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From the Editor's Desk……

It gives great pleasure that the current issue (Vol. IX, No. I) of the B N Seal Journal of Science is published as usual before the Annual Day Celebration of the College. The present volume brings together a number of original and informative research/review articles of very high quality, which address the current global scenario. The topics encompass practically all disciplines of Science and also interdisciplinary subjects, intimately linked together. We hope that the current issue of this journal has not failed to live up to the expectation, reputation and excellent academic standards set up by the preceding volumes. The readers will definitely find it stimulating, inspiring and thought-provoking.

We would like to thank all the contributors for their scholarship and research acumen. Thanks are due to the entire editorial team for their hard work and support, contribution in critically reviewing the articles and preparation of this issue of the B N Seal Journal of Science. It is worthwhile to acknowledge the help and support rendered by The Publication & Published Material Distribution Cell of this College for bringing out this issue of the Journal on time. I would also like to thank everybody who has contributed in any way, however great or small. Last but not the least; we are grateful to Dr. Bimal Kumar Saha, Officer-in-Charge of this College, for his patronage, support and enthusiasm.

Last but not the least, it is a pleasure to mention that recently the Journal has become UGC enlisted (No. 48724). The College takes pride in it.

From The Principal's Desk.....

It gives me immense pleasure that the first issue of the Volume 9 of the B N Seal Journal of Science is going to be published. It is very rich in form and content. It is also a matter of pride for the College that recently it has become UGC enlisted. I wish it all success.

BK Saha

Officer-in-charge
ABN Seal College
Cooch Behar

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Brojendra Nath Seal Journal of SCIENCE

Review Article

CARBON NANOTUBE DOPED LIQUID CRYSTALS

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A B S T R A C T

Carbon nanotube, an important allotrope of carbon, comprises of co-axial tube of graphene sheets. They are highly conducting along their length but poor conducting along diameter. They are non–responsive to any perturbations like electric or magnetic fields. Liquid crystals are self–assembled orientationally, partially positionally ordered soft materials, which can easily respond to such perturbations and orient themselves along the field. The basic compatibility between liquid crystals and carbon nanotubes is anisotropic nature of both. When carbon nanotubes are suspended in liquid crystals, they align themselves along the direction of liquid crystal molecules and the order parameter is enhanced. Ion density, threshold voltage, driving voltage, flickering of image, and degradation of display are observed to decrease in nematic liquid crystals due to doping of carbon nanotubes whereas in ferroelectric liquid crystals switching time, viscosity, dielectric increment decrease and critical frequency of Goldstone mode increases. Liquid crystal–carbon nanotube composites are capable of solving many issues of display technology.

Keywords: *Carbon nanotube; single wall carbon nanotube; threshold voltage; ion density; liquid crystal.*

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1. INTRODUCTION

A new type of finite carbon structure consisting of needle–like tube was discovered by Japanese Scientist Sumio Iijima in 1991, when examining carbon materials under an electron microscope. Electron microscopy reveals that each needle comprises of coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. On each tube the carbon–atom hexagons are arranged in a helical fashion about needle axis [Fig. 1]. The helical pitch varies from needle to needle and from tube to tube within a single needle [Iijima, 1991]. Sumio Iijima called these materials "carbon nanotubes", since they have a tubular structure of carbon atom sheets, with a thickness scaled in less than a few nanometers. The name has been

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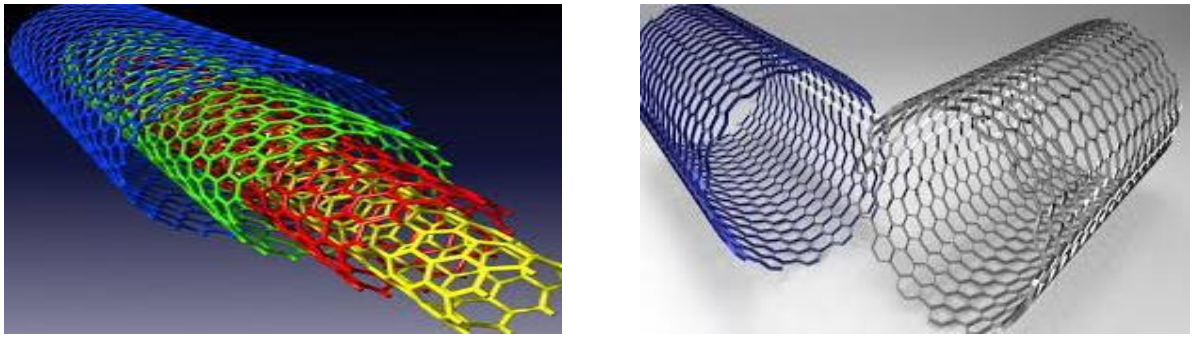
widely accepted now. Carbon nanotubes (CNTs) have attracted a lot of researchers in a wide range of fields from academia to industry, not only because of their uniqueness when compared with conventional materials, but also because they are very promising materials in *nanotechnology* in future technology. Their properties open a whole range of novel applications including nanoscale electronics, field emission sources, actuators, nanosensors for chemical and bio–logical molecular detection [Dierking *et al.*, 2004]. The simplest carbon nanotube is composed of a single graphite sheet of a honeycomb network of carbon atoms called graphene, it is rolled up seamlessly into a tubular form. The first reported carbon nanotubes were composed of multi–tubes [MWCNT] wrapped in a concentric fashion [Iijima, 1991]. Later, single–wall carbon nanotubes [SWCNT] were discovered [Iijima, 1993].



(a) MWCNT (b) SWCNT

Fig. 1: *(a) Multi–walled carbon nanotubes (MWCNTs), (b) single–walled carbon nanotubes (SWCNTs)*

CNTs are materials with extraordinary physical properties relating to their mechanical and electronic behaviour. They have strong anisotropy of conductivity i.e., they are highly conducting along the length of the tube and poor conducting along the diameters [Lynch *et at.*, 2002]. They find applications in diversified fields like–electromechanical devices, hydrogen storage, field emission devices, nanometer-sized electronic devices, sensors and probes etc. due to their fascinating properties of high conductivity with essentially no heating, exceptionally stiff and strong with high modulus of elasticity [Baughman *et al.*, 2002, Yu *et al.*, 2006], and enhanced surface area due to their high porosity. Liquid crystals (LC) are fascinating self–assembled soft materials in which the molecules are orientationally ordered and partially positionally ordered. Liquid crystals easily response to small perturbations like electric field, magnetic field, surface effect etc. for which they find applications in diversified fields along with display technology. The key feature behind the compatibility of LCs and CNTs is highly anisotropic nature of both.

But realize the practical application of CNTs in LC host; the primary challenge is to achieve perfectly aligned CNTs over large areas. Lynch *et al.* [Lynch *et al., 2002*] first aligned them by dispersing them in an anisotropic liquid crystalline medium and maneuvered the directionality of CNTs. The concept of application of the CNTs (in LC host) is that if they are dispersed in liquid crystalline medium, then on application of electric and magnetic fields the LC molecules will move along the direction field and the CNTs will also be aligned along the direction of liquid crystal molecules and hence the order parameter of the LC–CNT

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composite will be enhanced in comparison to the pure LC medium. Change of the electro–optical properties of CNT doped LC composite is a result of enhanced order parameter.
The LC–CNT composite system has drawn great interest in the recent years as they show lower operating voltage, higher contrast ratio and faster switching speeds [Qi *et al.,* 2008]. They exhibit a significant modification of physical properties of the host because of the outstanding interactions of CNTs with aromatic mesogenic units of liquid crystals. The enhanced conductivity and lowered threshold voltage for Freedricksz transition from planar to homeotropic configuration of the SWCNT doped nematic liquid crystals were observed by Dierking *et al.* [Dierking *et al., 2004*].

2. EFFECT OF CNT DOPING ON NEMATIC LIQUID CRYSTAL

Nematic liquid crystals (NLC), have been extensively used in display devices from the very beginning era of display technology with liquid crystals. Although a tremendous improvement in the quality of display as well as reduction of manufacturing cost has taken place over the years, there are many issues which the LC industry is trying hard to address. In order to obtain high quality performance in LCDs, it is an important issue to lower the concentration of charged impurities and maintain high resistivity [Nakanishi *et al.,* 2002]. Although twisted nematic (TN) liquid crystals are the most popular operation mode for nematic LCs in display markets due to their low operation voltage, high contrast ratio and nearly achromatic transition [Schadt *et al.*, 1971], their assymetric director alignment causes a narrow viewing angle in TN–LCD and limit their application. Performance degradation over the time of such display is another significant issue to be solved toward its application. The main cause of this degradation is adsorption of ion charges of only one sign by the alignment layers leads to building a sheet of ion charges of the other sign adjacent to each aligning layer. These electric bi–layers create strong electric fields in the region of the alignment layers, resulting in polar surface interaction responsible for changes in anchoring energy in the nematic LCs [H. Y. Chen *et al.*, 2005]. Suppression of ion–charge effect and modified electro–optical characteristics of TN–LCs are possible by doping CNTs [H. Y. Chen *et al.*, 2005]. The screening effect arising from the increased population of absorbed ion charges on the interface causes a decrease of the effective voltage for the LC layers and it increases threshold voltage (V_{th}) of the display. Decreased moving–ion density which suppressing the unwanted field screening effect and contributing to a reduction of the driving voltage is obtained by doping diamond nanoparticle in nematic LCs [P. Chen *et al.*, 2007]. Another issue of nematic liquid crystal is the flickering of image. This also arises due to the presence of free ions in the LCs. Therefore it is the prime goal to reduce the free ion density in the LC medium. CNTs have higher tendency to trap ions and hence decreases the free ion density in the LC medium and thereby reduces the threshold voltage, reduces flickering of the image and reduces the degradation of the display.

3. EFFECT OF CNT DOPING ON FERROELECTRIC LIQUID CRYSTAL

Enhanced dielectric and electro–optic properties are observed in ferroelectric liquid crystals because of minute addition of CNTs. Doping of CNTs in ferroelectric liquid crystal reduces dielectric increment of Goldstone mode ($\Delta\varepsilon_G$) [Huang *et al.*, 2006], but increases its

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critical frequency (f_G) significantly. Decrease in dielectric dispersion and increase in relaxation frequency due to doping of carbon nanotubes in ferroelectric, deformed helix ferroelectric and antiferroelectric liquid crystals were reported by several authors [Podgornov *et al.* 2009, Sood *et al.* 2012, Ghosh *et al.* 2015]. The complex dielectric dispersion (ε^*) can be expressed as [Botcher *et al.*, 1978]:

$$\varepsilon^* = \varepsilon - i\varepsilon = \varepsilon + \sum_k \frac{\Delta\varepsilon_k}{1 + (i\omega\tau_k)^{1-\alpha_k}} - i\frac{\sigma}{\omega\epsilon_0} \qquad (1)$$

where ε' is the real part and ε'' is the imaginary part of complex dielectric dispersion, ε_∞ is the real part of dielectric dispersion at high frequency limit, $\Delta\varepsilon_k$ is dielectric increment, τ_k is relaxation time, α_k is asymmetry parameter of *k*–th mode relaxation process, σ is the conductivity of the capacitive cell, arises due to presence ions and ϵ_0 is the permittivity of free space. CNTs have higher electron affinity thereby reduces the free ion density and hence reduces the conductivity in the CNT doped liquid crystal suspension and, hence the dielectric dispersion (ε') (or dielectric increment $\Delta\varepsilon$) is reduced in the composite in comparison to the pure LC.

The decrease of dielectric increment and increase of critical frequency of Goldstone mode, soft mode can be explained with the help of Landau equation of free energy. Considering the bi–quadratic coupling between tilt (θ) and polarization (*Ps*), T. Carlsson *et al.* [Carlsson *et al.*, 1990] derived simple relations for parameters which define the thermodynamic properties of Goldstone mode and soft mode. They derived the expression for dielectric increment of Goldstone mode ($\Delta\varepsilon_G$) and critical frequency (f_G) as

$$\Delta\varepsilon_G = \frac{1}{2\epsilon_0 K_\varphi q^2}\left(\frac{Ps}{\theta}\right)^2 \qquad (2)$$

$$f_G = \frac{K_\varphi q^2}{2\pi\gamma_G} \qquad (3)$$

The rotational viscosity (γ) of ferroelectric liquid crystal is related to spontaneous polarization (*Ps*) switching time (τ) and electric field (*E*) though the relation [Pozhidaev *et al.*, 1988]

$$\gamma_G = \tau \cdot Ps \cdot E \qquad (4)$$

The ratio (*Ps*/θ) decreases significantly in the CNT doped ferroelectric system due to decrease of *Ps* [Ghosh *et al.*, 2015] and increase in θ and the twist elastic constant (K_φ) increases due to dispersion of rigid carbon nanotube in soft liquid crystal medium which refers the decreasing value of $\Delta\varepsilon_G$ from equation (2) .

The reduced switching time in ferroelectric and antiferroelectric liquid crystals due to CNT doping was reported by several authors [Lee *et al.* 2004, Malik *et al.* 2012, Ghosh *et al.* 2015]. From equation (4) the faster switching time leads to the reduction of torsional

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viscosity of the CNT composite which in turn implies from equation (3) the increase in critical frequency of Goldstone mode. Similar explanation holds good for soft mode dielectric increment ($\Delta\varepsilon_S$) and soft mode critical frequency f_S.

4. SUMMARY

The carbon nanotubes influence the properties of LCs significantly when suspended in liquid crystals, by aligning themselves along the direction of molecules of liquid crystal and enhancing the order parameter. In nematic liquid crystals the reduced ion density, threshold voltage, driving voltage, flickering of image, and reduced degradation of display, higher contrast ratio are observed due to doping of carbon nanotubes whereas in ferroelectric liquid crystals faster switching time, reduced viscosity, dielectric increment and increased critical frequency of Goldstone mode are generally observed. Future technology is nanotechnology and therefore liquid crystal–carbon nanotube composites will take a major role in solving of many issues of display technology.

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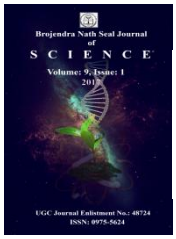

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Review Article

DISCOVERY IN SCIENCE: NECESSITY, METHODOLOGY AND OUTCOME

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A B S T R A C T

It is a common practice to judge the importance of scientific research leading to a discovery in terms of its immediate utility, applicability and impact on the society. This is, of course, important. But it should also be borne in mind that at the fundamental level science is the study of nature and its laws - the truth and beauty underlying natural phenomena and processes. As one goes through the History of Science, one sees that there could be many avenues originating from the main road of scientific discovery to reach the goal. On the other hand, a goal may be set but a different target may be reached. So the means and the ultimate results are manifold, and these may not be comprehensible right at the beginning. Consideration of all these is very fascinating, as outlined in this article.

This write-up is based on the 18th Ramatosh Sarkar Memorial Lecture delivered by the author at Bangiya Bijnan Parishad on 15.02.17. The talk was delivered in Bengali entitled "বিজ্ঞানে আবিষ্কার: প্রয়োজন, প্রকরণ ও পরিণাম".

Keywords: *Scientific research, invention and innovation, discovery, methodology, outcome of a scientific work*

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1. INTRODUCTION

A conversation was going on between a scientist (say, Mr. X) and his wife (Mrs. Y), of which I was a witness. It was on the occasion of publication of a paper by Mr. X, in an international journal of repute, which contained many formidable looking equations and all very complex staff. Seeing all these, Mrs. Y asked Mr. X, "What are all these meant for? Do all these really matter for the mankind, or even for common people like us? Will these lead to

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any new discovery? To me, these are of no value. You better go for the discovery of, say, some machine or instrument which serves our daily need. Or else, discover some life-saving drug. Can you do that? Say 'yes' or 'no'. See, a team of scientists has discovered another system of planets orbiting a star over 'there' in the sky, with one planet at a favourable distance from the parent star, just like earth in our solar system. These are 'real' discoveries."

Mr. X had a pause for a moment. Then he answered his wife, which could be the subject matter of a popular oral presentation. But he said something only about what a scientific discovery is and the possibility of the result or outcome of any scientific work leading to a discovery. I shall add something more to it. No, it is not like making some discovery in Nuclear Science and ending up in the Manhattan Project, leading to the mass destruction of Hiroshima and Nagasaki in Japan. For the sake of completeness, I would also say something about the need or necessity of a discovery. The methods/means adopted and the way things are discovered will also be elaborated. This will amply bring out the importance of a scientific exercise otherwise out of context or seemingly meaningless to the ordinary people.

I start by saying what a discovery is. Any layman already has some idea about a discovery, but I have to make it concise. For this, let us have a look at the list of some very important breakthroughs in the history of human civilization a common man would cite. I go with the progress of civilization: introduction of the number system and the number zero, use of fire, use of weapons (made of wood, stone, ultimately metal), use of wheel, design and construction of steam engine, recognition of the universal law of gravitation (by Issac Newton), identification of oxygen, new studies of penicillin (antibiotics) and vaccinations of rabies/anthrax, formulation of the electromagnetic theory, formation of the periodic table of elements, knowing radioactivity for the first time, emergence of a subject like quantum mechanics, knowledge of the double helix structure of DNA, propounding the special theory and the general theory of relativity, the big bang theory and many others – the attentive reader could add many more to this list. But I curtail it because of shortage and limitation of scope. So a discovery is knowing/recognising the importance/utility of things/matter that already exist in nature and sometimes making them suitable for use by mankind at the ground level, knowing the fundamental laws of nature and how things work in natural processes This is also associated with knowing the ultimate truth that is inherent in nature. A discovery is, of course, different from an invention and then innovation. One can learn the use of an optical lens in seeing nearby or faraway objects. Then one notices that by placing two such lenses at the two ends of an open tube, thereby covering the openings, one can see very small nearby objects or astronomical bodies lying at great distances. This is invention and thus one has primitive versions of a microscope and a telescope. Further improvements on these result in technologically advanced ways of looking into the microcosm and the macrocosm. This advancement could, in turn, help us and lead to more fundamental discoveries, which are fascinating. Thus discovery and invention go hand-in-hand in meeting needs of daily life, in contributing to industrial and technological achievements and in revealing the ultimate truth about nature. The recently concluded experiments at the Large Hadron Collider (LHC), although aimed at studying nature at the miniscule scale, need instrumentation and

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technology working at the highest possible levels and bring forth the fruit of technological advancements.

2. NECESSITY OF A DISCOVERY

So why is a discovery necessary? There are two basic reasons and I shall touch upon these one by one. First reason is based on needs in daily life. From time immemorial one has been looking at the skies to check the positions, motions of the stars, planets, the sun, the moon and other heavenly bodies and make a note of them. The positions of the sun and the moon of course have direct bearings on the weather system, the seasons, formation of clouds and occurrence of rain/storm, the formation of tide and ebb, the cultivation of crops etc. The positions of stars were helpful in navigation in the absence of any mariner's guide or compass. They used to guide sailors on high seas. It was found that the annual flooding of the river Nile in Egypt occurs when the very bright star Sirius (*Lubdhak*, in Bengali) rises before sunrise. Sirius is the brightest of stars in the sky, if one excludes our parent star Sun. It belongs to the constellation *Canis Majoris* (the big dog), the companion dog of the constellation *Orion* (*Kalpurush*, in Bengali – the hunter).

The relative configurations of the stars do not change with time and there are fixed star-clusters or constellations. Among different star-clusters are some special congregations of stars (the '*Rashis*' - collections of stars, given names associated with objects, animals and human beings in specific forms associated with everyday life) - the twelve Signs of the Zodiac - *Aries* (the Ram), *Taurus* (the Bull), *Gemini* (the heavenly twin - a man and a woman), *Cancer* (the Crab), *Leo* (the Lion), *Virgo* (the Virgin Girl), *Libra* (the Weighing Balance), *Scorpius* (the Scorpion), *Sagittarius* (an animal with the head of a human being and a four-legged body, holding bow and arrow in its hand), *Capricorn* (the He-goat), *Aquarius* (the Water-pitcher), *Pisces* (Two Fishes, disposed head-to-tail at each other). The reader is asked to look into any popular book on sky watching.

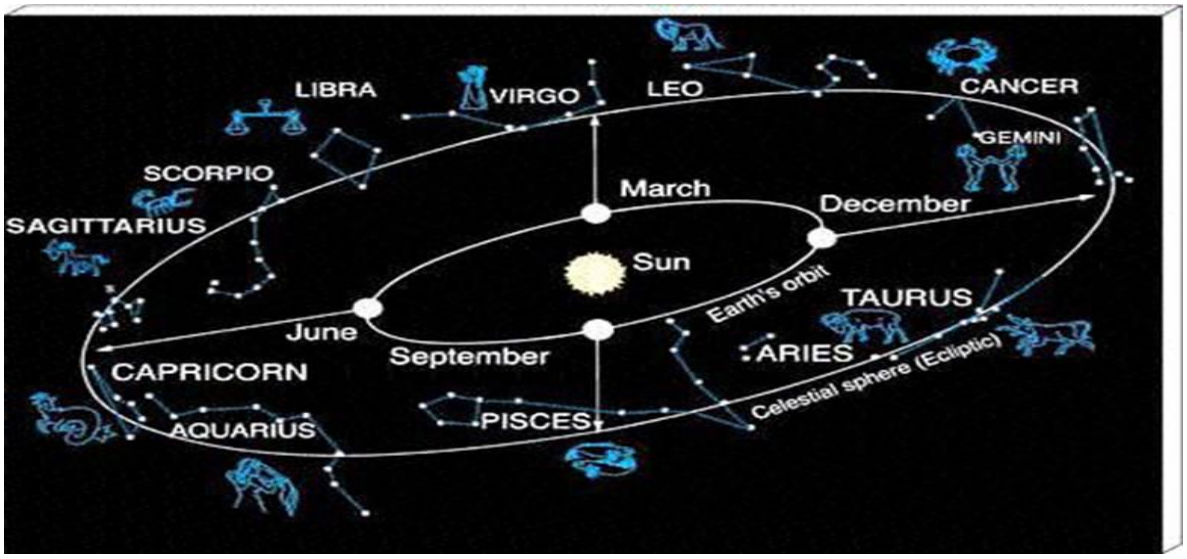

Fig. 1: *Twelve signs of the Zodiac*

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People saw that the sun, the moon and usually the planets in our solar system move over the 'fixed' (fixed over a considerable period of time of several thousand years) background of these *rashis*. The planets, the sun, the moon and the stars were observed also for astrological reasons - people tried to make out whether their positions in different *rashis* could be statistically correlated with different happenings in the life of a human being and his/her ultimate fate. Different rituals, customs and social occasions were held depending upon their positions also. This also resulted in finding out the systematics associated with their motions. Thus the twelve Hindu months in the year were linked with the position of the sun in the twelve different *rashis* and its complete transit across each one of them. There are twenty seven stars equally distributed on the apparent monthly path of the moon on the sky; these are (in Bengali or Sanskrit) *Asvini, Bharani, Krittika, Rohini, Mrigashira, Ardra, Punarbasu, Pushya, Ashlesha, Magha, Purba phalguni, Uttar phalguni, Hasta, Chitra, Swati, Bishakha, Anuradha, Jyeshtha, Mula, Purbashara, Uttarashara, Shrabana, Dhanishtha, Shatabhisha, Purba bhadrapada, Uttar bhadrapada, Rebati*. In mythology, they are thought to be the twenty seven beautiful wives of the Moon God. On the full moon day (*Purnima*) in each Hindu month, the moon was observed to be close to one of these specific stars. So in the month of *Baishakha*, the moon lied close to the star *Bishakha* etc. The names of the twelve months in the year came this way. But let me mention that this is not the case nowadays - one will not see the moon lying close to *Bishakha* on the full moon day in the month of *Baishakha*. This is because the stars are not really fixed. They are actually moving away from one another on the average with tremendous speed. So although not apparent in, say, two or three thousand years, their relative motion will be noticeable in an appreciable period of time. Another consequence is that the relative configuration of the stars will keep changing with time. The precession of the axis of rotation of the earth (with a time period of around 26,000 years) is also responsible for this. So the current pole star will no longer be a fixed star (*Dhrubatara*) in, say, some five thousand years.

Secondly, a human being has got the natural inquisitiveness to learn the ultimate truth inherent in nature and natural processes. 'Why', 'what' and 'how' are always there to be answered by him or her. He/she cannot rest without resolving the mysteries of nature and getting satisfied. I give two examples from the field of astronomical observations - one linked with the other. First I give the name of Tycho Brahe, the nobleman, astrologer and astronomer of the 16th century Denmark. According to Edwin Arthur Burtt in "The Metaphysical Foundations of Modern Physical Science: A Historical and Critical Essay (1925)", he had the first competent mind in modern astronomy to feel ardently the passion for exact empirical facts. The use of a telescope was not known to him and with his own instruments sextant and quadrant he went on to watch the sky. Tycho had his own system, the Tychonic system, of the universe in which the motions of the sun and the moon were around the earth but all other planets moved around the sun. In 1572, he saw the supernova SN 1572 (*De Stella Nova*) in the constellation *Cassiopeia* (resembling the English letter 'W' in shape) and commented that he saw nothing like this - not even the halo of a star or the moon. For nights together, he kept watching and recording the positions of the planet Mars on the sky, usually favourably visible all throughout the year. It was a very painstaking and persistent effort. People thought that these planets could influence our lives in various possible ways

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and so astrology contributed also in leading to astronomical observations. In this context let me say that the sight of the famous comet in 1577 (in Tycho's time) in Europe cast apprehensions in the mind of people.

His student and follower Johannes Kepler (from Germany) started from where Tycho Brahe ended. He was also keenly interested in star-gazing. He saw another supernova - that occurred in 1604 (in the constellation *Ophiuchus* – the serpent bearer). Unlike Tycho, Kepler believed in the heliocentric model of the universe, in which all the planets keep orbiting around the sun and he was interested in discovering any rule prevalent in their motion. He compiled three books – *Astronomia Nova, Harmonices Mundi* and *Epitome of Copernican Astronomy*. Kepler did a very critical study of the huge amount of data on the motion of Mars collected by Tycho and was successful in what could be said as finding the needle in a stack of hay. He systematized and generalized the observations in the form of three famous laws of planetary motion (see any good text book in Physics) and this was a remarkable achievement. Thus empirical observations of nature backed with the natural curiosity to know the unknown lead to discoveries.

3. METHODS/MEANS/WAYS OF DISCOVERY

Theoretical, experimental and empirical – there are three methods of making discoveries. A scientist should have the correct objective – the vision, a very clear understanding of the perspective – the mission and also the imagination. According to Einstein, "Imagination is more important than knowledge." But of course he/she should be potentially equipped with the expertise in his subject and should have the appropriate knowledge. By this time, it has already become apparent that empirical findings/observations provide ways leading to a great discovery. However, this has to be substantiated by other findings and experiments. Theoretical support could also lead to confirmation of empirical facts and help generate new ideas. Thus the three laws of planetary motion were theoretically derived later by no other than Sir Issac Newton from his law of universal gravitation. But new theories and their predictions will also have to survive the test of experiments. For example, the fact that light bends in a strong gravitational field, as given by Einstein in his general theory of relativity, was experimentally verified by Sir Arthur Eddington during the 1919 total solar eclipse. Stars lying close to the sun are normally invisible because of the intense solar halo. However, during an eclipse they may be visible and light coming from them, if bent in the gravitational field of the sun, will see them at positions different from what the recordings are. This was found to be the case. So, experimental verification is the ultimate necessity in the claim of a genuine discovery. New experimental results may also seek the explanation by theory. Thus all these methods go hand-in-hand in arriving at the truth.

The ways things are discovered are wonderful to know sometimes. One might accidently make some very important discovery while studying something quite different. Thus radio engineers Arno Penzias and Robert Wilson got Nobel Prize in Physics by discovering cosmic microwave background radiation at a temperature around 3 K – the relics of the Big Bang. They were working at Bell Labs in Holmdel, New Jersey, USA in 1964 with their horn

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antenna to receive radio signals bounced off echo balloon satellites. To their surprise, they kept receiving a low, steady, mysterious noise which they attributed to one or more of the following reasons: spurious signals from the adjacent urban regions, results of possible nuclear radiation or test, or even pigeons nesting on the antenna. Astrophysicists like Robert H. Dicke at nearby (some 60 km away) Princeton University were also searching for these signals, but the credit for the discovery went to Penzias and Wilson. Similarly another discovery was made when Alexander Fleming, the Scottish Biologist was working on bacteria, like staphylococci and went on holidays for a few days, leaving some soiled dishes used for eating in the laboratory and also some bacteria cultures. Coming back there, he found some strange moulds grown on the leftover edibles and also on the cultures, which destroyed the growth of bacteria. These were the penicillin fungi (*Penicillium Notatum* and *Penicillium Chrysogenum*) and with this started the subject matter of bacteriology, leading to the discovery of penicillin and many other antibiotics. Antoine Henri Becquerel, a French physicist, was the first person to discover evidence of radioactivity and this too happened accidentally. He was working on some naturally available substance – crystals containing uranium and found some 'rays' coming out of it, tarnishing or fogging photographic paper. He first thought that to be due to rays of the sun falling on it. So on a cloudy day, he stopped doing his experiment and left some experimental material in a dark shelf, wrapping it up with photo-paper. Surprisingly he found blackening of the photo-paper even in the absence of sunlight and gave hint of some radiation like X-rays being emanated from the object. Later Marie Curie and Pierre Curie investigated it to be due to the radioactive property of uranium and got the Nobel Prize.

Fig. 2: *Penicillium Chrysogenum growth*

It is also interesting to note that there are occasions on which more than one scientist belonging to different places/countries independently made the same discovery at slightly different times. The backgrounds/needs may be different. Thus Lavoisier, Scheele and Priestley discovered oxygen separately. Issac Newton from England and Wilhelm Gottfried Leibnitz from Prussia independently discovered Calculus according to different necessity. Charles Darwin and Alfred Russell Wallace independently arrived at the discovery of the theory of evolution of natural species.

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The legacy of discoveries may also be hierarchical or may go on from one generation to others. J. J. Thomson discovered electron. His student Ernest Rutherford discovered proton (the structure of the atom) and later Rutherford's student James Chadwick discovered neutron (see Fig. 3 below).

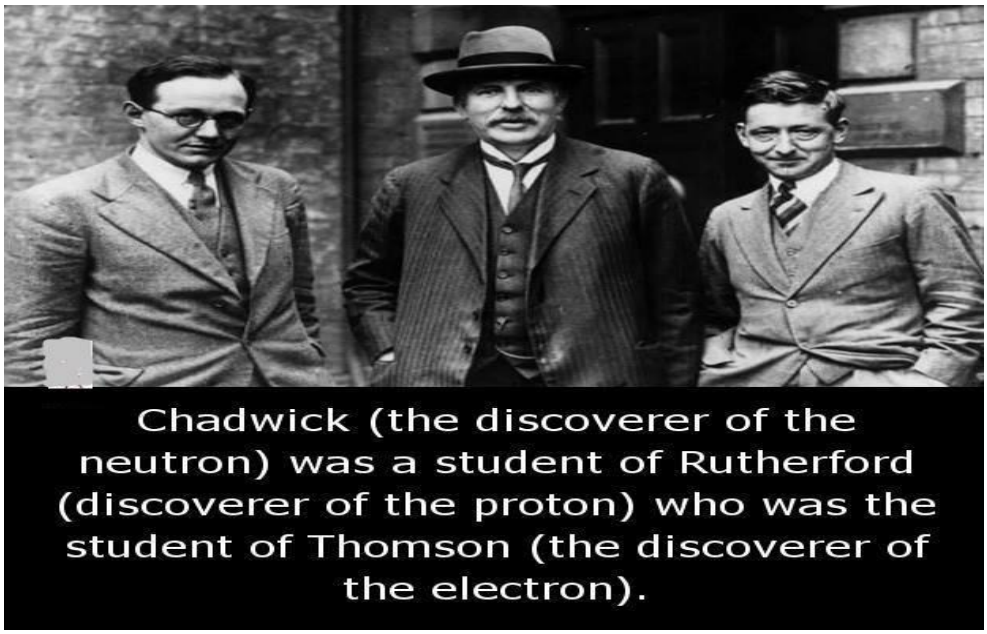

Fig. 3: *Hierechy of scientific research*

4. RESULTS/OUTCOME OF A DISCOVERY

Now we describe the result of a discovery and its possible outcome. This is the crux of the subject matter. I try to cite some spectacular instances.

Let me mention that the development of the subject of thermodynamics, an extremely important domain of Physics, was due to necessity arising out of engineering applications. An engineer contributes to the development of technology, industry, leading to significant improvement of standards of living. Within the scope of thermodynamics, he/she thinks of designing engines, refrigerators, automobiles and machines. However, usually Physics or science in general is fundamental in this context and an engineer thinks of realistic applications of whatever he learns from Physics/Mathematics. There is a famous joke which illustrates the mind-set of an ordinary man, an engineer, a physicist and a mathematician, and presents a nice comparison. It is said that they were separately asked the same question – how many legs a cat would have if it is given a wooden leg? The layman said, "It will have five legs." Then the physicist said, "It all depends on how one defines a leg. If a wooden leg is also another leg, I would say that it would have five legs. If not considered to be a leg, it will have four legs." The mathematician was approached then. He said, "One does not specify what has happened to the other legs. So I would say that it would have at least one wooden leg." (Note that the physicist and the mathematician, although extremely wise, do not find it meaningless to give a thought to an apparently unrealistic question.) Lastly the engineer was

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asked the question. He said, "See, I am not bothered to give answer to such foolish, unrealistic questions. So please go away and leave me."

Fig. 4: *Picture of Sadi Carnot*

Now let me tell you about a brilliant French engineer in particular – Nicolas Lėonard Sadi Carnot (1796-1832), who died very young unfortunately. He was thinking of the development of heat engines and ways of maximising its efficiency. A heat engine delivers work at the cost of heat, cycle after cycle. It is well known that the total amount of energy is constant in this universe and there are changes of energy from one form to another. Also, it is possible to do work with energy. Heat, another form of energy, is also converted into work. However, there are limitations in this respect. Let me make it clear. It is possible to convert work fully into heat. Thus if one rubs his hands together there is 100 percent conversion of work into heat. At the end of the process, one has his hands left at the same initial temperature. But is the opposite possible? From the point of view of conservation of energy, there should not be any problem. It is of course possible for heat getting fully converted into work. But then the substance or the system, which is made to work with the application of heat, is not left in the same initial state or configuration. A simple example will illustrate this. Let us consider some gas confined inside a closed container fitted with a movable piston carrying a weight at the top. When heated, the gas expands and pushes the weight upwards against the force of gravity, thus doing work. The temperature of the gas can be made to remain constant at each step of the process of expansion. The heat going into the gaseous system is fully converted into work, if we neglect friction. But the important thing is that the initial volume and temperature are not the same as the final ones. So the system is not in a position to repeat the entire process in order that same work is delivered again and again. However, if the gas goes through a series of processes, bringing it back to its initial state, we design what is known as a heat engine. But will there be full conversion of heat into work then or could there be some

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device whose efficiency is 100 percent? Carnot considered all these very critically and wrote a book "Rẻflexions sur la puissance motrice du feu" (in French) or "Reflections on the motive powers of fire" (in English). He came to the very important conclusion that it is not possible to construct a heat engine which only absorbs heat from a hot reservoir and fully converts it into work. It led to the formulation of one fundamental law of nature – the second law of thermodynamics, which states that there exists no process in nature whose sole effect is the absorption of heat from a hot body and its complete conversion into work, without producing any other changes in the universe. The consequences of this is really far reaching (which I do not refer to any more here) and thus something very important was discovered in physics from the necessity of engineering development.

If engineering lends its hand to the development of physics, the reverse is of course possible and that too, may be, from a seemingly impossible idea. Let me elaborate on this by taking examples from nature. If one asks, "What is the smallest possible structural unit of matter which makes it chemically different from one another?" Or, "what are the seeds of different elements?" The answer would be the nuclei of elements. Where do they come from and how? Starting from very light elements like hydrogen, helium etc, nuclei of the chemical elements are synthesized in the primordial universe, at the cores of stars and at various other cosmic sites under extreme conditions (supernova explosions etc.) in steps through nuclear reactions like fusion. Once the nuclei are synthesized, they will make up the atoms by gathering electrons from nature. Then the structure of the universe comes up as we see it today, locally through the operation of electromagnetic processes and through gravitational forces at the cosmic scale. So there will be atoms, ions, molecules, molecular association, inanimate objects, plants and animals, mountains, rivers, seas, forests, countries, continents, planets, star systems, galaxies and so on. So we are born in the stars and every chemical element inside our body owes it origin to them. Now the problem is that these nuclei are positively charged and in order to fuse them, one has to surmount the Coulomb repulsive barrier in the first place, which is formidable. When two positively charged nuclei start toward each other to combine into a heavier and chemically different nucleus inside a star, say, the initial motional energy keeps decreasing at the expense of gain in potential energy and it may be that over some region of relative motion between them, the potential energy is larger than the initial energy, making the kinetic energy over this region negative. This is of course not allowed by classical physics. However, the lighter nuclei do combine, yielding heavier nuclei and producing large amount of energy according to Einstein's relation: $E = \Delta m.c^2$, where Δm is the mass difference of the nuclei fusing together and the product(s). There are so many nuclei fusing inside a star and the colossal amount of energy resulting from there is radiated out by the stars in the form of heat, light, x-rays and other forms of electromagnetic energy. A significant portion is carried out into space through charged particles and neutrinos also. So, how to solve this apparent riddle?

The answer came from quantum mechanics through the work of George Gamow, R. W. Gurney and E. U. Condon. Let us have a simple look at it. What is a quantum system and how are prescriptions for such a system different from a classical one? A body in motion has got something called a de Broglie wavelength (dimension) which is given by the amount of

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its motion (momentum). If the physical dimension of a body is comparable to its de Broglie wavelength, then we say that the system can be treated quantum mechanically and then the prescriptions for it become meaningful. Thus a bus is motion has got de Broglie wavelength much much smaller than its size and so its motion is classical – according to Newton's laws of motion. However, atomic, subatomic particles and nuclei in motion can be treated quantum mechanically. A very important aspect of quantum prescriptions is the probabilistic interpretation. Thus in the previous seemingly impossible situation of nuclei fusing at the core of stars, there exists a finite, non-zero probability of relative motion becoming possible over a region of space in which the kinetic energy is negative. This is known as barrier penetration through tunnelling. Thus nuclear combination becomes a reality, although not permitted by classical physics.

If one takes mental snapshots of all the steps of relative motion between two nuclei leading to fusion and rewinds them, one considers the time-reversed process – the nuclear fission. For this process also, the quantum prescription is relevant. It is possible to utilise fission to generate electricity for use by mankind in domestic processes and industry. This is done in a nuclear reactor where nuclear fission is harnessed for peaceful use of energy. So an engineer designs a nuclear reactor after getting the answer from a quantum physicist and this is extremely important to meet the growing demand of energy with the advancement of civilization. It is worthwhile to mention that the fission of one gram of uranium-235 can meet the energy requirement of a small town over almost a year. However, if coal is burnt to produce the same amount of electricity in a thermal power station, it can be shown that something like 3000 kg of coal will be needed. Advanced countries like Japan, France use electricity generated by nuclear power plants. Note that it has not been possible to design a fusion reactor since till date we do not have the technology to control and sustain nuclear fusion reactions, which yields more energy than fission considered in the bulk.

5. CONCLUSION

So the possibilities of a scientific exercise in any form leading towards great discoveries are immense and no meaningful venture can be degraded. One may be smart enough to make a quick breakthrough for the reward of a Nobel Prize. I admit that this is necessary but there are problems which are more complex and demand attention for their solution. They may not be that much rewarding in terms of money or recognition but gives fun and brings a human being very close to nature. Then there is always the need for research at the very fundamental level. For example, some twenty years ago, one thought that nuclear physics has become an obsolete subject. But with the possibilities of studying the exotic nuclei both theoretically and experimentally, one realizes that even today one does not have full knowledge of one of the fundamental interactions of nature – the strong interaction. And the treatment of the many-body problem in Nuclear Physics still remains the hardest task a physicist can possibly think of. But this will not have any significant appeal to a common man and it will not bother him. On the other hand, there are many *not-so-sophisticated* problems which still need to be resolved. For example, a concrete theory of the frictional force does not exist till date. These are challenging and appealing.

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As it is written in the Holy Bible, when confronted with the choice between Heaven and Knowledge, Adam and Eve opted for knowledge. So with the advancement of knowledge, let us keep discovering the truth and beauty of nature with an aim to sustain peaceful coexistence and live happily.

ACKNOWLEDGEMENT

This article is dedicated to my dear wife for her valuable criticism and inspiration. Thanks are due to Rajkumar Chakraborty for his valuable suggestion. I also thank my very dear friends and colleagues for their support and enthusiasm. Last but not the least; I dedicate the presentation to my dear little daughter for her keen interest in the subject.

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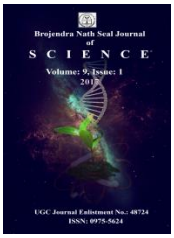

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Research Article

COSMOLOGICAL MODELS OF THE UNIVERSE WITH NONLINEAR DISSIPATIVE EFFECTS

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A B S T R A C T

We study here the phenomenological cosmological models in the presence of nonlinear dissipative effects in Einstein's theory of gravity. The evolution of the universe is explored considering the imperfect fluid described by nonlinear Israel Stewart Theory (nIS). The corresponding cosmological dynamics is obtained for a flat homogeneous isotropic Friedman-Robertson walker spacetime.

Keywords: *nonlinear bulk viscosity, dark energy.*

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1. INTRODUCTION

The recent cosmological observational data [Riess 1998; Riess 2008; Astier 2006; Spergel 2007] strongly suggest that the most part of the present universe filled with dark matter (~26.8 %) and dark energy (~68.3 %) and the rest (~ 4.9 %) are usual baryonic matter. Dark matter which is supposed to consist of weakly interacting massive particles (WIMPS) with zero effective pressure particle axions (a particle present in the multiplet of grand unified theories) and neutrinos (light particles present in broken supersymmetric models). Dark energy which is a mysterious entity is responsible for negative pressure. The cosmological constant (Λ) (which arises as the result of the combination of quantum field theory and general relativity) and its generalizations are the simplest way to describe dark energy. However, the theoretical value of the magnitude of Λ is 60-120 orders greater than the observed value [Permutter 1999; Sen 2002]. However, there are other candidates [Wetterich 1998; Hannestad 2006] for the dark energy namely self interacting scalar-field dark energy models known as quintessence, Kinessence, Brane, Modified gravity field etc.

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The recent predictions from the observational Astronomy, i.e. supernovae light curve data to WMAP data [Riess 1998, 2008; Astier 2006; Spergel 2007] indicate that the present universe is accelerating. It is also known that the universe might have emerged to the present state from an inflationary phase in the past. In the evolutions of the universe a number of processes might have occurred leading to a dissipative effect. Infact, some processes in cosmology and astrophysics can't be understood without a dissipative process. In the early universe a number of processes may occurred that could lead to a viscosity in the cosmological fluid. Viscosity may be arises due to the decoupling of neutrinos from the radiation era, the decoupling of matter from radiation during the recombination era, creation of superstrings in the quantum era, particle collisions involving gravitons, cosmological quantum particle creation processes and formation of galaxies [Misner 1968; Barrow 1977; Hu 1983]. It has been predicted from observations that a non negligible dissipative bulk stress on cosmological scales at the late universe phase might be important. To describe a relativistic theory of viscosity, Eckart [Eckart 1940] made the first attempt. However, the theories of dissipation in Eckart formulation suffer from serious shortcoming, viz., causality and stability [Hiskock1985; Muller 1967]. It has been shown that the problems of relativistic imperfect fluid may be resolved by including higher order deviation terms in the transport equation [Hiskock1985; Muller 1967]. Israel and Stewart [Israel 1970] developed a fully relativistic formulation of the theory taking into account second order deviation terms in the theory, which is termed as "transient" or "extended" (IS) irreversible thermodynamics (*EIT*).

These theories are based on small departures from equilibrium and the transport equation is linear with bulk viscous pressure. However, the viscosity-driven inflation demands nonlinear bulk viscous pressure [Maartens 1995]. Nonlinear Israel Stewart (nIS) [Maartens 1997] is developed to describe the nonlinear bulk viscous process and the departure does not need to remain close to equilibrium. Using the nIS, several works are done [Chimento 1997; Acquaviva 2015] to describe evolution of the universe. The objective of the present work is to investigate nIS theory in the evolution of the universe. This paper is organized as follows. In Sec. 2, gravitational action and field equations are presented. Cosmological solutions are given in Sec. 3. The results obtained are discussed in the last section 4.

2. THE RELEVANT FIELD EQUATIONS

We consider the homogeneous and isotropic space-time metric given Friedmann Robertson-Walker (FRW)

$$ds^2 = -dt^2 + a^2(t)\left[\frac{dr^2}{1-k_1 r^2} + r^2(d\theta^2 + \sin^2\theta\, d\phi^2)\right], \qquad (1)$$

where $a(t)$ is the scale factor of the universe. The constant k defined curvature of the space time, $k_1 = 0, 1, -1$ represents flat, closed and open spaces respectively. The field equations and conservation equation yield

$$H^2 = \frac{\rho}{3} - \frac{k_1}{a^2}, \qquad 2\dot{H} + 3H^2 = -p - \Pi - \frac{k_1}{a^2}, \qquad (2)$$

$$\dot{\rho} + 3(\rho + p)H = -3\Pi H. \qquad (3)$$

Where $H = \frac{\dot{a}}{a}$ is the Hubble parameter and an over dot represents derivative with respect to cosmic time (t). Where we consider the standard unit $8\pi G = c = 1$, p is the isotropic pressure

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of the universe, ρ is the energy density of the universe and $\Pi\ (\leq 0)$ is the bulk viscous pressure. The nIS evolution equation [Maartens 1997] for the bulk viscous stress Π satisfies the transport equation given by

$$\Pi(1+3\tau_* H)+\tau\dot{\Pi}\left(1+\frac{\tau_*}{\zeta}\Pi\right) = -3\,\zeta\,H-\frac{1}{2}\tau\Pi\left[3H+\frac{\dot{\tau}}{\tau}-\frac{\dot{\zeta}}{\zeta}-\frac{\dot{T}}{T}\right]\left(1+\frac{\tau_*}{\zeta}\Pi\right). \qquad (4)$$

The nIS model recover to IS theory for $\tau_* \to 0$. Where $\zeta\ (\geq 0)$ is the coefficient of bulk viscosity, $\tau\ (\geq\ 0)$ is the linear relaxation time, T is the temperature of the universe and $\tau_*\left(\geq \sqrt{\frac{\zeta\tau}{2nTS}}\right)$ is the nonlinear relaxation time, S is the specific entropy. We consider linear equation of state (EoS) $p=(\gamma-1)\rho$. We assume barotropic behavior of temperature i.e., $T=T_0\rho^{\frac{\gamma-1}{\gamma}}$. The linear relaxation time is defined as $\tau=\frac{\zeta}{v^2\gamma\rho}$, v is the dissipative part of sound speed. We assume following phenomenological relation

$$\zeta=\alpha\,\rho^{\delta}, \qquad \tau_*=k^2\,\tau \qquad (5)$$

where α and k are constant. The deceleration parameter(q) is related to H as

$$q\ =\frac{d}{dt}\left(\frac{1}{H}\right)-1\,. \qquad (6)$$

The value of deceleration parameter is negative for accelerating and positive for decelerating phase of evolution of the universe.

3. COSMOLOGICAL SOLUTIONS

The observations of Cosmic Microwave Background (CMB) anisotropy indicate that the universe is flat and total energy density is very much closed to the unity $\Omega_{tot}\cong 1$ [Spergel 2003]. Hence in the proceeding we use the concept of flat universe $k_1=0$. Using equations (2), (3), (4), (5) and (6) we obtain following expression of the evolution of the universe in nIS theory,

$$(q+1)Hq'+\frac{1}{\gamma}(q+1)^2-3(q+1)+\frac{9\gamma}{4} +\frac{\left[\frac{3\gamma}{2}-(q+1)\right]\times\left[3k^2+\frac{3v^2\gamma}{\alpha}H^{1-2\delta}\right]-\frac{9}{2}v^2\gamma}{1-\frac{k^2}{v^2}+(q+1)\frac{2k^2}{3v^2\gamma}}=0 \qquad (7)$$

Where prime $(')$ represents derivative with respect to Hubble Parameter (H). To find a analytic solution of equation (7) we assume $\delta=\frac{1}{2}$ for simplicity. Equation (7) becomes

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$$\frac{(q+1)^2+c(q+1)}{(q+1)^3+h(q+1)^2+e(q+1)+g}q^{'}+\frac{1}{\gamma}=0 \qquad (8)$$

where $c=\frac{3v^2\gamma}{2k^2}\left(1-\frac{k^2}{v^2}\right), h=c-3\gamma, e=\frac{9}{4}\gamma^2-3c\gamma-\gamma A,\ g=\frac{9}{4}\gamma^2 c+\gamma AB, A=\frac{9v^2\gamma}{2k^2}\left(k^2+\frac{v^2\gamma}{\alpha}\right)$ and $B=\frac{3\gamma}{2}(1-\frac{v^2}{k^2+\frac{v^2\gamma}{\alpha}})$. For $g=0, h=2c$, we obtain following relation between deceleration parameter and Hubble parameter

$$\frac{3(2c-d)\tan^{-1}\left(\frac{d+2(q+1)}{\sqrt{4e-d^2}}\right)}{\sqrt{4e-d^2}}+\frac{1}{2}\ln[\ (q+1)^2+h(q+1)+e]=c_0H^{-\frac{6}{\gamma}}, \qquad (9)$$

c_0 is a constant. For $g=0, h=2c$, we obtain following relation between deceleration parameter and Hubble parameter $(q+1)^2+h(q+1)+e=c_0H^{-\frac{6}{\gamma}}$. As the equation (7) is highly nonlinear to find a general analytic solution we adopt a numerical technique to find its solution. To find a numerical solution [Das 2006; Debnath 2007] one can plot $q\ vs\ H$ with an initial condition $(q[1])$ and for a given set of other parameters. If we choose at present value of age of the universe is $H=1$, then present value of deceleration parameter is $q[1]=-0.50$, which is compatible with observational data [Spergel 2003]. Figures show two phase of evolution of the universe, present accelerating phase early decelerating phase in the presence of nIS theory. The early exponential $(\dot{H}=\ddot{H}=0)$ inflation phase $(a(t)=a_0t^{H_0t}$, where a_0, H_0 are positive constants) can be obtained for $H_0=\left[\frac{\alpha}{2v^4\gamma}(v^2-k^2)(2v^2-1)\right]^{\frac{1}{1-2\delta}}$. So an exponential expansion is possible for $v>k,\ 2-\gamma\geq v^2>\frac{1}{2}$. Figure (1) shows how evolution of the universe depends on δ for a given set of initial constant and other parameter. Here early phase of evolution are obtained for $H>1$ and later phase of evolutions are obtained for $H<1$. The figure (1) indicates that there may be future deceleration phase for higher value of δ. Figure (2) shows how evolution of the universe depends on v for a given set of initial constant and other parameter. The figure (2) indicates that the rate of past deceleration is higher for higher value of v.

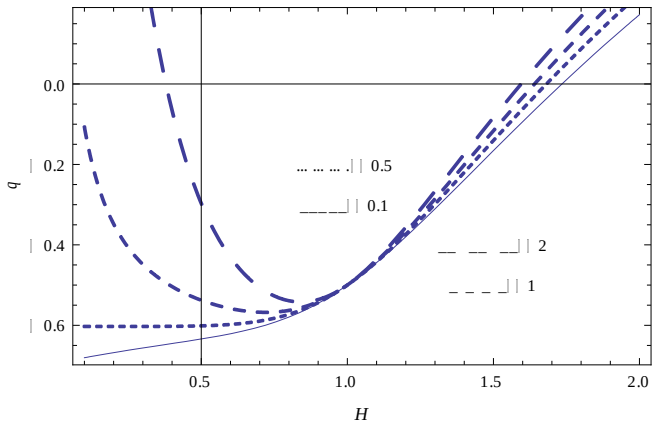

Fig. 1: *Show q vs H for different value of* $\boldsymbol{\delta}$ *of a given set of other parameters* $\boldsymbol{\gamma=\frac{4}{3}, k=0.1, v=0.6,\ \alpha=10}$ *and* $\boldsymbol{q[1]=-0.5}$.

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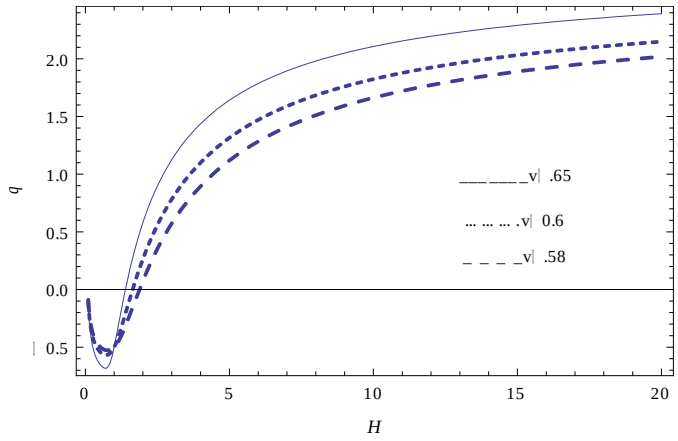

Fig. 1: *Show q vs H for different value of* $\boldsymbol{v}$ *of a given set of other parameter* $\boldsymbol{\gamma = \frac{4}{3}}$, $\boldsymbol{k = 0.1}$, $\boldsymbol{\delta = 1}$, $\boldsymbol{\alpha = 10}$ *and* $\boldsymbol{q[1] = -0.5}$.

4. DISCUSSION

In this paper, we explore cosmological models of the universe in the presence of non linear dissipative effects described by nIS theory for homogeneous and isotropic spacetime in Einstein's gravity. The early inflation phase of the universe are obtained for $v > k$, $2 - \gamma \geq v^2 > \frac{1}{2}$ and $\dot{H} = \ddot{H} = 0$. We adopt here a technique similar to that used in *Ref* [Das 2006; Debnath 2007] to solve equation (7). The relevant equations are written in terms of Hubble parameter H and the deceleration parameter q. We plot $q\ vs\ H$ for different parameters, namely, δ, v for a given set of other parameters. The figures show the present accelerating phase of the universe is followed by past decelerating phase. It may be noted that the universe may remain present accelerating phase, for the small value of δ. Figure (2) indicates that the rate of past deceleration is higher for higher value of v for a given set of other parameters.

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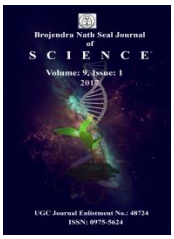

Brojendra Nath Seal Journal of SCIENCE

Review Article

ON SOME PROPERTIES OF ALMOST CLIQUISH FUNCTIONS

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A B S T R A C T

In this paper, a new concept of generalized continuous functions viz. almost cliquish functions on a topological space has been introduced. An attempt has been made to characterize points of almost cliquish functions and study some algebraic properties of almost cliquish functions.

Keywords and phrases: *Quasicontinuity, almost quasicontinuity, cliquish functions.*

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1. INTRODUCTION

In what follows, X is a topological space and Y is a metric space with metric d. Through the paper R is the space of real numbers with the usual metric. Furthermore, N, Q stand for the sets of natural numbers and rational numbers respectively.

We use the notation $cl(A)$, $\text{int}(A)$ to denote the closure and the interior of a set $A \subseteq X$. A set A is called preopen(or β-set) if $A \subseteq \text{int}(cl\, A)$, [D Andrijevic(1986), O Njastad(1965)]. The union of any family of preopen sets is preopen and the intersection of a preopen and an open one is preopen[O Njastad(1965)].

Recall that a function $f : X \to Y$ is said to be at $x_0 \in X$:

---quasicontinuous, if for each open neighborhood U of x_0 and each open neighborhood V of $f(x_0)$, there is a non empty open set $G \subseteq U$ such that $f(G) \subseteq V$ [T Neubrunn (1988-89)].

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---almost quasicontinuous, if for each open neighbourhood U of x_0 and each open neighbourhood V of $f(x_0)$, there is a non empty preopen set $G \subseteq U$ such that $f(G) \subseteq V$ [J Ewert(1993)].

---cliqish, if for each $\varepsilon > 0$ and each open neighbourhood U of x_0, there is a non empty open set $G \subseteq U$ such that $d(f(x'), f(x'')) < \varepsilon$ for all $x', x'' \in G$ [H P Thielmen(1953)].

A function f is called quasicontinuous, almost quasicontinuous, cliquish if it has this property at each point.

With $C(f), Q(f), AQ(f)$ and $A(f)$ we define the sets of all points at which f is continuous, quasicontinuous, almost quasicontinuous and cliquish respectively.

From the definitions: $C(f) \subseteq Q(f) \subseteq A(f)$ and $Q(f) \subseteq AQ(f)$.

It is known that $A(f)$ is closed set, $A(f) \setminus C(f)$ is of first category [A. Neubrunnova(1974)].

Here we introduce a new concept of almost cliquish function as follows:

A function $f : X \to Y$ is said to be almost cliquish at a point $x_0 \in X$ if for each $\in > 0$ ad each open neighbourhood U of x_0, there is a non empty preopen set $G \subseteq U$ such that $d(f(x'), f(x'')) < \varepsilon$ for all $x', x'' \in G$. f is said to be almost cliquish if it has the property at each point of X. By $AE(f)$, we denote the set of all points at which f is almost cliquish.

2. THE POINTS OF ALMOST CLIQUISH FUNCTIONS

From the definitions it is evident that $A(f) \subseteq AE(f)$. But the converse is not true. It follows from the following example:

Example 2.1: Let $f : R \to R$ be given by $f(x) = \begin{cases} 1 ; & x \in Q \\ 0 ; & \text{otherwise} \end{cases}$

Then f is almost cliquish on R. But f is not cliquish at any real number.

Almost cliquish functions need not to be bounded which follows from the following example:

Example 2.2: Let $f : [-1,1] \to R$ be given by $f(x) = \begin{cases} 1/x ; & 0 < x \le 1 \\ 0 ; & -1 \le x \le 0 \end{cases}$

f is almost cliquish in $[-1,1]$. But not bounded. Also, a real valued cliquish function defined on a compact space is not necessarily bounded which follows from example 2.2. Again, a bounded function need not be almost cliquish .

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Example 2.3: Let $f : R \to R$ be given by $f(x) = \begin{cases} 1 ; & x \in N \\ 0 ; & \text{otherwise} \end{cases}$

f is bounded but not almost cliquish on R.

It also be clear that the restriction of almost cliquish function to an open subspace is almost cliquish.

Theorem 2.4: For a function $f : X \to Y$, $AE(f)$ is a closed set.

Proof: Let x_0 be a limit point of $AE(f)$, U be an open neighbourhood of x_0 and $\varepsilon > 0$. Let $x_1 \in U \bigcap AE(f)$. Then ther is a preopen set $G \subseteq U$ such that $d(f(x'), f(x'')) < \varepsilon$ for all $x', x'' \in G$

So, $x_0 \in AE(f)$.

Corollary 2.5: If $f : X \to Y$ is almost cliquish at each point of a set dense in X then f is almost cliquish.

Corollary 2.6: For a function $f : X \to Y$ if $A(f)$ is dense in X then f is almost cliquish.

3. PROPERTIES OF ALMOST CLIQUISH FUNCTIONS

In this part Y denotes a normed linear space.

Proposition 3.1: If $f : X \to Y$ is cliquish and $g : X \to Y$ is almost cliquish then $f + g$ is almost cliquish.

Proof: Let $x_0 \in X$, U be an open neighbourhood of x_0 in X and $\varepsilon > 0$. Since f is cliquish at x_0, there exists a non empty open set $G \subseteq U$ such that $\| f(x) - f(y) \| < \frac{\varepsilon}{2}$ for all $x, y \in G$.

Choose a point $y_0 \in G$. Since g is almost cliquish at y_0, there exist a nonempty preopen set $H \subseteq G$ such that $\| g(x) - g(y) \| < \frac{\varepsilon}{2}$ for all $x, y \in H$.

Let $x, y \in H$. Then $\| (f+g)(x) - (f+g)(y) \| \leq \| f(x) - f(y) \| + \| g(x) - g(y) \| < \frac{\varepsilon}{2} + \frac{\varepsilon}{2} = \varepsilon$

So, $f + g$ is almost cliquish at x_0.

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Remark 3.2 : If f is cliquish at x_0 and g is almost cliquish at x_0 then it is not necessary that $f+g$ is almost cliquish at x_0. It follows from the following example.

Example 3.3: Let $f:[-1,1]\to R$ and $g:[-1,1]\to R$ be given by

$$f(x)=\begin{cases} 1/x\ ; & 0<x\le 1 \\ 0\ ; & -1\le x\le 0 \end{cases} \qquad g(x)=\begin{cases} 1/x\ ; & -1\le x<0 \\ 0\ ; & 0\le x\le 1 \end{cases}$$

Then $$(f+g)(x)=\begin{cases} 1/x\ ; & x\neq 0 \\ 0\ ; & x=0 \end{cases}$$

Clearly f is cliquish at 0, g is almost cliquish at 0, but $f+g$ is not almost cliquish at 0.

Proposition 3.4: If $f:X\to Y$ is almost cliquish at a point $x_0\in X$ and $c\in R$ then cf is almost cliquish at x_0.

Proof: If $c=0$ then $(cf)(x)=0$, for all $x\in X$. Clearly cf is almost cliquish at x_0.

Suppose that $c\neq 0$. Let U be an open neighbourhood of x_0 in X and $\varepsilon>0$. Then there exists a non empty preopen set $G\subseteq U$ such that $\|f(x)-f(y)\|<\dfrac{\varepsilon}{|c|}$ for all $x,y\in G$.

Let $x,y\in G$. Then $\|(cf)(x)-(cf)(y)\|<\varepsilon$ for all $x,y\in G$. So, cf is almost cliquish at x_0.

Proposition 3.5: If $f:X\to Y$ is bounded and cliquish and if $g:X\to Y$ is bounded and almost cliquish then fg is bounded and almost cliquish.

Proof : Since f and g are bounded , fg is bounded.

Put $M=Sup\{\|f(x)\|;x\in X\}$ and $K=Sup\{\|g(x)\|;x\in X\}$

Let $x_0\in X, U$ be an open neighbourhood of of x_0 in X and $\varepsilon>0$. Since f is cliquish at x_0 , there exists a non empty open set $G\subseteq U$ such that $\|f(x)-f(y)\|<\varepsilon$ for all $x,y\in G$.

Choose a point $y_0\in G$. Since g is almost cliquish at y_0, there exists a nonempty preopen set $H\subseteq G$ such that $\|g(x)-g(y)\|<\varepsilon$ for all $x,y\in H$.

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Let $x, y \in H$. Then

$\|(fg)(x)-(fg)(y)\| \le \|f(x)\|\|g(x)-g(y)\| + \|g(y)\|\|f(x)-f(y)\| < (M+K)\varepsilon.$

Hence fg is almost cliquish at x_0.

Proposition 3.6: If f is a bounded real valued cliquish function defined on X and g is abounded real valued almost cliquish function defined on X then

(i) $f \vee g$ and (ii) $f \wedge g$ are also bounded, almost cliquish on X ,where $(f \vee g)(x) = Max\{f(x), g(x)\}$ and $(f \wedge g)(x) = Min\{f(x), g(x)\}$.

Proof of (i): Let $x_0 \in X$. Let U be an open neighbourhood of of x_0 in X and $\varepsilon > 0$. Since f is cliquish at x_0, there exists a non empty open set $G \subseteq U$ such that $\|f(x)-f(y)\| < \frac{\varepsilon}{2}$ for all $x, y \in G$.

Choose a point $y_0 \in G$. Since g is almost cliquish at y_0, there exists a nonempty preopen set $H \subseteq G$ such that $\|g(x)-g(y)\| < \frac{\varepsilon}{2}$ for all $x, y \in H$.

Let $x, y \in H$. Then $\|f(x)-f(y)\| < \frac{\varepsilon}{2}$

$-\frac{\varepsilon}{2} < f(x)-f(y) < \frac{\varepsilon}{2} \Rightarrow f(y) < f(x)+\frac{\varepsilon}{2}$ and $f(x) < f(y)+\frac{\varepsilon}{2}$

So, $f(y) < (f \vee g)(x)+\frac{\varepsilon}{2}$ and $f(x) < (f \vee g)(y)+\frac{\varepsilon}{2}$

Similarly, $g(y) < (f \vee g)(x)+\frac{\varepsilon}{2}$ and $g(x) < (f \vee g)(y)+\frac{\varepsilon}{2}$

Hence $(f \vee g)(y) \le (f \vee g)(x)+\frac{\varepsilon}{2}$ and $(f \vee g)(x) \le (f \vee g)(y)+\frac{\varepsilon}{2}$

$\Rightarrow |(f \vee g)(x)-(f \vee g)(y)| \le \frac{\varepsilon}{2} < \varepsilon$

So $(f \vee g)$ is almost cliquish at x_0.

The proof of (ii) follows from the fact that $f \wedge g = -((-f) \vee (-g))$ and from (i).

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Review Article

A DISCRETE IN TIME STOCHASTIC INVENTORY MODEL UNDER TRADE CREDIT FINANCING DEPENDENT ON THE ORDERING QUANTITY

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A B S T R A C T

In this paper attempt has been made to study a probabilistic EOQ model under permissible delay in payments where delay period is not fixed dependent upon the ordering quantity and demand is random.

Keywords: *EOQ model, random demand, trade credit financing, variable credit period, ordering quantity.*

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1. INTRODUCTION

The classical economic order quantity (EOQ) model is based on the implicit assumption that the retailer must pay for the items as soon as he/she receives the items from a supplier. In real life situations, suppliers usually offer their customers a delay period (credit period) for settling the account and no interest is charged on the outstanding account if the account is settled by the end of the credit period. The supplier will charge higher interest if the account is not settled within the trade credit period. The suppliers often make use of this policy to promote their commodities.

Goyal (1985) first established an EOQ model under permissible delay in payments. Chung (2001) developed an alternative method to determine the optimal ordering policy under the condition of delay in payments. Shah et al. (1993) studied the same model by allowing shortages. Shah and Shah (1993) first studied a probabilistic model where delay in payment is permissible. Shah and Shah (1998) extended the same model, where time was treated as a continuous variable. In another paper, Shah and Shah (1998) developed a discrete-time

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probabilistic inventory model under permissible delay in payments. Many researchers , such as Aggarwal and Jaggy (1995), Hwang and Shinn (1997), Jamal et al. (1997), Sarker et al. (2001), Shah and Shah (1998)and Huang (2003)also developed inventory models taking permissible delay in payment into account.

All inventory models mentioned above were made under the consideration that the trade credit policy is independent of the order quantity. Recently Chang et al.(2003) and Chung et al. (2001) developed EOQ models under permissible delay in payment, where the trade credit period is linked to the order quantity. When the order quantity is less than the quantity at which the delay in payment is permitted, the payment for the items must be made immediately. Otherwise, a fixed trade credit is permitted.

The supplier uses this policy to encourage retailer to order a larger quantity. However these above mentioned models were completely deterministic in nature. In reality, this trade credit period cannot be fixed. If it is fixed, then the retailer will not be interested in buying higher quantity than the fixed quantity at which delay in payment is permitted. To reflect this situation, we have developed an inventory model under the assumption that the trade credit period is not only linked to ordering quantity but also varies with the ordering quantity. We have also assumed that the demand is a continuous random variable following some probabilistic distribution.

In this chapter, we have developed a stochastic inventory model under variable trade credit period dependent on the ordering quantity. We have assumed that the demand is a continuous random variable following some probability density function. We have optimized the relevant cost for the retailer. We have developed our model for discrete cycle time. Lastly, results obtained in this chapter are illustrated with the help of a set of numerical examples.

2. ASSUMPTION AND NOTATION

The inventory models under consideration are formulated with the following assumptions and notations:

(i) On hand inventory of the system is reviewed regularly at an interval of length T, which is the fixed cycle length. At the end of each scheduling period T, units are ordered so as to bring the on-hand inventory level to a level Q.

(ii) The demand x during any scheduling period, follows a probability density function (p.d.f.) $f(x|T), a(T) \le x \le b(T)$ with $\mu(T) = E(x|T) = \sum_{a(T)}^{b(T)} xf(x|T) = RT$ (say) in discrete sense, where $\mu(T)$ is the mean demand during T and $R = \frac{\mu(T)}{T}$ denotes the average expected demand per unit time during a cycle. It is further assumed that the p.d.f. $f(x|T)$ of the demand x during T is sufficiently well behaved so that all the expected costs discussed below exist. Also the distribution of the demand is assumed to be stationary over the planning horizon.

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(iii) In the process of obtaining the exact solution, we have assumed the forms of the maximum annual demand $b(T)$ as $b(T) = PRT$, where $P \geq 1$ is a known constant.

(iv) The rate of replenishment is infinite.

(v) Lead-time is zero.

(vi) Shortages are not allowed.

(vii) W is the fixed quantity at which the delay in payment is permitted.

(viii) A, C, S, H are the ordering cost per order, unit purchase cost per item, unit selling cost per item and unit stock holding cost per item per unit time, respectively, and are known constants. It is also assumed that $S \geq C$.

(ix) To encourage retailer to buy larger items or quantity, we have assumed that if the retailer buys items from supplier less than a fixed quantity W (say) then the retailer will not get some facilities such as delay in payment, otherwise if the retailer buys more than others. Therefore delay period is increasing function of Q. For simplicity, in our paper, we have assumed the delay period is linearly dependent on ordering quantity. i.e., if $Q \geq W$, a variable credit period $M(M_0 + \alpha Q; \alpha \in [0,1])$, is permitted; otherwise a delay in payment is not permitted. The reasons for choosing such values of α is that if $\alpha < 0$ then $M_0 + \alpha Q$ will be a decreasing function of Q which is unrealistic assumption. If $\alpha > 1$ then the delay period will be so high that the supplier may face some problem to capitalize his own profit. Therefore we have assumed. But generally α should be in $[0, a]$, where a is close to 0 and less than 1.

(x) M and N are the retailer's trade credit period offered by the supplier and the customer's trade credit period offered by the retailer respectively where $M \geq N$.

(xi) When the retailer must pay the amount of purchasing cost to the supplier, the retailer will borrow 100% purchasing cost from the bank to pay off the account with rate I_p, When $T \geq M$, the retailer returns money to the bank at the end of the inventory cycle. However, when $T \leq M$, the retailer returns money to the bank at $T = M$.

(xii) If the credit period is shorter than the cycle length, the retailer can sell the items, accumulate sales revenue and earn interest with rate I_e throughout the inventory cycle, where $I_p \geq I_e$.

(xiii) $TVC(T)$, a function of T, is the total relevant cost and T^* is the optimal cycle time.

3. MODEL FORMULATION

Since the inventory level decreases due to demand of the items, the difference equation describing the inventory level $Q_x(t)(t = 0,1,2,....T)$ of the system at different points of time during scheduling period T is

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$$Q_x(t+1) = Q_x(t) - \frac{x}{T}, \qquad t = 0,1,2,...T \qquad (1)$$

Using the boundary condition $Q_x(0) = Q,$ the solution of equation (1) becomes

$$Q_x(t) = Q - \frac{x}{T}t, \qquad t = 0,1,2,...T \qquad (2)$$

Since shortages are not allowed, using the condition $Q_x(T) = 0$, when $x = b(T),$ we obtain

$$Q = b(T) \qquad (3)$$

Using equation (3), equation (2) becomes

$$Q_x(t) = b(T) - \frac{x}{T}t, \qquad t = 0,1,2,...T \qquad (4)$$

The average expected inventory in the system per unit time is

$$\frac{1}{T}\sum_{t=0}^{T} E(Q_x(t)) = (2P-1)(T+1)\frac{R}{2}.$$

The total annual variable cost consists of the following elements. Two situations may arise.

$$(I)\ \frac{W}{PR} \leq M = M_0 + \alpha PRT.$$

$$(II)\ \frac{W}{PR} > M = M_0 + \alpha PRT.$$

Case I: $\frac{W}{PR} \leq M = M_0 + \alpha PRT.$

(a) Ordering cost per unit time = $\frac{\mathrm{A}}{T}$.

(b) Stock holding cost per unit time $= (2P-1)(T+1)\frac{RH}{2}$

(c) Now according to our assumption, three possible cases can occur namely $0 < T < \frac{W}{PR}$, $\frac{W}{PR} \leq T \leq M$ and $T \geq M$. These three cases are treated separately which are discussed below.

Case (i) $0 < T < \frac{W}{PR}$

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Expected interest payable per unit time = $\frac{CQTI_p}{T} = CI_pPRT$.

Expected interest earned per unit time = $\frac{SI_e}{T}\sum_{t=o}^{T} E(\frac{x}{T})t = \frac{SI_eR(T+1)}{2}$.

Case (ii) $\frac{W}{PR} \le T \le M = M_0 + \alpha PRT$

Expected interest payable per unit time =0.

Expected interest earned per unit time = $\frac{SI_e}{T}\left[\sum_{t=0}^{T} E(\frac{x}{T})t + E(\frac{x}{T})T(M-T)\right]$

$$= \frac{RSI_e}{T}\left[M_0 + \alpha PRT - \frac{(T+1)}{2}\right]$$

Case(iii) $T \ge M = M_0 + \alpha PRT$

Expected interest payable per unit time = $\frac{CQ(T-M)I_p}{T} = \frac{CPR(T-M_0-\alpha PRT)I_p}{T}$.

Expected interest earned per unit time= $\frac{SI_e}{T}\left[\sum_{t=0}^{T} E(\frac{x}{T})t\right] = \frac{RSI_e}{2}(T+1)$

From the above arguments, the relevant total cost per unit time for the retailer can be expressed as

$$TVC(T) = \begin{cases} TVC_1(T) & if\ 0 < T < \frac{W}{PR} \\ TVC_2(T) & if\ \frac{W}{PR} \le T \le M \\ TVC_3(T) & if\ \ T \ge M \end{cases} \quad (5)$$

Where $TVC_1(T) = \frac{A}{T} + (2P-1)(T+1)\frac{RH}{2} + CI_pPRT - \frac{SI_eR(T+1)}{2}$ (6)

$$TVC_2(T) = \frac{A}{T} + (2P-1)(T+1)\frac{RH}{2} - \frac{RSI_e}{T}\left[M_0 + \alpha PRT - \frac{(T+1)}{2}\right] \quad (7)$$

$$TVC_3(T) = \frac{A}{T} + (2P-1)(T+1)\frac{RH}{2} + \frac{CPR(T-M_0-\alpha PRT)I_p}{T} - \frac{RSI_e}{2}(T+1) \quad (8)$$

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Case II: $\frac{W}{PR} > M = M_0 + \alpha PRT.$

I this case equation (5) can be written as follows:

$$TVC(T) = \begin{cases} TVC_1(T) & if\ 0 < T < \frac{W}{PR} \\ TVC_3(T) & if \quad T \geq \frac{W}{PR} \end{cases}$$

(9)

4. COMPUTATIONAL PROCEDURE

Since T must be non-negative integer, the necessary condition for $TVC(T)$ to be a minimum at T^* is $\Delta TVC(T^* - 1) \leq 0 \leq \Delta TVC(T^*)$, where $\Delta TVC(T) = TVC(T+1) - TVC(T)$.

5. ALGORITHM FOR COMPUTATION

Step 1. Find T^* from $TVC(T)$ present in equation (5) using computational procedure.

Step 2. If $\frac{W}{PR} \leq M_0 + \alpha PRT^*$, then $T_0^* = T^*$.

Step 3. Find T^* from $TVC(T)$ present in equation (9) using computational procedure.

Step 4. If $\frac{W}{PR} \geq M_0 + \alpha PRT^*$, then $T_{00}^* = T^*$.

Step 5. If only T_0^* exits and T_{00}^* does not exits, then T_0^* is the optimal cycle time.

Step 6. If only T_{00}^* exits and T_0^* does not exits, then T_{00}^* is the optimal cycle time.

Step 7. If both T_0^* and T_{00}^* exits, then calculate $TVC(T_0^*)$ and $TVC(T_{00}^*)$

Step 8. If $TVC(T_0^*) \geq TVC(T_{00}^*)$, then optimum cycle time is T_{00}^*, otherwise T_0^* is the optimal cycle time.

6. NUMERICAL EXAMPLE

Let us consider inventory system with the following parameters in appropriate

units.

(i) $A = 50$, $H = 0.5$, $C = 10$, $S = 12$, $\alpha = 0.5$, $M_0 = 2$, $I_e = 0.005$, $I_p = 0.05$, $P = 2$, $R = 10$, $W = 30$.. Hence optimal cycle time is 5 and optimal cost is 18.0345

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(ii) A = 50, H =0 .5, C = 10, S = 12, α=0.5, M_0 =2, I_e =0.005, I_p =0.05,P =2, R = 9, W = 30.. Hence optimal cycle time is 3 and optimal cost is 28.7847

7. CONCLUSION

This chapter deals with a probabilistic economic order quantity inventory model under condition of permissible delay in payments to take the order quantity into account. To reflect realistic business situations, I assume that the trade credit period is not only linked to the order quantity but also varies with the ordering quantity. If $Q < W$, the delay in payments is not permitted. Otherwise, a variable trade credit period $M = M_0 + \alpha Q$ is permitted. It is also assumed that demand rate follows a probability density function. Under these assumptions, the model is developed. I develop an algorithm, which will help one to determine the optimal T^* efficiently. Numerical examples are provided for illustration.

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Research Article

SOME RESULTS ON STRONGLY k^{th} HÖLDERIAN FUNCTIONS

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A B S T R A C T

The concept of strongly k^{th} Hölderian functions on an interval $[a, b]$ which generalizes the notion of Hölderian function of positive order on $[a, b]$ is introduced.

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1. INTRODUCTION, NOTATIONS AND PRELIMINARIES

A function f of a real variable is said to be Hölderian (Lipschitzian) of order $\alpha > 0$ on $[a, b]$ if there exists a positive constant k such that for any two points

$$x, y \in [a, b],\ |f(x) - f(y)| \leq K|x - y|^{\alpha}.$$

Symbolically we write as $f \in L_{ip}(\alpha, K, [a, b])$.

Generalization of Hölderian functions and locally k^{th} Hölderian functions was presented by De Sarkar and Panda; Barman and De Sarkar. The use of higher order divided differences was first applied by A. M. Russell to obtain BV_kfunctions on an interval$[a, b]$. Consequently many workers pursued Russell's idea to generalize many related concepts.

We denote by $\pi(x_0, x_1, x_2, \ldots, x_k)$ a sub-division of the closed interval $[a, b]$ of the form $a \leq x_0 < x_1 < x_2 < \ldots < x_k \leq b$.

Let f be a real valued function defined on the closed interval $[a, b]$ and let $k(> 1)$ be a positive integer. If $x_0, x_1, \ldots, x_k$ are any $(k + 1)$ distinct points, not necessarily in linear order, in $[a, b]$. Then the k^{th} divided difference of f is defined by

$$Q_k(f; x_0, x_1, x_2, \ldots, x_k) = \sum_{i=0}^{k} \{\frac{f(x_i)}{\prod_{j=0, j\neq i}^{k}(x_i - x_j)}\}.$$

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Definition 1.1. The function f is said to be k^{th} Hölderian of order $\alpha > 0$ with constant $M > 0$ on $[a, b]$ if for any set of $(k+1)$ points $x_0 < x_1 < x_2 < \ldots < x_k$ in $[a, b]$, we have

$$|Q_{k-1}(f; x_0, x_1, \ldots, x_{k-1}) - Q_{k-1}(f; x_1, x_2, \ldots, x_k)| \leq M(x_k - x_0)^{\alpha}$$

In this case we write, $f \in H_k(\alpha, M, [a, b])$.

2. MAIN RESULTS

Definition 2.1. The function f is said to be strongly k^{th} Hölderian of order $\alpha > 0$ with constant $M > 0$ at the point $p \in [a, b]$, if there exists a $\delta > 0$ such that for any set of $(k+1)$ points $x_0 < x_1 < \ldots < x_k$ in $[p - \delta, p + \delta]$, we have

$$|Q_{k-1}(f; x_0, x_1, \ldots, x_{k-1}) - Q_{k-1}(f; x_1, x_2, \ldots, x_k)| \leq M(x_k - x_0)^{\alpha}$$

It is to be noted that at the end points a and b we define such functions by considering right and left closed neighborhoods respectively and we write, $f \in S_k(\alpha, M, p, [a, b])$.

Clearly $f \in H_k(\alpha, M, [a, b])$ then $f \in S_k(\alpha, M, p, [a, b])$ for all $p \in [a, b]$.

***Remark* 2.1**. If $f \in S_k(\alpha, M, p, [a, b])$ for all $p \in [a, b]$, where $\alpha > 1$ then it can be shown that $f^k(x) = 0$ for all $x \in (a, b)$ and $f_+^k(a) = f_-^k(b) = 0$. Hence f is a polynomial of degree $(k-1)$ atmost and so $f \in H_k(\beta, M, [a, b])$, for all $\beta > 0$.

Theorem 2.1. If $f \in S_k(\alpha, M, p, [a, b])$, $k \geq 0$, $\alpha > 0$ then $Q_k(f; x_0, x_1, x_2, \ldots, x_k)$ is bounded when $p - \delta \leq x_i \leq p + \delta$, $(i = 0,1,2, \ldots, k)$.

Proof. We consider a fixed subdivision $\pi(a_0, a_1, \ldots, a_k)$ of $[p - \delta, p + \delta]$ and write

$A = |Q_k(f; a_0, a_1, \ldots, a_k)|$. Let $x_0, x_1, x_2, \ldots, x_{2k+1}$ be any collection of points with

$p - \delta \leq x_0 < x_1 < x_2 < \ldots < x_{2k+1} \leq p + \delta$. We see that

$|Q_k(f; x_0, x_1, \ldots, x_k) - Q_k(f; x_{k+1}, x_{k+2}, \ldots, x_{2k+1})|$

$= |[Q_k(f; x_0, x_1, \ldots, x_k) - Q_k(f; x_1, x_2, , \ldots, x_{k+1})] +$

$[Q_k(f; x_1, x_2, \ldots, x_{k+1}) - Q_k(f; x_2, x_3, , \ldots, x_{k+2})] + \cdots +$

$[Q_k(f; x_k, x_{k+1}, \ldots, x_{2k}) - Q_k(f; x_{k+1}, x_{k+2}, , \ldots, x_{2k+1})]|$

$\leq |Q_k(f; x_0, x_1, \ldots, x_k) - Q_k(f; x_1, x_2, , \ldots, x_{k+1})| +$

$|Q_k(f; x_1, x_2, \ldots, x_{k+1}) - Q_k(f; x_2, x_3, , \ldots, x_{k+2})| + \cdots +$

$|Q_k(f; x_k, x_{k+1}, \ldots, x_{2k}) - Q_k(f; x_{k+1}, x_{k+2}, , \ldots, x_{2k+1})|$

$\leq M(x_{k+1} - x_0)^{\alpha} + M(x_{k+2} - x_1)^{\alpha} + \cdots + M(x_{2k+1} - x_k)^{\alpha}$

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$< (\mathrm{k}+1)\mathrm{M}[(p+\delta)-(p-\delta)]^{\alpha}$

$= (\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}$

$\therefore |Q_k(f; x_0, x_1, x_2, \dots, x_k) - Q_k(f; x_{k+1}, x_{k+2}, , \dots, x_{2k+1})| < (\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}$ … (1)

We shall show that for all choices of $y_0, y_1, \dots, y_k$ such that $p-\delta \le y_0 < y_1 < \dots < y_{2k+1} \le p+\delta$

$|Q_k(f; y_0, y_1, y_2, \dots, y_k)| \le (\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha} + \mathrm{A}$ … (2)

Suppose first that $y_k < p+\delta$ and choose $(y_{i+k})_{i=1}^{k+1}$ such that

$max(a_k, y_k) < y_{k+1} < y_{k+2} < \cdots < y_{2k+1} \le p+\delta.$

Applying (1) to the subdivision $(x_i)_{i=0}^{2k+1}$, where $x_i = y_i$ for all i, we deduce that

$|Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1})| < (k+1)M(2\delta)^{\alpha}$

and applying (1) to the subdivision $(x_i)_{i=0}^{2k+1}$, where $x_i = a_i$, $(0 \le i \le k)$ and

$x_i = y_i$, $(k+1 \le i \le 2k+1)$ we obtain

$|Q_k(f; a_0, a_1, a_2, \dots, a_k) - Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1})| < (k+1)M(2\delta)^{\alpha}.$

Therefore, $|Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; a_0, a_1, \dots, a_k)|$

$= |Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1}) +$

$Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1}) - Q_k(f; a_0, a_1, \dots, a_k)|$

$\le |Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1})|$

$+ |Q_k(f; y_{k+1}, y_{k+2}, \dots, y_{2k+1}) - Q_k(f; a_0, a_1, \dots, a_k)|$

$< 2(k+1)M(2\delta)^{\alpha}$

Thus $|Q_k(f; y_0, y_1, \dots, y_k)|$

$= |Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; a_0, a_1, \dots, a_k) + Q_k(f; a_0, a_1, \dots, a_k)|$

$\le |Q_k(f; y_0, y_1, \dots, y_k) - Q_k(f; a_0, a_1, \dots, a_k)| + |Q_k(f; a_0, a_1, \dots, a_k)|$

$\le 2(\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha} + \mathrm{A}$ …(3)

Hence (2) follows in this case.

Again, if $p-\delta < y_0$ and $y_k = p+\delta$, we can deduce this case, by choosing $(y_{i+k})_{i=1}^{k+1}$ such that $p-\delta \le y_{k+1} < y_{k+2} < \cdots < y_{2k+1} < \min(a_0, y_0)$ and setting $x_0 = y_{k+i}$, $x_i = y_{k+i+1}$, $(1 \le i \le k)$ and $x_{k+i} = a_{i-1}$, $(1 \le i \le k+1)$, to the previous case.

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The last case when $p-\delta=y_0$ and $y_k=p+\delta$, we choose $y_{k-1}<\beta<y_k=p+\delta$ then by the previous case, we must have $|Q_k(f;y_0,y_1,\dots,y_{k-1},\beta)|\leq 2(\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}+\mathrm{A}$ and

$|Q_k(f;y_1,\dots,y_{k-1},\beta,y_k)|\leq 2(\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}+\mathrm{A}$.

We now have $|Q_k(f;y_0,y_1,\dots,y_k)|$

$=|\alpha Q_k(f;y_0,y_1,\dots,y_{k-1},\beta)+\gamma Q_k(f;y_1,y_2\dots,y_{k-1},\beta,y_k)|;\alpha+\gamma=1$

$\leq(\alpha+\gamma)[2(\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}+\mathrm{A}]$

$=2(\mathrm{k}+1)\mathrm{M}(2\delta)^{\alpha}+\mathrm{A}$ …(4)

Hence the theorem.

Definition 2.2. We define

$$S_k(\alpha,p,[a,b])=\bigcup_{M>0}S_k(\alpha,M,p,[a,b])\quad\left(=\bigcup_{M=1}^{\infty}S_k(\alpha,M,p,[a,b])\right)$$

and

$$S_k(p,[a,b])=\bigcup_{M>0}S_k(\alpha,p,[a,b])$$

The function $f\in S_k(\alpha,p,[a,b])$ $\left(f\in S_k(p,[a,b])\right)$ are called Strongly k^{th} Hölderian of order $\alpha>0$ (Strongly k^{th} Hölderian) at the point $p\in[a,b]$.

Also we define

$$S_k[a,b]=\bigcap_{p\in[a,b]}S_k(p,[a,b])$$

The function $f\in S_k[a,b]$ are called Strongly k^{th} Hölderian on $[a,b]$.

Again we define

$$S_k(\alpha,M,[a,b])=\bigcap_{p\in[a,b]}S_k(\alpha,M,p,[a,b])$$

The function $f\in S_k(\alpha,M,[a,b])$ are called uniformly strongly k^{th} Hölderian of order α on $[a,b]$.

Theorem 2.2. Let $0<\alpha_1<\alpha_2$, $p\in[a,b]$ and $M>0$, then

(i) $S_k(\alpha_2,M,p,[a,b])\subset S_k(\alpha_1,M,p,[a,b])$

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(ii) $S_k(\alpha_2, p, [a,b]) \subset S_k(\alpha_1, p, [a,b])$.

Proof. We can assume in the definition of $S_k(\alpha, M, p, [a,b])$ that $\delta < 1$ and $\delta < \frac{1}{2}$ respectively. Then for any set of points $x_0 < x_1 < x_2 < \ldots < x_k$ in $(p-\delta, p]$, we have

$(x_k - x_0)^{\alpha_1} \geq (x_k - x_0)^{\alpha_2}$.

Similarly for any set of points $x_0 < x_1 < x_2 < \ldots < x_k$ in $[p, p+\delta)$, we have

$(x_k - x_0)^{\alpha_1} \geq (x_k - x_0)^{\alpha_2}$.

From these inequality *(i)* follows. It is easy to see that *(ii)* follows from *(i)*.

Note: We note that $S_k(p, [a,b]) = \cup_{n=1}^{\infty} S_k\left(\frac{1}{n}, p, [a,b]\right)$.

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Review Article

CONDUCTOMETRIC INVESTIGATION: PHYSICO-CHEMICAL STUDIES IN DIFFERENT SOLVENT SYSTEMS

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A B S T R A C T

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte of solutions. The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Fortunately for us, accurate theories of electrolytic conductances are available to explain the results even upto a concentration limit of $K\,d$ (K = Debye-Huckel-length, d = distance of closest approach of free ions). Recent development of experimental technique provides an accuracy to the extent of 0.01% or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation however, is the colligative-like nature of the information obtained.

Keywords: *Ion-ion interaction, ion-solvent interaction, short range cation anion interaction, solvent separated pair, contact pair*

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1. INTRODUCTION

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilised to determine the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents. The conductometric method in conjunction with viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions. However, the choice and application of theoretical equations as well as equipment and experimental techniques are of great importance for precise measurements. These aspects

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have been described in details in a number of authoritative books and reviews [Evans *et al.* 1973 and Banthel *et al.* 1971].

The study of conductance measurements were pursued vigorously both theoretically and experimentally and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects and our discussion will be related to the studies in aqueous, non-aqueous, pure and mixed solvents.

The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager in deriving the Kohlrausch's equation:

$$\Lambda = \Lambda_0 - S\sqrt{c} \qquad \ldots\ldots\ldots(1)$$

where, $$S = \alpha \Lambda_0 + \beta \qquad \ldots\ldots\ldots(2)$$

$$\alpha = (Ze)^2 K/3(2+\sqrt{2})\varepsilon_r R T c^{1/2} = 82.406 \times 10^4 Z^3/(\varepsilon_r T)^{3/2} \qquad \ldots\ldots\ldots(3)$$

$$\beta = Z^2 e F K/3\pi\eta c^{1/2} = 82.487 Z^3/\eta(\varepsilon_r T)^{1/2} \qquad \ldots\ldots\ldots(4)$$

The equation took no account for the short range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent. In the subsequent years, Pitts and Fuoss and Onsager independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned. The original F.O. equation was modified by Fuoss and Hsia who recalculated the relaxation field, retaining the terms which had previously been neglected.

The equation usually employed is of the form:

$$\Lambda = \Lambda_0 - \alpha\Lambda_0 c^{1/2}/(1+\kappa a)(1+\kappa a/\sqrt{2}) - B c^{1/2}/(1+\kappa a) + G(\kappa a) \qquad \ldots\ldots\ldots(5)$$

where $G(\kappa a)$ is a complicated function of the variable. The simplified form:

$$\Lambda = \Lambda_0 - S\sqrt{c} + E c \ln c + J_1 c - J_2 c^{1/2} \qquad \ldots\ldots\ldots(6)$$

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is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini. Further, correction of the equation (6) was made by Fuoss and Accascina.

They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + E\,c \ln c + J_1\,c - J_2\,c^{3/2} - B\,\Lambda_0\,c \qquad \ldots\ldots\ldots(7)$$

In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions.

2. IONIC ASSOCIATION

The equation (4) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against $\sqrt{c}$ (limiting Onsager equation) are used to assign the dissociation or association of electrolytes. Thus, if Λ^0_{expt} is greater than Λ^0_{theo}, i.e., if positive deviation occurs (ascribed to short range hard core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviation ($\Lambda^0_{expt} < \Lambda^0_{theo}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_0 + B$) occurs, the electrolyte may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in Λ^0_{expt} and Λ^0_{theo} would be considerable with increasing association.

Conductance measurements help us to determine the values of the ion-pair association constant, K_A for the process:

$$M^{z+} + A^{z-} = MA \qquad \ldots\ldots\ldots(8)$$

$$K_A = (1 - \alpha) \,/\, \alpha^2\, c\, \gamma_{\pm}^2 \qquad \ldots\ldots\ldots(9)$$

and,
$$\alpha = 1 - \alpha^2\, K_A\, c\, \gamma_{\pm}^2 \qquad \ldots\ldots\ldots(10)$$

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For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation or Shedlovsky's equation:

$$T(Z)/\Lambda = 1/\Lambda_0 + K_A/(\Lambda_0)^2 c\gamma_{\pm}^2 \Lambda / T(Z) \quad \text{.....(11)}$$

where $T(Z) = F(Z)$ (Fuoss-Kraus method) and $1/T(Z) = S(Z)$ (Shedlovsky's method):

$$F(Z) = 1 - Z(1 - Z(1 - Z(1 - \cdots)^{1/2})^{1/2})^{1/2} \quad \text{.....(12)}$$

and $$1/T(Z) = S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \cdots \quad \text{.....(13)}$$

The plot of $T(Z)/\Lambda$ against $c\gamma_{\pm}^2\Lambda/T(Z)$ should be a straight line having $1/\Lambda_0$ for its intercept and $K_A/(\Lambda_0)^2$ for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (11).

The Fuoss-Hsia conductance equation for associated electrolytes is given by:

$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + \overline{E(\alpha c)} \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A\Lambda\gamma_{\pm}^2(\alpha c)$ ...(14)

The equation was modified by Justice. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c}) + \overline{E(\alpha c)} \ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \quad \text{.....(15)}$$

$$(1 - \alpha)/\alpha^2 c\gamma_{\pm}^2 = K_A, \quad \text{.....(16)}$$

$$\ln\gamma_{\pm} = -Kq^{1/2}/(1 + KR\sqrt{\alpha c}) \quad \text{.....(17)}$$

The conductance parameters are obtained from a least square treatment after setting:

$$R = q = e^2/2\varepsilon KT \quad \text{(Bjerrum's critical distance)} \quad \text{.....(18)}$$

According to Justice, the method of fixing the J-coefficient by setting $R = q$ clearly permits a better defined value of K_A to be obtained. Since the equation (15) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as must as possible by J_2 rather than by K_A, whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction.

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From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach, a^o, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss:

$$K_A = (4\pi N a^3/3000) \exp(e^2/a\varepsilon\kappa T) \quad \text{.....(19)}$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^o. The distance parameter was finally determined from the more general equation due to Bjerrum:

$$K_A = 4\pi Na/1000 \int_{r=a}^{r=q} r^2 \exp(Z^2 e^2/r\varepsilon\kappa T)\, dr \quad \text{.....(20)}$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret.

3. ION SIZE PARAMETER AND IONIC ASSOCIATION

For plotting, equation (5) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - E\,c \ln c = \Lambda_0 + (J - B\Lambda_0)\,c = \Lambda_0 + J_1 c \quad \text{.....(21)}$$

with J_2 term omitted.

Thus, a plot of Λ_0 vs c gives a straight line with Λ_0 as intercept and J or $(J - B\Lambda_0)$ as slope. Assuming $(B\Lambda_0)$ to be negligible, a^o values can be calculated from J. The a^o value obtained by this method for DMSO were much smaller than would be expected from sums of crystallographic radii. One of the reasons attributed to it is ion-solvent interactions which are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in a^o values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction (which should be $B\Lambda c$ rather than $B\Lambda_0 c$) leads to a larger value of a^o [Tissier *et al.* 1978] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J.

Fuoss in 1975 proposed a new conductance equation. He subsequently put forward another conductance equation in 1978 which replaces the old equations suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

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(i) Those which find an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij} = a$. The nearest neighbours to a contact pair are the solvent molecules which form a cage around the pairs.

(ii) Those with overlapping Gurney's co-spheres (solvent separated pairs). For them $r_{ij} = (a + ns)$, where n is generally 1 but may be 2, 3 etc.; 's' is the diameter of sphere corresponding to the average volume (actual plus free) per solvent molecule.

(iii) Those which find no other unpaired ion in a surrounding sphere of radius R, where R is the diameter of the co-sphere (unpaired ions).

Thermal motions and interionic forces establish a steady state, represented by the equilibria:

$$A^+ + B^- = (A^+ \ldots\ldots\ldots B^-) \quad = \quad A^+B^- \quad = \quad AB \qquad \ldots\ldots\ldots(22)$$

Solvent separated pair Contact pair Neutral molecule

Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$

e.g.. H_3O^+ and CH_3COO^-. Let γ be the fraction of solute present as unpaired ($r > R$) ions. The concentration of unpaired ion becomes $c\,\gamma$, if α is the fraction of paired ions ($r \leq R$), then the concentration of the solvent separated pair is $c\,(1-\gamma)\,(1-\gamma)$ and that of contact pair is $\alpha\, c\,(1-\alpha)$.

The equation constants for (22) are:

$$K_R = (1-\alpha)(1-\gamma)/c\,\gamma^2 f^2 \qquad \ldots\ldots\ldots(23)$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_S/KT) = e^{-\epsilon} \qquad \ldots\ldots\ldots(24)$$

where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations and can be calculated by continuum theory. K_S is the constant describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_S is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ϵ is E_S measured in units of KT. Now:

$$(1-\alpha) = 1/(1+K_S) \qquad \ldots\ldots\ldots(25)$$

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And the conductometric pairing constant is given by:

$$K_A = (1 - \alpha)/\ c\,\gamma^2 f^2 = K_R/(1 - \alpha) = K_R\,(1 + K_S) \qquad \ldots\ldots\ldots(26)$$

The equation determines the concentration of active ions which produce long-range interionic effects. The contact pairs react as dipoles to an external field, X and contribute only to changing current. Both contact pairs and solvent separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculated long-range effects (activity coefficients, relaxation field ΔX and electrophoresis $\Delta\Lambda_e$). The various patterns can all be reproduced by theoretical fractions of the form:

$$\Lambda = p[\ \Lambda_0\,(1 + \Delta X/X) + \Delta\Lambda_e\ ]\ = p[\ \Lambda_0\,(1 + R\,X) + E\,L\ ] \qquad \ldots\ldots\ldots(27)$$

which is a three parameter equation $\Lambda = \Lambda_0\ (c,\ \Lambda_0,\ R,\ E_S)$ $\Delta X/X$ (the relaxation field, RX) and $\Delta\Lambda_e$ (the electrophoretic counter current, EL) are long-range effects due to electrostatic interionic forces and p is the fraction of solute which contributes to conductance current. R is the diameter of the Gurney co-sphere.

The parameter K_S (or E_S) is a catch-all for all short-range effects:

$$p = 1 - \alpha(1 - \alpha) \qquad \ldots\ldots\ldots(28)$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity $(-E_S/K\,T) >> 1$ and the equation becomes:

$$\Lambda = \gamma\,[\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e] \qquad \ldots\ldots\ldots(29)$$

The equilibrium constant for the effective reaction, $A^+ + B^- = AB$, is then:

$$K_\Lambda = (1 - \alpha)/c\,\gamma^2 f^2 \approx K_R\,K_S \qquad \ldots\ldots\ldots(30)$$

as $K_S >> 1$. The parameters and the variables are related by the set of equations:

$$\gamma = 1 - K_R\,c\,\gamma^2 f^2/(1 - \alpha) \qquad \ldots\ldots\ldots(31)$$

$$K_R = (4\pi\,N\,R^3/3000)\ \exp\,(\beta/R) \qquad \ldots\ldots\ldots(32)$$

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$$-\ln f = \beta^{k/2}(1 + \kappa R),\ \beta = e^2/\varepsilon\kappa T \quad \text{.....(33)}$$

$$K^2 = \pi\beta N\gamma c/125 \quad \text{.....(34)}$$

$$-\varepsilon = \ln[\alpha/(1-\alpha)] \quad \text{.....(35)}$$

The details of the calculations are presented in the 1978 paper. The shortcomings of the previous equations have been rectified in the present equation which is more general than the previous equations and can be used in the higher concentration region (0.1 N in aqueous solutions).

4. LIMITING EQUIVALENT CONDUCTANCE

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surroundings solvent molecules as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad \text{.....(36)}$$

At present, limiting equivalent conductance is the only function which can be divided into ionic components using experimentally determined transport number of ions, i.e.,

$$\lambda_+^0 = t_+\Lambda_0 \quad \text{and} \quad \lambda_-^0 = t_-\Lambda_0 \quad \text{.....(37)}$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions [Fuoss 1978]. However, accurate transference number determinations are limited to few solvents only. Spiro and Krumgalz have made extensive reviews on the subject.

In absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting equivalent conductances in organic solvents for which experimental transference numbers are not yet available.

The methods have been summarized by Krumgalz [Krumgalz 1985] and some important points are mentioned below:

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(i) Walden equation [205], $(\lambda^{0}_{\pm})^{25}_{\text{water}} \cdot \eta_{0\,\text{water}} = (\lambda^{0}_{\pm})^{25}_{\text{acetone}} \cdot \eta_{0\,\text{acetone}}$ (38)

(ii) $\lambda^{0}_{\text{pic}}\,\eta_0 = 0.267$ [205, 206] based on $\Lambda^{0}_{Et_4Npic} = 0.563$ .....(39)

$\lambda^{0}_{Et_4N^+} \cdot \eta_0 = 0.296$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda^{0}_{Et_4Npic}$ values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii) $\lambda^{0}_{25\ Bu_4N^+} = \lambda^{0}_{25\ Ph_4B^-}$ [206] .....(40)

This equality holds good in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

(iv) $\lambda^{0}_{25\ Bu_4N^+} = \lambda^{0}_{25\ Bu_4B^-}$ [207] .....(41)

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^-.

(v) The equation suggested by Gill [208] is:

$$\lambda^{0}_{25\ R_4N^+} = Z F^2/6\,\pi N \eta_0 [\, r_i - (0.0103\ \varepsilon_0 + r_y)] \quad .....(42)$$

where Z and r_i are charge and crystallographic radius of proper ion, respectively; η_0 and ε_0 are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively.

However, large discrepancies were observed between the experimental and calculated values. In a paper, Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

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(vi) $\lambda^{0}_{25\ [\ (i\text{-}Am)_3\ BuN^{+}]} = \lambda^{0}_{25\ Ph_4B^{-}}$ [209] .....(43)

It has been found from transference number measurements that the $\lambda^{0}_{25\ [\ (i\text{-}Am)_3\ BuN^{+}]}$ and $\lambda^{0}_{25\ Ph_4B^{-}}$ values differ from one another by 1%.

(vii) $\lambda^{0}_{25\ Ph_4B^{-}} = 1.01\ \lambda^{0}_{25\ i\text{-}Am_4B^{-}}$ [210] .....(44)

The value is found to be true for various organic solvents.

Krumgalz suggested a method for determining the limiting ion conductances in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_0 values into ionic components for non-aqueous electrolytic solutions.

Considering the motion of solvated ion in an electrostatic field as a whole it is possible to calculate the radius of the moving particle by the Stokes equation:

$$r_S = |Z| F^2 / A \pi \eta_0 \lambda^{0}_{\pm} \quad .....(45)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in case of perfect slipping). Since the r_S values, the real dimension of the non-solvated tetraalkyl (aryl) onium ions must be constant, we have:

$$\lambda^{0}_{\pm}\ \eta_0 = \text{constant} \quad .....(46)$$

This relation has been verified using $\lambda^{0}_{\pm}$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i - Am_4B^{-}$, Ph_4As^{+} and Ph_4B^{-} ions and for tetraalkylammonium cations starting with $n\text{-}Et_4N^{+}$. The relationship can be well utilized to determine $\lambda^{0}_{\pm}$ of ions in other organic solvents from the determined Λ_0 values.

5. SOLVATION NUMBER

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can easily be determined from the Stokes' law. The volume of the solvation shell V_S, can be written as:

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$$V_S = (4\pi/3)\ (r_S{}^3 - r_C{}^3) \qquad \text{.....(47)}$$

where r_C is the crystal radius of the ion; the solvation number, n_S would then be obtained from:

$$n_S = V_S / V_0 \qquad \text{.....(48)}$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects from:

$$V_S{}^0 = 4.35\ r_S{}^3 \qquad \text{.....(49)}$$

where $V_S{}^0$ is expressed in mol/litre and r_S in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical equations and theoretical corrections have been suggested to make the general method.

6. STOKES' LAW AND WALDEN'S RULE

The limiting conductance, $\lambda_i{}^0$ of a spherical ion of radius, R_i moving in a solvent of dielectric continuum can be written according to Stokes' hydrodynamics, as:

$$\lambda_i{}^0 = |Z_i e|\, \hat{e}\, F/6\ \pi\ \eta_0 R_i = 0.819\,|Z_i| / \eta_0 R_i \qquad \text{.....(50)}$$

where η_0 = macroscopic viscosity by the solvent in poise, R_i is in angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case in case of bulky organic ions, we get:

$$\lambda_i{}^0\, \eta_0 = 0.819\,|Z_i| / R_i = \text{constant} \qquad \text{.....(51)}$$

This is known as Walden's rule. The effective radii obtained using the equation can be used to obtain solvation number. The failure of Stokes' radii to give the effective size of the solvated ion for small ions is generally ascribed to the inapplicability of Stokes' law to molecular motions.

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Robinson, Stokes, Nightingale have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's product with temperature. The idea of microscopic viscosity was invoked without much success but it has been found that:

$$\lambda_i^{\,0}\,\eta^p = \text{constant} \qquad \ldots\ldots\ldots(52)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions.

Attempts to explain the change in the Stokes' radius R_i have been made. The apparent increase in the real radius, r has been attributed to ion-dipole polarization and the effect of dielectric saturation on R. The dependence of Walden product on the dielectric constant led Fuoss to consider the effect of the electrostatic forces on the hydrodynamics of the system. Considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion Fuoss proposed the relation:

$$\lambda^0_{i,\,0} = F\,e|Z_i|/6\,\pi R_\alpha(1 + A/\,\varepsilon R_\alpha^2) \qquad \ldots\ldots\ldots(53)$$

or,
$$R_i = R_\alpha + A/\varepsilon \qquad \ldots\ldots\ldots(54)$$

where R_α is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and A is an empirical constant.

Boyd gave the expression:

$$\lambda^0_i = F\,e|Z_i|/6\,\pi\,\eta_0 r_i[1+ (2/27\,\pi\,\eta_0\,.\,Z_i^2\,e^2\,\tau\,/\,r_i^4\,\varepsilon_0)] \qquad \ldots\ldots\ldots(55)$$

considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles.

Zwanzi treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda^0_i = Z_i^2\,e\,F/A_v\,\pi\,\eta_0 r_i + A_D\,[\,Z_i^2 e^2\,(\varepsilon_r^{\,0} - \varepsilon_r^{\,\alpha})\,\tau\,/\,\varepsilon_r^{\,0}(2\,\varepsilon_r^{\,0}+1)\,r_i^3\,] \qquad \ldots\ldots\ldots(56)$$

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where ε_r^0, ε_r^α are the static and limiting high frequency (optical) dielectric constants. A_υ = 6 and A_D = 3/8 for perfect sticking and A_V = 4 and A_D = 3/4 for perfect slipping. It has been found that Born's and Zwanzig's equations are very similar and both may be written in the form:

$$\lambda^0_i = A\, r_i^3 / \,(r_i^4 + B) \qquad \text{.....(57)}$$

The theory predicts that λ^0_i passes through a maximum of $3^{3/4}A/4B^{1/4}$ at $r_i = (3B)^{1/4}$ Å . The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius.

For comparison with results in different solvents, the equation (56) can be rearranged as:

$$Z_i^2\, e\, F/\lambda^0_i\, \eta_0 = A_\upsilon\, \pi\, r_i + A_D Z_i^2/r_i^3\; e^2(\varepsilon_r^0 - \varepsilon_r^\alpha)/\; \varepsilon_r^0(2\;\varepsilon_r^0 + 1)\tau\,/\,\eta_0 \qquad \text{...(58)}$$

or,
$$L^* = A_\upsilon\, \pi\, r_i + A_D\; Z_i^{\,2}/r_0^3 P^* \qquad \text{.....(59)}$$

In order to test Zwanzig's theory, the equation (59) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available. All the plots were found to be straight line. But the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobilities and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.

It is found that the Zwanzig's theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large, i.e., for solvents of high P^* and for ions of small r_i. Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features, e.g.,

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(i) It does not allow for any correlation in the orientation of the solvent molecules as the ion passes by and this may be the reason why the equation does not apply to the hydrogen bonded solvents.

(ii) The theory does not distinguish between positively and negatively charged ions and therefore, cannot explain why certain anions in dipolar aprotic media possess considerably higher molar concentrations than the fastest cations.

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA + water [Bahadur *et al.* 1981] mixtures and other aqueous binary mixtures [Das *et al.* 1988 and Gill *et al.* 1982]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts have been made with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because (i) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression and (ii) it is not possible to account for some specific properties of different kinds of ions and solvent molecules.

Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Zwanzig's expression though account for a change in Walden product with solvent composition but does not account for the maxima. Hemmes suggested that the major deviation in the Walden product is due to the variation of the electrochemical equilibrium between ions and solvent molecules with the composition of mixed polar solvents.

In cases where more than one type of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarization deficiency has been introduced.

7. CONCLUSION

However, quantitative expression is still awaited. Further, improvements [Roy *et al*. 2015 and Borun *et al.* 2016] naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions.

From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to attack this problem using different experimental techniques.

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Research Article

DETERMINATION OF THE PHYSICO-CHEMICAL PARAMETERS AND WATER QUALITY STATUS IN TORSA RIVER FOR IRRIGATION USED IN COOCH BEHAR DISTRICT, WEST BENGAL

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A B S T R A C T

The present study intended to calculate the water quality index (WQI) of Torsa river in Cooch Behar district, West Bengal for irrigation, agriculture and drinking purpose throughout a year. The seasonal variation of the physico-chemical parameters like p^H, electrical conductivity (EC), total hardness (TH), Total Alkalinity (TA), Chloride(Cl), Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) of river water at five selected sites was determined. Result showed the moderate variation of the different physico-chemical parameters in their concentration for all seasons. Moreover, water quality index of Torsa River is good indicating suitability of water for irrigation and drinking purpose.

Keywords: *Water quality index, physicochemical parameters, irrigation*

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1. INTRODUCTION

Water is the universal solvent, abundant and most useful component, without it life is impossible. The Surface water bodies, which are the most important sources of water for human activities are unfortunately under severe environmental stress as well as are being threatened as a consequence of human developmental activities like unplanned urbanization and industrialization [Kumar 1995]. So all these factors lead to spoil the water. Recent report of World Health Organization (WHO) on 2009 revealed that the approximately 36% of urban and 65% of rural India's were without access to safe drinking water. Indian agriculture is usually based on river water but now-a-days due to domestic waste of big towns and cities,

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discharge of industrial pollutants there is a drastic change of the physico-chemical parameters of river water [Prakash 1982]. The quality of river water at any point reflects several major natural influences like lithology of the basin, atmospheric inputs and climatic conditions but on the other hand modern industrial and municipal activity continuously pollute the river water in all season. This polluted water in particular for agriculture work crop the productivity as well as deteriorates the quality of soil. It further reflects the quality as well as quantity of the agriculture products. The objectives of the present investigation were to assess the seasonal variation of physico-chemical parameters and water quality status of Torsa River for agri-irrigation purpose of Cooch Behar district in West Bengal.

2. EXPERIMENTAL SECTION

2.1. Study Area

Torsa is an international river which is known as Machu and Ama Chhu. It rises from Chumbi valley, Tibet where it is known as Machu. After then it flows into Bhutan with name Ama Chu. Total length of this river is 358 km, out of which 113 km in Tibet and the rest 145 km in Bhutan before flowing into the northern part of West Bengal in India. The Torsa river enters in West Bengal through the border towns, Phuntsholing (Bhutan) and Jaigaon (Alipurdur District, West Bengal, India). After crossing a distance of 45.06 km the river flows to CoochBehar district through Patlakhaowa and leaves the district from Gitaldah, Dinhata and enters into Banga Desh. This river water is useful for the agriculture, domestic, drinking and industrial purpose of the villages and towns in CoochBehar district. Now a day there is a big question regarding the suitability of water for the agriculture purpose throughout the year due to modern civilization, sewage water and modern industrialization. Under this circumstances, the present investigation was studied under the five important sites *viz*, Dalsingh para (near Jaigaon) (**site 1)**, Madhupur (**site 2**), Phasighat (**site 3**), Ghughumari (**site 4**) and Kalighat (**site 5**) to investigate the water quality status of the torsa river. In this connection it has to point out that Cooch Behar lies between $25^0 57' 47''$ to $26^0 36' 2''$ north latitude and between $89^0 54' 35''$ to $88^0 47' 44''$ east longitude. The total area of the district is 3387 sq. kms, which contributes 3.82% of the land mass of the state of West Bengal.

2.2. Materials and Methods

The water sample from the river torsa were collected for all the season (pre-monsoon and post monsoon) on monthly basis for the period of one year. The water samples were collected from five different sites and it was kept in one liter polyethylene bottles properly cleaned and were analyzed for different physiochemical parameters as per the standard procedure of APHA (1998). Parameters like p^H, electrical conductivity (EC), total dissolved solids (TDS) were measured using digital p^H, EC and TDS meters respectively. On the other hand, parameters like total hardness (TH), dissolved oxygen (DO), Chemical oxygen demand (COD), Biological oxygen demand (BOD), chloride (Cl) were analyzed in the laboratory.

2.3. Results and Discussion

The values of different physiochemical parameters of the torsa river for both pre and post monsoon season was given in Table 1.

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Table 1: *Values of different physiochemical parameters of Torse River for different Season*

I. PREMONSOON SEASON

Parameters	Site1	Site 2	Site 3	Site 4	Site 5	Average
p^H	8.6	7.5	7.9	8.1	8.4	8.1
Conductivity	168	175	205	198	235	196.2
Total Hardness	92	48	64.9	52	43	59.98
TDS	96	82	97	88	104	93.4
TSS	36.8	56	52.9	47	91.2	56.78
Alkalinity	58	52	104	98	115	85.4
Chloride	4.9	4.5	4.4	5.1	7.9	5.36
DO	8.2	6.8	7.7	6.2	8.5	7.48
BOD	1.1	0.6	0.9	1.3	1.2	1.02
COD	6.9	4.8	3.7	2.7	4.8	4.58
Total Phosphate	66.7	45	47.7	43.9	56.2	51.9
Total Nitrate	12.5	9.6	12.2	8.4	6.9	9.92

II. POSTMONSOON SEASON

Parameters	Site1	Site 2	Site 3	Site 4	Site 5	Average
p^H	7.7	7.1	7.6	8.0	8.2	7.72
Conductivity	152	166	189	176	202	177
Total Hardness	78	44	76	85	41	64.8
TDS	123	96	120	119	129	117.4
TSS	125.8	67	146	134	174	129.36
Alkalinity	86	69	148	134	196	126.6
Chloride	5.8	5.1	5.2	5.4	8.3	5.96
DO	7.7	6.9	8.1	7.3	8.9	7.78
BOD	1.5	0.7	1.1	1.1	1.4	1.16
COD	7.3	4.9	3.8	2.9	4.9	4.76
Total Phosphate	77	42	79	45	89.4	66.48
Total Nitrate	9.6	7.8	11.9	4.3	5.1	7.74

(All the values shown in Table 1 are in ppm unit except conductivity and p^H)

From Table 1 it was observed that twelve physicochemical parameters of the Torsa River showed wide fluctuation in their concentration for different seasons. It is well documented

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that the three (physical, chemical and biochemical) are the most important characteristics of any water body system. Since p^H is an important parameter which determines the suitability of water in various purposes, therefore in the present investigation the p^H of water fluctuated from 8.1 to 7.72. The high p^H value may be attributed [Magudeswaran *et al* 2007] enhanced organic compound degradation or due to production of salicylic acid by the hydrolysis of silicates in the rock beds of Site 1 & 5 in particular. The electrical conductivity and total dissolved solids were found to be moderate range. Chloride is the most important parameters for the measuring of the water quality. In the present investigation the concentration of the chloride varied from 5.36 mg/lit to 5.96 mg/lit indicating the good quality of water. So this water may be used for drinking purpose. The concentration of the dissolved oxygen regulates the distribution of flora and fauna. The present investigation indicated that the concentration of the dissolved oxygen varied from 7.48 mg/lit to 7.78 mg/lit. The low value of dissolved oxygen is an indication of a tendency towards an anoxic condition. The value of alkalinity varied from 85.4 mg/lit to 126.6 mg/lit. The increase in concentration of total alkanity at site 5 may be attributed to chemicals present [Sinha *et al* 2011] in the effluent which are drained into the river water. Biological Oxygen Demand (BOD) represents [Bhandari *et al* 2008] the quantity of oxygen required by bacteria and other micro-organism during the biochemical degradation and transformation of organic matter present in water body system under aerobic conditions. In the present investigation the value of BOD ranged from 1.02 mg/lit to 1.16 mg/lit. From the above table it was observed that the enhanced concentration of different parameters of river water (hardness, BOD, COD, Phosphates, Chloride, TDS) appeared in post-monsoon period compared with the pre-monsoon period. This variation may be attributed by the activities like discharge of sewage in the river and decreased periodical flow of water in the river after monsoon season.

Determination of Water Quality Index (WQI)

Water quality index is a 100 point scale that summarizes results from a total of nine different measurements [Singh *et al* 2012]. These parameters are temperature, p^H, Dissolved Oxygen, fecal coliform, total phosphate, nitrates, turbidity, Total Suspended Solid (TSS) and Biological Oxygen Demand (BOD). This concept was first developed in 1965 in the USA. The following Table 2 summarizes these nine parameters used as water quality factors and their corresponding weight. In this connection it has mentioned that conversion of dissolved oxygen (ppm) to % of saturation for calculation of water quality was carried out by the ratio of DO in the study sample and maximum DO at the temperature of the sample.

Table 2: *Nine different parameters of water body system and their corresponding weight.*

Factor	DO	Fecal Coliform	P^H	BOD	Temperature change	Total phosphate	Nitrates	Turbidity	Total Solids
Weight	0.17	0.16	0.11	0.11	0.10	0.10	0.10	0.08	0.07

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Overall water quality index was calculated based on five factors in the following Table 3. (Source Code: Keith Alcock's Javascript WebMaster: webmaster@alcock.vip.best.co)

Table 3: *Overall water quality index of Torsa River*

Factor	DO	Fecal Coliform	P^H	BOD	Temperature change	Total phosphate	Nitrates	Turbidity	Total Solids
Weight	0.17	0.16	0.11	0.11	0.10	0.10	0.10	0.08	0.07
Quality Index	95		87	94		2			84

Based on the above five factors the water quality index of the river torsa was 75. The 100 point index can be divided into several ranges corresponding to the general descriptive terms shown in the following Table 4.

Table 4: *Water Quality Index (WQI) and the status of water quality*

Range	90-100	70-90	50-70	25-50	0-25
Quality	Excellent	Good	Medium	Bad	Very Bad

Since the water quality index is 75, which is in the range of 70 to 90 so the water quality of the study sites is good for irrigation.

3. CONCLUDING REMARKS

From the present study it may be concluded that quality of the Torsa River is good since the water quality index for this river water is 75, based on five quality parameters indicating suitability of water for irrigation and agriculture purpose. A relatively lower concentration of chlorides also indicates the suitability of water for domestic use. Hence application of water quality index technique for the overall assessment of the water quality of any water body system is a useful tool.

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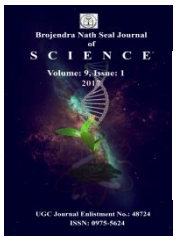

Brojendra Nath Seal Journal of SCIENCE

Review Article

TITANIUM DIOXIDE (TIO2): A GREEN PHOTO CATALYST FOR DESTROYING HAZARDOUS POLLUTANTS

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A B S T R A C T

Studies on photo catalysis have started about two and a half decades ago. The theme of Green chemistry is the *prevention is better than cure*. Titanium dioxide (TiO_2), which is the most important materials in our life, has the promising role in the photo catalytic air purification, sterilization and cancer therapy. In this paper the promising role of TiO_2 was described.

Keywords: *Titanium Dioxide, Photocatalysis, Green Chemistry, Decomposition of organic hazardous pollutants*

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1. INTRODUCTION

Green Chemistry deals with the design the chemical reactions and synthesis of new products which reduce or eliminate the use and formation of hazardous substances during the carrying out of the various type of chemical reactions. Therefore it needs to prevent or minimize the formation of the products in particular the hazardous substances either through the development of the greener synthesis or through the use of some green photo catalysis *viz.* TiO_2. It is now well documented that titanium dioxide (TiO_2) is one of the most superior materials for decomposing organic compounds due to its strong photocatalytic property [Blake *et al* 1999; Zili *et al* 1999]. It has become the most important photocatalyst in environmental bio-decontamination for a large variety of organics, bacteria, viruses, fungi and cancer cells, which can be totally degenerated and converted to CO_2, H_2O and harmless inorganic anions. The nanoparticles of titanium dioxide (TiO_2) absorb the UV component of sunlight, acting as a catalyst to form reactive hydroxyl (OH) radicals in the presence of

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atmospheric moisture. These radicals can oxidize and destroy the most pollutant molecules. The photo catalytic activity can be significantly enhanced by reducing the size of the TiO_2 particle [Qunighong *et al* 2000; Liqiang *et al* 2003]. By reducing the size of the TiO_2 particle, the surface area of TiO_2 increases leading to improvement of photo efficiency and photocatalytic property. The present paper describes the properties of TiO_2 as a green photocatalyst [Paxton *et al* 1998] for destroying hazardous pollutants.

2. DISCUSSION

It has been observed that most of the man-made chemical reactions released organic pollutant like VOCS (hydrocarbon). Such type of hydrocarbon contributes to make the air pollution. TiO_2 can favor the aerial oxidation of the type of organic pollutants [Khan *et al* 1991]. The photocatalytic property of TiO_2 was first reported by Mastsunaga and his coworkers. They observed that when TiO_2-Pt catalyst in contact with the microbial cell is exposed to near UV light, the microbial cells in water would be killed. For searching the ideal semiconductor photocatalyst[Halley *et* al 1987] several factors must be taken into consideration- among them one is oxidation potential and another one is energy of the band gap. The oxidation potential is vital since it has the ability to form photogenerated valance band holes and to create hydroxyl radicals, which is the key for using the substances as a photo catalyst for the oxidation of organic molecules. At the same time reducing behavior of the excited conduction band electron which must have sufficient energy to reduce the molecular oxygen to produce super oxide. Usually aerial oxidation of the organic compounds without catalyst consists of two barriers. First step is the reaction between triplet O_2 and singlet organic compounds which is the quantum mechanically forbidden. So it needs high activation energy. The second step is the oxidizing behavior of O_2 (E^0= +1.23V) which is consist of four electron transfer process and if it occurs at a single step then it become quite unlikely. So the step wise electron transfer is likely to occur. In presence of catalyst this barriers may be removed in different ways. Herein we shall discuss the promising role of TiO_2 as a photo catalyst for the oxidation of organic substance of the dioxygen molecule. TiO_2 acts as an ideal photocatalyst in several aspects. It is highly stable chemical substances, relatively inexpensive, and photogenerated holes are highly oxidizing [Wunderlich *et al* 2004]. TiO_2 acts as a semiconductor having band gap about 3.23eV. So it works well in the UV region. This band gap gives the energy difference between the HOMO (= VB) and LUMO (=CB), where VB donates the valence band and CB donates conduction band. The outermost filled orbitals of elemental titanium (Ti) are $4s^2$ and $3d^2$ and that of oxygen (O) are $2s^2$ and $2p^4$. In TiO_2, the Ti ions are in a distorted octahedral environment and formally have a Ti^{4+} ($3d^0$) electronic configuration. The valence band of TiO_2 is composed primarily of oxygen 2p orbitals hybridized with Ti 3d states, while the conduction band is made up of pure 3d orbital of titanium. When TiO_2 is exposed to near-UV light, electrons in the valence band are excited to the conduction band leaving behind holes. The excited electrons in the conduction band are now in a pure 3d state and since the nature of valence and conduction band is completely different, i.e. dissimilar parity, the transition probability of e^- to the valence band reduces leading to reduction of $e—h^+$ recombination. During photo excitation, an electron is promoted from VB to CB which is the delocalized LUMO. This excited

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photoelectron from the delocalized LUMO is transferred to molecular di-oxygen to generate O_2^-. This is energetically favorable.

$$O_2 + e \text{ (LUMO of } TiO_2) \rightarrow O_2^- \text{ (superoxide)}$$

So the thermodynamically hindered step *viz.* formation of O_2^- from molecular di-oxygen molecule is overcome. In fact, the subsequent steps of reduction are energetically favorable. So O_2^- is formed, then oxidizing action can go without facing any thermodynamic barrier. In fact O_2^- can oxidize the organic pollutants. Moreover oxidation of hydrocarbons through free radical mechanism can also be started in presence of O_2^- and moisture. Photo excitation in TiO_2 promotes an electron from VB to CB. During the photo excitation, an electron from the oxide lone pairs is excited to the delocalized LUMO. It can be represented as follows:

$$(Ti^{4+})(O^{2-})(O^{2-}) \rightarrow (Ti^{4+})\ (O^{2-})\ (O^{2-}) + \text{electron (LUMO)}$$

The above reaction was carried out in the presence of sunlight having wavelength 384 nm.

The O^- (7electron system) can react with the moisture to generate the radicals both OH^- and OH. The OH radical is effective oxidizing agent [Linsbigler *et al* 1995; Tanaka *etal* 1991*]*. It acts as a strong oxidant to destroy the organic pollutants. The detailed mechanistic pathway of TiO_2 as a photo catalyst is given in the following equations.

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+ \quad \text{..(i)}$$

$$H_2O + h^+_{vb} \rightarrow HO^{\cdot} + H^+ \quad \text{..(ii)}$$

$$O_2 + e^-_{cb} \rightarrow O_2^{\cdot -} \quad \text{...(iii)}$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \quad \text{..(iv)}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad \text{..(v)}$$

$$H_2O_2 + e^-_{cb} \rightarrow HO^{\cdot} + HO^- \quad \text{.. .. (vi)}$$

$$D + h^+_{vb} \rightarrow D^{\cdot +} \quad \text{... (vii)}$$

$$A + e^-_{cb} \rightarrow A^{\cdot -} \quad \text{. (viii)}$$

$$e^-_{cb} + h^+_{vb} \rightarrow TiO_2 + \text{heat} \quad \text{..(ix)}$$

D = absorbed donor molecule

There are three types of crystal structure in TiO_2 *viz.* anatase, rutile and brookite type. The band gap [Mills *et al* 2003; Basca *et al* 1998] value for the anatase, rutile and brookite type is 3.2 eV, 3.02 eV and 2.96 eV respectively. Thus, wavelength of light having less than 385 nm, will excite e^- from the valence band to the conduction band, producing an e—h^+ pair. Among the three structures only anatase and rutile are commonly used as photocatalysts. However, it is interesting to note that there exist controversial results regarding the photocatalytic activity among these two phases. But, in general, it is considered that anatase phase has greater photocatalytic activity than rutile [Maruska *et al* 1978]. There are also studies that the rutile

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phase has greater photocatalytic activity and some studies even claim that a mixture of anatase (70–75)% and rutile (30– 25)% is more active than pure anatase. The reason is still not understood and more detailed and careful experiments are required to understand this discrepancy. The disagreement of the results may be due to various reasons, such as crystal size, surface area, defects, porosity and pore size distribution. One can reason out that since the anatase phase has a higher Fermi level than the rutile phase by about 0.1 eV, the anatase phase will have lower capacity to absorb oxygen and higher degree of hydroxylation (i.e. number of hydroxy groups on the surface) and thus should have greater photocatalytic activity [Gerischer *et al* 1992] than the rutile phase. Another essential difference is that the anatase phase has a wider optical absorption gap and may have smaller electron effective mass and hence higher mobility. It has also been reported that the anatase phase has an indirect band gap, whereas the rutile phase has a direct band gap [Bickley *et al* 1991]. The indirect band gap will cause further decrease in the recombination rate of the e—h^+ pair generated upon illumination. Thus, more detailed experimental and theoretical work is required to determine the e^- effective mass and mobility of the photo-generated e^-. Research group of Prof. S. Banerjee extensively studied the photo catalytic activity of of TiO_2 using AFM (atomic force microscopy). Moreover besides the studies on the photocatalytic phenomena of titanium dioxide studies on the photo-induced superhydrophilicity has recently discovered. This property was discovered accidently at the laboratories of TOTO Inc., in the year 1995 [Mo *et al* 1995]. It was found that if a TiO_2 film is synthesized with a certain percentage of silicon dioxide, it acquires superhydrophilic properties after UV illumination. In this case, electrons tend to reduce the tetravalent titanium cations to the trivalent cations and the holes oxidize the oxide ions. In this process oxygen atoms are ejected, creating oxygen vacancies. Water molecules can occupy these oxygen vacancies producing adsorbed OH groups, which tend to make the surface sufficiently hydrophilic. There is an extremely wide application for superhydrophilic technology. Some of the applications are anti-fogging property, self-cleaning and bio-compatibility. Besides it, TiO_2 can destroy chlorobenzene, smoke, microorganism etc. This property arises due to the generation of powerful oxidizing agent like OH^-, O_2^- radicals. Some useful applications of photocatalysis are: (i) Self cleaning and anti soiling property of TiO_2 (ii) water purification and air purification. It should be pointed out that the use of TiO_2 as photocatalyst we achieve more environmental benefits. This arises due to the nontoxic behavior of TiO_2 and all over process is economic. But besides these advantages there are some disadvantages. The band gap indicated that it can be activated by light of wavelength lies that 384-385 nm. So from sunlight only 3% can be utilized for photo catalysis by TiO_2. If electrical energy is utilized to generate the UV light of appropriate wavelength, then the process becomes costly.

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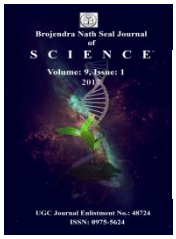

Brojendra Nath Seal Journal of SCIENCE

Research Article

A NOVEL RARE-EARTH POLYOXOMETALATES: SYNTHESIS, AND THEIR CHARACTERIZATION THROUGH CRYSTALLOGRAPHY AND SPECTROSCOPY

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A B S T R A C T

New rare earth or Lanthanide encapsulated molecule $Na_{10}[Ce(PW_{11}O_{39})_2].12H_2O$ has been prepared by the hydrothermal method and was characterized by elemental analyses, IR, UV spectra, luminescence spectra and single crystal X-ray diffraction techniques. The asymmetric unit consists of $[Ce(PW_{11}O_{39})_2]^{10-}$ with cerium as a linking central atom flanked between two giant phosphotungstate Keggin POM units and the charge of which are counter balanced by ten hydrated univalent sodium ions. The molecular structure of the title complex reveals a 3D supramolecular framework formed through intermolecular hydrogen bonds. This constitutes the first example, where two POMs are linked through a lanthano-bridge.

Keywords: *Keggin Polyoxometalates; Hydrothermal synthesis; Lanthanotungstate; Emission spectrum, Contour view*

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1. INTRODUCTION

The synthesis of rare earth polyoxometalates or Lanthanopolyoxometalates (Ln-POMs) has received current interest due to their special spectroscopic and magnetic properties, as well as their potential use as luminescent probes, NMR shift agents and magnetic resonance imaging agent. Polyoxometalates have a rich background in structural engineering and synthetic world. Its discovery was arguably almost two century ago. Since its inception, different scientists have nurtured the versatile aspects of POMs to enrich our knowledge in this relatively unexplored field. In 1826, Berzelius [Lin *et al.* 2002] reported the first POM, the phosphomolybdate of formula $[PMo_{12}O_{40}]^{3-}$. Marignac [Berzelius *et al.* 1826] soon followed him by observing two isomeric forms of $[SiW_{12}O_{40}]^{4-}$. In the early 1930s, Keggin solved the structure of the related anion $[PMo_{12}O_{40}]^{3-}$ [Marignac *et al.* 1864] which opened the floodgate. Since then, innumerable number of structures of different varieties of POM

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have been synthesized and carefully characterized. The epoch making era came when spectroscopic techniques were used for characterization. The end of the 19th century and the early decades of the 20th century were very eventful for the chemistry of POMs. [Keggin *et al.* 1933] In the last half of the decade, a lot of experimental information has been collected. Since the inception, POMs constitute an immense class of polynuclear metal-oxygen clusters [Copaux *et al.* 1906; Pope *et al.* 1983] usually formed by Mo, W or V and different mixtures of these elements. Nowadays, polyoxometalate chemistry continues its development, both as a pure chemical science, and also with many new dimensions in a multidisciplinary context interacting with other aspects like materials, [Hill *et al.*1998] nanotechnology, [Pope *et al.* 1991] biology, [Khan *et al.* 2000] as anti cancer, antiviral [Long *et al.2006*] and even as insulin mimetic, [Ma *et al.* 2005] surfaces, [Yamase *et al.*2005] catalysis, [Hasenknopf *et al.* 2005] supramolecular materials, [Nomiya *et al.* 2001] colloid science, [Rhule *et al.* 1998] and electronic materials including electro/photo chromic systems, [Errington *et al.* 2005] sensors, [Vasylyev *et al.* 2004] molecular materials [Neumann *et al.* 2000] and magnetism [Mizuno *et al. 2005*] Several elements have been reported as taking part in POM compounds. In addition, beyond this unusual chemical flexibility, they have an 'organic-like' structural diversity and the number of frameworks synthesised increases daily. More recently, the syntheses of lathanopolyoxometalates (Ln-POMs) have received current interest due to their versatile features as stated earlier. More specifically, rare earth-POMs become very popular as NMR shift agents and magnetic resonance imaging agent [Mbomekalle *et al.* 2003; Attanasio *et al.* 1990; Wang *et al.* 2000]. Continuing interest in this field largely focuses on rational syntheses of complexes with extended polymeric structure. The complexes of multidimensional frameworks in which transition-metal ions and lanthanide ions serve as inorganic bridging linker have been widely reported [Liu *et al.*1999; Fu *et al.* 2001; Fu *et al.* 1998; An *et al.* 2005]. However, examples of the multidimensional complexes built up of POM building blocks and alkali cations are still rare. Howell RC et al. have reported a two-dimensional (2D) network using potassium cations as linkers [Mialane *et al.* 2003]. In 2002, Noritaka et al. have reported the first extended POM structure wherein sodium connects lacunary Keggin molecule $[PW_{11}O_{39}]^{7-}$ into a 1D linear chain [Honma *et al.* 2002] and subsequently they obtained another linear chain with monovacant Keggin anions $[SiW_{11}O_{39}]^{8-}$ units also joined by sodium cations [Chiba *et al.* 2006]. So far, such 1D chain consisting of sandwich-type Ln-POM units with linker of alkali metal cations are scarely reported. Here, I report the synthesis and crystal structure determination of a novel sandwich-type polyoxometalate $Na_{10}[Ce(PW_{11}O_{39})_2].12H_2O$, in which a 1D zigzag chain constructed from sandwich-type $[Ce(PW_{11}O_{39})_2]$ building block and the sodium cations.

2. EXPERIMENTAL

2.1.Materials and methods

Chemicals were readily available from commercial sources and were used as received without further purification. Sodium tungstate Na_2WO_4 (AR Loba, India), ammonium cerium nitrate $(NH_4)_2[Ce(NO_3)_6]$ (Merck, India), were of reagent grade and were used as received. Deionized water was used as the solvent.

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2.2. Preparation of the precursor ligand $Na_9[PW_90_{34}]$ (1)

Sodium nonatungsto phosphate $Na_9[PW_90_{34}]$ is prepared as per the reported literature [Fan *et al.* 2006]. 24 gm $Na_2WO_4.2H_2O$ is dissolved in 30ml of water, then 85% H_3PO_4 is added drop wise with stirring (0.8ml) to achieve just alkaline pH at 8. 4.5 ml of Glacial acetic acid AcOH is then added drop wise with vigorous stirring to achieve final pH 7.5. During addition of AcOH, large quantities of white precipitate is formed. The solution is then stirred for 1hr & the precipitate is collected & dried by suction filtration. Crude yield of the product is 13.6 gm which does agree with the reported value.

2.3. Synthesis of the complex $Na_{10}[Ce(PW_{11}O_{39})_2].12H_2O$ (2)

2.44gm (1m. mol) $Na_9[PW_9O_{34}]$ is dissolved in 20 ml of water followed by the drop-wise addition of 1 ml 6 (M) HNO_3 under constant stirring and heating. The temperature is maintained up to 80°C for 15 minutes. 1.644 gm (3m mol) $(NH_4)_2[Ce(NO_3)_6]$ is then dissolved in minimum quantity of acid- water (3ml H_2O + 2ml 6 (M) HNO_3) which is again added dropwise to the aforesaid whirling solution. Finally the resulting solution was heated and stired for 40 minutes. The temperature was maintained up to 80^0C. The final recorded pH of the solution was 3. The solution was kept for cooling at room temperature, filtered and the filtrate was kept in the fridge for crystallization. After a couple of weeks, golden yellow block shaped crystals were formed. Many factors can affect the isolation of final products, such as initial reactants, the concentrations of counter cations, pH values, reaction time and temperature. In our case, the pH value of the reaction system was of crucial importance for the product formation.

2.4. Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Spectrophotometric measurements were made in aVarian Cary 1E UV-visible spectrophotometer with 1.00 cm glass cells. IR (400–4000 cm-1) was recorded in KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Molecular structure of $Na_{10}[Ce(PW_{11}O_{39})_2].12H_2O$ (2)

As depicted by Fig. 1, the building block of 1 contains an 8-coordinate lanthanide cation Ce(IV) in antiprismatic geometry sandwiched between two lacunary anions $[\alpha\text{-}PW_{11}O_{39}]^{7-}$. Each $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion acts as a tetra dentate ligand by its four unsaturated oxygen atoms (O13, O15, O38, and O39) to coordinate with the tetravalent cerium Ce(IV) metal center. There are two long Ce –O bonds (Ce –O13, Ce–O15) with the oxygen atoms originating from edge-shared W octahedra and two short Ce –O bonds (Ce –O38, Ce –O39) with the oxygen atoms originating from corner-shared W octahedra. The bond lengths vary from 2.451 A° to 2.474 A° and the average value is 2.461 A °. In addition, complex molecule 2 contains strong hydrogen bonding interactions between oxygen atoms of heteropolyanions and the oxygen atoms from ligand water molecule coordinated to the Na atoms.

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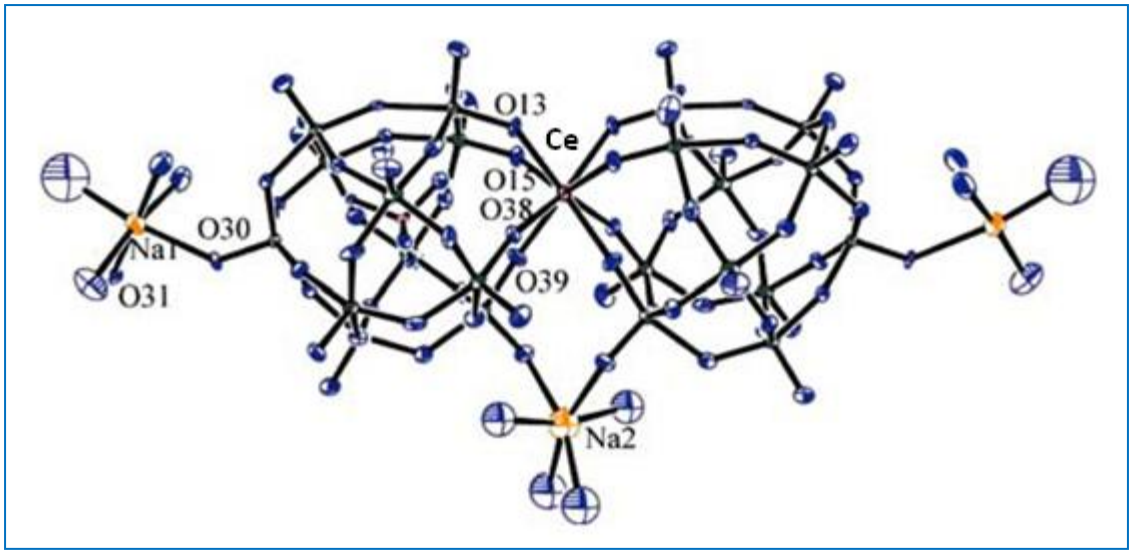

Fig. 1: *Ortep view structural unit of complex 2. The lattice water molecules are omitted for clarity.*

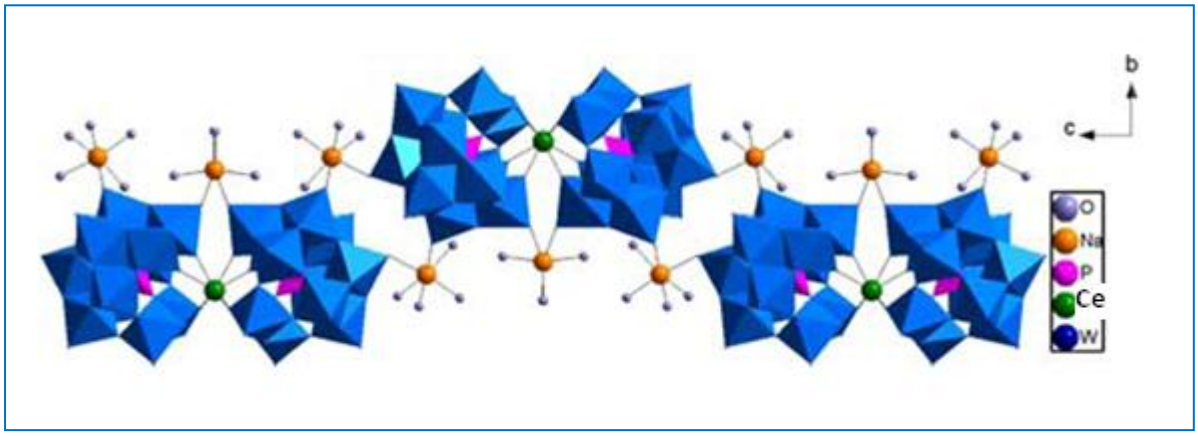

Fig. 2: *Polyhedral view of 1D zigzag chain of compound 2. The lattice water molecules are omitted for clarity.*

3.2. Vibrational Spectra

The IR spectra of 1 display the characteristic features of a Keggin-type structure as shown in Fig.3. Five strong vibration bands are indeed observed for ν (P–O), ν (W=O), and ν (W–O–W) at 1104.8, 1060, 957, 889, and 796.5 cm^{-1}. That shows a splitting of the P–O stretching band (1104.8 and1058.7 cm^{-1}), indicative of the lacunary anion and originating from the loss of an{W–O} unit from $[PW_{12}O_{40}]^{3-}$, which is identical with that of $[Ln(PMo_{11}O_{39})_2]^{11-}$ [Gaunt *et al.* 2003]. The red shifts of ν (W=O) and ν (W–O–W) can be ascribed to the influence of incorporating Ce ions into the polyanions frameworks . Apart from these, the IR spectrum of the title compound has some characteristic bands for the polyoxoanion at 510, 940, 878, 770 and 1320 cm^{-1} which are attributed to ν (W=Ot terminal), ν (W–Ob-W octahedral edge sharing), ν (W–Oc-W octahedral corner sharing) and (Ce-O-W) respectively. In addition, a strong broad peak observed at 3350 cm^{-1} is assigned to ν (−OH) absorption along with the hydrogen bonds which proves the presence of lattice water.

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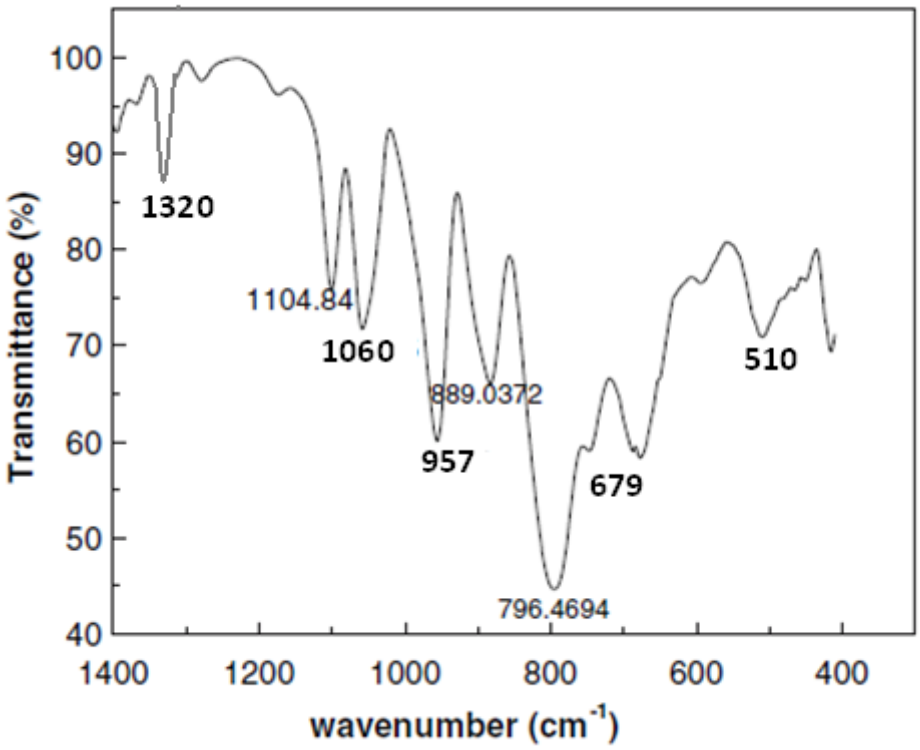

Fig. 3: *FTIR spectrum of complex 1, taken as KBr pellet*

3.3. Electronic spectra

The excitation bands for Ce (IV) anionic complex under the orange emission of 596 nm show four main peaks, 222.5 nm, 242 nm, 259 nm and 271 nm. Moreover, lanthanide ions do not contribute to the spectra of their complexes since f-f transitions are Laporte-forbidden and very weak (molar absorptivity coefficients of the order of only 0.5–3.0M^{-1} cm^{-1}) [*et al.*32]. On the other hand, charge-transfer bands involving lanthanide orbitals are also typically not observed in the near-UV and spectral regions [Armaroli *et al.* 1999]. Hence the absorption bands of samarium complexes in different solvents as well as in viscous or polymeric media are completely attributable to the ligand-centered (LC) transitions, although with respect to the corresponding free ligand, some perturbation is observable upon complexation [Sabbatini *et al.* 1996]

3.4. Mapping as fingerprint

A three dimensional plot could be exploited profitably as a powerful analytical tool and is required for a complete description of the luminescence, which are given in Figures 6, 8, and 10. It may be represented as the so-called excitation/emission matrix [Wolfbeis *et al.* 1983]

Furthermore, connection of data points with the same luminescence intensity (i.e., same height) by lines results in tomograms of two-dimensional representation (luminescence mapping). Such diagrams always represent a top view as in Figures 6 and 7.

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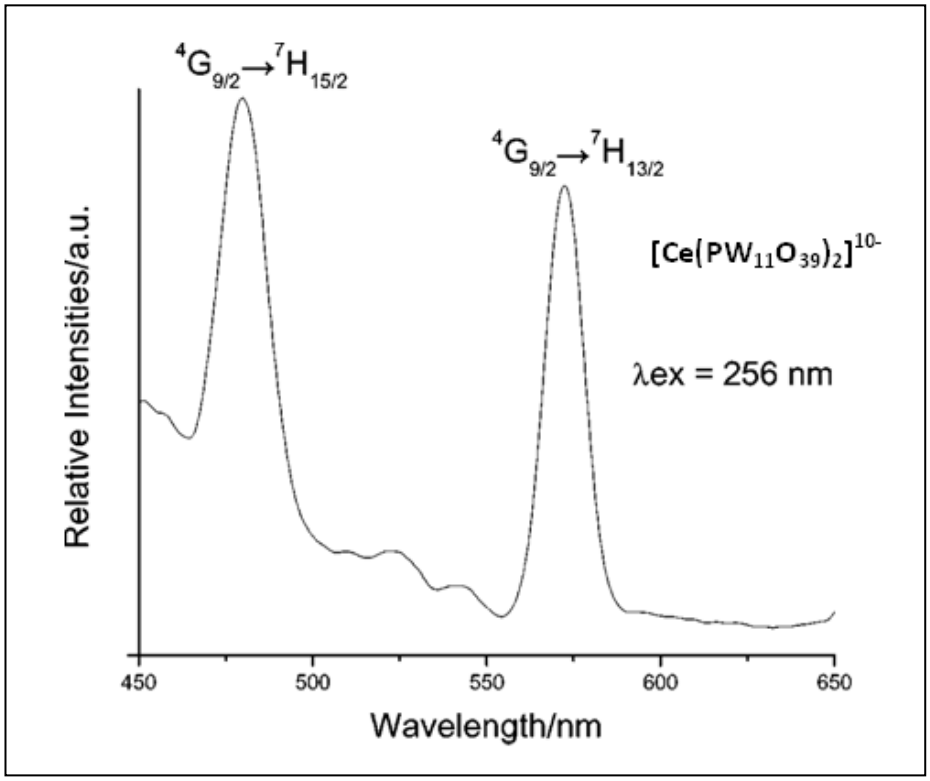

Fig. 4: *Emission spectrum of* $[Ce(PW_{11}O_{39})]^{10-}$ *polyoxo complex in aqueous solution*

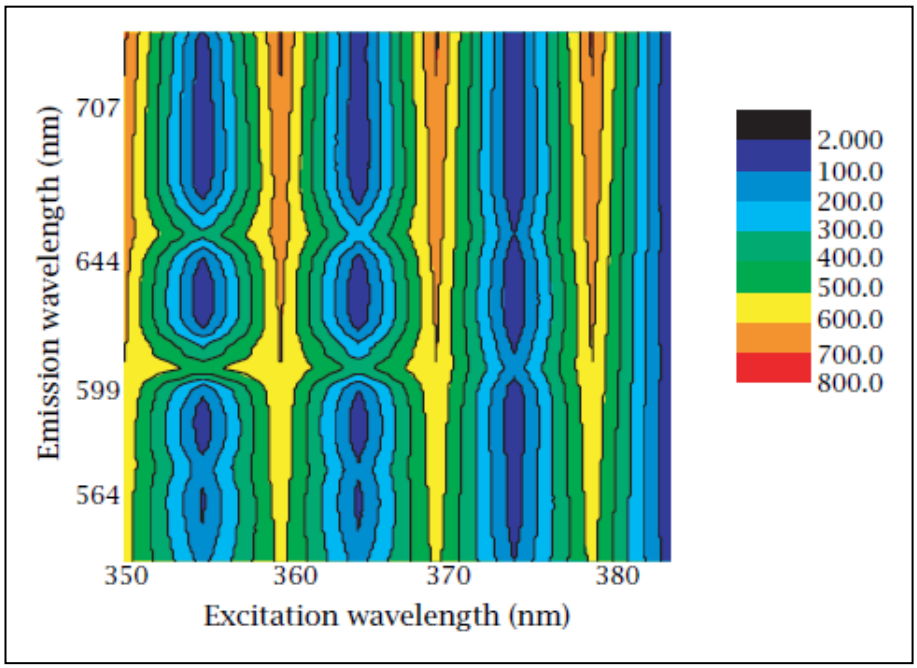

Fig. 5: *Contour view of the emission spectra of* Ce^{4+} *ion in* $[Ce(PW_{11}O_{39}]^{10-}$ *complex in* H_2O *atdifferent excitation wavelengths.*

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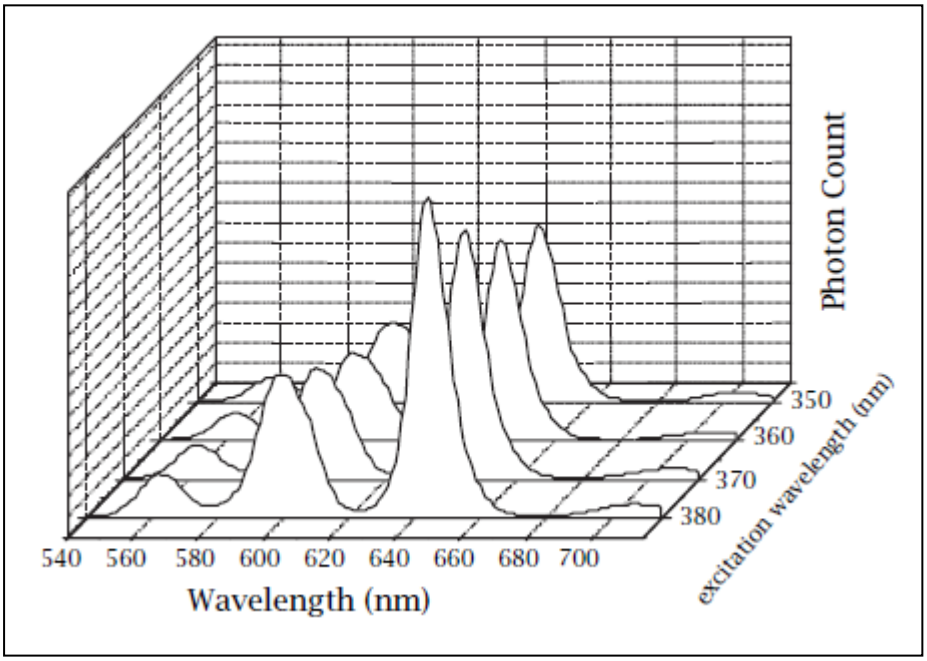

Fig. 6: *3D-View of the emission spectrum of Ce^{4+} ion in $[Ce(PW_{11}O_{39}]^{10-}$ complex in H_2O at different excitation wavelengths*

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Review Article

SARCO (ENDO) PLASMIC RETICULUM CA^{+2}-ATPASE (SERCA): THE UNIQUE TRANSPORT ENZYME AND ITS MODULATORS

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A B S T R A C T

Sarco (endo) plasmic reticulum Ca^{+2}-ATPase (SERCA) is membrane bound enzyme that pumps $Ca^{+2}$from the cytoplasm into lumen, with simultaneous hydrolysis of ATP and is a very important enzyme for maintaining calcium concentrations in our body. SERCA activity has been shown to be affected by a wide range of substances such as proteins and peptides, drugs, hormones and growth factors etc. and under different conditions they serve to activate or inhibit Ca^{+2}-ATPase activity in different cells and tissues and can be collectively referred to as modulators of SERCA. The present study lists a detailed report of such modulators with special reference to their mechanism of enzyme regulation.

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1. INTRODUCTION

Transport enzymes are those responsible for the transport of ions across the cell membranes. The transport takes place against ion gradient, energy required for the process is provided by ATP, which is hydrolyzed to ADP and inorganic phosphate (P_i) during these transport phenomena. These ion pumps are found in bacteria, archaea and higher eukaryotes and belong to P-type ATPases (includes Na^+, K^+, Ca^{2+}, H^+, K^+-ATPases) and are involved in performing different fundamental processes in biology and medicine, ranging from the generation of membrane potential to muscle contraction, the removal of toxic ions from cells, maintaining proper acidity inside cells etc [Kühlbrandt 2004]. Mutation or dysfunction of these ATPases leads to several diseases. Malfunction of Ca^{2+}-ATPase may lead to defect in cardiac function, infertility, diabetes and even cancer [Tempel *et al.* 2008]. Impairment of sodium pumps, on the other hand, cause diseases including osteoporosis, hypertension etc.

2. ABOUT SERCA

Ca^{2+}-ATPase or the Ca^{2+}-pump is responsible for the transport of Ca^{2+} across cell membranes and thus maintains intracellular calcium concentration. Because of its peculiar flexibility as a ligand, calcium regulates all important aspects of cellular activity, beginning

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with the creation of new life at fertilization and ending with the dramatic event of apoptotic suicide at the end of the life cycle. The evolutionary choice of Ca^{2+} appears to be dictated by a number of its properties. First of all, it can reversibly bind to complex molecules in the intracellular ambient, as it can bind to sites of irregular geometry, such as those normally offered by proteins. Secondly, Ca^{2+} is peculiarly capable of autoregulating its messenger function i.e. its production and movements inside cells eg. membrane transporters are regulated by Ca^{2+}. Ca^{2+} Itself may liberate Ca^{2+} from intracellular stores, thus adding one step to the signaling cascade, as if the liberated Ca^{2+} were a third messenger. In addition, Ca^{2+} may also function as a bonafide first messenger in that it can interact on the exterior of cellular membrane as if it were a hormone or growth factor. Finally, and most importantly, Ca^{2+} is distinctly ambivalent. Cells have an absolute dependence on the messenger function of Ca^{2+}. In order to function properly, its homeostasis must be controlled with absolute precision; failing which, there can be a sustained cellular Ca^{2+} overload leading to apoptotic and/or necrotic cell death [Carafoli 2004].

The cytoplasmic free Ca^{2+} concentration in all cell types at rest is very low (50-150 nM) which is 10^3-10^4 times lower than the free Ca^{2+} concentration in the extracellular space (usually 1 mM) or in the lumen of sarco(endo)plasmic reticulum (SR/ER) (0.1-2.0 mM). Such large Ca^{2+} gradients across cellular boundaries are established and maintained by the powerful calcium pumps located in the cell surface or plasma membranes and in sarco(endo) plasmic reticulum [MacLennan *et al.* 1997; Philipson *et al.* 2000] with contributions from other cellular organelles. The SR Ca^{2+} pump catalyzes the electrogenic transport of two Ca^{2+} ions per ATP molecule hydrolyzed from the cytoplasm into the lumen of SR. The Ca^{2+}-ATPase has been localized in sperm and is known to play an important role in regulating cellular motility and fertility.

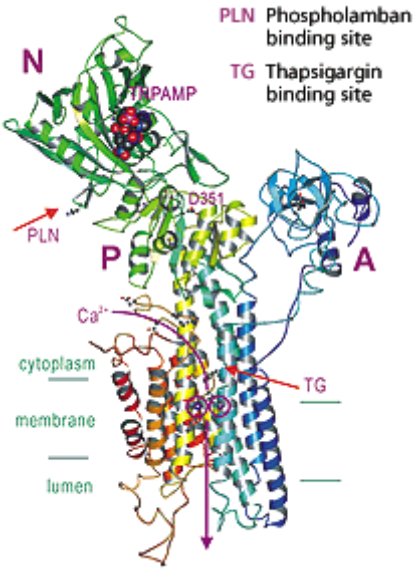

Fig. 1: *Structure of Ca^{2+}-ATPase involved in calcium ion transport across the sarcoplasmic reticulum (SR) membrane*

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The Ca^{2+} transporting systems can be classified into four basic transporting modes *i.e.* ATPases, exchangers, channels and uniporters. In general, whenever the situation demands the fine regulation of Ca^{2+} in submicromolar concentrations, the ATPase mode are chosen, since this appears to be the only transport system with the ability to interact with high Ca^{2+} affinity and is therefore used by plasma membrane and sarcoendoplasmic reticulum.

The ATP dependent Ca^{2+} pumps of sarco (endo) plasmic reticulum (SERCA) constitute a large family of proteins of 100 kDa-138 kDa [Toyoshima *et al.* 2000; Toyoshima *et al.* 2002; Toyoshima *et al.* 2004; Lee 2002] and a proteolipid of molecular mass 6 kDa-12 kDa, belonging to P2 subfamily (subtype 2A) of P-type ATPases. They are structurally distinct from the Ca^{2+} pump of the plasma membrane, but share similarities in the mechanism of calcium translocation. The intracellular location of SERCA exclusively in SR/ER membranes is maintained by the presence of specific retention/retrieval motifs in their primary sequences. The Ca^{2+} transport is reversible and under favourable condition results in the hydrolysis of ATP molecule for two Ca^{2+} ions released from the lumen of SR [Sumbilla *et al.* 2002]. Counter-transport of H^+ and fluxes of ions through the anion and cation channels of SR prevent large changes in membrane potential during Ca^{2+} transport. The SERCA pumps have high affinity for Ca^{2+} (K_m about 0.1 μM), and are capable of maintaining a resting cytoplasmic Ca^{2+} concentration of 10 nM-20 nM.

The plasma membrane Ca^{2+}-ATPase (PMCA) is the only high affinity Ca^{2+} transporting system present in the plasma membrane and belongs to the P2 (subtype 2B) subfamily of P-type ATPases [Lutsenko *et al.* 1995] The molecular mass is 130 kDa-140 kDa and are characterized by the formation of an aspartyl phosphate intermediate as part of their reaction cycle [Strehler et al. 2001]. At variance with the closely allied SERCA, PMCA contains only one Ca^{2+} binding site, and indeed transports one Ca^{2+} as one ATP molecule is hydrolyzed.

In addition to Mg^{2+}-dependent Ca^{2+}-ATPase, another Ca^{2+}-ATPase which can be activated without any Mg^{2+} has also been reported from a number of tissues and sources with varying sensitivity to calcium and insensitivity to magnesium [Post *et al.* 2002; Sanchez-Luengo *et al.* 2004; Da Silva *et al.* 2002] and is known as Mg^{2+}-independent Ca^{2+}-ATPase. Both these ATPases have similar properties [Sikdar *et al.* 1991]. They may either be the two forms of the same enzyme having separate catalytic sites or same catalytic site with different sensitivities to Mg^{2+} [Sikdar *et al.* 1999; Sikdar *et al.* 1993]. Mg^{2+}-dependent Ca^{2+}-ATPase is present in most mammalian tissues whereas the reproductive tissues are enriched with Mg^{2+}-independent Ca^{2+}-ATPase.

3. MODULATORS OF SERCA

The regulation of Ca^{2+}-ATPase is affected by a wide variety of substances, protein/peptide factors, hormones, growth factors, organic compounds, drugs etc. under different conditions. They either activate or inhibit Ca^{2+}-ATPase activity in different cells and tissues and are known as modulators of Ca^{2+}-ATPase.

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Ca^{2+}-ATPase activity is inhibited by vanadate [Barrabin *et al.* 1982], lanthanum chloride [Fujimori *et al.* 1990], ruthenium red [Alves *et al.* 1986] etc. Inhibition of Ca^{2+}-ATPase is also exhibited by the sulfhydryl reagents like salyrgan and N-ethylmaleimide [Taylor *et al.* 1979]. Apart from these reagents, Ca^{2+}-ATPase is also inhibited by calcium channel blockers. These are benzothiazipines like diltiazem, dihydropyridines like nifedipine, nimodipine and phenylalkylamines like verapamil. A calmodulin antagonist, trifluoperazine is also known to inhibit Ca^{2+}-ATPase [Lichtman *et al.* 1982]. Chlorpromazine, an antipsychotic drug, appears to inhibit Ca^{2+}-ATPase by binding to unsaturated fatty acids and inhibition of dephosphorylation step.[173] The aromatic amines like reserpine, prenylamine and imipramine inhibit Ca^{2+}-ATPase by reversibly interfering in the hydrolytic reaction step [Balzer *et al.* 1968]. Thapsigargin (TG), a tumour promoting sesquiterpene lactone is found to be a very potent inhibitor of ER Ca^{2+}-ATPase [Thastrup *et al.* 1990; Lytton *et al.* 1991].

Some toxins, like the mycotoxin cyclopiazonic acid (CPA), produced by certain species of the common fungal genera *Aspergillus* and *Penicillium* have been found to inhibit SERCA specifically. 2,5-Di(tert-butyl)-1,4-benzohydroquinone (tBHQ) is another specific inhibitor of SERCA [Wictome *et al.* 1992].

Interleukin-2 (IL-2), one of the most important cytokines, generally produced by activated helper T-lymphocytes, stimulates proliferation and effector functions in various cells of immune system; it has been shown to increase the activity of SR Ca^{2+}-ATPase in rat cardiomyocytes. It has been demonstrated that 3,5,3'-tri-iodo-L-thyronine (T3), in rat thymocytes, increases plasma membrane Ca^{2+}-ATPase activity [Segal *et al.* 1989].
The amphiphilic peptide mastoparan, isolated from wasp venom, has been shown to be a potent inhibitor of the sarcoplasmic reticulum Ca^{2+}-ATPase. Myotoxin a, a polypeptide of 43 amino acids from the prairie rattle snake *Crotalus viridis viridis*, also inhibits the activity of the Ca^{2+}-ATPase of skeletal muscle sarcoplasmic reticulum [Baker *et al.* 1995]. Mellitin, a basic peptide isolated from bee venom also inhibits SR Ca^{2+}-ATPase [Voss *et al.* 1991]. Palytoxin, a coral toxin significantly reduces Ca^{2+} pumping of isolated SR vesicles [Kockskamper *et al.* 2004]. Nonylphenol and 3,5-dibutyl-4-hydroxytoluene (BHT) have also been shown to inhibit Ca^{2+}-ATPase activity of skeletal muscle sarcoplasmic reticulum [Michelangeli *et al.* 1990]. Disulfiram [bis(diethylthiocarbamoyl)disulphide] has been found to stimulate the Ca^{2+}-ATPase of skeletal muscle sarcoplasmic reticulum reversibly [Starling et al. 1996]. The skeletal muscle SR Ca^{2+}-ATPase is also stimulated by jasmine, which increases the rate of dephosphorylation of the ATPase. Methyl jasmonate has shown to be a potent stimulator of SR Ca^{2+}-ATPase. Reports show that ceramide stimulates the plasma membrane Ca^{2+}-ATPase activity. Sphingosine, on the other hand, inhibits the calmodulin stimulated enzyme. Ivermectin, a macrocyclic lactone, was shown to be a potent Ca^{2+}-ATPase inhibitor (IC_{50} = 7μM), inhibiting SERCA1 and SERCA2b. Cyclosporin A, a cyclic oligotide and an immunosuppressant, inhibits the skeletal muscle Ca^{2+}-ATPase (SERCA1). Curcumin, a compound derived from the spice, turmeric, is a potent inhibitor of the SERCA Ca^{2+} pumps [Bilmen *et al.* 2001].

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Fewer reports are available on endogenous protein stimulators/inhibitors of Ca^{2+}- ATPases. Calmodulin is the naturally occurring activator of plasma membrane Ca^{2+}- ATPase. Phospholamban and sarcolipin are two small proteins which reversibly regulate the Ca^{2+} pump of sarcoplasmic reticulum. A protein activator of molecular weight 63 kDa has been reported from human erythrocyte membrane as an activator of Ca^{2+}-ATPase [Mauldin *et al.* 1980]. Another report describes a protein of molecular weight ~56-60 kDa from dog and beef heart sarcolemma which stimulates plasma membrane Ca^{2+}-ATPase from human erythrocytes as well as from cardiac sarcolemma [Reinlib *et al.* 1984]. Regucalcin, a calcium binding protein has been found to activate sarcoplasmic reticulum Ca^{2+}-ATPase. PDC-109, the major secretory protein from bull seminal vesicles has also shown to stimulate bovine sperm membrane Ca^{2+}-ATPase. A 12 kDa endogenous regulator protein purified from rat brain cytosol has exhibited inhibitory activity on Mg^{2+}-independent Ca^{2+}-ATPase while stimulating the Mg^{2+}-dependent form of the enzyme prepared from goat spermatozoa. Narayanan et al. reported a cytosolic protein fraction, termed CPF-I, obtained by $(NH_4)_2SO_4$ fractionation of rabbit heart cytosol which caused marked inhibition (upto 95%) of ATP-dependent Ca^{2+} uptake by cardiac sarcoplasmic reticulum. An endogenous inhibitor of SR Ca^{2+}-ATPase has been isolated from human placenta [Javed *et al.* 2000]. A protein kinase (cyclic AMP dependent) inhibitor (PKI) purified from bovine heart stimulates Ca^{2+}-ATPase activity in human erythrocytes. Recently protein isolated from goat testis cytosol and goat spermatozoa have also shown to stimulate Mg^{2+}-independent Ca^{2+}-ATPase [Sengupta *et al.* 2007; Sengupta *et al.* 2008]. Ghoshal et al. have also reported a low molecular mass protein isolated from bovine brain to stimulate the Mg^{2+}-independent Ca^{2+}-ATPase [Ghoshal *et al.* 2006; Ghoshal *et al.* 2008]

4. CONCLUSION

Reports on regulation of SERCA and elucidation of their mechanism of enzyme modulation will continue to throw light on the various aspect of enzyme action. Since SERCA plays a very important role in sperm cells, especially sperm motility, such reports will be of immense interest for endocrinologists and to reproductive science.

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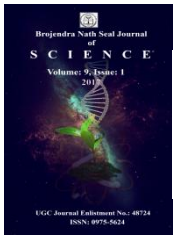

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Review Article

ANION–π AND LONE–PAIR–π INTERACTIONS: SPECIAL TYPE OF NON–COVALENT SUPRAMOLECULAR FORCES

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A B S T R A C T

Anions are essential species in biological systems and, particularly, in enzyme–substrate recognition. Therefore, the design and preparation of anion receptors is a topical field of supramolecular chemistry. Most host–guest systems successfully developed are based on noncovalent (ionic and hydrogen-bonded) interactions between anions and ammonium-type functionalities or Lewis acid groups. The ability of aromatic rings to act as acceptors in hydrogen bonds has been demonstrated extensively both by experimental and by theoretical means. Countless examples of D-H-π (H-π, D = O, N, C) interactions have been found in the three-dimensional structures of proteins. Much less is known with regard to the occurrence of other possible noncovalent interactions with aromatics in macromolecular structures, those with a geometry that points oxygen lone pairs into the face of a π system. However, since the past 5 years, an alternative route toward the synthesis of efficient anion hosts has emerged, namely, the use of "anion–π" interactions involving nitrogen-containing electron deficient aromatic rings, as the result of several favorable theoretical investigations. There also has been a growing interest in lone pair - π interactions in recent years In this Account, the state of the art in this growing area of anion-binding research and lone pair - π noncovalent interactions are presented and several selected examples have been discussed.

Keywords- *Non-covalent interactions, anion–π interactions, lone pair–π interactions, biological systems, nitrogen heterocycles*

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1. INTRODUCTION

A recently developed branch of supramolecular chemistry has unveiled novel types of non-covalent forces between electron deficient aromatic ring and anion (anion-π interaction) as well as between electron deficient aromatic systems and lone-pair of electrons. Anions are essential species in biological systems in which they often play crucial structural and functional roles.[1] Therefore, the design and preparation of anion receptors is a burgeoning field of research in supramolecular chemistry.[2] Most of the anion

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receptors successfully developed are based on hydrogen bonding,[3] electrostatic interaction[4] and coordination bonds to metal ions.[5] Since 2004, an alternative route for the synthesis of anion hosts involving π-electron deficient aromatic rings has emerged[6] as a sequel to the results of several theoretical investigations.[6a,6b,7] Such investigations also reveal that π-π-stacking motif interacts more efficiently with anion than single π-system, indicating that the interplay between anion-π and π-π interactions strengthens the anion-π interactions (Figure 1).[8] Non-covalent interaction between neutral molecule (Lewis base) and electron deficient aromatic molecule is crucial and plays an important role in both chemical and biological systems.[6a, 9] Studies on such noncovalent interactions may lead to the development of novel approaches for the design of effective systems capable of exhibiting noncovalent recognition properties at molecular level.

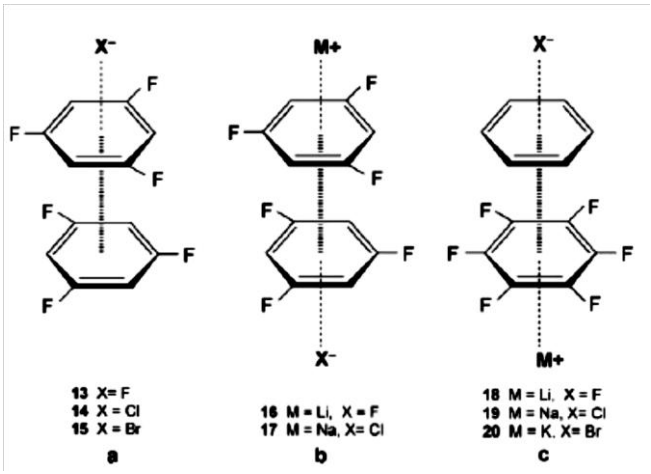

Fig. 1*: Schematic representation of systems with multiple non-covalent interactions*

2. INCIDENCE OF ANION-π AND LONE-PAIR-π INTERACTIONS IN BIOLOGICAL SYSTEMS

Several electron deficient aromatic moieties are found to be present in biomolecules. In biological system anion recognition is of prime importance since more than 70% of enzyme substrates and cofactors are anions.[10] Several halide-nucleobase interactions are evident in literature. Close contacts between the centroids of coordinated adenine, guanine and thymine nucleobases and fluorine atom of tetrafluoroborates are observed in cobalt(II), palladium(II) and copper(II) complexes respectively (Figure 2). These crystallographic evidences of halide-nucleobase interactions are suggestive of the existence of similar anion-π interactions in the biological domain.

Chloride channels, for example, are vital for living organism.[11] Malfunctions of such channels create serious diseases.[12] Therefore, design of efficient chloride channels are of great significance. Very recently Mackinson et al[13] have reported the crystal structure of chloride channel from *Salmonella enterica* serovar *typhimurium* (StCIC) (Figure 3). Three of the six amino acid found in the binding site of this chloride channel are aromatic. The phenyl rings, especially Phe348 (Figure 4) may have a crucial role to play in chloride recognition and sliding of the ions through the channel.

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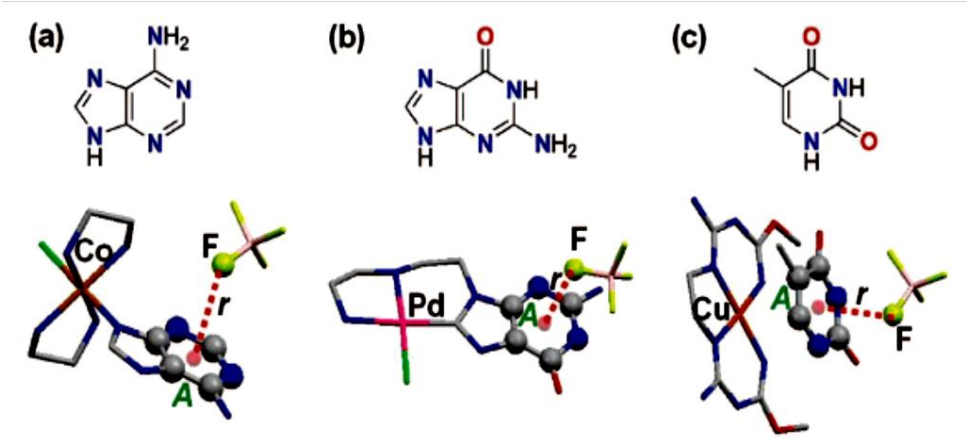

***Fig. 2**: Attractive contacts between DNA bases. (a) tetrafluoroborate-adenine interaction, distance of F---centroid A, r = 3.271 Å (Cambridge Structural Database code ICIDII). (b) Tetrafluoroborate-guanine interaction; r = 3.241 Å (CSD code IBIDIG) and (c) tetrafluoroborate-thyamine interaction; r = 3.282 Å (CSD code IVOROA)*

Lately, Motile et al have published a remarkable synthetic ion channel based on anion-π recognition[14] (Figure 4).

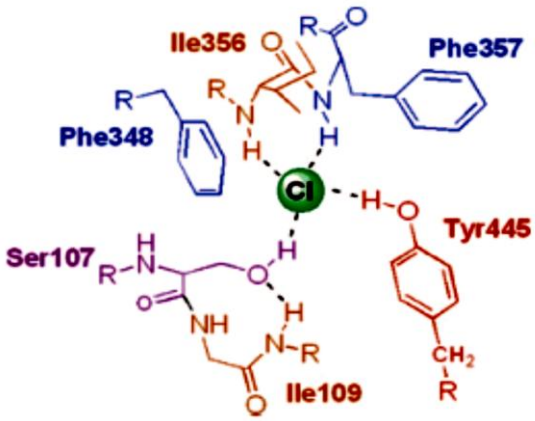

***Fig. 3**: Schematic representation of the receptor site of a CIC chloride channel, revealing the presence of six amino acids at the binding sites.[13]*

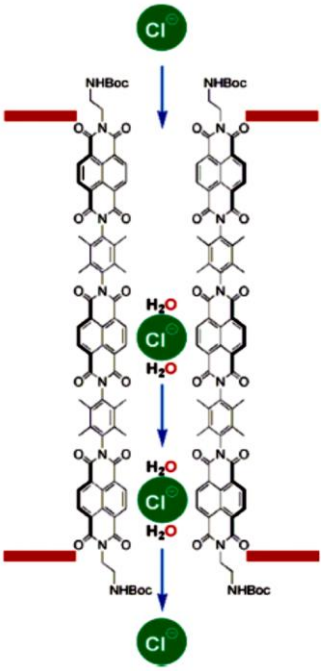

***Fig. 4**: Electron deficient rod as chloride-π slides in lipid bilayer membrane.[14]*

The involvement of lone-pair-π interactions in biological systems is also of extreme importance and is receiving great deal of attention from the scientific community in recent time.[6a,9,15] Couple of interesting examples of H_2O-π interactions within RNA pseudoknot

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have been demonstrated by Egli et al[16] (Figure 5). Such water- nucleobese interactions are of prime importance for the frame-shifting activity of pseudoknots and for the stability of sugar-nucleobase intramolecular interactions. Such lone-pair-π interactions have also been observed in several proteins.[9]

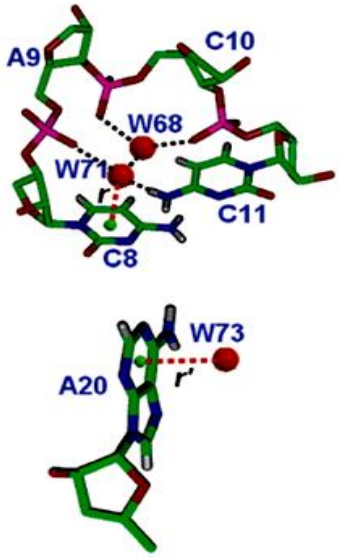

***Fig. 5**: O_{water}- π interactions observed in a RNA molecule.*[16]

3. ROLE OF NITROGEN HETEROCYCLES IN ANION-II AND LONE-PAIR-II INTERACTIONS: EXPERIMENTAL EVIDENCES

Several pioneering theoretical and experimental studies revealed that *N*-heterocycles can participate effectively in key supramolecular interactions like anion-π and lone-pair-π types.[6a,6b,9,17] These heteroaromatic moities when electron deficient, can act as Lewis acid which favorably interacts with anions and electron rich neutral molecules with binding energies comparable to those achieved in cation-π interaction (~20-50 kJ/mole) as well as in moderate hydrogen bonding (~15-20 kJ/mole).[17d]

Ever since the first experimental evidences of anion-π interactions, reported independently by Mayer et al and Reedijk et al in 2004, which involve *N*-heterocycles as π-electron deficient aromatic moiety, a number of interesting examples of anion-*N*-heterocycle interactions have been reported in literature. Mayer et al[6i] reported a Cu(II) complex of hexakis(pyridine-2-yl)-[1,3,5]-triazine-2,4,6,-triamine (L_A, Figure 6) ligand where Cl^- counter-anion establishes anion-π interaction with triazine ring of L_A (Figure 7). Almost simultaneously, Reedijk et al[6h] also reported a Cu(II) complex $[Cu_4(L_B)Cl_4][Cl]_4(H_2O)_{13}$ involving N, N′, N″, N‴-tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-triazyl}-1,4,8,11-tetraazacyclotetradecane (L_B, Figure 6). In this complex molecule two Cl^- anions are in close contact to the triazine rings (Figure 8).

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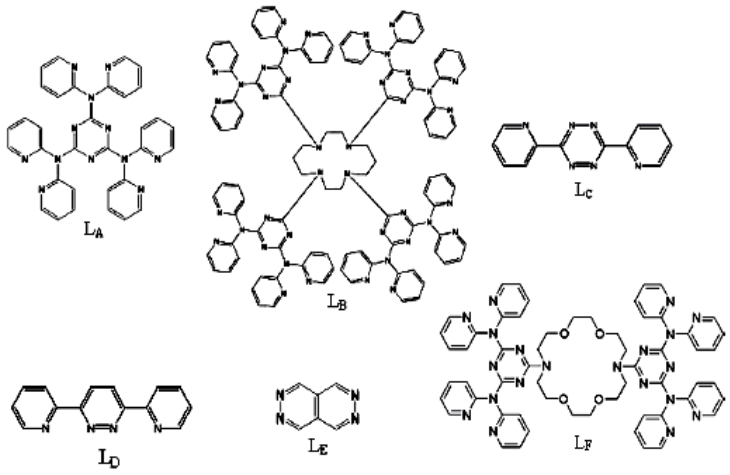

***Fig. 6**: Different types of electron deficient N-heterocyclic ligands which are effective for establishing anion-π and lone-pair-π interactions*

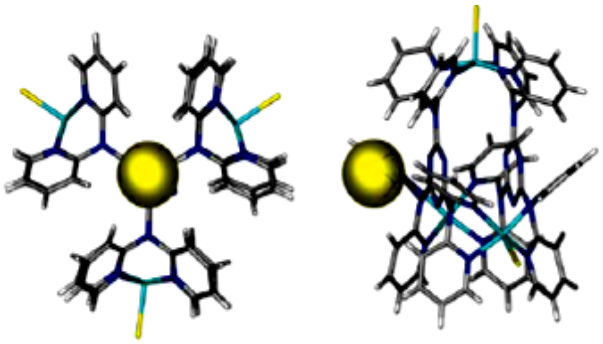

***Fig. 7**: Schematic drawing of front (left) and side (right) views of $[[L_A(CuCl)_3](Cl)]^{2+}$.*

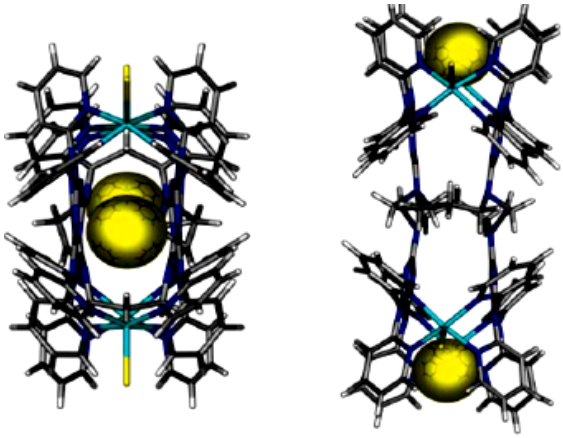

***Fig. 8**: Crystal structure of $[Cu_4(L_B)Cl_4](Cl)_4(H_2O)_{13}]$ from two different perspectives.[6h]*

A series of attractive interactions between polynuclear anions and the tetrazine-based-ligand (L_C, Figure 6) or the pyridazine-based ligand (L_D, Figure 6) have been reported by Dunbar et al.[6f] For instance, the solid state structure of $[Ag_4(L_D)_4](PF_6)_4$ formed from the reaction of $AgPF_6$ with L_D in nitromethane shows several strong binding interactions between the PF_6^- ions and pyridazine rings (Figure 9).[6f] Structure of $[Ag_2(L_C)_3](SbF_6)_2$ exhibits a rare crystallographic example of an anion-π_6 system where six anion-π interactions are present per participating SbF_6^- anion (Figure 10). These ring-π systems further participate in π-π-stacking interactions to establish anion-π-π interactions.[6f] Strong anion-π binding interactions have been demonstrated by Domasevitch et al[6d] using *N*-heterocycle pyridazo[4,5-d] pyridazine (L_E) (Figure 6) as ligand. A series of remarkable anion-pyridazine supramolecular associations have been observed in the reported molecule (Figure 11).

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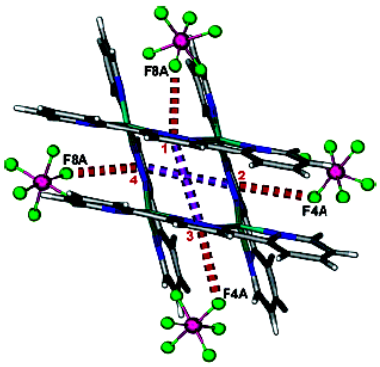


***Fig. 9**: Grid-type structure of $[Ag_4(L_D)_4](PF_6)_4$ depicting the π-π and anion-π interactions*

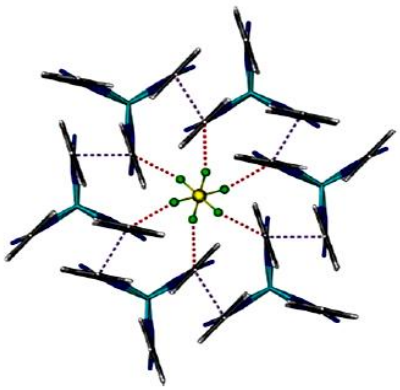
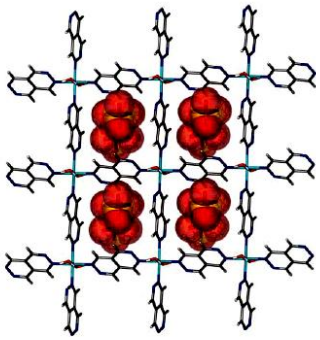


***Fig. 10:** Anion-π interactions between a SbF6- anion and six tetrazine rings in [Ag2(LC)3] (SbF6)2.*



(a)

***Fig. 11**: 2D square grid structure of $[Cu(H_2O)_2(L_E)_2](ClO_4)_2.4H_2O$ with each of the square meshes encapsulating two perchlorate anions with short O---π contacts.[6d]*

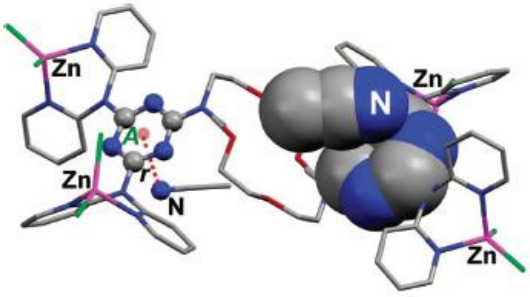


***Fig. 12**: Representation of the zinc complex $[Zn_4(L_F)Cl_8](CH_3CN)_2$ showing the interaction of acetonitrile molecules with each triazine unit of the ligand.[17d]*

Recently, Reedijk et al[17d] have described the first crystallographic evidence of acetonitrile-π interactions with the electron deficient nitrogen heterocyclic L_F (Figure 6). The reaction of this ligand with $ZnCl_2$ in 1:1 methanol/acetonitrile solvent mixture yields a tetranuclear zinc complex $[Zn_4(L_F)Cl_8](CH_3CN)_2$, whose solid state structure (Figure 12) suggests the presence of acetonirile-triazine close contacts.

4. CONCLUDING REMARKS

Anion-π and lone pair-π interactions are being recognized as important supramolecular bonding contacts by the scientific community. Thus, research investigations are increasingly dedicated to the study of these noncovalent contacts. The illustrative examples cited here clearly indicate that interactions between anion and electron-rich molecules with π-acidic rings are certainly important bonding contacts that should be used by the supramolecular chemist to build multidimensional molecular structures.

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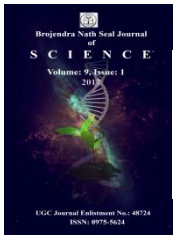

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Review Article

GREEN CHEMISTRY: A TOOL FOR SUSTAINABLE DEVELOPMENT

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A B S T R A C T

The concept of sustainable development is deeply interrelated to the very existence of mankind and living bodies on the mother earth. Sustainable development aims to maintain economic advancement and progress with the protection of long-term value of the environment. It is defined [1] as the "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." On the other hand the scientific progresses, particularly chemical advancements have undeniable contribution to development of modern civilization. But there are a large number of instances where various chemical developments also bring new environmental problems and harmful unexpected side effects. In this context Green Chemistry plays a vital role to achieve the sustainable development.

Keywords: *Green chemistry; Atom economy; biocatalysts; environmentally benign chemistry*

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1. INTRODUCTION

The term Green Chemistry is defined [2] as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances." Since its initial introduction in the early 1990s, Green Chemistry has spread throughout all aspects of the international chemical enterprise. It is now well recognized that Green Chemistry affects all of the various subdisciplines of chemistry and maintains a correlation with industry, academia and government. A central goal of Green Chemistry is to avoid hazard in the design of new chemicals. To achieve this objective it is essential for the chemists to have precise information about the hazardous potential of the chemicals in advance. Selection of proper synthetic procedure also plays a critical role. Hence, Green Chemistry is a new "philosophy" of how to make chemical products in the chemical industry and laboratories. It seeks innovative design and changes in the chemical

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processes that can eliminate hazards and helps scientists achieve the goal of sustainable development.

2. OBJECTIVES OF THE PAPER

It is now established that the science of chemistry is central to addressing the problems facing by the environment. Thus there is an increasing appreciation that the practice of Green Chemistry is imperative in design and attainment of sustainable development. A central driving force in this increasing awareness is that green chemistry accomplishes both economic and environmental goal. Being the part of the environment and society, every citizen in general and the researchers in particular should have a sound idea about sustainable development and how Green Chemistry serves as an efficient tool to achieve it. The present paper aims to provide an introductory idea about Green Chemistry, its basic principles and future perspective of this emerging field. It also intends to encourage the young researchers and students to practice and research on Green Chemistry to attain the sustainable development.

3. HISTORICAL CONTEXTS OF GREEN CHEMISTRY

Green Chemistry traces back several decades and can be linked to the public awareness on environmental pollution in USA and other industrial countries of the 1960s and 1970s. In 1969 the US Government under the pressure from society established the Citizen's Advisory Committee on Environmental Quality and a Cabinet-level Environmental Quality Council "The Environmental Protection Agency" (EPA). Two decades after the implementation of the EPA, The Pollution Prevention Act (PPA) came into existence in 1990, which enforced eco-friendly strategies and made considerable efforts to reduce source waste. In 1991, the Office of Pollution Prevention and Toxics (OPPT) launched a model research grants programme named "Alternative Synthetic Pathways for Pollution Prevention." In 1993, it was expanded to include other topics, such as greener solvents, safer chemicals, and used the name "Green Chemistry". Paul Anastas, A chemist, who was responsible for these programmes, deeply associated with it and coined the term "Green Chemistry". In 1997 the first International Green Chemistry Conference took Place in Venice under the patronage of IUPAC [3]. In the same year The Green Chemistry Institute of the American Chemical Society was established. The inaugural edition of the Journal of Green Chemistry [4], sponsored by the Royal Society of Chemistry, appeared in 1999.

4. TWELVE PRINCIPLES OF GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT

As pointed out earlier, Paul Anastas coined the term "Green Chemistry" to focus attention on this area of research and development. He also developed a set of guidelines that chemists use in order to perform Green Chemistry in a better way. The most important aims of Green Chemistry were defined in those principles which are popularly known as 'Twelve Principles

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of Green Chemistry'. These principles are very intuitive and simply good to practice. The guide lines help chemists to fulfill their unique role in achieving sustainable development. If we carefully observe of these principles it becomes clear that each of them is directly or indirectly connected with the very aim of sustainable development. These principles are:

4.1.Prevention

It is better to prevent waste than to clean or to treat after its formation. This is a fundamental principle and most of the other principles are framed in the light of this principle. It is well known that an ounce of prevention is worth a pound of cure. The spirit of preventive measure has inspired the scientists to develop many new methodologies and techniques in the last few decades. By adopting new innovative techniques and synthetic approach Green Chemistry aims to prevent waste and toxic byproduct in advance. Throughout the history there have been many cases of environmental disaster (like Bhopal, India) which took place only due to lack of preventive measures.

4.2.Atom economy

This principle states that it is best to use all the atoms in a chemical process. In an ideal reaction, all reactant atoms end up within the useful product molecule. In this connection it should be remembered that a reaction may have a high percentage yield but a low percentage atom economy, or vice versa. As Trost has outlined [5], a synthetic transformation can achieve 100% yield of product and still generate a substantial amount of waste if the transformation is not 'atom economic'.

Mathematically the percentage of atom economy is expressed by:

% Atom Economy = (Formula Weight of Product ÷ Formula Weight of Reactants) X 100%

4.3. Less hazardous chemical synthesis

This principle emphasizes on how we make molecules and materials. The goal is to reduce the hazards of a particular chemical synthesis. Traditionally chemists have not paid much attention about what reagent they are using and the hazards that are associated with them. Usually chemists use whatever means to carry out a particular synthesis. But today's chemists search for less toxic reagent and less hazardous pathway. Less toxic materials reduces hazards to workers in industries and laboratories, which in turn make little pollution to the environment. In brief, this principle focuses on choosing reagents that pose minimum risks and generate only benign-products.

4.4. Designing safer chemicals

This principle focuses on the products that we make. The products can be generated that are inherently safer for the desired target application. Everyone wants safe products. This principle is aimed at designing products which are safe, non-toxic and efficacious. At present there are millions of chemical substances and materials in the market which are consumed by community. But all of these compounds are not equally safe and target specific. Thus, synthesis of target specific chemicals is a big challenge to the researchers. For example, researchers are now trying to synthesize pesticides that are highly specific to a particular pest organism, but at the same time non-toxic to the surrounding wildlife and ecosystem. This principle is equally applicable in drug designing.

4.5. Safer solvents and auxiliaries

Most of the chemical reactions are carried out in solvents. And traditionally used most of the organic solvents pose hazards and toxicity in nature. They provide volatile organic

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compounds (VOC's) which add to pollution and can be extremely hazardous to human. Green chemistry initiated a big challenge in search of less toxic solvents. The widely used solvents are alcohol, benzene (carcinogenic in nature), CCl_4, $CHCl_3$, CH_2Cl_2 etc. Chlorinated solvents are exceedingly harmful to environment. These traditional solvents are now being replaced by safer greener solvents. The safer solvents includes ionic liquids, super critical CO_2 fluid or super critical water. Solvent free approaches successfully utilize clays, zeolites, silica and alumina etc. Reactions in aqueous medium are always preferred to other mediums.

4.6. Design for energy efficiency

The energy requirement of a chemical processes is a vital issue and should be recognized for their environment and economic impacts. This principle focuses on creating products and materials in a highly efficient manner so that the energy involved with the production of materials gets minimized. It also reduces the pollution and cost. This principle searches for the most energy efficient pathway of chemical synthesis. Reactions which take place at room temperature and pressure are highly encouraged. It reduces the energy requirement of a chemical transformation. Introduction of microwave irradiation and sono-chemistry (ultrasound energy) is very much relevant in this regard.

4.7. Use of renewable raw materials and feedstocks

Now a days, starting materials for majority of synthetic processes are of petroleum origin or products of refining. Near about 90-95% of the products in our daily life are made from petroleum. Hence, petroleum is used not only for transportation and energy but also in making products. This principle aims to shift our petroleum dependence by using renewable raw materials that can be gathered or harvested locally. Biodiesel is one of the excellent examples which are being used as an alternative fuel. Polylactic Acid (PLA) is another bio-based plastic made from renewable feedstocks such as corn and potato waste. Therefore, it is an essential task of the Green Chemist to find out alternative manufacturing processes which use renewable raw materials. This has a profound impact on the economic growth of a country.

4.8. Reduce intermediate derivative

This principle aims to reduce unnecessary derivatization (use of blocking group, protection /deprotection, temporary modification of physical and chemical processes) in the synthetic route. The use of derivatization requires additional reagents, which in turn are wasteful and produce large amount of by-products. This principal insists chemists to change their traditional outlook in chemical synthesis. Because majority of traditional synthesis follow multistep reactions accompanied by additional materials. Instead of that, more selective, tactfully chosen synthetic path is preferred where multistep route is avoided as well as protection of functional group is not required.

4.9. **Catalysis and catalytic reagent**

The use of catalyst in a chemical reaction reduces the activation energy and dramatically enhances the rate of a reaction. Hence, a catalyst finds an important place in green chemistry practice. A green catalyst has little or no toxicity and to be used in a cyclic process which ensures the high efficiency of a chemical reaction. Enzymes are the important class of biocatalyst which perhaps meets all the criteria of green catalyst. Green Chemistry aims to mimic the catalytic activity of enzymes. As a result of extensive research the toxic heavy

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metal catalysts are getting replaced with softer catalysts like zeolite, phase transfer catalyst, crown ether etc. In near future nanocatalysts will play a crucial role in this regard.

4.10. Design for degradation

It is a big trouble for the environmental chemists that most of the chemical products and consumer items are not biodegradable. Their persistence nature causes permanent environmental problem. Green Chemistry aims at designing products so that at the end of their function it will break down into hazardless substances. Plastics are the well known example of non degradable substances which pose serious environmental problem. Similarly pharmaceutical drugs such as antibiotics; widespread use of pesticides build up in our water streams. Thus green chemistry targets the pollutants at its very origin.

4.11. Real-time analysis for pollution prevention

In order to avoid the formation of hazardous substances analytical methodology needs to be further developed. The specially designed sophisticated analytical tools and techniques enable a chemist for real time analysis, in process monitoring and also help control prior to the formation of hazardous substances. This may reduce the generation of waste. Moreover it saves time as well as energy.

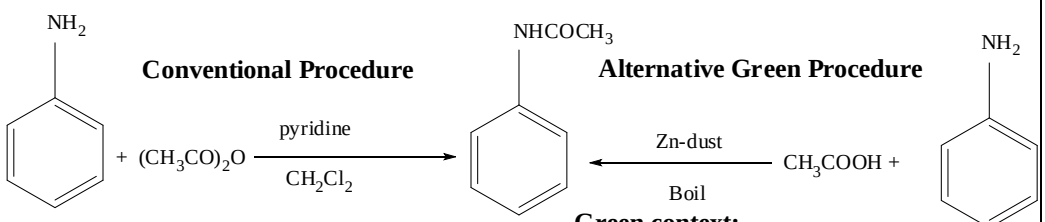
4.12. Inherently safer chemistry for accident prevention

This principle emphasizes on the safety of the involved persons as well as the surrounding community of the industry. Utmost care should be taken in the selection of raw materials, related chemical substances and the methodology adopted for a process. The reactants, products and the process should be inherently safe. This means that the concerned chemicals and their degraded products to be non-toxic, not dangerous (e.g. they will be non-explosive, non-allergic, non-inflammable etc.).

5. DIFFERENCES AND COMPARISONS AMONG THE CONVENTIONAL AND "GREENER METHOD"

At present there are large numbers of green methods which chemists adopt instead the conventional way of synthesis. Here, one representative chemical reaction (Fig-1) namely acetylation of primary amine [6] has been taken to highlight the beauty of the Green Chemistry.

Figure -1 (Preparation of acetanilide from primary amine)



Non-green Components:
Use of chlorinated solvent like CH_2Cl_2
Pyridine is also not eco-friendly
Acetic anhydride leaves one molecule of acetic acid unused (not atom-economic)

Green context:
Avoids use of acetic anhydride (usage banned in some states, due to its utility in narcotic business)
Minimizes waste by-products
Avoids hazardous solvent

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6. SUSTAINABLE DEVELOPMENT, ENVIRONMENTAL CHEMISTRY AND GREEN CHEMISTRY

The concepts of sustainable development aim to maintain economic development and progress while protecting the long-term value of the environment. Living within our environmental limits is one of the central principles of sustainable development. One implication of not doing so is climate change. But the focus of sustainable development is far broader than just the environment. It is also about ensuring a strong, healthy and just society. The terms 'Environmental Chemistry' and 'Green Chemistry' are two different aspects of environmental pollution studies. The former is the study of chemical pollutant in natural environment while the later is an attempt to design chemical products and processes to reduce or eliminate the harm they cause to the environment. Environmental chemistry focuses on the study of pollutant chemicals, whereas Green Chemistry seeks to reduce pollution at source. In brief, the Green Chemistry is the tool, the approach is Environmental friendly and the aim is to achieve the Sustainable development.

7. CONCLUSION

Green chemistry has come a long way since its birth in 1990, growing from a small grassroots idea into a new approach to scientifically-based environmental protection. All over the world, government and industries are working with green chemists to transform the economy into a sustainable development. It goes without saying that sustainability must be achieved if civilization is to survive with a reasonable living standard on Planet Earth. There's no denying that Chemists can play a key role in achieving the desired sustainability. While many exciting new greener chemical processes are being developed it is clear that a far greater number of challenges lie ahead. In this context the inception of Green Chemistry is very much timely. Green chemistry may be the next social movement that will set aside all the world's differences and allow for the creation of an environmentally commendable civilization.

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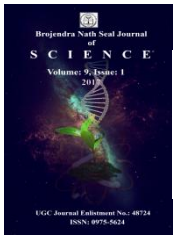

Brojendra Nath Seal Journal of SCIENCE

Research Article

SOLVENT EFFECT ON PHOTOPHYSICAL PROPERTIES OF NAPTHOXAZINONE DERIVATIVES

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A B S T R A C T

Biologically important napthoxazinone derivatives were synthesized. The UV-vis and emission spectra were recorded. The effects of polarity of various solvents on the absorption and fluorescence spectra of the compounds were studied.

***Key words**: Napthoxazinone, UV-vis spectra, fluorescence, solvent effect.*

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1. INTRODUCTION

Important class of biologically active natural and non natural products have been a part of nitrogen containing heterocycles which are of special interest in present day research [Turgut *et al.* 2007; Swinbourne *et al.* 1987; Imran *et al.* 2010; Rehman *et al.* 2010; Adib *et al.* 2006]. Among those 1,3-oxazines and their derivatives are reported to have potential biological activities like antibacterial, antitumor, analgesic, anticonvulsant and they are receptors of progesterone and melatonin. [Kurz *et al.* 2005; Zhang *et al.* 2003; Poel *et al.* 2002; Rehman *et al.* 2010; Adib *et al.* 2006]. They have generated interests as they are probable receptors of seretonin [Zhou *et al.* 2005] and dopamine [Jones *et al.* 1984]. Benzo-1,3-oxazines were reported as biologically active antihypertensive, antirheumatic, antimalarial, anti-anginal agents [Damodiran *et al.* 2009]. Among 1,3-oxazines systems naphthoxazine derivatives have therapeutic potential in the treatment of Parkinson's diseases [Joyce *et al.* 2003; Kerdesky *et al.* 2005] and naphthalene-condensed 1,3-oxazin-3-ones have been reported to act as potent antibacterial agents [Latif *et al.* 2002]. Again they are good synthetic precursors in the preparation of phosphinic ligands for asymmetric catalysis [Wang *et al.* 2002]. The effect of solvent on photophysical properties of organic compounds have immense scienific and technological importance. It is well known that the photo-physical

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behavior of a dissolved organic compound depends on the nature of its environment, the intensity, shape, and maximum absorption wavelength of the absorption band of a compound in solution depends strongly on the solvent-solute interactions, polarity of solvent, viscosity and other solvent nature [Zakerhamidi *et al.* 2012; Haidekkar *et al.* 2005; George *et al.* 2007]. We have synthesized various naphthalene-condensed 1,3-oxazin-3-ones from reported method [Dabiri *et al.* 2007] and studied the effect of various solvents on the UV-vis and emission spectra of the synthesized compounds.

2. EXPERIMENTAL

The solvents were purchased from Merck and the Sisco Reasearch Laboratories without further purification. UV-vis spectra of compounds were recorded in HPLC grade solvents on a Perkin-Elmer UV/VIS spectrometer (Model: Lambda 25). Fluorescence spectra were generated on a Perkin Elmer Fluorescence spectrometer (Model: LS 55). All the spectral studies including absorption and emission spectra were performed in quartz cells. In all the cases the concentrations were maintained at 5×10^{-5} M.

The oxazinones (Scheme 1) were synthesized and purified according to the literature method in our laboratory [Dabiri *et al.* 2007].

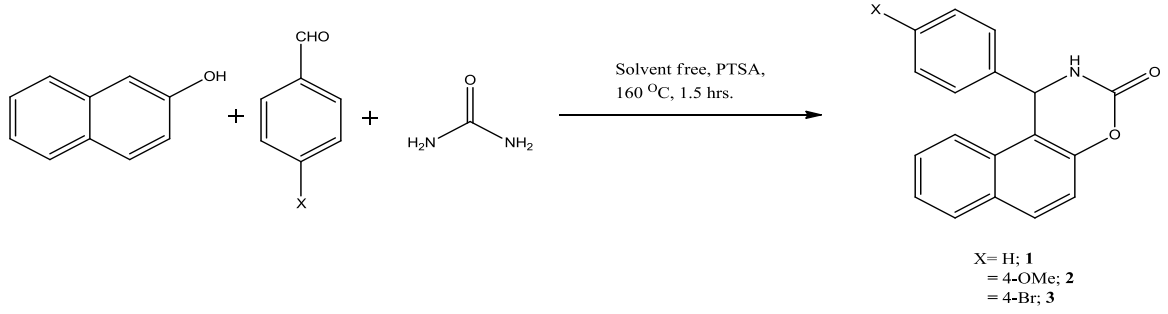
General method:

A mixture of β-naphthol (1mmol), aromatic aldehyde (1 mmol), urea (1.5 mmol) and PTSA (0.3 mmol) were finely mixed.The reaction was placed in a screw capped vial and heated at 160 ˚C for 1.5 hr. After cooling the reaction mixture was washed with water and recrystallized from ethyl acetate-hexane(1:3) to afford product.

1-phenyl-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**1**): yeild: 57%; mp: 218 ˚C; δ: 6.19 (d, J = 2.1 Hz, 1 H, CH), 7.22-8.00 (m, 11 H, Ar-H), 8.9 (br s, 1 H, NH).

1-(4-methoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**2**): yeild: 57%; mp: 186 ˚C; δ: 2.98 (3H, s, OCH_3) 5.66 (s, 1 H, CH), 6.75-7.75 (m, 10 H, Ar-H), 8.8 (br s, 1H, NH).

1-(4-bromophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (**3**): yeild: 60%; mp: 220 ˚C; δ: 5.76 (s, 1 H, CH), 7.17-7.86 (m, 10 H, Ar-H), 8.91 (br s, 1H, NH).



Scheme 1

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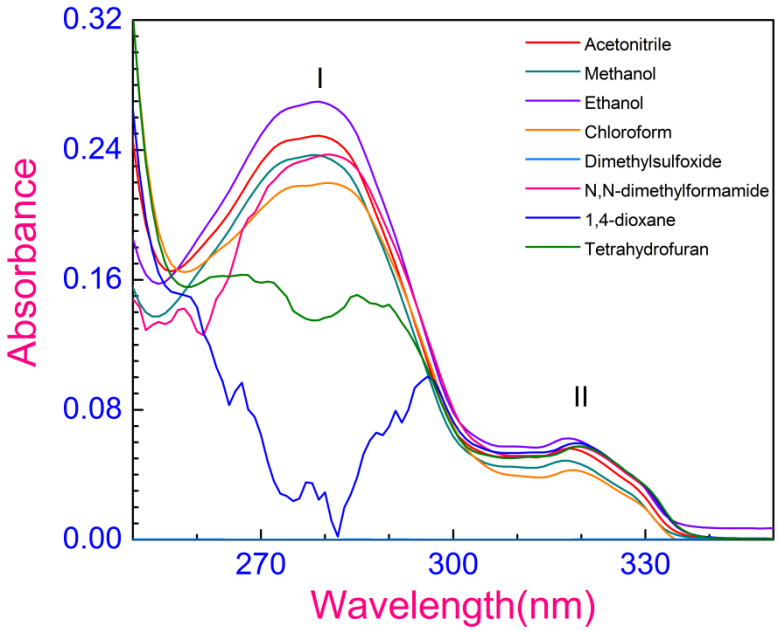

Fig. 1: *Solvent effect on absorption spectra of compound* ***1*** *(5 × 10^{-5} M).*

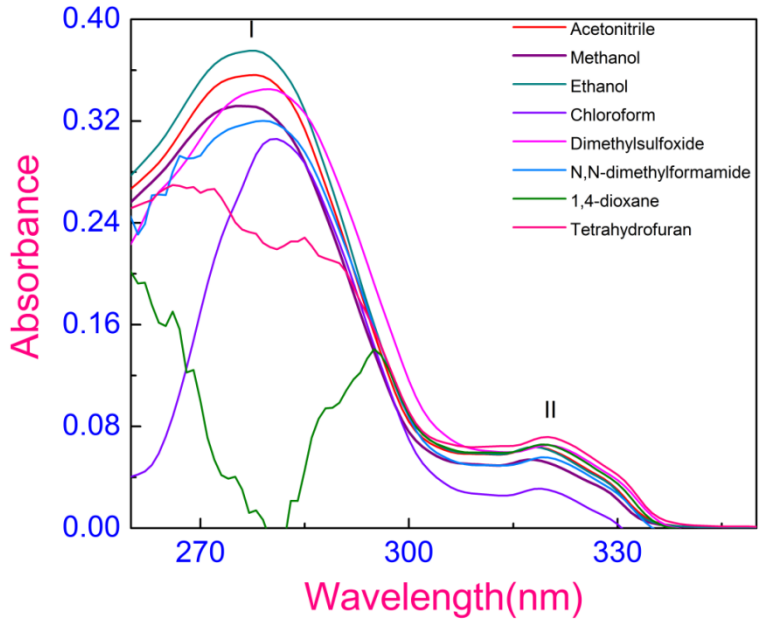

Fig. 2: *Solvent effect on absorption spectra of compound 2(5 × 10-5 M).*

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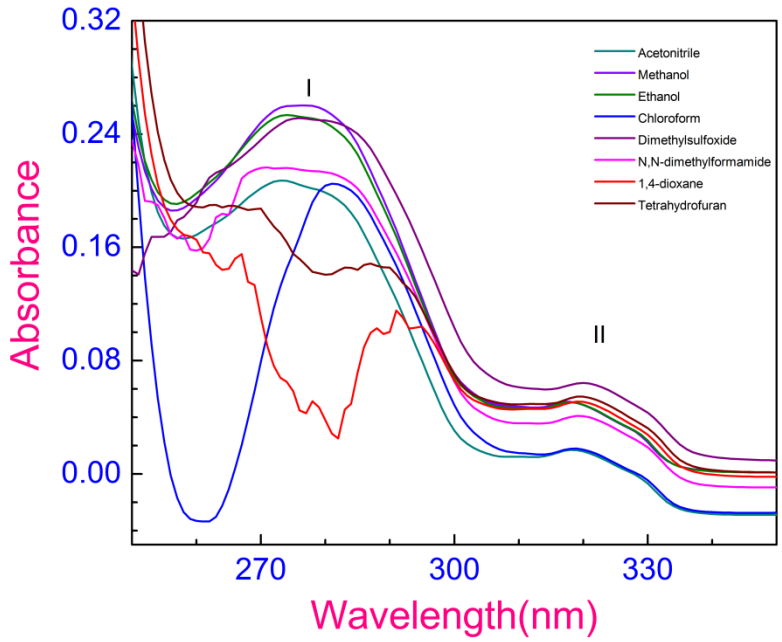

Fig. 3: *Solvent effect on absorption spectra of compound 3 (5 × 10-5 M).*

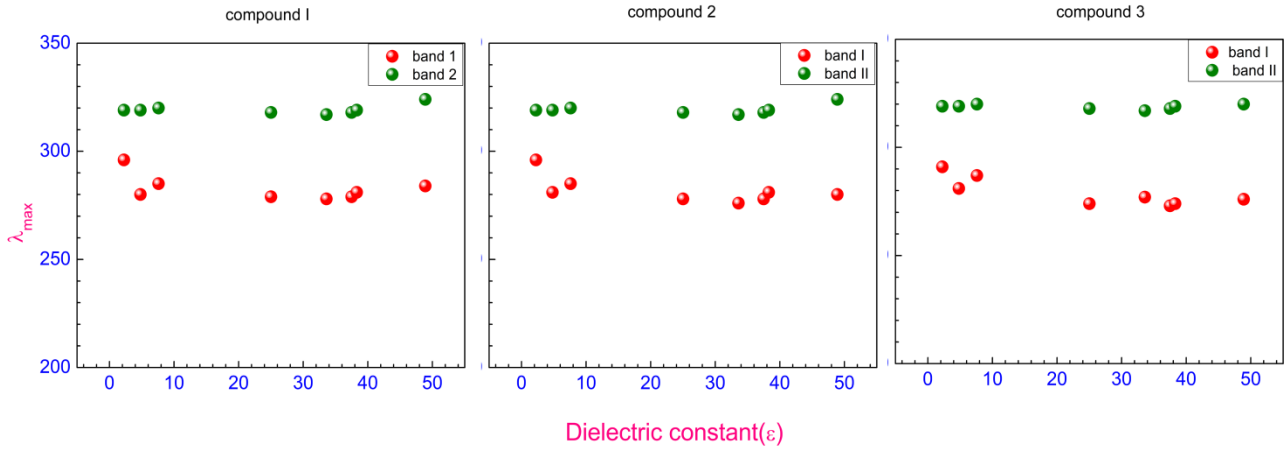

Fig. 4*: Plot of λ_{max} of compound 1,2.3 vs dielectric constant of the solvents*

3. RESULT AND DISCUSSION

The compounds **1**, **2** and **3** were synthesized by a one pot solvent free condensation method following a reported literature. The purification was checked by thin layer chromatography, melting point ^{1}H-NMR spectroscopy.

The absorption spectra of the three napthoxazine derivatives were taken in various solvents with an aim to visualise the effect their polarity effects on the electronic absorption spectra of the compounds. In these compounds an absorption band centered around 276 nm to 295 nm (band I) and another centred around 317 nm to 324 nm (band II) were noticed. The first one due to the presence of the ester carbonyl and the second one due to the presence of

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the napthalene ring system. It was seen that a general trend followed for all the three compounds **1**, **2** and **3** ie., for the solvent with least polarity as for example 1,4-dioxane followed by tetrahydrofuran there was a red shift of the absorbtion band I from 285 to up above 290 nm. In case of highly polar solvents the maxima for band I centred between 276 to 280 nm. For the band II the aforesaid trend was not followed the band remained more or less the same in all the solvents. For the compound **1** the band II got a slight red shift for highly polar dimethyl sulfoxide. Aprobable reason for the red shift of the absorption band I in least polar solvents due to absence of solvent dipoles interacting with carbonyl dipoles which lead to an interaction between the carbonyl dipoles of the each molecule further leading to stabilsation of the π^* orbital. The UV/vis spectroscopic shifts of compounds **1**, **2** and **3** are depicted in Fig. 1, Fig. 2 and Fig. 3 and Table 1.

A plot of λ_{max} versus dielectric constant for dependance on solvent polarity on absorption maxima was done for further corroboration (fig. 5).

Table 1: *Absosorbtion maxima of the compounds in various solvents*

Compounds	*Band*	*Wavelength at absorbtion maxima (in nm) in various solvents*							
		Acetonitrile	*Methanol*	*Ethanol*	*Chloroform*	*Dimethyl sulfoxide*	*Dimethyl formamide*	*Dioxane*	*Tetrahydrofuran*
1	I	279	278	279	280	284	281	296	285
	II	318	317	318	319	324	319	319	320
2	I	278	276	278	281	280	279	295	285
	II	318	317	318	319	320	319	319	320
3	I	273	277	274	281	276	274	291	287
	II	318	317	318	319	320	319	319	320

Emission studies

In emission studies in all the three compounds **1**, **2** and **3** a more or less showed their emission maxima at 345.5 nm when excited at 278 nm with excitation slit at 12.5 nm and emission slit at 2.5 nm. The oxazinone moities showed a slight stoke shift at 348 nm. The emission intensities for the probes were much high in polar solvents than non polar solvents. The fluorescence dependance of the compound were depicted in fig. 5, 6 and 7.

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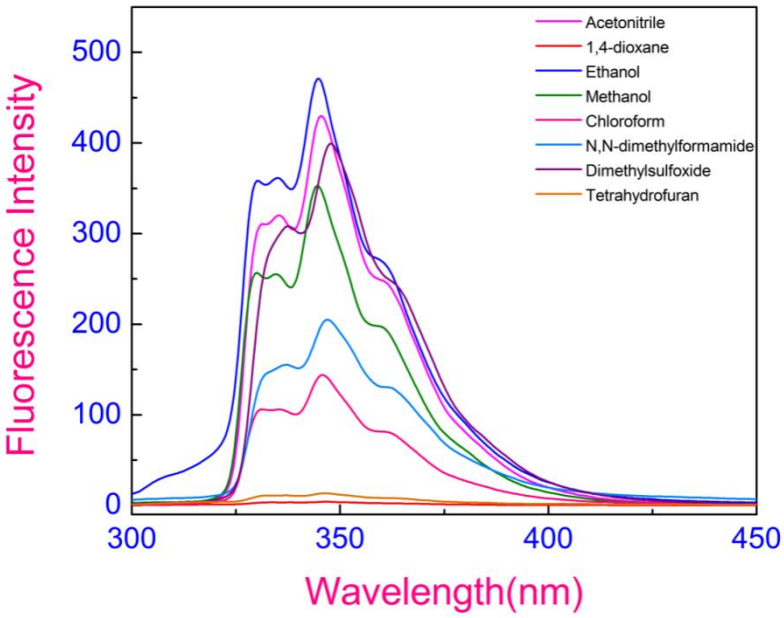

Fig. 5: *Solvent effect on emission spectra of compound 1 (5×10^{-5} M).*

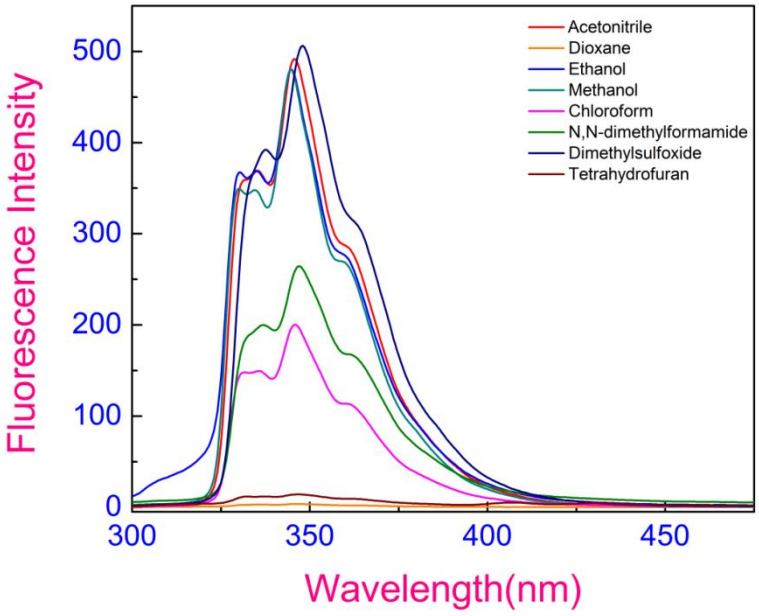

Fig. 6: *Solvent effect on emission spectra of compound 2 (1 × 10-5 M).*

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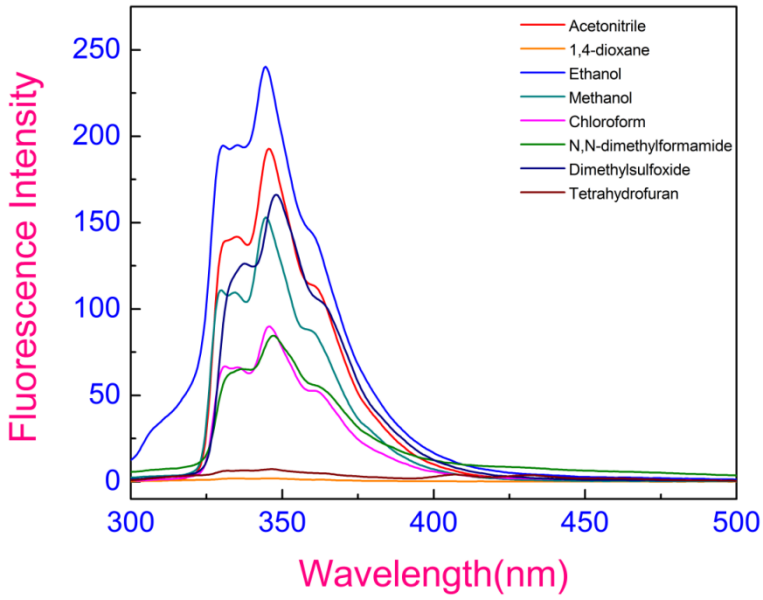

Fig. 7: *Solvent effect on emission spectra of compound* ***3*** *(5×10^{-5} M).*

4. CONCLUSION

In conclusion we can say that we have synthesized three known oxazinone based compounds which have been biologically important and studied the effect of solvent in their absorption and emission spectra. Our study can extended to various physical studies in future works with these important heterocycles.

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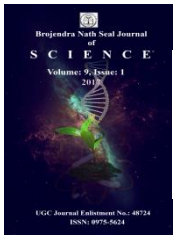

Brojendra Nath Seal Journal of SCIENCE

Research Article

STUDY OF SURFACE TENSION OF BENZONITRILE + ACETONITRILE AND BENZONITRILE + OCTANOL MIXTURE AT 293 K TO 313 K

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A B S T R A C T

Surface tensions have been measured for benzonitrile- acetonitrile and benzonitrile-octanol binary liquid mixtures over the entire mole fraction range at 293K, 303K and 313K. The surface tension values in mixed binary liquids are not simple mole fraction average of pure values. Excess surface tensions at each composition are calculated, at all the three temperatures studied. Surface enthalpy and surface entropy values at each mole fraction are measured from temperature study of surface tension. The results so found are explained.

Keywords: *Surface tension, Excess surface tension, Surface enthalpy, Surface entropy*

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1. INTRODUCTION

The thermodynamic properties of liquids and liquid mixtures have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer and fluid flow [Kim et al. 1988]. Surface tension is an essential thermo-physical property and needs to be well studied because it plays an important role in the design of contacting equipment involved in production processes - such as catalysis, adsorption, distillation and extraction [Lopez Lazaro et al. 2015]. The literature dealing with surface tension of binary liquid mixtures is extensive, but the systems involving alcohols are interesting [Peng et al. 2004; Luning Prak et al.2014; Taylor et al. 1996; Yoshimoto et al. 2002; Conor et al. 2010] because of their inherent nature of forming associations in the form of H-bonds within themselves or with other components (nitriles) in a liquid mixture. In this study, the surface property (surface tension), of a protic polar (octanol) – aprotic polar (benzonitrile) and an aprotic polar (benzonitrile) – aprotic

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polar (acetonitrile) liquid mixture is studied over the entire composition range. In order to have information regarding temperature dependence of this property such study is done at three different temperatures.

2. EXPERIMENTAL

The liquids used were of spectroscopic grade and used as received. All the mixtures were prepared by mass in glass stoppered flasks. The balance precision was $\pm 1 \times 10^{-4}$ g. The accuracy of the mole fractions was estimated to be within ±0.0001. The surface tensions of pure components and mixtures at the liquid-vapor interface were measured using the ring detachment method by a tensiometer. The temperature of the measurement cell was controlled within ± 1 K by a thermostatic water bath via an external circulating loop. Each value reported was an average of three measurements with an uncertainty of ± 0.01 mNm^{-1}.

3. RESULTS AND DISCUSSION

The measured values of surface tension (γ) of acetonitrile + benzonitrile and octanol + benzonitrile mixture at three different temperatures from 293 K to 313 K are listed in Table 1.

Table1: *Experimental Values of surface tension,γ, and calculated excess Surface Tension, γ^E, at different temperatures for the binary mixtures.*

System: Benzonitrile (1) + Acetonitrile (2) mixture						
X_1	γ/mNm^{-1}	γ^E	γ/mNm^{-1}	γ^E	γ/mNm^{-1}	γ^E
	293 K		303 K		313 K	
0.0000	29.21	0.00	27.92	0.00	26.61	0.00
0.1002	30.68	0.45	29.32	0.37	27.92	0.31
0.2003	31.89	0.63	30.58	0.60	29.16	0.55
0.2980	33.12	0.87	31.79	0.80	30.32	0.73
0.4005	34.25	0.95	32.95	0.91	31.45	0.84
0.5010	35.42	1.09	34.12	1.04	32.58	0.97
0.5992	36.29	0.96	35.01	0.92	33.44	0.84
0.7001	37.04	0.68	37.78	0.66	34.18	0.58
0.8006	37.99	0.61	36.76	0.60	35.08	0.47
0.9001	38.75	0.35	37.42	0.24	35.78	0.18
1.0000	39.42	0.00	38.21	0.00	36.60	0.00
System : Benzonitrile (1) + Octanol (2) mixture						
0.0000	26.18	0.00	25.33	0.00	24.39	0.00
0.1008	27.04	-0.47	26.34	-0.289	25.44	-0.18
0.1999	28.06	-0.77	27.44	-0.46	26.46	-0.37
0.3001	28.90	-1.25	28.02	-1.18	26.96	-1.09
0.3990	29.26	-2.20	28.43	-2.04	27.58	-1.68

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0.4996	30.16	-2.63	29.18	-2.58	28.09	-2.40
0.5980	30.94	-3.16	30.22	-2.81	29.21	-2.48
0.6997	32.46	-2.98	31.68	-2.66	30.64	-2.29
0.8008	34.01	-2.77	33.24	-2.40	32.43	-1.74
0.9003	36.74	-1.36	35.66	-1.27	34.28	-1.10
1.0000	39.42	0.00	38.21	0.00	36.60	0.00

The graphical variation of surface tension with mole fraction is shown in figure 1a. & b.

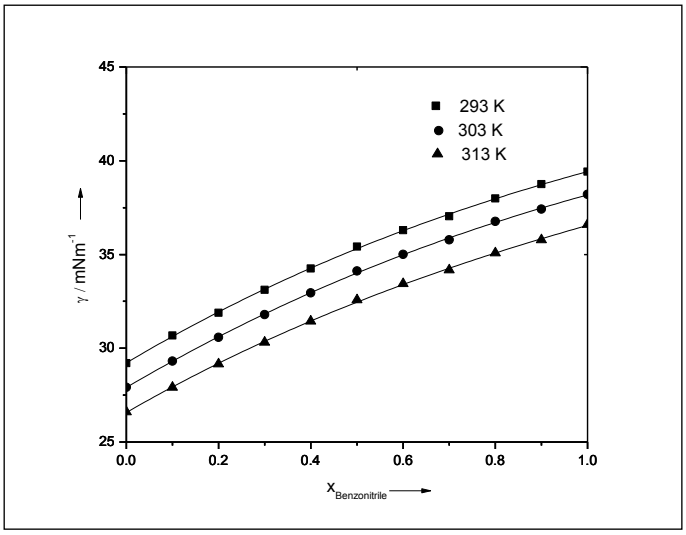

Fig.1a)*: Variation of surface tension with mole fraction for Acetonitrile + Benzonitrile mixture at different temperatures.*

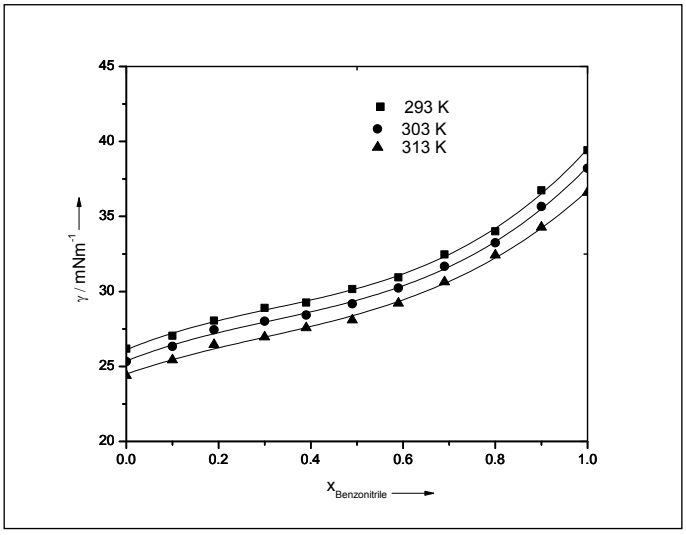

Fig.1b)*: Variation of surface tension with mole fraction for Octanol + Benzonitrile mixture at different temperatures.*

The figure shows non linear variation in both the cases. The excess surface tension, γ^E, was calculated by the following equation:

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$$\gamma^{E} = \gamma - (x_1\gamma_1 + x_2\gamma_2) \qquad \text{--- (1)}$$

where γ is the surface tension of mixture, x_1 & x_2 are the mole fraction and γ_1 & γ_2 are the surface tension of the pure components 1 & 2 respectively. The excess surface tension values of the liquid mixtures are also listed in Table 1. It has been found that excess surface tension values are positive for acetonitrile + benzonitrile mixture over the entire composition range at all three temperatures studied. But the case of octanol + benzonitrile mixture is completely different, when negative excess surface tension is found. The variation of excess surface tension as a function of mole fraction is shown in figure 2a. & b.

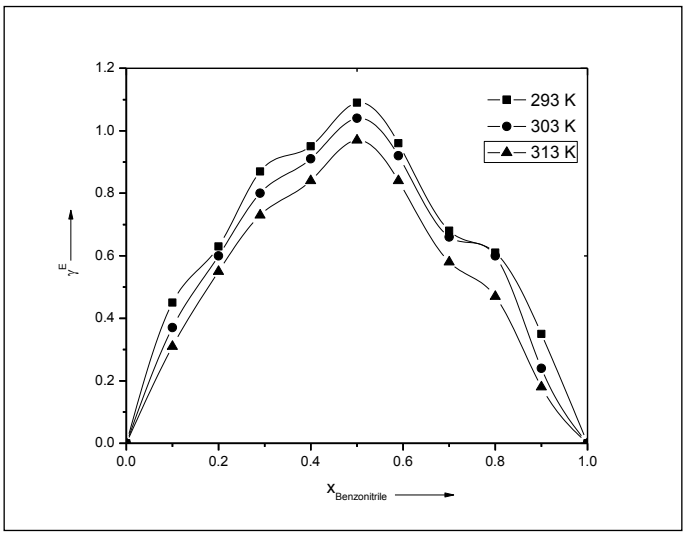

Fig.2a): *Variation of excess surface tension with mole fraction for Acetonitrile + Benzonitrile mixture at different temperatures.*

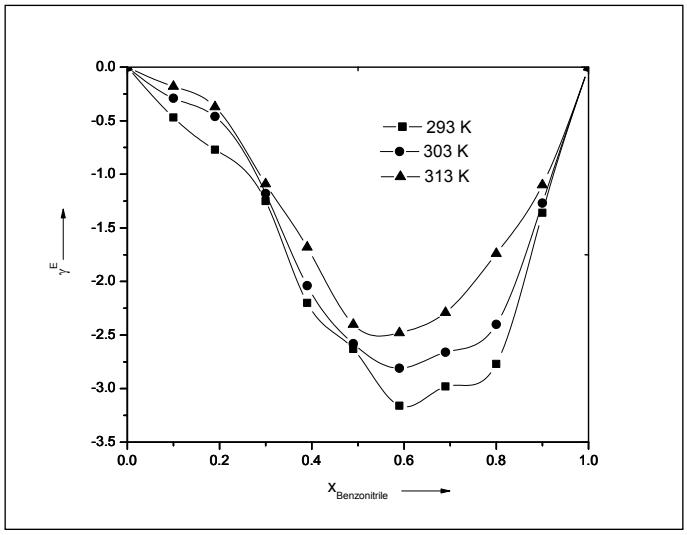

Fig.2b:) *Variation of excess surface tension with mole fraction for Octanol + Benzonitrile mixture at different temperatures.*

Tsierkezos and Filippous [Tsierkezos et al. 2006] suggest that the excess surface tensions indicate an uneven distribution of the components between the surface region and the bulk region. In case of acetonitrile + benzonitrile mixture, as benzonitrile is added to acetonitrile,

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the surface tension increases but this increase is greater than mole fraction average value. Actually due to addition of higher surface tension component (in this case benzonitrile) to a mixture, the added component accumulates more in the surface for positive excess surface tension. Therefore in terms of interactions, it definitely states that acetonitrile-benzonitrile interactions are less favourable than acetonitrile-acetonitrile or benzonitrile-benzonitrile interactions. On the other hand, for benzonitrile + octanol mixture negative excess surface tension definitely suggests that benzonitrile (in this case higher surface tension component) accumulates less in the surface than ideal state because of strong octanol – benzonitrile interactions [Tahery et al. 2006]. Specific H-bond interaction is intelligible in this case.

The temperature variation of surface tension values, allow the estimation of surface entropy ($S^{\gamma}/Jm^{-2}K^{-1}$) and surface enthalpy (H^{γ}/Jm^{-2}). At a given composition, the surface tension values, γ, can be fitted linearly with temperature (T/K) by the following equation:

$$\gamma = A + B(T/K) \quad \ldots(2)$$

The parameters A and B give the values of H^{γ} and S^{γ} respectively as:

$$\gamma = H^{\gamma} - S^{\gamma}(T/K) \quad \ldots(3)$$

The definition of these quantities are $H^{\gamma} = \gamma - T(\frac{\partial \gamma}{\partial T})_P$ and $S^{\gamma} = -(\frac{\partial \gamma}{\partial T})_P$ where S^{γ} represents the variation of entropy per unit surface area due to interface formation and is equal to the negative temperature parameter of the surface tension. Surface enthalpy, H^{γ}, is the sum of surface free energy required to extend the surface and the latent heat required to maintain isothermal conditions. The calculated values of H^{γ} and S^{γ} are listed in Table 2.

Table 2: *Derived surface enthalpy, H^{γ}, and surface entropy, S^{γ} for the binary mixtures:*

Benzonitrile (1) + Acetonitrile (2)			Benzonitrile (1) + Octanol (2)		
X_1	H^{γ}/mJm^{-2}	$S^{\gamma}/mJm^{-2}K^{-1}$	X_1	H^{γ}/mJm^{-2}	$S^{\gamma}/mJm^{-2}K^{-1}$
0.0000	67.30	0.13	0.0000	52.42	0.14
0.1002	71.12	0.14	0.1008	50.60	0.14
0.2003	71.90	0.14	0.1999	57.85	0.10
0.2980	74.16	0.14	0.3001	60.40	0.12
0.4005	75.30	0.14	0.3990	55.13	0.14
0.5010	79.54	0.15	0.4996	62.03	0.11
0.5992	78.09	0.14	0.5980	71.71	0.09
0.7001	78.99	0.14	0.6997	67.69	0.11
0.8006	80.69	0.15	0.8008	63.11	0.10
0.9001	82.31	0.15	0.9003	77.27	0.08
1.0000	80.79	0.14	1.0000	80.49	0.09

Surface enthalpy of the mixture increases as benzonitrile is added to the mixture. Surface entropies of benzonitrile + acetonitrile mixture do not change very much for composition change but in case of benzonitrile + octanol mixture surface entropy increases slowly as benzonitrile is added to the mixture.

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4. CONCLUSION

Thus the above study concludes that:

i) Surface tension of both the mixtures, benzonitrile + acetonitrile and benzonitrile + octanol system deviate from idealily.

ii) Positive surface excess is found for nitrile + nitrile system while negative surface excess is the case of nitrile + alkanol system.

iii) The positive surface excess can only be explained due to unfavorable 1-2 interactions while negative surface excess definitely suggests strong 1-2 interaction between benzonitrile and octanol by H bonding.

iv) In both the cases the excess surface tension decreases with increasing temperature.

v) Surface enthalpy and surface entropy values can be calculated from temperature study of surface tension.

vi) In both the cases, surface enthalpy increases as mole fraction of benzonitrile increases. Surface entropy remains almost constant for nitrile mixture but increases slowly for nitrile + alkanol mixture as benzonitrile is added.

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Review Article

INCLUSION OF HERBAL EXTRACTS IN DIABETOPATHY- DREAMS TO REALITY

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A B S T R A C T

As our lifestyle is getting techno savvy we are moving away from nature, while we cannot escape from nature because we are a part of it. What nature has stored in for us we have not yet fully explored. This fact can be disturbing point with humans. With life on tech-route for every individual in the 21st century humans sufferings are coming out with different diseases as like diabetes. The basic herbs have the answer, the overall key has no side effects and effective remedies. The remedies are in linked with the nature which is the biggest plus point where no other medicine can claim this fact. The golden fact is use of herbal treatments is dependent of any age group. Herbal medicines are bit slowly in treatment but it cure disease from the root. Plants provide a potential source to control diabetes and are widely used in several traditional systems of medicines to prevent diabetes. Several phytonutrients have been identified from medicinal plants and this presents on exciting opportunity for the development of new types of therapeutics for diabetes. In this paper attempts are undertaken to explore pharmaceutical properties of locally available herbs in Cooch Behar district and try to see the efficacy and ethno medical importance of these species as well as awareness of the indigenous people of this locality.

Keywords: *Diabetes, Insulin, Ayurveda.*

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1. INTRODUCTION

One of the million dollar question to every scientific community of the world today is how to control multifactorial diseases while million of people are suffering? When the internal environment of the human body system cannot maintain the balance or homeostasis with the external environment of the nature, many symptomic disorders occurs in the human body system by affecting many multifactorial organs with a particular syndrome and arises as a disease. In recent times, some of diseases are due to recent change in lifestyle of due to

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stress. One of such disease which is due to modern lifestyle change is diabetes which is gradually booming into the study. Diabetes is a common and a very prevalent disease affecting the citizens of either developed or developing countries. Classically Diabetes is regarded as a disease related with Sweet Urine and excessive muscle loss (Bordoloi *et.al.* 2014). Elevated levels of blood glucose (hyperglycemia) lead to spillage of glucose into the urine, hence the term sweet urine. It is also results in metabolic disorder which is characterized as chronic hyperglycemia.(Kalita *et. al*, 2014). The multifactorial disease is classified as Insulin dependent diabetes mellitus and Non insulin dependent diabetes mellitus. First one is due to destruction of beta cells in pancreatic islet, which are responsible for insulin synthesis. Due to some abnormalities in glucoreceptor, appropriate amount of insulin is not uptake by different tissue and caused Type – II diabetes mellitus. There are lots of complication seen in diabetes mellitus patients including long term damage, dysfunction and eventually failure of organs, especially the eyes, kidneys, nerves, heart and blood vessels. This disease requires medical diagnosis, treatment and changes in life style. The disease is associated with reduced quality of life and increased risk factors for mortality and morbidity. It is projected to become one of the world's main disablers and killers within 25 years. Now a days there is increasing interest in herbal medicine in developing countries in Diabetic care due to their low price, natural origin and less side effect (Rawat and Parmer, 2013).

2. GLOBAL SCENARIO AND INDIA'S POSITION IN GLOBAL DIABETIC MARKET

People with diabetes is increasing due to population growth, aging and urbanization and increasing prevalence of obesity and physical inactivity. The dynamics of the diabetes epidemic are changing rapidly. Once a disease of the west, Type-2 diabetes has now spread to every country in the world. Type-2 diabetes is a global public health crisis that threatens the economics of all nations, particularly developing countries. Fueled by rapid urbanization, nutrition transition and increase in sedentary lifestyle, the epidemic has grown in parallel with the worldwide rise in obesity. Asian's population and rapid economic development have made it an epicenter epidemic. Several factors contribute to accelerate diabetic epidemic in worldwide, including "normal weight-metabolically obese" phenotype high prevalence of smoking and heavy alcohol intake; high intake of refined carbohydrates (e.g White rice) and dramatically decreased physical activities. Poor nutrition in utero and in early life combined with over nutrition in later life may also play a role in Asia's diabetes epidemic. Westernised diet and lifestyle and genetic background accelerate the growth of diabetes in context of rapid nutrition transition (HU,B. Frank, 2011).

Modern lifestyle, advanced food habits, less physical work, mental workloads and other parameters maybe responsible for diabetes. It is estimated that nearly 380 million adults worldwide will have diabetes by 2025. India has 41 million diabetics and this number is expected to increase to 69.9 million by 2025 (Ramachandran, 2016). Currently India has got the largest number of diabetics and is being called as diabetic capital of the world.

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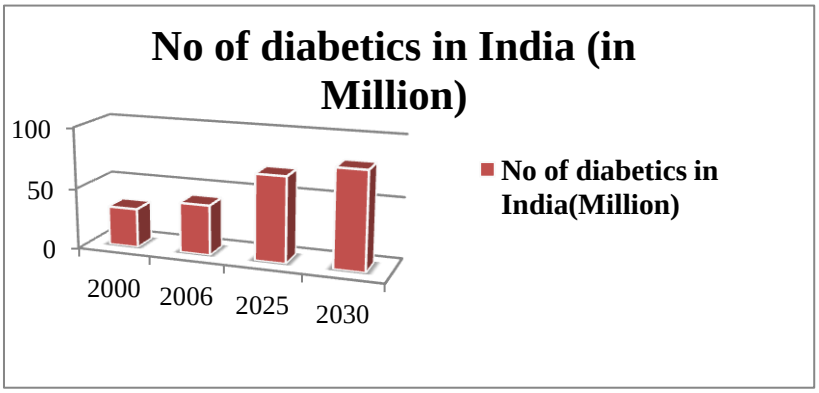

Fig. 1: *Trends in increasing diabetic population in India.*

Table 1: *Top ten diabetic countries in 2013 and future projection in 2035 (Adopted from Govindappa, 2015)*

Top 10	Countries	Diabetic people in 2013 (millions)	Countries	Diabetic people in 2035 (millions)
1	China	98.4	China	142.7
2	India	65.1	India	109
3	U.S.A	24.4	U.S.A	29.7
4	Brazil	11.9	Brazil	19.2
5	Russian Federation	10.9	Mexico	15.7
6	Mexico	8.7	Indonesia	14.1
7	Indonesia	8.5	Egypt	13.1
8	Germany	7.6	Pakistan	12.8
9	Egypt	7.5	Turkey	11.8
10	Japan	7.2	Russian Federation	11.2

Table 2: *Diabetic prevalence, deaths and expenditure from the data provided by 219 countries and territories for the year 2013. (Adopted from Govindappa, 2015)*

IDF Code	Seven IDF Regions	Prevalence of diabetes for 2013(millions)	Diabetic deaths under sixty years of age people in 2013(%)	Diabetic expenditure (USD) in 20-79 years of age group(Billions)
AFR	Africa	20	76	4

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EUR	Europe	56	28	147
MENA	Middle East and North Africa	35	50	14
NAC	North America and Caribbean	37	38	263
SACA	South and Central America	24	44	26
SEA	South East Asia	72	55	6
WP	West Pacific	138	44	88

3. TREATMENT STRATEGY

As Diabetes Mellitus is a metabolic disorder in the endocrine system and also diabetes is a multifactorial disease leading to several complications, and therefore demands a multiple therapeutic approach. Patients of diabetes either do not make enough insulin or their cells do not respond to insulin. Incase of total lack of insulin, patients are given insulin injection. Where as in case of those where cells do not respond to insulin many drugs are developed taking into consideration possible disturbances in carbohydrate metabolism. There are lots of synthetic drugs that have been used to control and treat diabetic patients with partial recovery from this dreaded disease. There are certain limitations due to high cost and side effects such as development of Hypogycemia, weight gain, gastro-intestinal disturbances, liver toxicity etc. The diseases associated with reduced quality of life and increased risk factors of mortality and morbidity. There is a growing interest in herbal remedies due to side-effects associated with the oral hypoglycemic agents for the treatment of diabetes. Alternative to synthetic drugs, plants provide a potential source of hypoglycemic drugs and are widely used in several traditional systems of medicine (Ayurvedic and Unani) to prevent diabetes. Hypoglycemic activity has been reported in many plants during the last 20 years.(Kumar,2015).

There are many herbal remedies suggested for diabetes and diabetic complications. Description of widely used plant having potential utility in curing diabetes found in Coochbehar Town-

1. *Wattakaka volubilis*

Family: Asclepiadaceae

Local name: Perun Kurinjan

Distribution: Common in the plains from coast to 1300 m. Subtropical Himalaya, India, East-West and South China, Taiwan, Malayasia, Sri lanka.

The plant is a very fleshy and large climber. Leaf powder is taken orally along with cow's milk.

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Recommended Dosage:- 50-75 ml of mixture is taken twice a day after food for 90 days.

2. *Abras precatorius*

Family:Fabaceae

Local name: Kundumani

Distribution: Found almost throughout the plains of India.

The plant is a climber commonly known as Wild Liquorice. Leaf of this plant is mixed with the leaves of *Andrographis paniculata, Gymnema sylvestre* and seeds of *Syzygium cumini.* The mixture is shade dried into powder and taken orally along with cow's milk.

Recommended Dosage- About 50 ml of mixture is taken twice a day before food for 120 days.

3. *Trigonella foenum graecum*

Family: Fabaceae

Local name: Fenugreek

Distribution: It is found all over India.

Fenugreek seeds are usually used as one of the major constituents of Indian spices. 4-hydroxyleucine, a novel amino acid from fenugreek seeds increased glucose stimulated insulin release by isolated islet cells in both rats and humans.

Recommended Dosage:- Oral administration of 2 and 8 gm/kg of plant extract produce dose dependent decrease in the blood glucose level in both normal as well as diabetic rats. Few seeds are soaked in 50ml water overnight. In the morning, the water after removing seeds is given.

4. *Aloe vera and Aloe barbadenis*

Family: Asphodeloideae

Local name: Dhritokumari

Distribution: Widely cultivated throughout the world. Mainly occur in the southern half of Arabian peninsula through North Africa(Morocco, Mauritania, Egypt) as well as Sudan and neighboring countries.

Recommended Parts to be used:- Aloe, a popular house plant can be separated into two basic products- gel and latex. Aloe vera gel is the leaf pulp or mucilage, aloe latex commonly referred to as "Aloe Juice", is a bitter yellow exudates from the pericyclic tubules just beneath the outer skin of the leaves. Extracts of Aloe gum effectively increases glucose tolerant in both normal and diabetic rats. Leaves of *Aloe barbadensis* show hypoglycemic effects in rats. Aloe vera stimulates the release of insulin from pancreatic beta cells.

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5. *Mangifera indica*

Family:Anacardeaceae

Local name: Aam

Distribution: The mango is native to South Asia, and from where it has been distributed to become one of the most cultivated fruits in the tropics.

Recommended Parts to be used:- The leaves of this plant are used as an antidiabetic agent. When the aqueous extract of mango given orally did not alter blood glucose level in either normoglycemic or streptozotocin induced diabetic rats. However, anti diabetic activity was seen when the extract and glucose were administered simultaneously and also when the extracts were given to the rats 60 minutes before the glucose . The results indicate the aqueous extract of *Mangifera indica* posses hypoglycemic activity. This maybe due to an intestinal reduction of the absorption of the glucose.

6. *Tinospora cordifolia*

Family: Menispermaceae

Local name: Guduchi

Distribution: It is widely distributed throughout India.

Recommended Dosage:- Oral administration of extract, root for 6 weeks resulted in a significant reduction in the blood and urine glucose and in lipids in serum and tissues in alloxan diabetic rats. The extracts also prevented a decrease in body weight. *Tinospora cordifolia* is widely used in Indian Ayurvedic medicine for treating diabetes mellitus.

7. *Acasia arabica*

Family:Fabaceae

Local name: Babhul

Distribution: It is found all over India, mainly in the wild habitat.

Recommended Dosage:- The plant extract acts as an anti diabetic agent by acting as secretagouge to release insulin. It induces hypoglycemia in control rats but not in alloxanised animals. Powdered seeds of this plant when administered (2,3 and 4 gm/kg body weight) to normal rabbits induced hypoglycemic effect by initiating release of insulin from pancreatic beta cells.

8. Alium cepa

Family: Liliaceae

Local name: onion

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Recommended Dosage:- Various ether soluble fractions

as well as insoluble fractions of dried onion powder show anti hyper glycemic activity in diabetic rabbits. When diabetic patients were given single oral dose of 50 gm of onion juice it significantly controlled post prandial glucose levels.

9. Alium sativum

Family: Liliaceae

Local name: Garlic

Distribution: It is a perennial herb cultivated throughout India.

Allicin , a sulphur containing compound is responsible for its pungent odour and it has been shown to have significant hypoglycemic activity. This effect is thought to be due to increased hepatic metabolism, increased insulin release from pancreatic beta cells.

Recommended Dosage:- Aqueous homogenate of garlic (10 ml/kg/day) administered orally to sucrose fed rabbits (10 gm/kg/day in water for 2 months) significantly increased hepatis glycogen and free amino acid content, decreased fasting blood glucose and triglyceride levels in serum in comparison to sucrose controls.

10. Ocimum sanctum

Family: Lamiaceae

Local name: Tulsi

Distribution: Native to the tropical and warm temperate regions and of all six inhabited continents, with the greatest number of species in Africa.

Since ancient times this plant is known for it's medicinal properties.

Recommended Dosage:- The aqueous extract of leaves showed the significant reduction in blood sugar level in both normal and alloxan induced diabetic rats. Oral administration (200 mg/kg) for 30 days led to decrease in the plasma glucose level by approximately 9.06 and 26.4% on 15 and 30 days of the experiment respectively. Renal glycogen content tenfold by skeletol muscle and hepatic glycogen levels decreased by 68% and 75% respectively in diabetic rats as compared to control.

11. Momodica chanantia

Family: Cucurbitaceae

Local name: Bitter gourd

Distribution: Found in India as well as other Asian countries.

Recommended Dosage:- Extracts of fruit pulp, seed, leaves and whole plant was shown to have hypoglycemic effect in various animal models. Polypeptide-p, isolated from fruits, seeds

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and tissues from this plant and showed significant hypoglycemic effect when administered subcutaneously to langoors and humans. Ethanolic extracts of this plant (200 mg/kg) showed an anti hyperglycemic and also hypoglycemic effect in normal and diabetic rats. Unripe fruits are taken orally along with food. 2,3 or 4 fresh unripe fruits are taken at any time per day for 3 months is generally recommended for adults.

12. Azadirachta indica

Family: Melieceae

Local name: Neem

Distribution: Native to India and the Indian Subcontinent including Nepal, Pakistan, Bangladesh and Sri lanka.

Pharmacological efficacy:- Hydroalcoholic extracts of this plant showed antihyper glycemic activity in streptozotocin treated rats and this effect is of increase in glucose uptake and glycogen deposition in isolated rat hemidiaphragm .

13. Psidium guajava

Family: Myrtaceae

Local name: Guava

Distribution: It is widely cultivated in tropical and subtropical regions around the world. It is frequently cultivated in North east India.

Pharmacological Efficacy:- Flavonoid glycosides such as strictinin, isostrictinin, and pedunculagin are the effective constituents of *Psidium guajava*, which has been used in clinical treatment of diabetes due to improved sensitivity to insulin.

14. *Panax ginseng*

Family: Araliaceae

Distribution: Found in North America and in Eastern Asia (mostly North East China, Korea, Bhutan, Eastern Siberia) typically in cooler climates.

Pharmacological Efficacy:-The antidiabetic potential of different ginseng species has been evaluated. This activity is to mediated by a number of different mechanisms, including regulation of pancreatic beta cell function by stimulation of insulin secretion and bio synthesis. This activity has been assigned to it's saponin and polysaccharide constituents e.g. ginsenoside Rh2 and panaxan-β respectively, which were exhibited to promote plasma insulin level by stimulating insulin release and biosynthesis in a glucose independent manner.

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15. Phyllanthus amarus

Family:Phyllanthaceae

Local name: Bhuia mala

Distribution: It is occupied throughout the hotter parts of India, mainly Deccan, Kokhan and south Indian states.

Pharmacological Efficacy:- Traditionally it is used as hypoglycemic agent. Methanolic extract of this plant decreased the blood sugar in alloxanized diabetic rats.

Table 3: *Indian Medicinal Plants With Antidiabetic and Related Beneficial Properties (Adopted from Modak, 2007)*

Plant Name	Common Name	Antidiabetic effects
Annona squamosa	Sugar apple	Hypoglycemic and antihyperglycemic activities of ethanolic leaf extract, increased plasma insulin level
Artemisia pallens	Davana	Hypoglycemic, increases peripheral glucose utilization or inhibits reabsorption
Areca catechu	Supari	Hypoglycemic
Beta vulgaris	Chukkandar	Increases glucose tolerance in OGTT
Boerhavia diffusa	Punarnava	Increases in hexokinase activity, decrease in glucose-6- phosphatase and fructose bis phosphatase activity, increase plasma insulin level, mantioxidant
Bombax ceiba	Semul	Hypoglycemic
Butea monosperma	Palasa	Antihyperglycemic
Capparis decidua	Karir or pinju	Hypoglycemic, hypolipidemic
Camellia sinensis	Tea	Antihyperglycemic activity
Caesalpinia bonducella	Sagarghota, fevernut	Hypoglycemic, insulin secretagogue, hypolipidemic
Coccinia indica	Bimb or kanturi	Hypoglycemic
Emblica officinalis	Amla, dhatriphala, a constituent of herbal formulation “Triphala”	Hypoglycemic

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Eugenia uniflora	pitanga	Hypoglycemic, inhibits lipase activity
Ficus bengalansis	Bur	Increase hexokinase activity decrease glucose - 6 phosphatase and fructose 1,6 bis phosphatase activity. Dose dependent hypoglycemic activity
Gymnema sylvestre	Gudmar or Merasiigi	Antihyperglycemic effect, hyplipidemic
Hibiscus rosa - sinensis	Gudhal or Jasson	Initiates insulin release from pancreatic beta cells
Ipomea batatus	Sakkargand	Reduces insulin resistance
Momordica cymbalaria	Kadavanchi	Hypoglycemic, hypolipidemic
Murraya koenigii	Curry patta	Hypoglycemic, increases glycogenesis and decreases gluconeogenesis and glycogenolysis
Musa sp.	Banana	Antihyperglycemic
Phaseolus vulgaris	Hulga, White kidney bean	Hypoglycemic, Inhibit α-amylase activity
Punica granatum	Anar	Anti hyperglycemic
Salacia reticulata	Vairi	Inhibitory activity against sucrose, α-glucosidase inhibitor.
Scoparia dulcis	Sweet broomweed	Insulin secretagogue activity, Anti hyperlepidemic, Hypoglycemic
Swertia chirayita	Chirata	Stimulates insulin release from islets
Syzygium alternifolium	Shahjire	Hypoglycemic and Antihypoglycemic
Terminalia chebula	Hirda	Hypoglycemic
Terminalia belurica	Behada, a constituent of Trifala	Hypoglycemic
Tinospora crispa	-	Anti hyperglycemic stimulates insulin release from islets
Vinca rosea	Sadabahar	Antihyperglycemic
Vernonia anthelmintica	Kaalijiri	Hypoglycemic
Withinia somnifera	Ashvagandha, Winter cherry	Hypoglycemic, Diuretic and Hypocholesterolemic

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4. INDIA'S POSITION IN GLOBAL BIODIVERSITY DOMAIN IN CONNECTION WITH TRADITIONAL PLANT

India is one of the richest in the world due to wide range of climate, topology and habitat in the country. The use of plants as a source of medicine has been a integral part of life in India from the earliest times. There are more than 3000 Indian plant species officially documented as possessing great medicinal potential. We can use these medicinal plants for the treatment of diabetes. India has a rich diversity of plant resources spread over a wide spectrum of habitats- desert, high mountains, highlands, tropical and temperate forests, swamplands, plains , grasslands , areas surrounding rivers as well as island, archipelago. The region is also heavily influenced by summer monsoons that cause major seasonal changes in vegetation and habitat. The great area of Indian subcontinent has wide range of climate and corresponding diversity in the vegetation .That is why India has been divided into the following botanical zones by D.Chatterjee (1962)

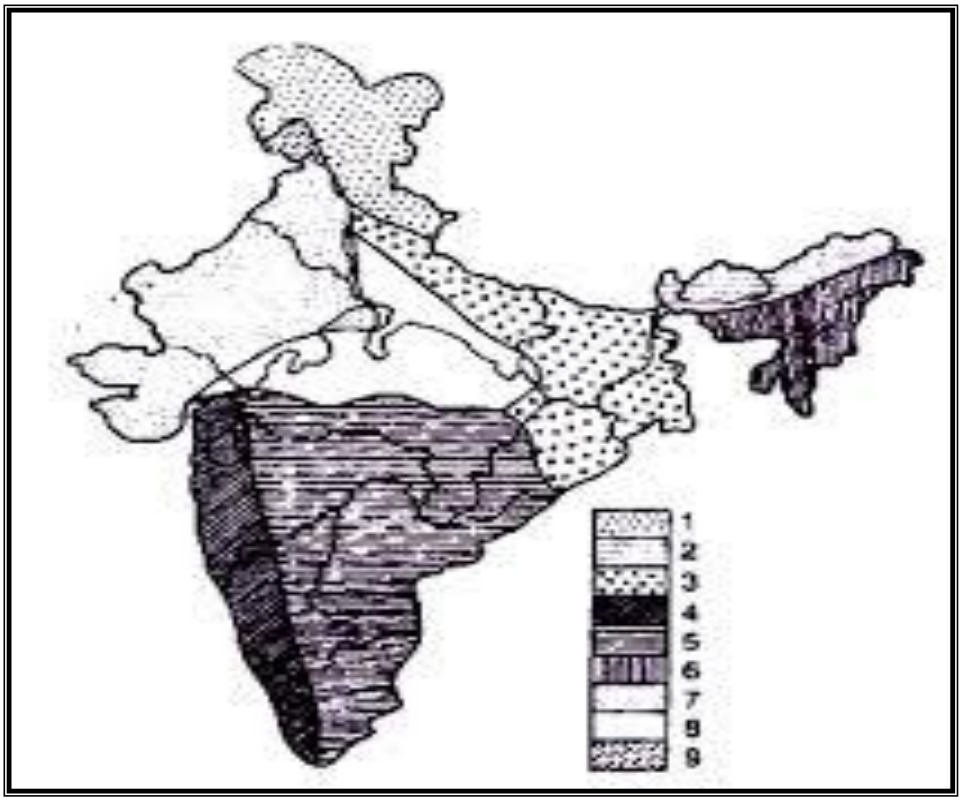

Fig.2: *hytogeographical provinces of India (After Chatterjee, 1962)*

Legends:

1. Western Himalayas 2. Eastern Himalayas 3. Indus Plain 4. Gangetic plain
5. Central India 6. Deccan 7. Western coasts of Malabar 8. Assam
9. Bay islands of Andaman and Nicobar

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Table 4: *Modalities of Treatment (Adopted From Dwivedi, 2013)*

Plants	Parts Used	Product patented	Activity utility
Aloe vera and Aloe barbadensis	Leaves gel and leaves extract	Barbaloin, emodin	Maintains glucose homeostasis by controlling the carbohydrate metabolizing enzymes.
Mangifera indica	Fruits extract and leaf extract	Cetechine, Mangiferin	Insulin secretion
Tinospora cordifolia	Plant extract	Tinosporoside	Root extract to alloxan diabetic rats caused a significant reduction in blood glucose and brain lipids. Widely used in Indian ayurvedic medicine for treating diabetes mellitus. Oral administration of the extract of *T.cordifolia* 6 weeks resulted in a significant reduction in blood and urine glucose and in lipids in serum and tissues in diabetic alloxan rats.
Alium sativam	Root extracts	Allicin, Allin	Increased hepatic glycogen and free amino acid content, decreased fasting blood glucose and triglyceride levels in serumin comparison to sucrose controls.
Acacia arabica	Leaves extract	Arabic acid	Insulin secretion
Allium cepa	Bulb,Plant extract	Sulfenic acid, 1-propenesulfenic acid	Control blood glucose as well as lipid in serum and tissues and normalize the activities in liver hexokinase, glucose-6-phosphatase and HMG co-A reductase . Oral

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			dose of 50 gm of onion juice is significantly controlled post prandial glucose levels.
Ocimum sanctum	Leaves extract	Eugonal, Carvecrol	Reduction in blood sugar level in both normal and alloxan induced diabetic rats, reduction in fasting blood glucose, uronic acid, total amino acid, total cholesterol,triglyceride and total lipid indicate the total hypoglycemic and hypolipidemic effects of Tulsi in diabetic rats.
Momordica charantia	Fruit extract	Momordicin I and II, Cucurbitacin B	Insulin secretion
Azadirachta indica	Leaves extract	Sugiol, Nimbiole, Limonodes, Nimbendiole, Azadirectin	Anti hyperglycemic activity, Antidiabetic activity.

5. PROS AND CONS OF HERBAL TREATMENT

Plants have always been an exemplary source of drugs and many of the currently available have been derived directly or indirectly from them. Ayurveda, the Indian system of traditional medicine provides a number of traditional plants to treat diabetes and an indigenous remedy has been used in the treatment of the diabetes since the time of the Charaka and Sushrata (6^{th} century B.C). Medical plants continue to provide valuable anti diabetic or hypoglycemic agents, in both modern science and traditional system. Most herbal medicines are well tolerated by the patient. Herbs typically have fewer side effects and safer to use over time. Herbal medicines are tend to be more effective for long standing health complains that don't respond well to conventional medicines.

The general public wants easy method to control diabetes. Sometimes anti diabetic herbal products can cause direct toxicity or adverse interactions with concurrent medications. These products can be very heterogenous in nature and have unpredictable levels of active ingredients with unpredictable and potentially harmful effects. No doubt plant origin natural

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products can be used as alternative medicine for treatment of diabetes, but they must need proper composition and formulation before being used.

Table 6: Some synthetic drugs and their side effects

AGENT	MECHANISM	SITE OF ACTION	ADVANTAGES	SIDE EFFECTS
Sulphonylureas	Stimulating insulin production by inhibiting the k - ATP channel	Pancreatic beta cells	Effective and inexpensive	Hypoglycemia and weight gain
Metmorphin	Decreases insulin liver resistance	Liver	Weight loss, does not cause hypoglycemia	Nausea and diarrhea. Hypoglycemia occurs when combined with sulfonylurea or insulin
Thiazolidinediones	Reduce insulin resistance by activating PPAR - γ	GI- tract	Low risk	Increased liver enzymes, weight gain, oedema, mild anaemia
α – glucosidase inhibitors	Reduces intestinal glucose absorption	Fat, muscle	Decrease postprandial plasma triglyceride levels	Diarrhoea, abdominal pain, serum levels of transaminases increases at doses.

6. ACHIEVEMENT RELATED WITH ETHNOZOOLOGICAL RESEARCH IN INDIA

Many works have been done in India since from ancient times. The early detection and treatment of diabetes has been mentioned in Sushrata samhita and Charak Samhita. A large number of antidiabetic minerals and drugs of plant origin have been described in classical ayurvedic literature. Many investigators contributed in the field of herbal medicine in relation to diabetes.

In recent times India have taken some initiative role in the treatment of Diabetes.

1. The council for scientific and Industrial Research launched the Blood Glucose regulator (BGR) – 34 , the countries first antidiabetic ayurvedic drug designed for

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type 2 diabetic mellitus which has been scientifically validated for its efficacy and safety.

2. A new antidiabetic medicine made from five ayurvedic medicinal plants. The Central Council of Research in Ayurvedic Sciences (CCRAS) has developed a new drug formulation AYUSH – 82 ,which has proven clinicaiiy efficient in treatment of diabetes.
3. Pills of *Momordica charantia* already been prepared been scientist. The investigators of CDRI Lucknow have walked out *Swertia chiratai* may be used in diabetes .
4. Indian Institute of Chemical Technology (CSIR- IICT) have discovered that the seeds and tubur of blue water lily are capable of effectively controlling the blood glucose in persons suffering from diabetes
5. T2DM in Indian patients with an emphasis on incretin pathway. Intestinal mucosa produces certain factors named incretin peptides such as glucose dependent insulinotropic polypeptide (GLP) and glucagon like peptide 1 (GLP-1) , which have the capacity to reduce blood glucose level by directly acting on the pancreatic beta cells. They found that the negative regulators of incretin peptides , dipeptidyl peptidase – 4 (DPP-4) plays a critical role in the pathogenesis of T2DM in Indian patients.

7. FUTURE PROSPECT

Nature is the best combinatorial chemist and till now natural products, compounds discovered from medicinal plants have provided many clinically useful drugs. In spite of the various challenges encounter in the medicinal plant based drug discovery, natural products isolated from plants will still remain an essential component in the search for new medicines. So, in future proper utilization of plant resources will certainly help in discovering novel lead molecules from plants by employing modern drug discovery and coordinating efforts of various disciplines to treat diabetes. And also the multiple activities of plant based of medicinal preparations meant for diabetes offers enormous scope for combating the threat of the diabetic epidemic

8. CONCLUSION

Diabetes is possibly the world's fastest growing metabolic disease and as knowledge of the heterogeneity of this disorder increases, so does the need for important appropriate therapies. As diabetes is dependent on lifestyle management, so "prevention is better than cure". Lifestyle changes and different food choices can help to reverse diabetes. Alternatively herbal medicines are used throughout the world for a range of diabetic presentations. The study of such medicines might offer a natural heal to unlock a diabetologists pharmacy for the future.

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Brojendra Nath Seal Journal of SCIENCE

Review Article

A MINI REVIEW ON HEAT SHOCK PROTEINS (HSPS): SPECIAL EMPHASIS ON HEAT SHOCK PROTEIN70 (HSP70)

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A B S T R A C T

Heat shock proteins (HSPs) are found in almost all types of eukaryotic cells and it is primary system for "intracellular self-defense" within a cell. HSP Expression is regulated by various factors such as temperature changes, environmental contaminants and infectious pathogens which facilitate protein unfolding, misfolding, and aggregation by interfering protein metabolisms. HSPs maintain protein structures, prevent non-native protein aggregation and target non-native or aggregated proteins for degradation and elimination from the cell. The primary heat-shock proteins are of some conserved classes: HSP33, HSP60, HSP70, HSP90, HSP100 and the small heat-shock proteins (sHSPs). The principle function of HSPs is thought to be thermo tolerance but it also interfere in immune system, aging and in several neurodegenerative diseases. Recently, HSP70 and other HSPs are used a lot as a marker of stress in research experiments as well as monitoring the environmental and anthropogenic stressor through *in vivo* and *in vitro* studies.

Keywords: *Chaperones, Drosophila, Heat shock protein, HSP70, Stress marker*

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1. INTRODUCTION

Heat shock proteins (HSPs) are a group protein that has intracellular expression with essential functions in various protein metabolisms (**Figure 1**). Expression of HSPs is regulated by various factors such as temperature changes, environmental contaminants, and infectious pathogens, which facilitate protein unfolding, misfolding, aggregation, or newly synthesized non-native proteins (**Iwama *et al.* 1998**).

HSPs reduce the effect of stress by several mechanisms which include maintenance of protein structures, prevention of non-native protein aggregation and targeting non-native or

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aggregated proteins for degradation and elimination from the cell (**Feder and Hofmann 1999**). In contrast, high concentrations of HSPs might interfere with continuing cellular processes occurring within the cell and the synthesis as well as break down of these proteins may be costly for the cell's energy budget and/or occupy a large portion of the synthetic/catabolic apparatus (**Feder and Hofmann 1999**).

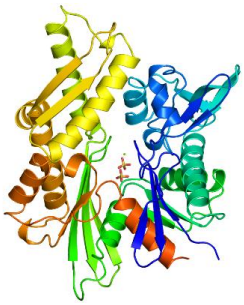

Fig. 1: *Human HSP70 (www.thesgc.org/structures/3l6q)*

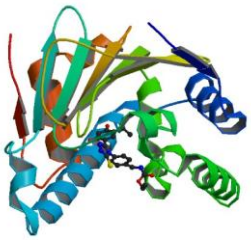

Fig. 2: *Human HSP90 (www.rcsb.org/pdb/explore.do?structureId=3hhu)*

2. HEAT SHOCK PROTEINS: MOLECULAR CHAPERONES

Most of the heat shock proteins are molecular chaperones **(Figure 3)**. Chaperones have been defined as "proteins that bind to and stabilize an otherwise unstable conformer of another protein – and, by controlled binding and release, facilitate its correct fate *in vivo*: be it folding, oligomeric assembly, transport to a particular subcellular compartment, or disposal by degradation" (**Hartl 1996**). The chaperones commonly prevent the aggregation of "sticky" protein folding intermediates. Chaperones are acting as "collectors" of damaged proteins through binding to their targets. Two classes of chaperones which are especially effective in completing this job are the small heat shock proteins. Thus, 90 kDa heat shock proteins (the Hsp90 family) may be considered as "recycling-concerned dustmen" of cells by binding their targets and keeping them in a folding competent state until the whole cell recovers, and provide energy for refolding process (**Figure 2**). Members of the 90 kDa chaperone family bind to both *in vitro* and *in vivo* various peptides (**Menoret *et al*. 1999**), which might play as "collector/dustman" role to free intracellular peptides. These residual peptides (released from the major cytoplasmic proteolytic apparatus) might seriously interfere in signaling processes (**Blum *et al*. 2000**) results a great threat to cellular functions.

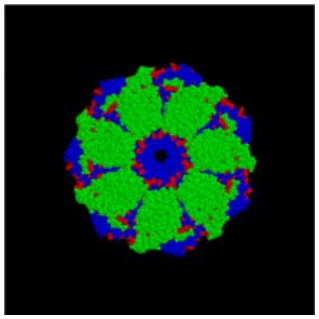

Fig. 3: *Model structure of a bacterial chaperone complex model (https://en.wikibooks.org/wiki/ Structural_Biochemistry/Protein_Folding_and_Chaperones)*

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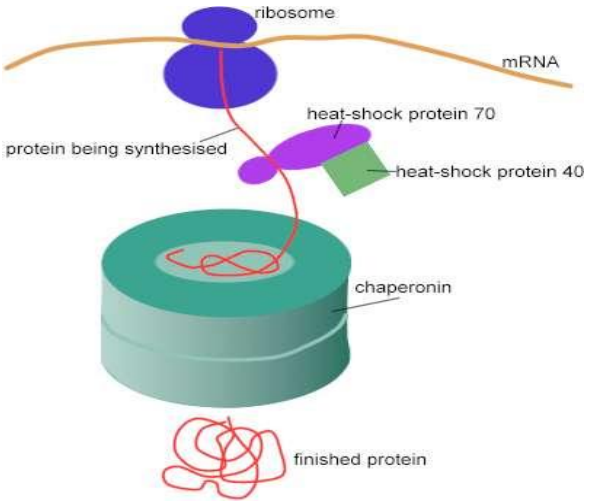

Fig. 4: *The diagram shows the role of heat-shock proteins and a chaperonin in protein folding. As the ribosome moves along the molecule of messenger RNA, a chain of amino acids is built up to form a new protein molecule. The chain is protected against unwanted interactions with other cytoplasmic molecules by heat-shock proteins and a chaperonin molecule until it has successfully completed its folding. (Courtesy: http://slideplayer.com/slide/4693681)*

3. HEAT SHOCK PROTEIN FAMILIES

The HSPs have been comprehensively studied, especially their cellular localization, regulation, and functions (**Lindquist and Craig 1988; Hightower 1991**). HSPs are found in both prokaryotic and eukaryotic cells, and their high level of conservation suggests that they have very crucial role in most of the fundamental cellular processes **(Sander 1993)**. **Ritossa** (**1962**) first discovered HSPs in *Drosophila melanogaster* larvae that were exposed to "heat shock". Several workers recognized a number of subsets of these proteins in the 70-kDa range (**Tissieres *et al.* 1974**). Over the past 30 years, a large number of additional proteins have been invented within this family, and these are collectively referred to as "HSPs" (**Sander 1993**).

Heat Shock Proteins are found in the cytosol, mitochondria, endoplasmic reticulum nucleus etc. The most well-studied and understood HSPs in mammals are those with molecular masses of ~60, 70, 90, and 110 kDa. These HSPs are expressed in response to temperatures (~37°C) and in conditions of stress (e.g. heat shock) and have distinct cellular locations and functional properties (**Table 1**). Moreover, small molecular-mass proteins also termed small HSPs, show tissue-specific expression and include heme oxygenase, HSP32, Hsp27, αB-crystallin, and HSP20 chaperone. The primary heat-shock proteins that have chaperone activity are of following conserved classes: HSP33, HSP60, HSP70, HSP90, HSP100 and the small heat-shock proteins (sHSPs) (**Schlesinger 1990**).

Although the most significant members of each family are summarized here, it should be noted that some species may express additional chaperones, co-chaperones, and heat shock proteins not listed. In addition, many of these proteins might have multiple splice variants (Hsp90α and Hsp90β, for instance) or conflicts of nomenclature (Hsp72 is sometimes called Hsp70).

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Table 1: *Cellular locations and proposed functions of mammalian heat shock protein families*

HSP Family	Cellular Location	Proposed Function
HSP27 (sHSP)	Cytosol, nucleus	Microfilament stabilization, antiapoptotic
HSP60	Mitochondria	Refolds proteins and prevents aggregation of denatured proteins, Proapoptotic
HSP70 family:		**Antiapoptotic**
HSP72 (Hsp70)	Cytosol, nucleus	Protein folding, cytoprotection
HSP73 (Hsc70)	Cytosol, nucleus	Molecular chaperones
HSP75 (mHSP70)	Mitochondria	Molecular chaperones
HSP78 (GRP78)	ER Cytoprotection,	Molecular chaperones
HSP90	Cytosol, ER, nucleus	Regulation of steroid hormone Receptors, protein translocation
HSP110/104	Cytosol	Protein folding

(HSP: heat shock protein; sHSP: small HSP; ER: endoplasmic reticulum)

4. THE HSP70 FAMILY

The proteins belong to ubiquitous HSP70 family of proteins are the most temperature sensitive and highly conserved of the HSPs. The HSP70s are reported as ATP-binding proteins and demonstrate a 60–80% base identity among eukaryotic cells (**Craig 1985; Lindquist 1986**). There are four distinct proteins in the HSP70 group (HSP72, HSP73, HSP75, and HSP78).

Proteins in the HSP70 group share common protein sequences but are synthesized in response to various stimuli (**Figure 5).** For example, the 73-kDa protein (HSP73 or Hsp70) is continually produced (hence, the term "constitutive"), whereas the 72-kDa protein (HSP72 or Hsp70) is highly inducible and its synthesis is increased in response to multiple stressors. The molecular structure of the HSP70 group of proteins and HSP70 gene regulation are summarized in **Figure 5**.

In eukaryotic organisms the expression of heat shock protein messenger RNA-s is facilitates by a family of transcription factors, called heat shock factors. Heat shock factor I (HSF-I) plays a major role in heat shock response, while other members of the family are activated after extended stress, or participate in course of embryonic development, or cell differentiation.

HSF-I is complexed with various heat shock proteins (HSP70 or with HSP90) in resting cells. Damaged proteins become abundant and liberate the heat shock factor from its HSP70/HSP90 complexes after stress.

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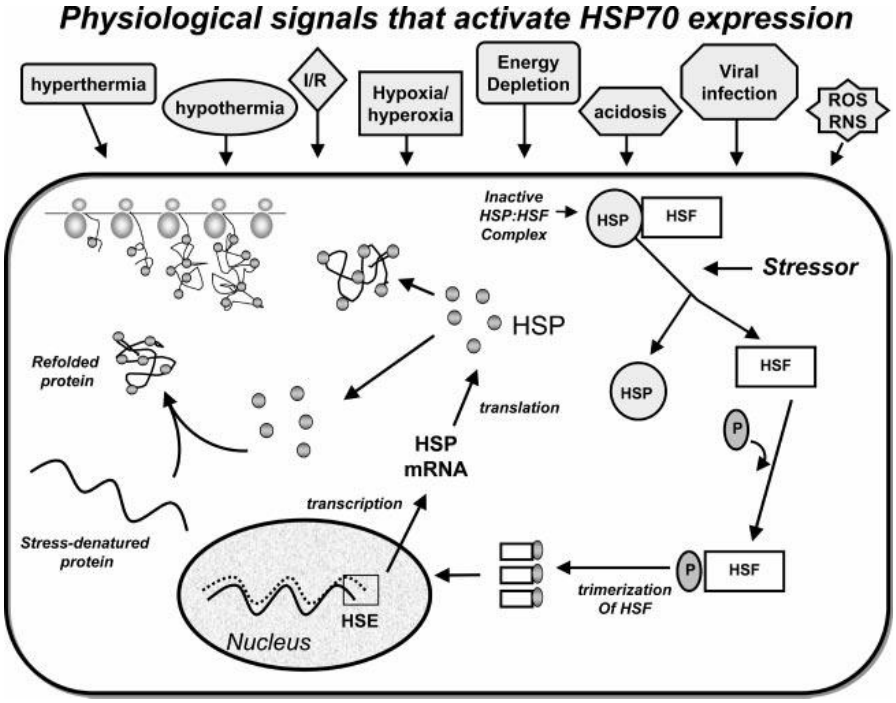

Fig. 5: *A summary of some of the major physiological signals that activate the inducible form of the 72-kDa heat shock protein (HSP70) synthesis (top) and a proposed mechanism for increased HSP70 expression within a cell. Heat shock factors (HSFs), present in the cytosol, are bound by heat shock proteins (HSPs) and maintained in an inactive state. A broad array of physiological stimuli ("stressors") are thought to activate HSFs, causing them to separate from HSPs. HSFs are phosphorylated (P) by protein kinases and form trimers in the cytosol. These HSF trimer complexes enter the nucleus and bind to heat shock elements (HSE) in the promoter region of the Hsp70 gene. Hsp70 mRNA is then transcribed and leaves the nucleus for the cytosol, where new HSP70 is synthesized. Proposed mechanisms of cellular protection for HSPs include their functioning as molecular chaperones to assist in the assembly and translocation of newly synthesized proteins within the cell and the repair and refolding of damaged (e.g., stress-denatured) proteins. (I/R, ischemia-reperfusion; ROS, reactive oxygen species; RNS, reactive nitrogen species.) (Courtesy:* ***Kregel 2012)***

This process involves trimerization, nuclear translocation and phosphorylation of HSF-I, which are all pre requisites for its binding to the promoter region of heat shock protein genes. All these steps are manifested by several co-chaperones of the major heat shock proteins, HSP70 and HSP90, and/or other proteins as well (**Morimoto 1999**). **Tsukiyama *et al.*** (**1994**) suggested GAGA-factor reorganize heat shock element present in DNA-segment of nucleosomal structure. Interestingly, numerous heat shock protein genes hire an active DNA-dependent RNA polymerase II even in the absence of heat shock factor. This "pausing polymerase" transcribes a small segment of the gene that becomes arrested by its binding to the initial complex of TATA-binding general transcription factors (**Figure 4**).

5. MAJOR FUNCTIONS OF HSPS

HSPs are reported very crucial for both normal cellular function and survival after a stress. The major functions are as follows:

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Thermo tolerance

The main physiological function associated with the stress-induced accumulation of the inducible HSP70 is a thermo tolerance. Thermo tolerance is the ability of a cell or organism to become resistant to heat stress after a prior sub-lethal heat exposure (**Landry *et al.* 1982; Lindquist 1986; Mizzen and Welch 1988,**). Several studies explained that the induction of HSP70 was associated with the development of tolerance to a variety of stresses, including hypoxia (**Hahn and Li 1982**), ischemia (**Marber *et al.* 1995**), acidosis (**Weitzel *et al.* 1995**), energy depletion (**Sciandra and Subjeck 1983**), cytokines such as tumor necrosis factor-α (TNF-α) (**Jäättelä and Wissing 1993**), and ultraviolet radiation (**Barbe *et al.* 1988**). The acquired thermo tolerance is transient in nature and depends principally on the intensity of the initial heat stress. The greater the initial heat stress, the greater the magnitude and duration of thermo tolerance. The expression of thermo tolerance following heat stress will occur within several hours and last 3–5 days in duration. Several workers suggested relation between the kinetics of thermo tolerance induction and decay with parallel changes in HSP70 induction and degradation (**Landry *et al.* 1982).**

The precise mechanism for the cellular thermo tolerance in association with an increase in HSP levels is still unclear. The plausible hypothesis might be the proteins in Hsp70 family are involved in preventing protein denaturation and/or processing denatured proteins and protein fragments, produced by stressors such as hyperthermia. **Mizzen and Welch** (**1988**) suggested through in vitro experiments that, heat stress results in translational arrest within a cell and this arrest is proportional to both the intensity and duration of the heat stress. Thus, resumption of translation resulted in HSP mRNA being translated into HSPs before the synthesis of other proteins occur within the cell.

6. FUNCTIONS OF HSP70 ASSOCIATED WITH STRESS TOLERANCE

The accumulation of HSP70 in response to heat stress and other stressors is general but the mechanisms by which HSPs confer stress tolerance are not clear. HSP70 acts as a chaperone and capable of cellular repair processes in response to heat, oxidative stress, activation of proteases, release of lysosomal and proteolytic enzymes, and alterations of the cytoskeleton. Several important cytoprotective functions have been attributed to HSPs and, in particular, the HSP70 family by several workers (**Mizzen and Welch 1988; Bakau and Horwich 1998**). These include

1. Protein folding in different intracellular compartments,
2. Structural protein maintenance,
3. Refold the misfolded proteins,
4. Translocation of proteins across membranes and into different cellular compartments,
5. Prevention of protein aggregation, and
6. Unstable protein degradation

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7. IMMUNE SURVEILLANCE AND ANTIGEN PRESENTATION OF HSP

Although the main purpose of HSPs research is to find out their functions and accumulation inside the cell in response to a physiological stress, but HSPs also serve as modulating signals for immune and inflammatory responses. This concept was recently suggested in a brief review by **Moseley (2000)**. Elevations in intracellular HSP levels have been found to improve cell tolerance to inflammatory cytokines such as TNF-α and interleukin-1 (**Jäättelä and Wissing 1993**). TNF-α and interleukin-1 secretion decrease in response to HSP accumulation within a cell (**Ensor *et al.* 1994**). **Kluger *et al.* (1998)** demonstrated that heat conditioning and the resultant increase in intracellular HSP70 levels protected animals from an endotoxin dose that was lethal in unconditioned rats. Moreover, after administration of endotoxin in the heat-conditioned animals revealed decrease in serum TNF-α level (**Kiang and Tsokos 1998**). These results points toward intracellular HSP accumulation might be responsible for reduction in inflammatory cytokine production with cellular challenge.

HSP70 is also recognized to assist antigen presentation in cells such as macrophages and dendrites (**Srivastava 1993**). When HSP70 is applied to the extra-celluiar environment of cell, macrophages and lymphocytes generate inflammatory cytokines. Finally, HSP70 have been found on the surface of tumor cells (**Roigas *et al.* 1998**), potentially functioning as recognition molecules for natural killer (NK) cells. Thus it might be concluded that, HSPs are significant modulators of antigen presentation, cytokine production, T-lymphocyte activation, and NK cell killing in response to both intracellular and extracellular physiological stress.

8. CHAPERONES IN AGING AND IN NEURODEGENERATIVE DISEASES

Aging is a consequence of an impaired function of repair processes (immune system, DNA-repair, elimination of free radicals, etc.). One of the crucial repair processes is refolding of damaged proteins by molecular chaperone. Aged organisms contain an increased amount of misfolded proteins, and the induction of HSP70 is impaired in both aged rats and humans. In contrast, better induction of heat shock proteins leads to an enhanced life expectancy in yeast, *Drosophila* and *C. elegans* (**Tatar *et al.* 1997**). Protein damage in neuronal cells (which, generally, cannot renew themselves by multiple mitotic events) may leads to several neurodegenerative diseases, such as Alzheimer's disease, Parkinson's disease, Huntington's disease, Wilson's disease, Alexander's disease etc. These diseases reveal massive protein aggregates in nerve cells that usually contain various heat shock proteins, such as ubiquitin-tags, the small heat shock protein, HSP27, HSP70 and HSP90 (**Mayer *et al.* 1991**). In accordance with this view, over expression of HSP70, or other heat shock proteins protects *Drosophila* from neurodegeneration in Huntington disease-like polyglutamine-induced aggregation.

9. AGING: ALTERATION IN HSP70 EXPRESSION

Cells, tissues, and whole organisms are capable to become resistant against stressors such as hyperthermia after a prior sub-lethal heat exposure (i.e., acquired thermo tolerance), and

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HSPs appear to play a crucial role in this process. One important and clinically relevant scenario in which tolerance to thermal stress is reduced is old age. In humans, the increased morbidity and mortality rates during aging process depends on heat exposure. For instance, age-related decrease in the stress response are thought to be associated with the increased incidence of death that has been reported for older individuals subjected to chronic heat waves (**Semenza *et al.* 1996**). Mostly, it has been suggested that older animals are less thermo tolerant and have higher mortality rates than their younger ones when exposed to repeat heat challenges (**Hall *et al.* 2000**). Moreover, cDNA studies revealed altered gene expression in response to heat stress that is indicative of decreased stress protein expression and influence aging (**Zhang *et al.* 2002**).

10. HSP: Its Use As A Marker Of Stress In Research Experiments

Organisms continuously exposed to environmental, toxic, physiological and metabolic stressors reveal a greater risk of adverse health effect. The higher degree of stress affects at the organismal level through the biochemical and cellular events **(Sarkar *et al.* 2015a, 2015b)**. The changes in altered biochemical and cellular parameters are used as stress indicators to evaluate the physiological condition of an organism (**Stegman *et al.* 1990**). Since organisms always try to resist the assault of stressful conditions by activating specific genes to produce specific proteins (**Choi *et al.* 2000**). The expression of such specific genes may provide an index of stress (**Atkinson *et al.* 1983).**

Elevated levels of HSP70 have been reported in the cells of organisms exposed to pesticides (**Sarkar *et al.* 2015a, 2015b**), food adulterants (**Mukhopadhyay *et al.* 2002**), solvents (**Nazir *et al.* 2003**), metals (**Urani *et al.* 2001**), and increased temperatures (**Krebs and Feder 1997**). For its being responsive even to minor assaults, HSP70 expression may prove useful as a molecular indicator for adverse biological effects. The efficiency of HSP70 expression as biomarker of environmental pollution has been advocated by many researchers (**de Pomerai 1996; Varo *et al.* 2002)**. The intensity of stress is indicated by the level of expression of heat shock proteins in that environment by that particular animal. With the help of heat shock proteins (HSPs), we can easily access the effects of any chemical on any non-target organisms as well as monitor environmental pollution.

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Review Article

HOW MANY ROADS MUST A MAN WALK DOWN BEFORE YOU CALL HIM A MAN: THE SAGA OF MARRIAGE AND MATE SELECTION – A SOCIO-ETHOLOGICAL PERSPECTIVE

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A B S T R A C T

One of the foremost instincts of all living creatures is to transmit its genes to the next generations. In order to achieve that goal, individuals, be it human or animal, need to find a partner. Individuals tend to ensure not only genetically superior partners, but also look for partners who can provide it with material benefits necessary for the survival of its offspring. Individuals also tend to ensure that a partner remains faithful to it, not carrying the genes of other individuals. In this context, human and animals show a striking resemblance. Human females prefer their spouses to be financially sound; similarly many female animals receive gifts from their mating partners in order to permit them to copulate. Such selective attitudes of females are widespread in the nature. On the other hand, males tend to be opportunists. Males in the nature have been proved to have lesser sexual threshold and inclined to practice polygamy. They also try to restrict their female counterparts from the accession to other males. This paper deals with the nature of sexual psychology in human and animals and depicts the conspicuous similarities in their selection and accession to mates.

Keywords: *Nuptial gift, Mate selection, Sexual psyche*

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1. INTRODUCTION

The idea of considering the human race to be at the apex of all other living creatures is perhaps the most important reason behind distrusting the omnipresence of all living beings and try to establish our dominance with the mouthful idea of superiority over all others. But does it really make sense? Have we really proceeded so far in the long run of evolution so as to leave all others behind? If we focus our discussion to the behavioural aspects, it will become very much evident that the idea of superiority is an artefact of justifying supremacy mostly in terms of scientific advancements. When it comes to behavioural aspects, humans are not too far from their other living counterparts. In fact, most of the behaviours are evident

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in case of animals as well in some form or other. And when it comes to the crucial question of sexual psychology and selection of partners, human and animals look much closer.

The underlying reason behind choosing partners is to transmit genes to the next generations. So, the behavioural aspects of mate selection will definitely tend to pacify the process of gene flow. From this point of view, mate choice seems to be a biological phenomenon. But, human behaviour is much more complicated as societies play an important role while shaping our behavioural responses. Therefore, the proposition of biological context is not beyond any question. This leads to the conflict between two ideas, whether it is biology or culture that paves the foundation of the behavioural attributes of partner selection.

2. THE RATIONALITY BEHIND PARTNER SELECTION

Evolution of reproductive tactics in both the sexes results from the selection pressure that is created by the interaction between males and females [Alcock 2001]. Since females produce eggs, nourish the immature and feed the newborn, at least in broader context, reproductive decision is supposed to be controlled by them. In the animal world, it is usually seen that the advanced animals show a significant trend in the involvement of females in parental care. Human males, although, provide noteworthy contribution in raising their children chiefly by providing monitory support and protection to their families irrespective of all cultures, mating decisions are not up to them, at least when successful fertilization is concerned. Human females can conceive only if they are within a certain fertile period of menstrual cycle. This makes males utterly insignificant in deciding whether they want to fertilize or not. Therefore the ratio between fertilizable eggs to mature sperms remains inclined towards the males [Alcock 2001], which in other words, means that the numbers of mature sperms capable of fertilizing the eggs are much more abundant than the numbers of available fertilizable eggs.

As the ratio between fertilizable eggs to sperms remains inclined towards the males, they face extreme competition in terms of accession to females. Therefore, each individual male must exhibit some sort of superiority to prove him competent enough to access females. Females, on the other hand, as because males are abundant, are expected to be selective. This selection is based on the enhanced attributes in their male counterparts that may increase their fitness. The domination of males in the most of the societies throughout the world is rooted into the fact that males in most societies are capable of providing monitory support to their families. Only the male providing financial support in a family is the most common and generalized scenario while the reverse is not always true. Therefore, female psychology tends to adhere to males who are capable enough in doing so. Such a trend ensures the safety of the females and her progenies. This is definitely costly to males and so, males, on the other hand, tend to stick to those females who are supposed to pay off the cost in terms of the certainty that she would conceive his child only and not of other males. This tendency of males is evolutionary conserved and the study of human reproductive psychology shows much similarity throughout the animal world in their reproductive behaviours.

3. FEMALES ARE SELECTIVE

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What we call financial responsibilities carried out by men might be considered similar to that of 'nuptial gifts', which animals, chiefly the male ones provide to their prospective female partners in order to access them for copulation. Mostly, the gifts are some palatable items that are believed to nourish the female and its eggs.

In this regard, the females of the blister beetles (*Neopyrochora flabellata*) exhibit a peculiar selective mate choice strategy. The male blister beetles consume a substance called cantharidin, which can be transferred to the females during mating along with the transmitted sperms. Further, females add the received cantharidin to their eggs for making the eggs less palatable for some egg-eating insects, thereby increasing the fitness of its offspring. At the time of copulation, the female scrutinises the amount of cantharidin secretion from a cephalic gland of its prospective mate and permits the male to inseminate it only if the female is certain about the secretion. If the male beetle fails to prove it to be an eligible partner in terms of the secretion, the female curls its abdomen so that the male fails to inseminate it [Eisner *et al.* 1996].

Another classic example of such selective mating by females is seen in case of the moth *Utetheisa ornatrix*, in which females copulate with multiple male moths. During intercourse, the males transfer spermatophores, which contain certain egg-protecting alkaloids [González *et al*. 1999]. Surprisingly, females of this moth can sense the mass of the transferred spermatophores. They shift sperms only from the heavier spermatophores to their sperm storing organs and use in fertilizing their eggs later [LaMunyon and Eisner 1993; LaMunyon and Eisner 1994].

Such instances are not restricted among insects; rather they are widespread in the animal kingdom. Females of fifteen-spined stickleback fish prefer males who are more efficient body shakers. Efficiency in shaking the body conforms to the efficiency in nest fanning once the eggs are laid. This ensures more oxygenation over the eggs and thereby successful hatching [Östlund and Ahnesjö 1998].

Turning towards the human race, the situation seems to be very much similar. Women around the world tend to look for mates who are financially much sound [Buss 1989]. At the same time, while advertising in matrimonial sections of the newspapers, women specify their preferences for rich men far more than men specifying rich women [Waynforth and Dunbar 1995]. This trend is not only seen in those societies where women are financially dependent on their husbands, but also in case of self supported women, moreover in heavier impetus. The well settled females have been seen to be more concerned about the economic robustness of their potential partners [Townsend 1989; Wiederman and Allgeier 1992].

Another trend that has been reported from the personal advertisements is the highest demand for grooms belonging to the age group of late thirties [Pawłowski and Dunbar 1999]. This might result from the fact that men in their late thirties are financially well settled and thus capable of mobilising their resources towards their families [Alcock 2001].

In spite of the clear evidences of higher demand for rich men, there are indications that females also give emphasis on overall masculinity when the matter of partner selection is

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concerned. It has been noted that women undergoing the fertile phase of menstrual cycle mostly prefers highly masculine phases [Penton-Voak and Perrett 2000]. Since, the copulation within the fertile phase has the maximum probability to result in pregnancy and therefore female psychology tends to accept men with 'good genes' which reflect their overall health condition, which is supposed to be represented by men's masculine architectures of faces.

What we denote as 'masculinity' in case of human has certain equivalent criterion in case of animals. Pied fly-catcher birds show morphological variations among their males, one variant is with jet black and white plumage while the other one with dull brownish plumage. Experimentally it is well established that female pied flycatchers conspicuously exhibit their preferences towards males with jet black and white feathers [Sætre *et al.* 1994]. Interestingly, experiments show that the bright coloured males are more efficient fathers [Sætre *et al.* 1995]. As their efficiency in 'baby-flycatcher-sitting', as we may call it, is reflected on their brighter plumage, females tend to inclined towards brighter 'masculine' males. The similar situation is observed in house finches, where the females prefer bright red feathered males over orange or yellow feathered males [Hill 1990].

4. MALES ARE OPPORTUNISTS

So far it is evident that the reproductive successes of the female animals are limited by their ability to conceive a certain number of offspring and accession to resources from their male partners in order to raise them. Although the phenomenon of mate choice is mostly associated with female-controlled mating preferences, males also exhibit their preferences in many instances. Logically, a male animal will have more fitness if it has adequate amount of accessible mature females. Therefore males tend to, if not practice in reality, to be polygamous. Upon finding a suitable partner in terms of its overall 'good look', which represents is overall genetic superiority of health and immunological conditions, males are prone to engage themselves in sexual activity more easily than the females do. Several studies have indicated this phenomenon.

In one study, a group of people were asked the likelihood of making themselves involved in sexual relationship with a person of the opposite sex after knowing each other for a certain duration of time which varied from 1 hour to 5 years. Males were found to be agreed to have sexual activity after knowing the potential mate for a shorter duration, whereas, females agreed to do so only after knowing their counterpart for a greater time period [Buss and Schmitt 1993]. This indicates the threshold for sexual activity in males is much lower than the females and indicates the opportunist tendency of male psyche when it comes to have sex.

The opportunist male sexual psyche is also evident from another study where people were asked about their preference of intelligence they would like to have in their partners, which varied widely from casual sex partners to stable dating partners and finally marital partners. Strikingly, when the matter of casual sex is concerned, males were found to be abruptly ready to date women with far below average intelligence, whereas, women were found to be much more selective [Kenrick *et al.* 1990]. This tendency of males to make themselves involved in

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sexual activity even compromising the minimum acceptable intelligence of their partners is once again an indication of male opportunist psychology.

This tendency is also supported by the fact that, since ages males have engaged themselves more in extramarital affairs compared to the females [Alcock 2001]. Polygamy, for males is proportionately correlated to chances to spreading genes in the next generation. Illegitimate children are extra gain in this term, because the genes of one male is successfully transmitted to the next generation even without costing its own parental care, as, in most cases, illegitimate children are reared by the extramarital partners and their husbands [Alcock 2001].

Another aspect of men's sexual psyche is jealousy and possessiveness. It has been found that, irrespective of cultures, adultery committed by women is considered as greater offence than committed by males. This trend of male dominated societies to monopolise females is a clear trend towards cementing up the probability of giving birth (and thus spreading genes) a child from a particular male only and not by other males. This is also supported by the social architecture of gorillas and human. Amongst gorillas, one male of the band controls the sexual activity of many females. Therefore, in gorillas, the chance of a female to conceive a baby from a gorilla other than the dominant one is extremely rare. This has resulted in testes in gorillas which are lighter in weight than the human testes [Harcourt *et al.* 1981] and a single ejaculation from a male gorilla contains lesser number of sperms than in human [Alcock 2001]. Humans, on the other hand, have restricted adultery artificially by enforcing laws. Criminal law and matrimonial law; both treat adultery as an offence against marriage [Yadav 2007].

Equivalent to the enforcement of laws to prevent extra-marital affairs, nature shows similar instances in the animal world. A lot of strategies male animals utilize to ensure its successful insemination, sometimes overruling the previous instances of insemination by other males. A prominent example of such strategy is seen in black winged damselfly (*Calopteryx maculate*) in which males scoops out 90 to 100 percent of the sperms of the female genital track inseminated by previously copulated male before undergoing intercourse [Waage 1979].

Apart from this, males in the animal world tend to restrict the accession to the copulated female by other males by involving many other strategies. Some of these include keeping the female occupied after copulation [Allen *et al.* 1994], sometimes by alluring new males to drive away from the female [Field and Keller 1993], sometimes by sealing the genital orifice of inseminated female by some secretions [Dickinson and Rutowski 1989].

In the parasitic wasp *Cotesia rubecula* copulation is followed by a time lag in which a second male may exploit a mated female to copulate again [Field and Keller 1993]. In order to distract rival males, recently mated male mimics a female for a certain period to deceit the rival. Female mimicry in this species acts as a post-copulatory mate guarding trick in order to increase its reproductive success [Field and Keller 1993].

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Likewise, the males of an Indonesian fish blueband goby (*Valenciennea strigata*) accompany its mating partner wherever it goes [Alcock 2001]. This is an instance of direct mate guarding.

Therefore, it is obvious that, throughout the animal world, including human, males show opportunist, jealous and possessive sexual mind-set towards their mating partners. This is evolutionary conserved, and meant for greater reproductive success of the males.

5. CONCLUSION

Human, although show striking resemblance with animals in their sexual psychology, it cannot be forgotten that human behaviour and psychology is a multidimensional aspect which involves genetic design as well as social upbringing. The analysis of sexual psychology with respect to animals can decipher the roots behind its sexual behaviour. We live in a world where many of the so called 'rational animals' tend to act far from a civilized manner, frequently committing brutal sexual crimes, enforcing savage laws to restrict and dominate women. Are these merely instincts, which are irresponsive to proper education, healthy culture and decent upbringing or can be surmounted towards an optimistic direction for the society by proper channelization? There are so many such questions which can be answered properly only when the origins of such behaviours are tracked down. Therefore, tracing the ethological root of human sexual psychology can throw light on the possible therapeutic, social, and academic directions which can rescue the mankind from a filthy sewage of social bondage and subjugation of human rights and instead, make it a better planet to live in.

ACKNOWLEDGEMENT

The title is inspired from the work of the legendary Bob Dylan. Having been to the timeless song 'Blowing in the wind', there is no other title I could have conceived for the paper.

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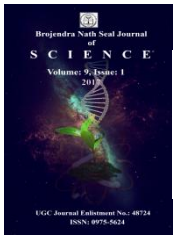

Brojendra Nath Seal Journal of SCIENCE

Review Article

THE MECHANISMS OF INNATE IMMUNITY IN INSECTS

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A B S T R A C T

The term "*immunity*" simply refers to "the state of protection from infectious diseases" by means of several mechanisms. These mechanisms are either highly specific or nonspecific. Insect possess both mechanisms but they have limitation in recognition of different particles. This is due to less diversity or variation in their peptidoglycan recognition particles (PGRPs). Like insect PGRPs, human has also four types of PGRPs that are PGRP-S, PGRP-L, PGRP-Iα & PGRP-Iβ, involved in innate immunity. Human PGRPs recognises foreign particles by their Pathogen associated molecular patterns (PAMPs). Insect PGRPs are of two types of which one directly lyses the foreign particles as an immediate immune measure. The other variety of PGRPs induces the Toll & Imd signalling pathway, termed as systematic activity, which is a delayed measure. These pathways direct the synthesis of antimicrobial proteins (AMPs) that lead to make a first line defence in insect body. These PGRPs of insect recognise foreign particles in a similar way like human PGRPs and engaged only in innate immune defence. From this it may be assumed that the genes that are involved in innate immunity in vertebrates or invertebrates may be conserved.

Keywords: *AMP, immunity, insects, PAMP, pathogens*

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1. INTRODUCTION

In this chancy living world all organisms are equipped with different systemic potential protective measures against intracellular or extracellular catastrophes due to pathogens. Such systems are differently manifested in different organisms depending on their metabolic complexities. However, all organisms possess a temporal set of metabolic pathways to do so.

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Immunity can be categorised into two different types namely, innate immunity and adaptive immunity. Innate immunity is the first line of defence against infection which is the less specific or non-specific one and eliminates infection within hours after introduction into body. Adaptive immunity is the second line of defence, which has more specificity and plays role few days after the initial infection. Further, immune responses can be divided into humoral and cell mediated immunity. Cell mediated immunity involves antibody producing cells and T-cells respectively. Mammalian immune system functions via both of these ways of immunity while insect immune system comprises only of innate immunity.

1.1. Insect innate immunity

The innate immune system in insects is composed of a large variety of specific and nonspecific responses that are activated in response to the presence of foreign agents **(Santoyo & Aguilar, 2011).**

Insect innate immunity can be categorised into humoral and cell mediated responses. In humoral response antimicrobial peptides (AMPs) are involved that produce intermediate reactive oxygen & nitrogen species, and by doing so they regulates melanisation of haemolymph and coagulation process. Cellular response includes haemocyte mediated actions such as phagocytosis, encapsulation & nodule formation.

1.2. Components of insect innate immunity

Insect innate immune system contains different types of Peptidoglycan recognition proteins (PGRPs). Insect PGRPs are of two types. The first type are amidase enzymes, which directly lyse the infectious foreign microorganisms and reduces its inflammatory activity. The second type of PGRPs evoke signal to activate proteolytic cascades and signal transduction pathways that generate antimicrobial products, induce phagocytosis, hydrolyse peptidoglycan **(Dziarski and Gupta, 2006)**. Like human adaptive immunity, this second type of insect PGRPs have recognition, signalling, and effector functions, all of which are crucial for enhancing antimicrobial innate immunity **(Dziarski and Gupta, 2006)**. But insect PGRPs are able to recognise only a limited number of foreign microorganisms.

The recognition of infectious microorganisms in innate immunity is done by the detection of pathogen-associated molecular patterns (PAMPs), which includes lipopolysaccharide (LPS), peptidoglycan (PGN), flagellin and nucleic acids from bacteria, fungi and viruses, which are essential for the microbial survival, but are not found in higher eukaryotes **(Yano & Kurata, 2011).**

Insects have nineteen types of PGRPs, which protect insects against microbial infections. The first PGRP was discovered in silkworm as a protein that induces prophenol oxidase cascade leading to melanisation and interferes with the bacterial PGN (**Dziarski & Gupta, 2006**). On the basis of size insect PGRPs are categorised as short PGRPs (PGRP-S) having smaller transcripts and are extracellular proteins, while other are long PGRPs (PGRP-L), which have longer transcripts and are intracellular, extracellular, or membrane-spanning proteins (**Dziarski & Gupta, 2006**). Thus S & L stands for short transcript and long transcript respectively and A, D, C are different isoforms e.g., PGRP-LC stands for C isoform of long transcript PGRP.

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Table 1: *Important pathogen associated molecular recognition proteins in insects.*

Sl. No.	Recognition proteins	Location	Function
1	PGRP-SA	Haemolymph	Binds with both lysine (Lys) type & Diaminopimelic (DAP) type PGN.
2	PGRP-SD	Haemolymph	Binds with lysine (Lys) type PGN.
3	PGRP-LC	On surface of immune cells	Binds with Diaminopimelic (DAP) type PGN.
4	PGRP-LE	Haemolymph	Binds with Diaminopimelic (DAP) type PGN.
5	Gram negative binding protein-1 (GNBP-1)	Haemolymph	Binds with Lipopolysaccharide (LPS).

2. HUMORAL DEFENCE

2.1. Antibacterial immunity: role of antimicrobial peptides (AMPs)

Antibacterial activity in insects was first observed in the bacteria-immunized pupae of the giant silk moths *Samia cynthia* and *Hyalophora cecropia* and later on in the bacteria-induced *Drosophila melanogaster* adult flies. The first insect AMP (Cecropin) was purified from the larvae of giant silk moth (*Hyalophora cecropia)* in 1980, and since then over 150 insect AMPs have been identified (**Yi *et al*, 2014**). AMPs play a vital role in antibacterial immunity.

Antimicrobial peptides (AMPs) are short cationic molecules that can be classified into three families on the basis of their protein structures and/ or amino acid compositions (**Viljakainen, 2015).** The nature and functions of the AMPs are detailed in Table 2.

Table 2: *Nature & functions of Antimicrobial peptides (AMPs)*

AMPs	Type	Molecular weight (kDa)	Function
Cecropin	Linear peptides forming α-helices	4	Lyse bacterial cell membrane, inhibit proline uptake & cause leaky membrane.
Moricin	Linear peptides forming a-helices	4	Increase permeability of bacterial cell membrane which kills the bacteria.
Defensin	Peptides containing cysteine residues	4	Disrupt the structure of bacterial cell membrane.
Drosomycin	Peptides containing cysteine residues	5	Act as antifungal & antibacterial peptide.

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AMPs	Type	Molecular weight (kDa)	Function
Apidaecin	Peptides containing proline residues	2.1084	Inhibits viability of gram negative bacteria.
Drosocin	Peptides containing proline residues	2.1986	Act on gram negative bacteria.
Lebocin	Peptides containing proline residues	3.433	Active against gram negative bacteria, gram positive bacteria & some fungi.
Attacin	Peptides containing glycine residues	20	Increase permeability of bacterial cell membrane and inhibits synthesis of cell membrane protein,
Gloverine	Peptides containing glycine residues	14	Inhibit synthesis of outer membrane proteins resulting in an increase in permeability of the outer membrane of the bacteria.

2.2. Molecular mechanism of synthesis of AMPs

During microbial infection, Toll like receptor (TLR) and Immuno deficiency (Imd) mediated pathway regulates the synthesis of AMPs. These two pathways exhibit striking similarities with the Toll like receptor (TLR) and Tumor Necrosis Factor-R (TNF-R) of the vertebrates that regulate NF-kB activity during the immune response, thereby suggesting common evolutionary lineage in respect of innate immunity **(Tembhare, 2016).**

2.3. Toll mediated signalling in Insects

Toll mediated pathway evokes immune response both against the gram positive bacteria and the fungi. But the pathway shows a few differences while functioning in fungi from that in gram positive bacteria. The pathways are separately discussed below.

2.4. Toll mediated pathway against gram positive bacteria

The Toll mediated signalling pathway functions stepwise as summarized below **(Lazzaro, 2008), (Tembhare, 2016)**:

I. Pathogen associated molecular patterns (PAMPs) of gram positive bacteria are Lys-type peptidoglycan (PG) of cell wall. Toll mediated Peptidoglycan recognition proteins (PGRP-SD) of Insects bind to this Lys-type PG and then recruits gram negative bacteria binding protein-1(GNBP1) & modular serine protease (MSP) zymogen in the presence of Ca^{2+}.
II. The PG-PGRP-SD-GNBP1 complex then induces the activation of MSP zymogen to active MSP.

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III. Active MSP induces the conversion of PGRP-SA zymogen to activated SPE protease which in turn cleaves Spatzle (SPZ) proprotein to processed SPZ.

IV. Spatzle protein then binds with Toll like receptor. So tube protein binds with Toll receptor protein via dMyD88 protein.

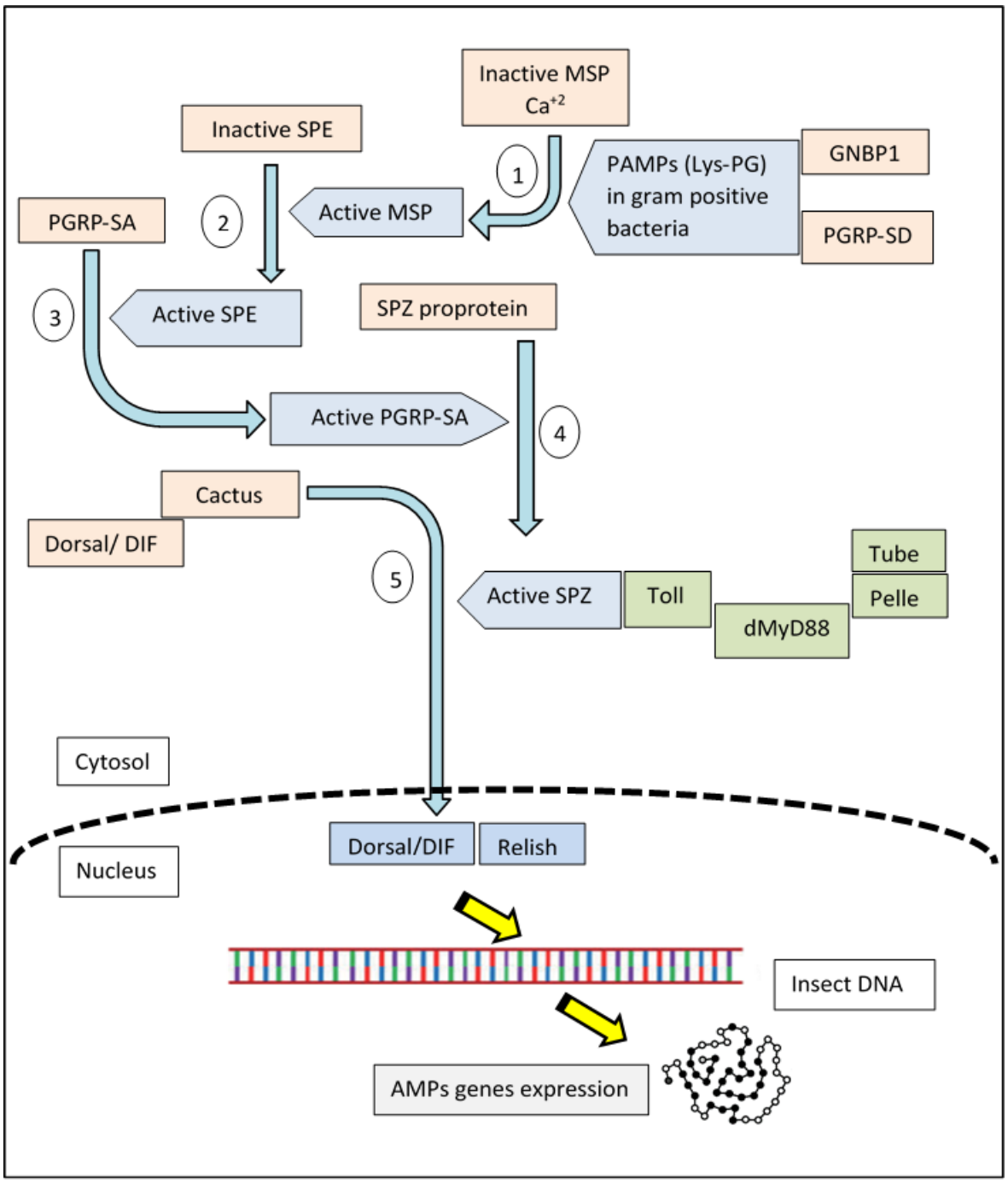

Fig. 1: *Diagrammatic representation of steps of Toll-mediated pathway in insects for AMPs expression against gram positive bacteria.*

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V. Tube protein then brings Pelle protein to toll protein and forms a complex of toll-tube-pelle.
VI. Pelle protein, a protein kinase phosphorylates Cactus protein. As a result, DIF/ Dorsal protein dissociated from cactus protein and enters into the nucleus.
VII. In nucleus, DIF/ Dorsal protein along with Relish protein (a NF-kB family protein, acts as transcription factor) binds with DNA and induces the expression of genes for AMP. AMPs then played their crucial role against gram positive bacteria.

2.5. Toll mediated signalling in Fungi

β-1, 3 glucan of fungi as PAMPs is recognised by GNBP3 or detection of protease virulence factors by activation of the persephone gene product. PGRP-SA has no role to detect the PAMPs of the fungi.

2.5.1. The steps of detection of PAMPs by GNBP3 and successive signalling cascades are summarized below **(Lazzaro, 2008) (Tembhare, 2016)**:

i. GNBP3 complex induces the activation of MSP zymogen to active MSP.

ii. Active MSP, induces the conversion of inactivated SPE to activated SPE protease which in turn cleaves SPZ proprotein to processed SPZ.

iii. Spatzle protein then binds with Toll like receptor. So tube protein binds with Toll protein via dMyD88 protein.

iv. Tube protein then brings pelle protein to toll protein and forms a complex of toll- tube-pelle.

v. Pelle protein, a protein kinase phosphorylates Cactus protein. As a result, DIF/ Dorsal protein dissociated from cactus protein and enters into the nucleus.

vi. In nucleus, DIF/ Dorsal protein along with Relish protein (a NF-kB family protein, acts as transcription factor) binds with DNA and induces the expression of genes into AMPs. AMPs then played their crucial role against gram positive bacteria.

2.5.2. The steps of detection of protease virulence factors by the activation of the Persephone gene product and mediated signalling are as follows **(Lazzaro, 2008) (Levitin & Whiteway, 2008)**:

i. Fungi release virulence factors. Then, Persephone protease (encoded from psh gene) was activated. It was crucial for the activation of the Toll receptor in response to fungal infection.
ii. On the other hand, Necrotic (*nec*) gene encoded serine protease inhibitor or serpin that inhibits the toll mediated signalling by blocking Persephone protease protein. Persephone induces the conversion of inactivated SPE to activated SPE protease which in turn cleaves SPZ proprotein to processed SPZ (SPATZLE).

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iii. Spatzle protein then binds with Toll like receptor. So tube protein binds with Toll protein via dMyD88 protein.
iv. Tube protein then brings pelle protein to toll protein and forms a complex of toll- tube- pelle.

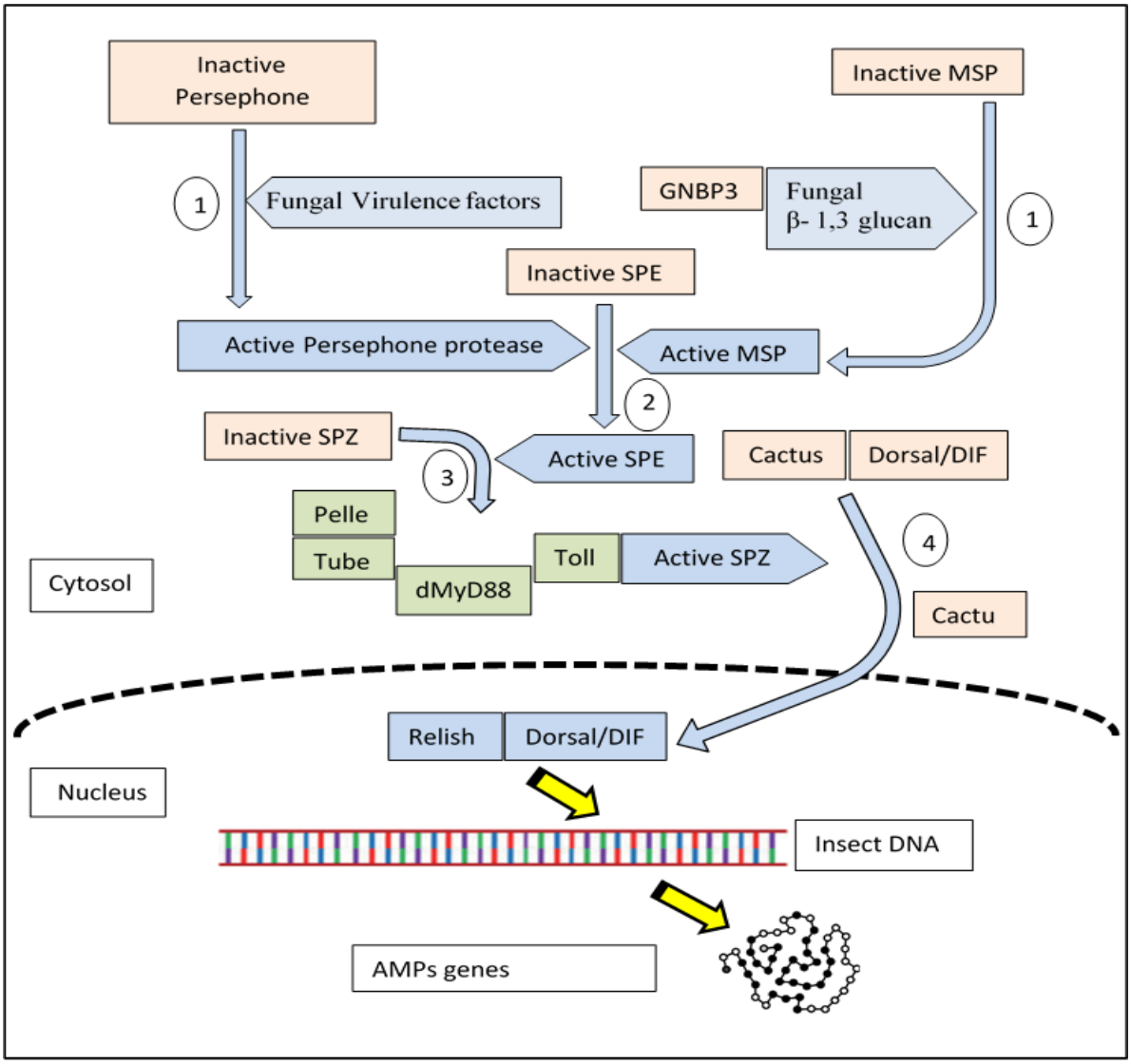

Fig. 2: *Diagrammatic representation of Toll- mediated pathway against Fungi.*

v. Pelle protein, a protein kinase phosphorylates Cactus protein. As a result, DIF/ Dorsal protein dissociated from cactus protein and enter into the nucleus.
vi. In nucleus, DIF/ Dorsal protein along with Relish protein (a NF- kB family protein, acts as transcription factor) binds with DNA and induces the expression of genes into AMPs. AMPs then played their crucial role against fungi or fungal infection.

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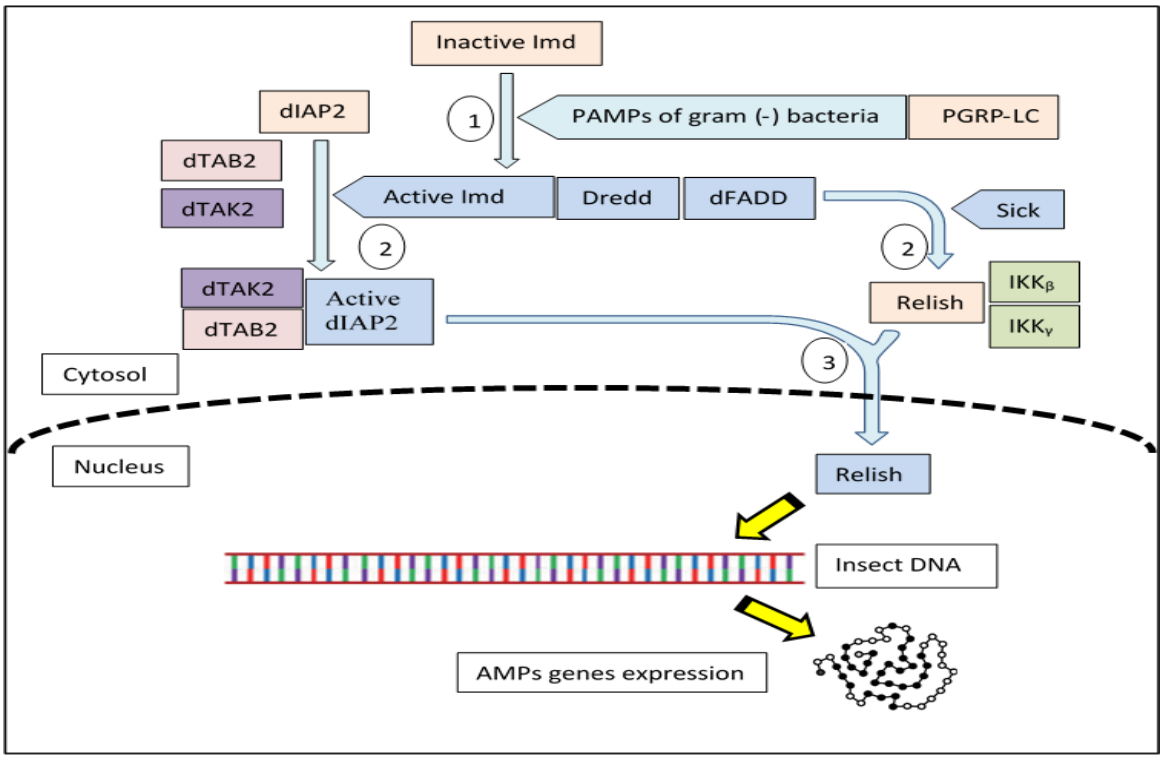

Fig. 3: *Diagrammatic representation of Imd signalling pathway against gram negative bacteria.*

2.6. Immuno deficiency (Imd) mediated signalling

Imd signalling pathway occurs against the infection or after attack of gram negative bacteria. In gram negative bacteria, lipopolysaccharides act as PAMPs that are recognised by PGRP-LC.

The steps of Imd signalling pathway are given below:

i. Lipopolysaccharides as PMPs from gram negative bacteria are recognised by PGRP-LC.
ii. PGRP-LC bound to the PMP activates the Imd receptor, which in turn associates with dFADD & Dredd proteins and forms Imd-dFADD-Dredd protein complex.
iii. Another protein Sick induces Imd-dFADD-Dredd protein complex to activate Relish protein. Although, Imd-dFADD-Dredd protein complex also activates dIAP2 protein. dIAP2 interacts with dTAB2 & dTAK2 proteins which further interacts with IKKβ & IKKγ. As a result, Relish is released from the IKKβ-IKKγ protein complex.

iv. PGRP-LC bound to the PMP activates the Imd receptor, which in turn associates with dFADD & Dredd proteins and forms Imd-dFADD-Dredd protein complex.
v. Another protein Sick induces Imd-dFADD-Dredd protein complex to activate Relish protein. Although, Imd-dFADD-Dredd protein complex also activates dIAP2 protein. dIAP2 interacts with dTAB2 & dTAK2 proteins which further interacts with IKKβ & IKKγ. As a result, Relish is released from the IKKβ-IKKγ protein complex.

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vi. Finally, Relish protein binds with respective gene and induces the gene expression of AMPs

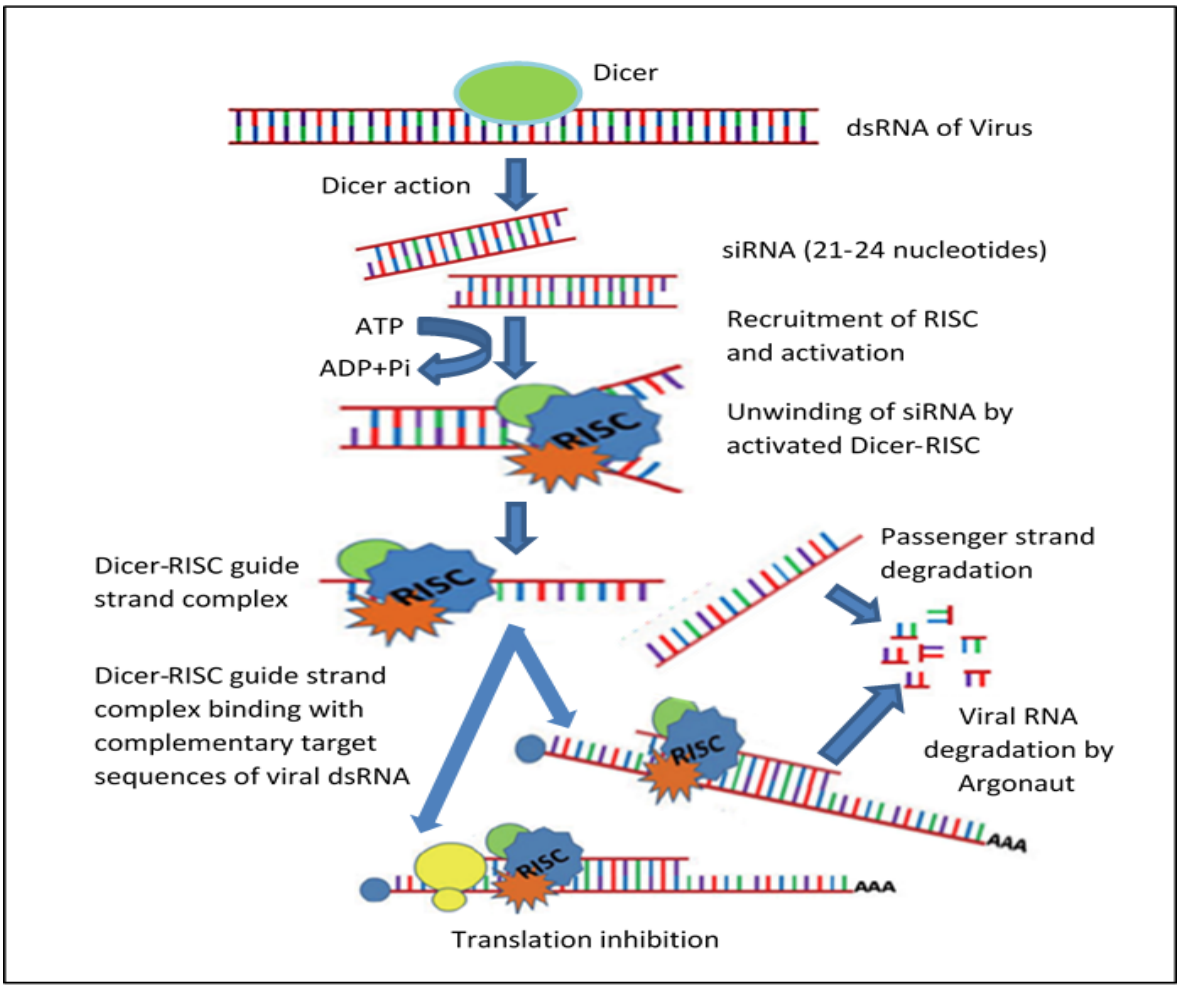

Fig. 4: *Diagrammatic representation of RNAi mediated signaling*

2.7. Antiviral immunity

The arbovirus or arthropod borne viruses are mostly RNA viruses. Their life cycle involves horizontal transmission by an arthropod vector or host between susceptible vertebrate hosts such as mammals, birds, domesticated animals and sometimes humans **(Tembhare, 2016)**.

Antiviral immunity involves RNA interference or RNAi mediated pathway and JAK- STAT mediated signalling pathway that are discussed below:

2.7.1. Antiviral RNAi response

The steps of this response pathway are given below:

i. After viral infection, the dsRNA of virus binds with DICER (RNase III family protein) and forms DICER-dsRNA complex.

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ii. Then, DICER cleaves the dsRNA to form small interfering RNAs (siRNAs), which are approximately 21 to 24 nucleotides long.
iii. RNA-induced silencing complex (RISC) is recruited, which degrades the passenger strand of the siRNAs.
iv. DICER-RISC-guide strand complex binds with complementary target sequence of viral dsRNA.
v. RISC contains argonaut protein, an endonuclease that degrades the complementary target sequence of viral dsRNA. As a result viral gene expression is inhibited.

2.7.2. JAK-STAT signalling pathway

The steps of this pathway are given below:

i. An extracellular ligand binds with domeless transmembrane receptor (DOME) and induces a conformational change.
ii. This conformational change leads to self-phosphorylation of its associated Janus Kinase (JAK) protein.
iii. This phosphorylation activates the JAK, which in turn phosphorylates the DOME protein. As a result, docking site is formed on DOME protein for STATs (signal transducers and activators of transcriptions) proteins.
iv. STATs then enter into the nucleus and enables specific gene transcription to form proteins that play crucial role against the viral infection.

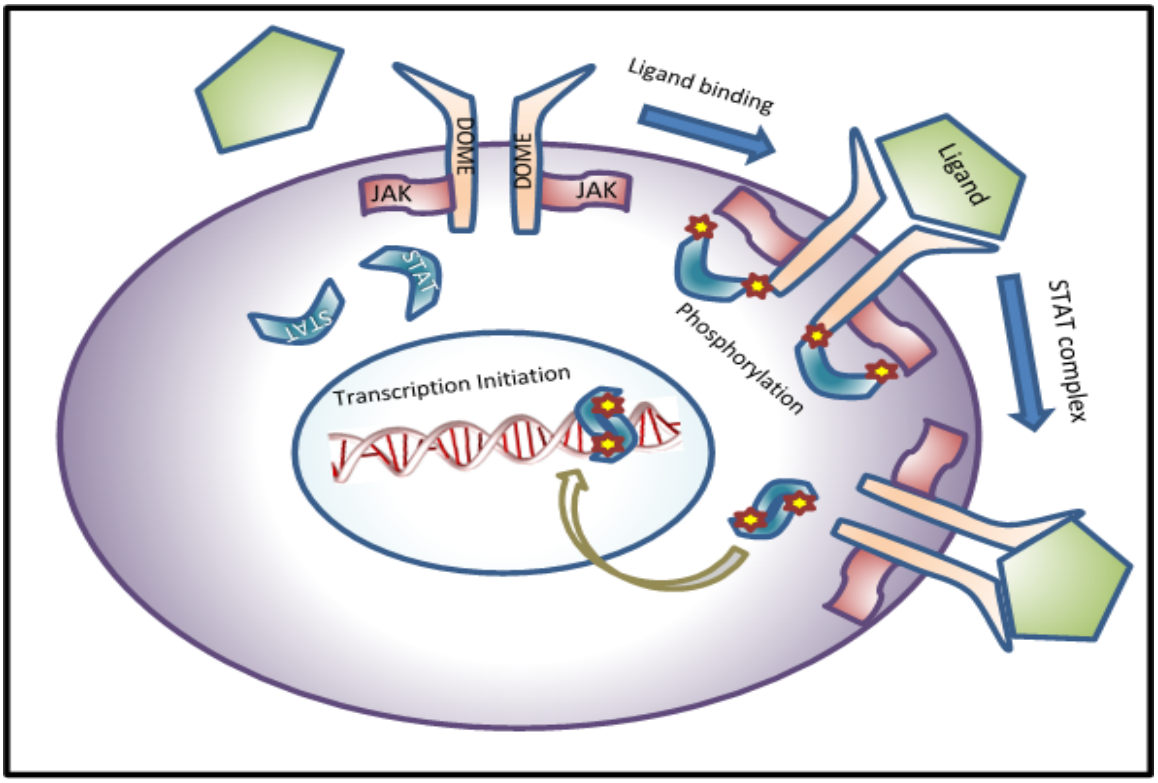

Fig. 5: *Diagrammatic representation of JAK-STAT mediated signalling*

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3. CELLULAR DEFENCE

Haemocytes, a variety of mesodermal, amoeboid, nucleated cell, plays crucial role in cellular defence mechanism. They are circulated freely in haemocoel and have similarity with vertebrate- leukocytes. Arnold (1974) has classified the haemocytes into nine different types, which are stated in Table 3 **(Tembhare, 2016)**.

Table 3: *Different types of haemocytes found in insects*

Haemocytes Type	Description
Prohaemocytes or Proleukocytes	Spherical cell with large nuclei shows mitotic division.
Plasmatocytes or Amaebocytes	Fusiform, pear shaped with large nuclei having cytoplasmic processes, do phagocytosis.
Granular haemocytes	Compact oval shaped cell, non- motile, metabolic in function.
Adipohaemocytes or Adipocytes	Large oval nuclei, vacuolated cytoplasm.
Coagulocytes	Spherical cell with large nuclei and hyaline cytoplasm.
Spherule cell	Elliptical cell with eosinophilic cytoplasm.
Crystal cell	Oval shaped cell with eccentric nuclei, clear crystalline basophilic cytoplasm.
Podocytes or Stellate cell	Stellate shaped with central large nuclei and radiating permanent podia.
Vermiform haemocytes or Nematocyte	Thread like with basophilic cytoplasm and are reported in last instar larvae of *Prodenia*.

3.1. Immune Activity of Haemocyte

3.1.1. Phagocytosis

Phagocytosis is a process in which virus, bacteria and different microorganisms engulfed or phagocytized by specific cells in order to protect the body from infection. The phagocytosis is carried out by forming pinocytic vesicles or by engulfing foreign bodies with pseudopodia or by making close contact with their plasma membrane. Mainly plasmatocytes play role in phagocytosis and some adipocytes also behave as phagocytes.

The efficiency of phagocytosis greatly varies among the different species of insects. Phagocytosis is a simple defensive mechanism in insects against foreign particles and also an effective means of removal of autolyzed tissues.

Phagocytosis occurs in three steps (https://en.wikipedia.org/wiki/Phagocytosis):

1. Unbound phagocyte surface receptors do not trigger phagocytosis.
2. Binding of receptors to the ligand at surface of the target particle causes them to cluster.
3. Phagocytosis is triggered and the particle is taken up by the phagocyte.

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3.1.2. Encapsulation

It is a defensive strategy in insect against large metazoan parasite. Although, plasmatocytes, lamellocytes, crystal cells, spherule cells play role in encapsulation but it is mainly carried out by plasmatocytes **(Tembhare, 2016)**. It is a major defensive strategy adapted by hymenopteran eggs, larvae etc.

Encapsulation is a process in which haemocytes aggregate around the large foreign bodies and initially form a consolidated capsule. This capsule is composed of two or more layers from deposition of different intercellular substances, mucopolysaccharides etc. to block the gaseous exchange. Complete encapsulation leads to death of foreign bodies due to lack of oxygen.

This process is ineffective in case of tachinid larvae because they possess respiratory funnel that remains directly connected with host's respiratory system.

3.1.3. Nodule formation

Nodule formation is a prompt response to clear microorganisms from the haemocoel **(Arai *et al*, 2013)**. In nodule formation, pathogens are at first recognised by specific molecules (such as PGRPs, LPs) and haemocytes aggregate surround the pathogen. The haemocytes release a flocculent material around foreign substances and these aggregated substances entrap foreign material and begin to melanise in that region within 30 minutes. After melanisation, the entire substance act like foreign body and is removed from the body by encapsulation process.

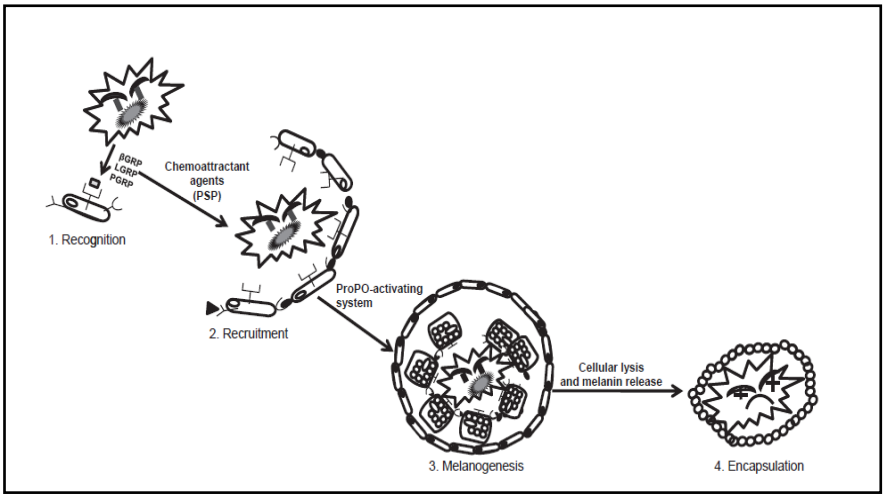

***Fig. 6:** Formation of nodule in insect **(Santoyo & Aguilar, 2011)**.*

AMPs, prophenoloxidase (proPO) factors are involved in humoral response which regulates melanisation process and functions of serine proteases, serine protease inhibitors, serine protease homologs, and lectins **(Arai *et al*, 2013)**. Besides, plasmatocytes, granular haemocytes & cystocytes are actively involved in nodule formation in insects **(Tembhare, 2016)**. Further studies demonstrated that C-type lectins & hemocytins are involved in aggregation process before nodule formation **(Arai *et al*, 2013)**.

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3.1.4. Melanin synthesis pathway

Phenyl oxidase (PO) helped in the synthesis of melanin which enhances the melanisation process. Melanin is synthesised through the following steps **(Santoyo & Aguilar, 2011)**:

i. Phenylalanine (Phe) is the precursor of the melanin in insect. The Phe is initially converted into Tyrosine (Tyr) by phenylalanine hydroxylase.
ii. Tyr is converted into (DOPA), by the action of PO.
iii. DOPA is either converted into Dopamine or Dopaquinone, catalysed by enzyme DOPA decarboxylase or PO respectively. Dopamine then further changes into Dopaquinone by enzyme PO.
iv. Dopaquinone then changes into 5, 6-Dihydroxyindole (DHI) via Dopachrome.
v. PO catalyses DHI to be converted into Indole-5, 6-quinone.
vi. Indole-5, 6-quinone is changed into melanochrome and finally polymerise to form melanin.

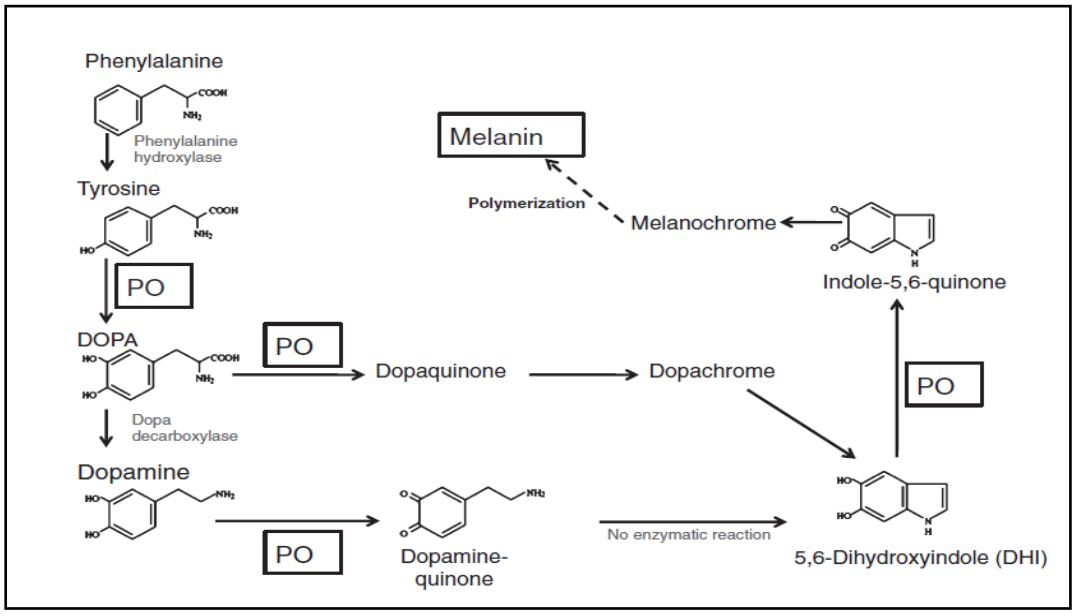

Fig 7: *Melanin synthesis pathway in insects* ***(Santoyo & Aguilar, 2011)***

4. BIOLOGICAL SIGNIFICANCE OF IMMUNITY IN INSECT

The insects are solely adapted to innate immune defence mechanism. The innate immune system comprises of molecular mechanisms to defend the host from infection by other organisms in a nonspecific manner and doing so, they are adapted to recognise and respond to pathogens in a generic way (**Tembhare, 2016**).

There are thousands of bacteria that live in association with insects. The action of bacterial infection helps in better evolution of insect immune system. Due to insect immune defence mechanism, evolutionary pressure in turn, plays on the microbes to develop resistance against insect immune system.

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In human, Major Histocompatibility Complexes (MHCs) are responsible for self & foreign cell recognition and for presenting antigen of either endogenous or exogenous in origin. Though insect PGRPs are capable only to recognise certain foreign particles, unlike the MHCs, yet insect PGRPs are quite efficient in inducing the signalling pathway for immunity.

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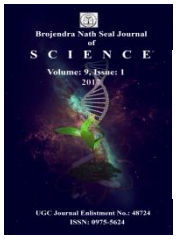

Brojendra Nath Seal Journal of SCIENCE

Research Article

A STUDY OF STUDENTS' PERCEPTION OF VIRTUAL ANIMAL DISSECTION AT UNDER GRADUATE ZOOLOGY COURSES IN WEST BENGAL

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A B S T R A C T

In today's world, the traditional hands-on laboratory practicals of the degree college programmes in the Zoology are declining. In some cases it is being replaced by virtual laboratories and tools. Information and communication technology (ICT) opens up a new world of creativity for students and teachers in this regard. The University Grants Commission has issued a guideline to discontinue zoological dissections in a phased manner since 2011. All the universities across India have revised their practical curriculum in Biological Sciences accordingly. The virtual animal dissection offers students a more humane, cruelty-free method of studying animals and animal anatomy. Now, it is time to have a look at the perception level of the students on this issue. The present study was designed to compare the perception of "real" and "virtual" dissections of the Zoology honours course students in the colleges of West Bengal. Data were collected from Zoology honours students using a self made survey questionnaire. The questionnaire was a closed ended one and had two parts. One corresponds to the information schedule with practice details and preference of the students. The second part of the questionnaire is related to actual experiences, views and opinions about real and virtual dissection. The response format was in a 5-point Likert scale. The split half reliability of the questionnaire was found to be 0.79. Random sampling technique was adopted to select the 398 Zoology Honours students (200 males and 198 females) as participants of the survey. Descriptive statistics like percentage was applied to analyze the data. The results showed that students who always preferred to practice interactive multimedia are 41%. However, 78.89 % of students preferred never to practise virtual microscopy. Real animal dissection was seldom preferable to 46.23% of students. 71.84% of the students favoured that recorded videos should replace real dissection of animals. 68.42% of the students believed that 3D animated videos provided a better understanding than real dissection of animals. But, majority of the students (65.79%) dismissed the idea of substituting real microscopy by Virtual microscopy. Interestingly, 63.16% of the students expressed their opinion that Virtual dissection can be a replacement for real dissection. These findings reinforce the need to offer a variety of learning experiences with special emphasis to the ICT based Virtual mode of learning.

Keywords: *Animal, virtual, dissection, Zoology.*

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1. INTRODUCTION

For decades, Zoology students in Indian colleges have studied the internal apparatus of animals by cutting them open. But, a set of guidelines, issued in 2011 by the University Grants Commission, overturned this 90-year-old practice. The move sparked several controversies. Animal rights and wildlife activists welcomed the guidelines while some scientists criticized them. The use of dissections in various branches of Biological Science, especially in Zoology like the mammals, birds, reptiles, amphibians and molluscs became more and more controversial these days. These led teachers and students to adopt alternative procedures in the practical classroom. Typical alternatives to using live animals for dissection are preserved specimens, three dimensional models, video clips of live dissection experiments, interactive multimedia experimentation and computer simulations etc. Studies have shown that when students are offered an alternative to dissection by using 3D models, charts and videos, there was no significant difference in their written examination results, in particular on those themes which were based on the dissection, compared to students who completed the dissection (Downie and Meadows, 1995). Similar findings is also reported by Kinzie, Strauss and Foss, 1993; Predavec, 2001. In India, the University Grants Commission (UGC) has issued a guideline to discontinue zoological dissections in a phased manner since 2011. All the universities across India have revised their practical curriculum in various subjects of Biological Sciences accordingly. The UGC, apex body for standardizing higher education in India has issued the guidelines to all universities and colleges that run Life Sciences and Zoology courses, saying animal dissection in their laboratories should be discontinued in a phased manner. The practice is to be replaced by field visits and digital virtual alternatives. Educators at all levels are increasingly choosing alternatives to animal dissection to meet their students' needs in the classroom. These modern practical methods include multimedia, animation, videos, interactive computer simulations and 3D models etc. It not only saves animal lives but also reduces the cost of animal purchased for dissection. This concept of virtual laboratory is more suitable for students, and is more effective than manually doing animal dissections. So, it seems to be an important issue for the students of Biological Sciences to gain an understanding of the relative usefulness of virtual animal dissections. Given this environment, this paper examines the perceptions of real and virtual dissections of Zoology Honours students in West Bengal, India.

2. BACKGROUND

Animal dissections in Zoology and Biological Sciences curriculum are being followed in the country for well over the past 90 years. The University Grants Commission (UGC) has announced phasing out of animal dissection for experimental purposes at the under-graduate (UG) and post-graduate (PG) levels in 2011. UGC recommended replacing these by alternative models including virtual dissection. The decision of UGC came on the recommendations of a task force in view of cruelty meted out to animals during experiments in laboratories by students, and biodiversity concerns. For both, UG and PG programmes started a reduction in the number of animal dissections and experimentation as well as in the number of species with all ethical considerations. Preference would be given to laboratory-

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bred animal models in mandatory requirements. All educational institutions coming under the purview of the UGC revised laboratory curriculum involving animals in such a way as it can incorporate virtual dissection. The laboratory curriculum involving animals tried to make students more compassionate towards the animals. The curriculum avoided experiments on animals in many cases, wherever possible, and used alternatives instead. Experiments on animals could not be performed merely for the purpose of acquiring manual skill. The animals protected under the Wildlife Protection Act 1972, particularly frogs and fishes could not be dissected. Further, "Animal ethics" would be included as a chapter in an appropriate course of study. In order to sensitize students and other stakeholders, the departments would display the highlights of the Acts in the laboratories and elsewhere. The departments might also adopt other modalities to popularize the science and sentiments of the provisions of these Acts.

3. REVIEW OF RELATED LITERATURE

Today, dissection is not a global phenomenon. It is no longer practised at schools in the Netherlands, Switzerland, Argentina, Slovak Republic, and Israel, and is rare in schools in Sweden, Germany, and England (Balcombe, 2001; Waltzman, 1999). The limited research studies conducted till date suggest that teachers mainly use alternatives as supplements, rather than substitutes, to conventional dissection. This is demonstrated in King et al.'s study (2004), where teachers reported using charts, videos, 3D models, CD-ROMs, and other computer-based resources, but only 31.4% agreed that alternatives were as good as dissection for teaching anatomy and physiology. Similar findings were noted by Almy et al. (2001), who found that teachers were split on the validity of computer simulation as a pedagogical tool, even though 78.1% of the teachers in the study who offered dissection also reported offering alternatives. Many variables can influence a teacher's decision to use alternatives, either in lieu of traditional dissection or in conjunction with it. In considering the factors that increase teachers' likelihood of using a virtual dissection alternative, Cockerham (2001) found that a teacher's positive attitude toward virtual dissection, their previous experience using a virtual dissection, and their intention to use a real animal dissection were all positively related to their likelihood of using a virtual dissection. Other variables that may influence a teacher's decision to use alternatives include their access to them, perceptions of their effectiveness, willingness to explore new modes of learning, attitudes toward animals and technology, preparedness to teach Biological Science, and available resources, budgets, time, and supports (Hart et al., 2008). The dissection of animals in laboratory work has been recognised as beneficial with arguments that dissection can help students to develop skills of observation and comparison, discover the shared and unique structures of specific organisms, and develop a greater appreciation for the complexity of life (NSTA, 2005). However, some authors have claimed that animal dissection is a controversial pedagogical practice. In educational contexts, it raises ethical and environmental concerns regarding the killing of animals, the ignoring of animal welfare standards, the weakening of respect for life (Balcombe, 2000; Bishop and Nolen, 2001; Hug, 2008; Jukes and Chiuia, 2003; Marr, 2001; Oakley, 2009; Sapontzis, 1995).

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It might be summarised that few studies the context of virtual animal dissections had been conducted, but all of them in the foreign countries. Currently, no reported research exits in regards to the use of virtual dissection at under undergraduate Zoology courses in the state of West Bengal. This prompted the researcher to conduct a survey on undergraduate Zoology students.

4. RATIONALE

Five countries (Argentina, Israel, the Netherlands, Slovakia, and Switzerland) do not conduct dissections, and the practice is rare or being phased out in other countries, including England, Sweden, and India (Oakley, 2011). As a replacement or substitute to this, the virtual animal dissection offers students a more humane, cruelty-free method of studying animals and animal anatomy. Using live animals in dissection may sometimes have negative psychological effects on students. With virtual animal dissection, it is possible to repeat steps and procedures as many times as is necessary for the student's learning process. Virtual animal dissection also requires less classroom time than live animal dissection as it eliminates the need for set up, clean up and disposal, allowing students more time to learn other material. It is also cheaper for schools to carry out virtual animal dissection in the long run with repeated use of the virtual animal dissection software. Virtual animal dissection also lessens the ecological impact of animal dissection. This is in contrast with the impact of doing six million live dissections each year which necessitates the collection of large numbers of animals. By avoiding the use of toxic preserving chemicals, the harvesting of animals and the disposal of body parts that are necessary for live animal dissection, virtual animal dissection has also less impact on the environment.

5. RESEARCH QUESTION

In view of the UGC guidelines regarding the phasing out of animal dissections, the present study is designed to assess and to address the issues related to the students' perception on ICT based Virtual Zoological Laboratory. The study is aimed at finding out the answers of the following research questions-

i) What does the Zoology Honours students in the colleges of West Bengal perceive regarding "real" and "virtual" dissections of animals?
ii) How do the students differ in their perceived preferences in "real" and "virtual" dissections for Zoology course?

6. UNIVERSE OF THE STUDY

The three- year undergraduate Zoology Honours (1+1+1) students in different General Degree Colleges of West Bengal correspond to the population for this study. The age groups of the students ranged from 19-21 years. A total of 398 students (200 males and 198 females) representing the sample of the study was randomly chosen from 20 colleges.

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7. MATERIALS AND METHODS

A self made questionnaire was used to collect the data. The questionnaire was a closed ended one and had two parts. One correspond to the information schedule with practice details and preference of the students. This part is used to collect demographic data about age, education and gender as well as information on real and virtual dissection practice. It had five options for 5 dimensions of practice preference – Always, Often, Sometimes, Seldom and Never. The second part of the questionnaire is related to actual experiences, views and opinions about real and virtual dissection. It had 5 dimensions – recorded dissection videos, 3D animated videos, interactive multimedia, virtual microscopy and real hands-on dissection. It consisted of 20 statements created to explore participants' perception of dissection as a college practice. The response format was a 5-point Likert scale, as follows: 1 = definitely disagree; 2 = disagree; 3 = can't say; 4 = agree; 5 = definitely agree. The split half reliability of the instrument was found to be 0.79.

8. ANALYSIS OF RESULT

The results from the data collected are analysed using descriptive statistics. Individual response was coded with 1 to 5 with ascending degree of positive perception. The analysed data is represented the form of tables (Table No. 1 and 2) and charts (Figure No. 1 and 2).

Table 1: *Students' practice preference in Zoological Dissection (percentage)*

Dimension of Preference in Practice	Always	Often	Sometimes	Seldom	Never
Recorded dissection videos	30.40	31.41	18.84	12.06	7.29
3D animated videos	15.58	18.34	30.40	27.64	8.04
Interactive multimedia	41.46	29.90	19.85	6.28	2.51
Virtual microscopy	7.04	3.77	2.51	7.79	78.89
Real hands-on dissection	5.53	16.58	28.39	46.23	3.27

The analysis indicated that the highest percentage students always prefer to practise interactive multimedia is 41%. However, 78.89 % of students preferred never to practise Virtual microscopy. Real animal dissection is seldom preferable to 46.23% of students (see Table 1).

The data in Table 2 indicate that the 71.84% (43.42% plus 28.42%) of the students favour that recorded videos should replace real dissection of animals. 68.42% (40.79% plus 27.63%) of the students believe that 3D animated videos provides better understanding than real dissection of animals. In case of their opinion about interactive multimedia to be a better option than killing and cutting open an animal, only 43.42% (14.47% plus 28.95%) students supported where as 32.37% students did not support and 28.95% remained undecided. But, in case of the Virtual microscopy to be a substitute for real microscopy majority of the students (39.47% + 26.32% = 65.79%) dismissed the idea. Lastly 63.16% of the students (38.16% plus 25%) expressed their opinion that Virtual dissection can be a replacement for real dissection.

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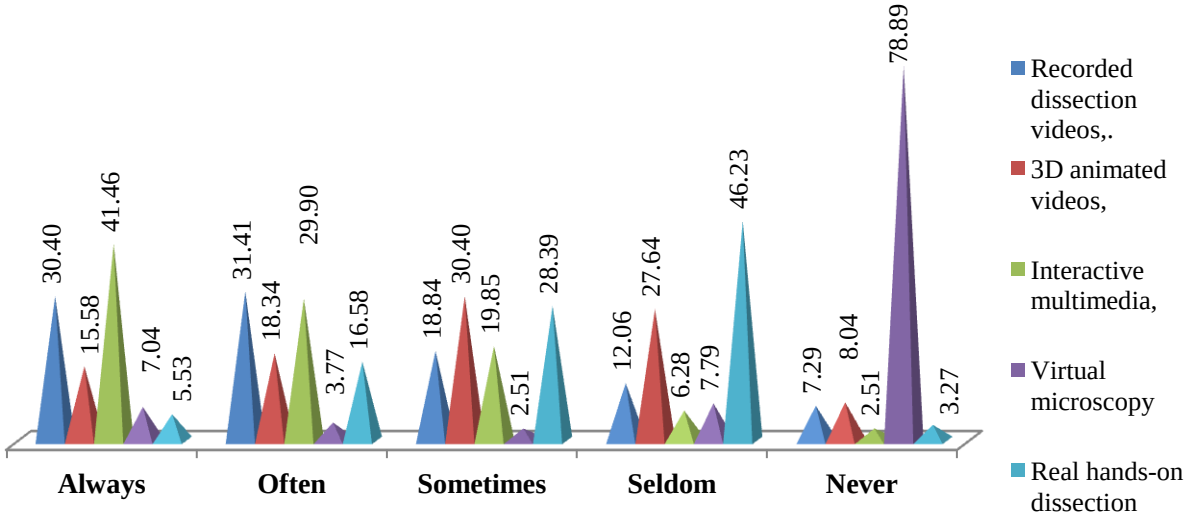

Fig. 2: *Students' practice preference in Zoological Dissection (percentage)*

Table 2: *Students' Perception of Zoological Dissection (in percentage)*

Students' Perception of Zoology Practical	Definitely agree	Agree	Can't say	Disagree	Definitely disagree
Recorded dissection videos should replace real dissection	43.42	28.42	11.84	17.11	3.95
	71.84			21.05	
3D animated videos provides better understanding	40.79	27.63	9.21	17.11	10.00
	68.42			27.11	
Interactive multimedia is better than killing and cutting open an animal	14.47	28.95	28.95	17.11	15.26
	43.42			32.37	
Virtual microscopy can be substitute for real microscopy	6.05	14.47	18.42	39.47	26.32
	20.53			65.79	
Virtual Dissection can not replace Real hands-on dissection	0.00	5.26	36.32	38.16	25.00
	5.26			63.16	

9. DISCUSSION

One of the debates within Zoology teaching is the appropriate use of animals to enhance the real learning experience. The time allotted for a practical session in Zoology ranges from 2 to 3 times that of a theory class. The curricula and syllabi had relevant practical experiences, including dissections, drawings, microscopy, experimentation and discussions with peers and tutor. For some reasons, a number of students are also unwilling to handle

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animals. At the same time in some cases financial cutbacks are making the real animal dissections more difficult.

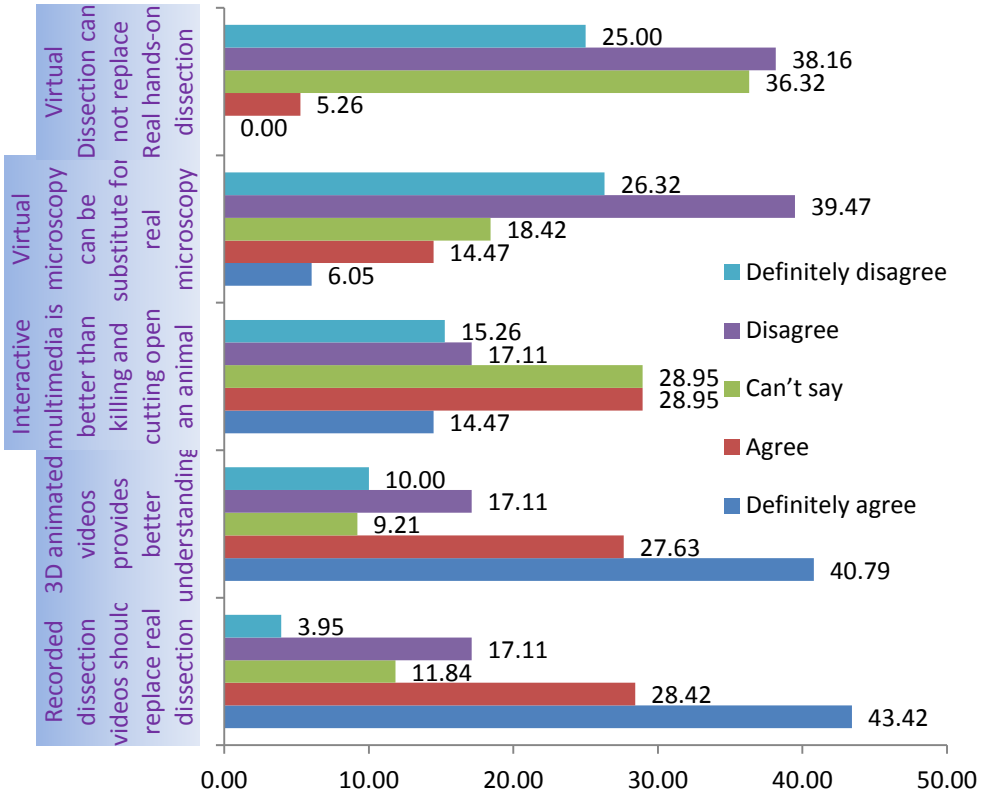

Fig 3: *Students' Perception of Zoological Dissection (in percentage)*

Finally the 2011 - UGC ruling to faze out dissection made teaching Zoology practical activities increasingly difficult. Information and communications technology (ICT) in the form of computers, television, literature databases, and audiovisual materials have been available for teachers in all disciplines for many decades. Several techniques developed simultaneously to harness the full benefit of ICT in the form of a learning tool in Zoology also. Today, many virtual learning experiences are available, which can be done in the laboratory, from home or from the college through computer and ICT access. Few of them are - virtual dissections, virtual microscopy virtual 3D experiments and virtual field trips etc. These are designed primarily to enhance the hands-on learning experience of students.

10. CONCLUSION

Globally, differences between countries in the views and position on dissection exist, largely based on the dominant teaching culture and values of a society, with trends for the exclusion of animal dissection or its replacement by virtual alternatives (Demirhan, 2014; Osenkowski, Green, Tjaden and Cunniff, 2015). The use of tactile and virtual learning approaches is common in several technical education courses. It is their preference to have hands-on practical, tactile experiences for exploration. But in this new "digital age", today's students are "digital natives".

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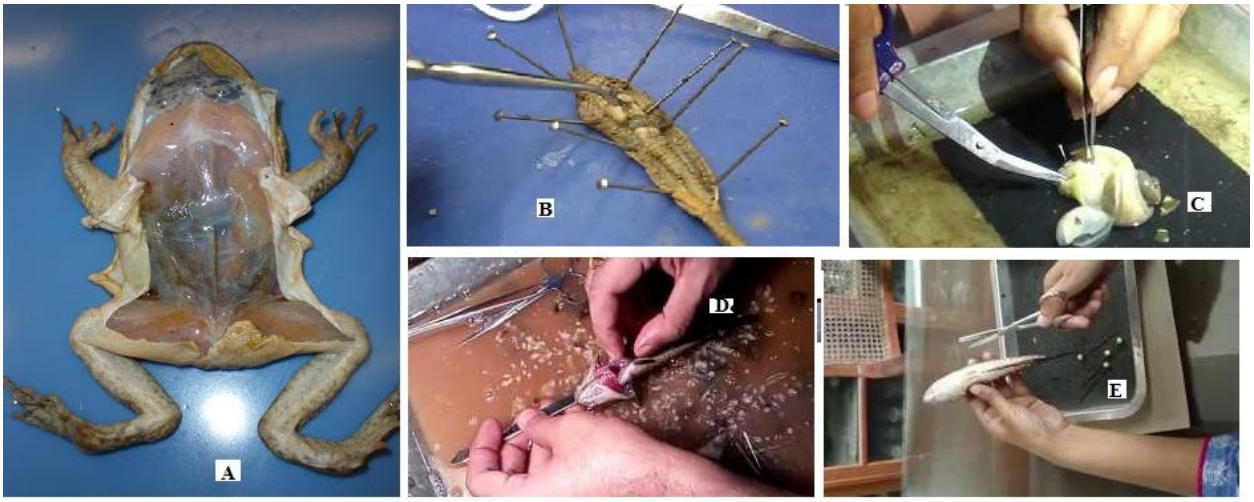

Animal Dissections in Zoology A -Toad, B - Earth Worm, C - Apple Snail, D& E - Lata fish

Image Source (McGraw-Hill)

The Educators must have sound assumptions about their learning preferences. We also found that gender may have an influence on students' preferences for the use of visuals in instruction. The present study is an initial in this field. This study is useful in addressing two questions - "How well do Zoology students discriminate between the real tactile and virtual learning experiences?" and "Virtual Dissection: how well can it replace authentic activities?". Evident from this study hands-on lab activities are not still the preferred activity of Zoology students. Virtual Dissections are getting increasingly preferred and valued for their flexibility

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of use, availability for revision and provision of additional information, ease of time and budgets.

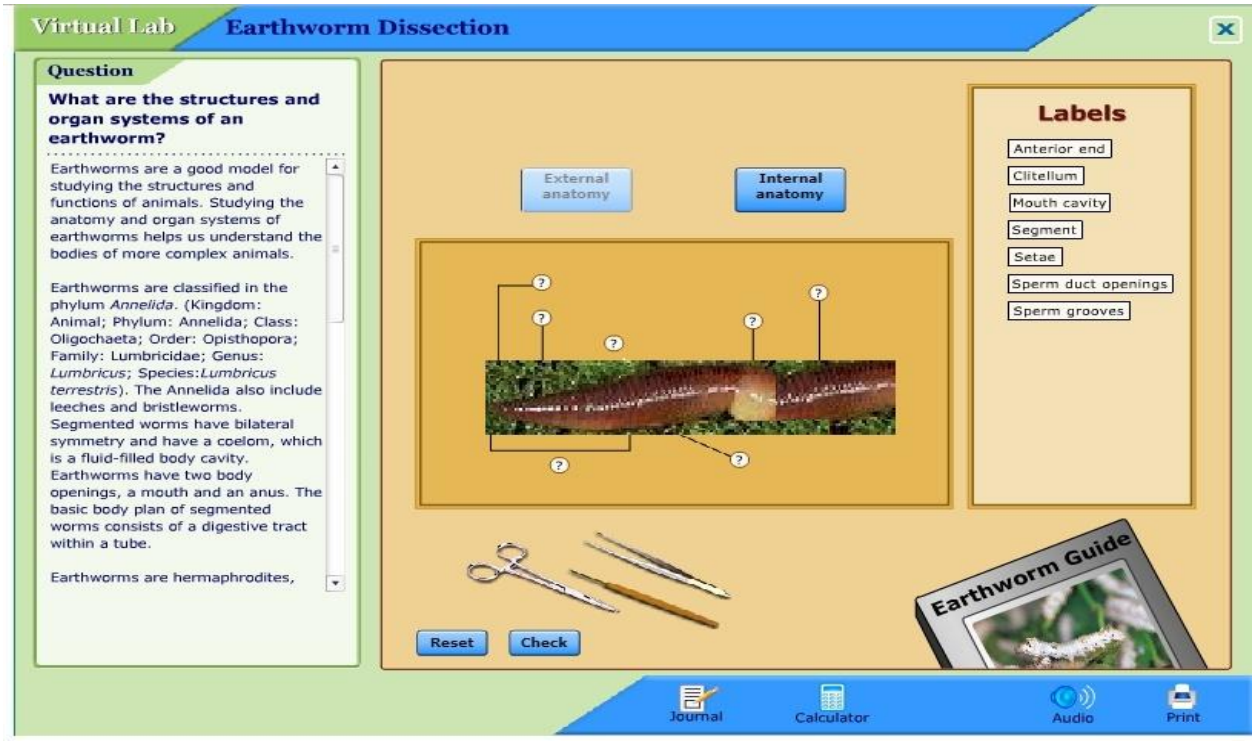

Image Source (McGraw-Hill)

The real dissections are valued for tactile learning and 3D nature. In this study, it is evident that students were willing to go for virtual dissection. This is a welcome trend. The perception trend also indicated that they were hesitant to accept Virtual microscopy probably due to lack of awareness and exposure. So there is a greater need to reinforce the offerings a variety of learning experiences with special emphasis to the ICT based Virtual mode of learning.

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Research Article

USING ICT AS A PEDAGOGIC TOOL: CHALLENGES

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A B S T R A C T

The quick advancement in technology in recent times has brought in tremendous changes in the way we live. The penetration of technology in educational arena has been massive. In this new digital age both the teachers and the students are getting increasingly dependent on information and communication technology (ICT). The ICT provides more opportunities for teachers and students to work better. ICT-based tools and resources are not only helpful to teach, but it also helps to refine work, to bring changes in classroom ambience and classroom relations, as well as to raise interest and increase motivation. But few barriers seem to discourage the teachers to integrate ICT and to introduce supporting ICT tools in the classroom. The present study is aimed to explore the teachers' views of using ICT tools in subject teaching. At the same time it also examines the obstacles, the teachers face to integrate ICT in their routine educational practices. For this purpose data were collected through a questionnaire from one hundred forty four secondary school teachers representing twenty four secondary schools of Kolkata educational district. Stratified random sampling was done taking account of three subject streams – science, social science and language group and four categories of school managements –government, government sponsored, government-aided and private. The data collected were interpreted using descriptive statistics. The key challenges faced by teachers are lack of time, lack of interest, inadequate training, hardware malfunction, lack of technical support, work overload and lastly lack of techno pedagogic skills. Finally, while many teachers welcomed opportunities of ICT, few were concerned that reshaping of teaching learning might displace precious human teaching. This study shows that there is a greater need to integrate observations from different angles and contexts of teaching with reference to man vs machine dependency. Future research in this field requires increasingly sophisticated approaches to understand scientific basis such perceptions.

Keywords: *ICT, perception, teachers, challenges.*

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1. INTRODUCTION

Information and Communication Technology (ICT) includes computers, the Internet, and a whole host of electronic devices such as radios, televisions, and projectors etc, and is widely used in today's education system . The use of technology as a tool has received great attention in recent times. The use of technological devices, such as televisions, tape recorders and video recorders has been incorporated as a tool for teaching since 1960s. There was evidence of many problems in terms of technical skills at the beginning, and it took about a generation for the technical skills and the technical problems to be ignored out (Taylor, 1980). Kent and Facer (2004) indicated that school is an important environment in which students participate in a wide range of computer activities, while the home serves as a complementary site for regular engagement in a narrower set of computer activities. ICT is considered a powerful tool for educational change and reform. A number of previous studies have shown that an appropriate use of ICT can raise educational quality and connect learning to real-life situations (Lowther, et al. 2008; Weert and Tatnall 2005). However, till date teachers are faced with some barriers that prevent them to employ information and communications technology (ICT) in the classroom or to develop supporting materials through ICT. Therefore, this study aims to explore the high school teachers' perceptions of the challenges and barriers of using ICT in the classroom.

2. REVIEW OF RELATED LITERATURE

Papert (1980) studied on 'Children, computer and powerful idea'. He understood the importance of digital media and how it could be used to enable children to learn better within a constructivist learning environment. He believed that the traditional tools such as pencils, copies and texts were inadequate. He felt that computers were the appropriate tool to enable the learner to take control of the learning process. He found that a complementary relationship exists between technology and constructivism**. Laird (1985)** worked on 'Approaches to training and development'. He believed that effective learning occurs when the sense organs are stimulated. Online instruction allows learners to use their sensory systems to register the information in the form of sensations. He found that the vast majority of knowledge held by adults (75%) is learned through seeing. Hearing is the next most effective (about 13%) and the other senses - touch, smell and taste account for 12% of what they know. He claims that the use of the Internet can enhance students' 29 organizational skills, **Davis (1993)** in his study 'Tools for learning' believes that there is no single magical formula for motivating students. Many factors affect a given students' motivation to work and to learn: Interest in subject matter, perception of its usefulness, general desire to achieve, self-confidence and self-esteem, as well as patience and persistence. With colorful and attractive graphics, interesting and illustrative animations, appropriate sound effects, ICT provides multisensory stimulations and real-world experiences. Teachers using ICT in teaching process can gain the learners' attention, motivate students to spend more time on learning activities with greater concentration, and engage them through production work. ICT can extend the range of alternative teaching methods beyond the conventional classroom. **Dalton (1998)** in his study 'Computers in schools' asserts that training is directed at changing

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people's knowledge, experience, skills and attitudes. The scarcity of adequately trained and experienced teachers, restrains ICT development in school education system. He emphasized the importance of training for the adoption and diffusion of computers in schools.

Bransford et al. (2000) reported the pedagogical paradigm needs to shift toward more student-centered learning. This shift is not easily accomplished, particularly in countries with teacher-centered educational traditions. The literature suggests that the changes in teachers' knowledge, beliefs, and attitudes should accompany the integration of ICT. ICT integration projects fall short of expectations because the educators continue working within a traditional vision of rote learning. Teachers need to believe that new approaches to teaching are effective and will make a difference for their students in order for them to continue using new approaches. Teachers' understanding and commitment are particularly important to sustain changes in areas such as project-based learning or student-centered techniques, which require core changes to a teacher's instructional practice. **Bauer and Kenton (2005)** stated in their study 'Towards technology integration in schools' that although teachers were having sufficient skills, were innovative and easily overcame obstacles, they did not integrate technology consistently both as a teaching and learning tool. Reasons are outdated hardware, lack of appropriate software, technical difficulties and student skills levels. The study found that professional development has a significant influence on how well ICT is embraced in the classroom. This implies that teachers training programmes often focus more on basic skills and less on the integrated use of ICT in teaching. Despite the numerous plans to use ICT in schools, teachers have received little training in this area in their educational training programmes. **Bahr (2009)** in his study 'Technological barriers to learning' found that the complex ICT environments may adversely impact on student learning. Learning is enhanced when pedagogies are employed to soften the high-load of ICT. **Wolcott et al. (2011**) in their study 'Faculty participation: Motivations, incentives, and rewards' found that intrinsic motives, such as job satisfaction and trying new technology tools and teaching strategies, were the most influential factors in faculty decisions to get involved in online learning. They found that faculty who wanted to participate were least influenced by extrinsic motivations such as monetary support, course release time, and tenure and promotion credit. Furthermore, some universities who did not provide faculty release time to develop online courses have had other staff members do this work, as with instructional designers, multimedia developers, and technology experts. **Jo Shan Fu (2016**) in his study 'ICT in Science Education', investigated the achievement, attitudes toward science, and career aspirations of Korean middle school students'. The research found some evidence that ICT assists high-achieving students and encourage enrolment in science.

By analyzing and synthesizing the different ways of classifying and categorizing ICT usage in the classrooms, the literature informs a repertoire of using ICT in teaching and learning. Children who exposed to school ICT programmes learned better. Also ICT was found to make school more interesting. When students participated in the ICT programmes, learning were more effective. Majority of the students and teachers had positive reaction to ICT programmes. Teachers and principals believed that teaching through ICT is better than traditional way of teaching. But few barriers seem to discourage the teachers to integrate ICT

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and to introduce supporting ICT tools in the classroom. The present study is aimed to explore the teachers' views of the use of ICT in subject teaching. At the same time it also examines the obstacles, the teachers face to integrate ICT in their routine educational practices.

3. OBJECTIVE OF THE STUDY

The present study aims to explore the teachers' perception in the context of challenges of using ICT by subject teachers. At the same time it also examines the obstacles, the teachers face to integrate ICT in their routine educational practices. Here, teachers' perceptions include their views, opinions and beliefs regarding use of ICT tools during teaching learning.

3.1. Sampling and Data Collection

Data were collected through a self made questionnaire. The questionnaire had two parts. One for collecting information of ICT facilities and usages, the other for collecting information on perception. The second part had options presented in 5 point Likert scale – 'Strongly agree', 'Agree', 'Not sure' 'Disagree' and 'Strongly disagree'. The questionnaire was tested for face validity and made reliable through 'test – retest' technique. The reliability co-efficient is found to be 0.78. One hundred forty four secondary school teachers representing twenty four secondary schools of Kolkata educational district correspond to the sample for the study. Stratified random sampling technique was applied, taking account of three subject streams – science, social science and language group and four categories of school managements –government, government sponsored, government-aided and private. The data collected were interpreted using descriptive statistics.

3.2. Analysis of Data

The key challenges faced by teachers during teaching learning falls into five broad categories which are lack of time, hardware malfunction, lack of technical support, work overload, lack of techno pedagogic skills, inadequate training and lack of interest.

Table 1: *Overall Challenges of using ICT*

Sl. No.	Challenges	Mean Score	Percentage
1.	Time constraints	79	22.83
2.	Fear of hardware malfunction	65	18.78
3.	Lack o technical support	55	15.89
4.	Work overload	45	13.00
5.	Techno Pedagogic Skills	42	12.13
6.	Inadequate training	35	10.11
7.	Lack of Interest	25	07.22

4. DISCUSSION

In this study it is evident that the highest level of obstacles faced by the school teachers is time limitation. The next challenge the very often face is the fear of hardware malfunction. If

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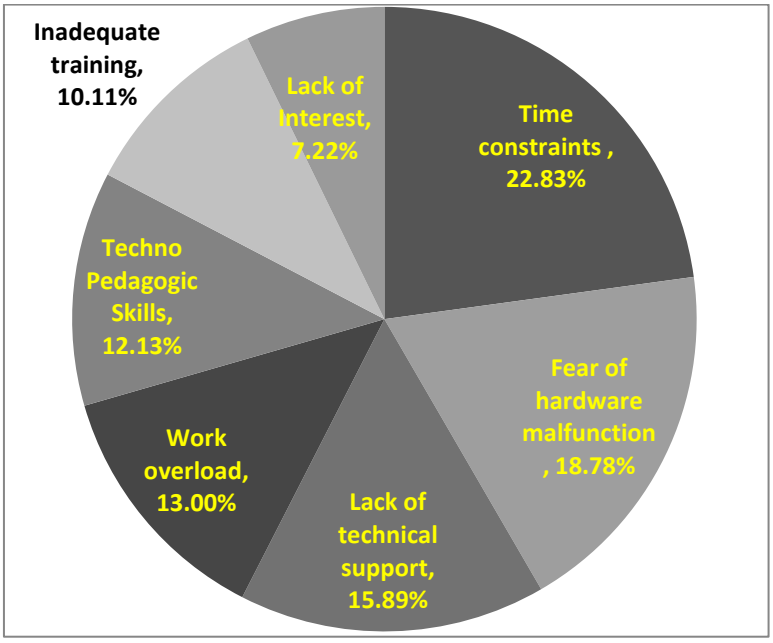
they manage to get time and the hardware does not betray, the tight schedule and heavy work load of most of the teachers make them skipping ICT. Many teachers acknowledge that they need training to develop proper techno pedagogic skills. Lack of personal interest is seen located at the bottom of the hierarchy.

Chart 1: *Overall Challenges of using ICT*



So the basic theme emerging out of this study is that teachers find it difficult to manage time with ICT tools. Generally a standard class period of 40 minutes duration turns out to be effective for half as to accommodate ICT tools to be ready for use and adjustments etc. This study is limited in regards to its sampling jurisdiction. This study may be extended to analyse the situational differences in facing challenges of ICT use with wider spectrum.

5. CONCLUSION

The majority of teachers in this study felt that ICT tools improve students' learning. ICT-based tools and resources are not only helpful to teach, but it also helps to refine work, to bring changes in classroom ambience and classroom relations, as well as to raise interest and increase motivation. While most of the teachers welcomed opportunities of ICT, many among them face problems while using such tools in classrooms. Few teachers were concerned that reshaping of teaching learning with ICT tools might displace precious human teaching. This study shows that there is a greater need to integrate observations from different angles and contexts of teaching with reference to man vs machine dependency. Future research in this field requires increasingly sophisticated approaches to understand scientific basis such perceptions. Another important effort would be to provide teachers with short term in-service training specifically on using ICT tools.

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Brojendra Nath Seal Journal of SCIENCE

Review Article

RNA INTERFERENCE: MECHANISTIC APPROACH AND APPLICATIONS

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A B S T R A C T

RNA interference (RNAi) is an evolutionary conserved mechanism which provides protection against invading viral particles or retrotrasposons and suppresses unnecessary expression of certain genes. Molecules like Dicer and RNA Induced Silencing Complex (RISC) are central to RNAi machinery. Dicer cleaves dsRNA into short ~21-22bp strands (miRNA or SiRNA) which is incorporated into the RISC. Guide strand of RISC base pairs with complementary sequences on target mRNA and Argonaute subunit of functional RISC catalyzes degradation of mRNA to block translation. Apart from usual cellular functions, RNAi is used in biotechnology, drug development, and medical science. It may be a ray of hope for several deadly diseases, but more research is needed to make it reliable for practical applications.

Keywords: *RNAi, RISC, Dicer, miRNA, siRNA*

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1. INTRODUCTION

RNA interference also termed as RNAi, Post-Transcriptional Gene Silencing (PTGS) or quelling is a novel bio-molecular mechanism utilized by cellular machinery to suppress expression of target genes. RNAi is usually triggered by introduction of double stranded RNA (dsRNA) within the cellular environment. These ~21-22bp dsRNAs have characteristic 3′ overhangs in their both ends which facilitate them to be incorporated and processed within enzymatic machinery of gene silencing. This is eventually followed by homology-dependent degradation of target mRNA **(Bender, 2001)**. The natural functions of RNAi include self-genome protection against invasion of viral or mobile genetic elements (transposones) into the cell and regulation of various developmental programs inside eukaryotes **(Agrawal et al., 2003)**.

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In a study conducted on *Escherichia coli* indicated that, small RNA molecules of 100 nucleotides in length can inhibit translation by binding to the specific complementary sequence of mRNA **(Nordström and Wagner, 1994)**. In 1990, Rich Jorgensen introduced a gene Chalcone Synthase-A (CHS-A) in excess to their normal copy in the petunia plant to intensify their red color for commercial purpose. Instead to intensification of red color, flowers became partially or fully white **(Napoli et al., 1990)**. This phenomenon, termed as co-suppression by researchers was an indication of gene silencing mechanism. Interestingly, such gene silencing phenomena were also noticed in fungi and were termed quelling.

2. DICER AND RISC: THE CENTRAL COMPONENTS OF RNAi

2.1. Dicer

Dicer is a 200kDa RNase III nuclease that shows high specificity towards dsRNAs. Dicer produces 3´ overhangs in dsRNAs which are recognized by downstream components of gene silencing machinery. Owing to its ability to digest dsRNAs into uniformly sized small RNAs (siRNAs), this enzyme was named Dicer. Dicer is evolutionary conserved in several groups of animals like fungi, nematodes, flies, plants and mammals. Dicer shows four structural domains- an amino terminal ATPase/RNA helicase domain, dual RNaseIII motifs (RIIIa and RIIIb), a dsRNA binding domain and a PAZ (Piwi, Argonaut and Zwille) domain.

In *Drosophila*, two subsets of Dicer protein have been detected: Dcr-1 and Dcr-2. Dcr-1 is ATP independent and shows high specificity towards stem-loop form of RNA i.e. precursor of micro-RNA (miRNA) **(Jiang et al., 2005)**. Dcr-1 interacts with a dsRNA binding protein-Loquacious (Loqs) and directs miRNA processing. Dcr-2 activity is ATP dependent and shows specificity towards siRNAs **(Jiang et al., 2005)**. Dcr-2 also interacts with a double stranded binding protein R2D2 to form a heterodimer complex (Dcr-2/R2D2). This complex is crucial for processing and loading of siRNA to the siRNA Induced Silencing Complex (siRISC) (**Xiang et al., 2006**).

In *C. elegans*, Dicer homologue K12H4.8 has been considered as Dcr-1 which is functional ortholog of *Drosophila* dicer protein **(Peele et al., 2001)**. Similar to this, CAF-1 of *A. thaliana* has been identified as Dicer homologue, but its role in PTGS is not clear. Structure of CAF-1 shows four structural domains that were identified in *Drosophila* Dicer protein.

2.2. RNA induced silencing complex (RISC)

RISC is a multimeric ribonucleoprotein that incorporates single strands (or guide strand) of miRNA or Si RNA in its core to identify complementary sequences on target mRNA. RISC has a protein of Argonaute family that binds guide strand to facilitate target recognition. Protein members of Argonaute family have been linked to either gene silencing mechanisms or control of developmental processes in several species. Argonaute proteins can either cleave target RNAs directly or recruit other gene-silencing proteins to identified targets. In *Drosophila*, protein of Argonaute family has been termed as AGO-2. AGO-2 is a ~130 kDa protein containing polyglutamine residues, PAZ and PIWI domains characteristic of other Argonaute proteins **(Agrawal et al., 2003)**. Additionally **Caudy et al., 2002** reported

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two other RNA binding proteins such as dFXR *(Drosophila* homolog of the fragile X mental retardation protein) and VIG (Vasa intronic gene) of RISC involved in target recognition and binding. In *C. elegans*, AGO-2 homologue RDE1 is required for dsRNA mediated gene silencing. Similar gene silencing protein of Argonaute family was also detected in *A. thaliana* and was termed AGO-1.

3. MECHANISM OF RNAi

3.1. microRNA mediated gene silencing

RNA Polymerase-II typically performs biogenesis of primary micro-RNA (Pri-miRNA) via transcription of endogenous genomic DNA. **(Fig. 1).** Pri-miRNA is then cleaved to a hairpin-loop of precursor-miRNA (Pre-miRNA) of 70 nucleotides by a microprocessor complex containing Drosha (RNase III enzyme) and Pasha/DGCR8 (dsRNA binding protein) **(Denli et al., 2004)**. Pre-miRNA is transported from nucleus into the cytoplasm by karyopherin Exportin-5 and Ran-GTP complex **(Yi et al., 2003)**. Cytoplasmic pre-miRNA becomes a substrate for Dicer and is cleaved into miRNA of ~22 nucleotides in length. miRNA with 3'-overhangs joins a multinuclease complex, called RNA-Induced Silencing Complex (RISC).

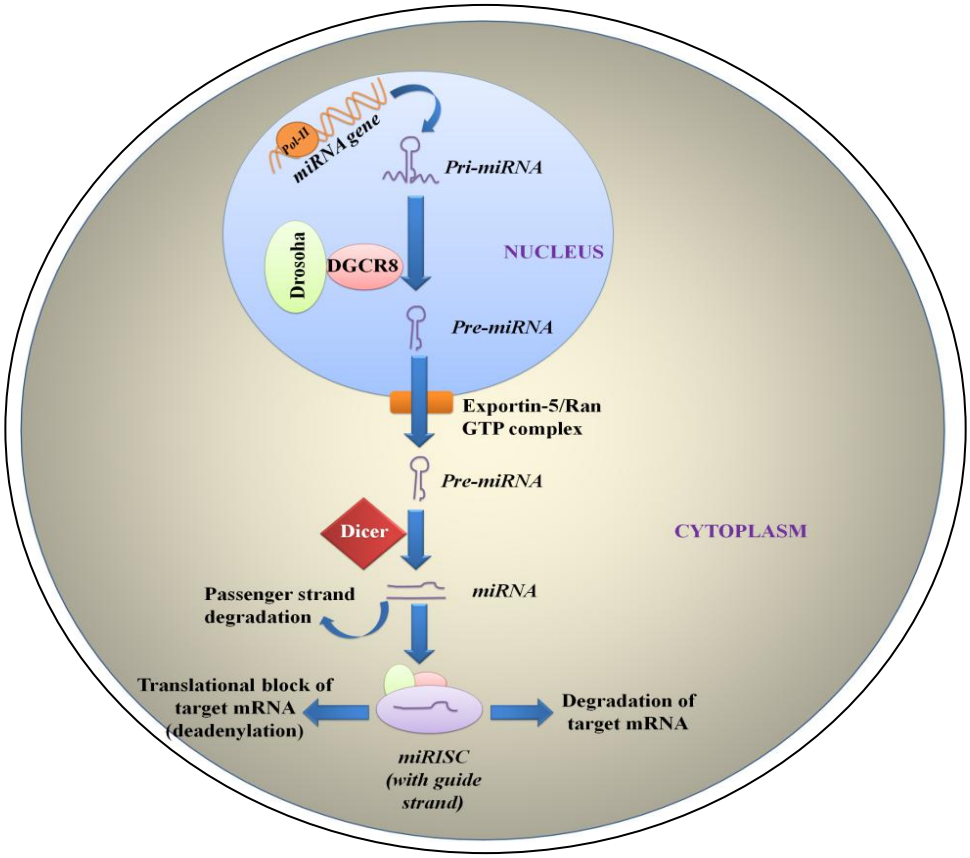

Fig.1: *Figure represents a molecular cascade involved in miRNA mediated gene silencing*

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Usually only one strand is tagged with the RISC complex and is known as guide strand whereas the other strand, called passenger strand is degraded by the Argonaute protein. Selection of guide strand is primarily based on the stability of the termini of the two ends of dsRNA. Strand with lower stable base pairing of the 2–4 nucleotides at the 5' end of the duplex preferentially associates with RISC and thus becomes the active miRNA **(Schwarz et al., 2003)**. Once guide strand is incorporated into the RISC, it searches for target mRNA having complementary sequences. When complementary sequences are detected, miRNA either perfectly or imperfectly base pairs with the 3' untranslated regions (UTRs) and causes transcriptional inactivation either by cleavage or blocking accessibility for translational machinery. miRNA also catalyzes deadenylation of target mRNA to block translation**.**

3.2. siRNA mediated gene silencing:

As indicated in **Fig. 2**, siRNA-induced RNAi machinery is activated when large dsRNA is introduced either naturally or artificially into the cell **(Mello and Conte, 2004)**. RNA-binding domain (RBD) of dicer recognizes dsRNAs and cleaves them into discrete ~21-25 nucleotide dsRNA fragments, utilizing ATP as energy source.

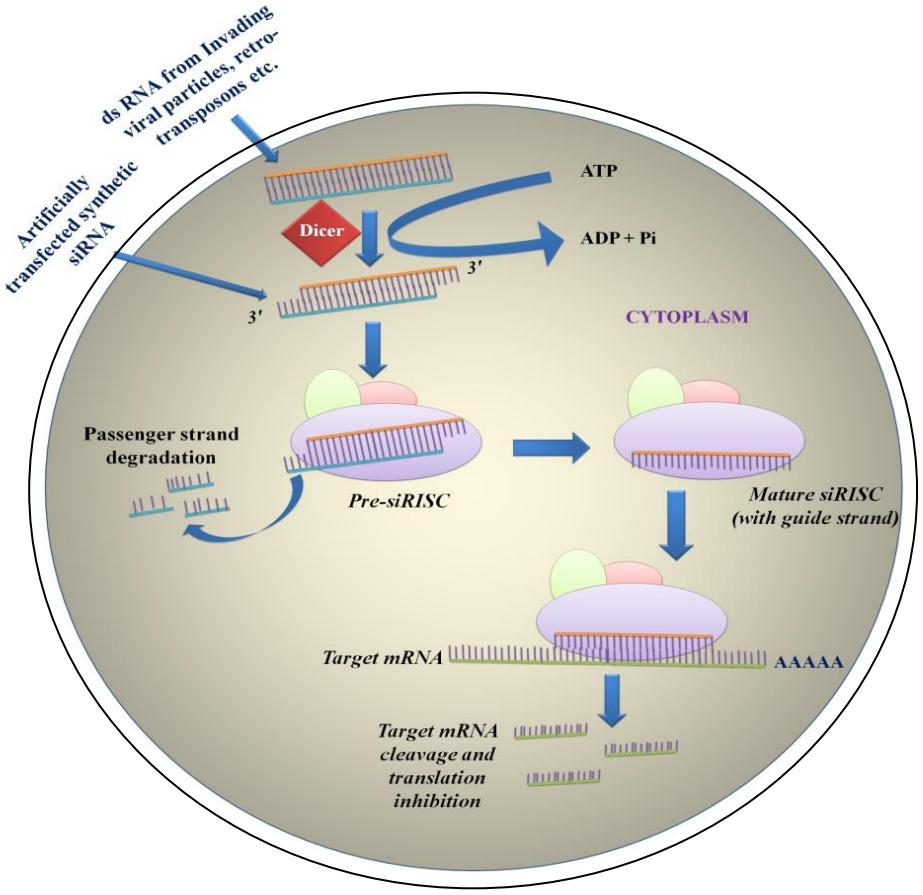

Fig. 2: *Figure represents siRNA based gene silencing in eukaryotes*

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Dicer has RNase III type endonuclease activity that makes staggered cuts at both strands producing 3'overhangs of 2 nucleotides. dsRNA is recruited to RISC (more accurately, pre-RISC) where argonaute identifies the end of the duplex with lower stability and unwinds the RNA. Only guide strand is retained to the RISC (now termed holo-RISC or functional RISC) whereas passenger strand is degraded by the Argonaute protein **(Tomari and Zamore, 2005)**. Guide strand recruits holo-RISC to the target mRNA having complementary sequence and allow PIWI domain of Argonaute protein to cleave phosphodiester linkage of target mRNA, resulting in the translational inhibition **(Fig. 2).**

4. APPLICATIONS

siRNA blocks genes expression and therefore multiplication of viral genome within the host cells. It also induces cytosine methylation and play significant role in chromatin remodeling. RNAi is important for the maintenance of heterochromatic state. RNAi also maintains genetic integrity by transcriptional inactivation of some undesired genes such as repeat sequences and retrotransposons.

Besides, biotechnology uses RNAi machinery for several other purposes. RNAi has been emerged as a pivotal tool in exposing functional aspects of several genes. Through RNAi mediated gene silencing, researchers can explore probable functions of a particular gene in several species. As for example, chromosome I and III of *C. elegans* have been screened by RNAi to unravel genes for cell division and embryonic development **(Fraser et al., 2000)**. Similarly RNAi technology has also been implemented for *D. melanogaster* to identify genes involved in embryonic development and cellular signaling cascades **(Clemens et al., 2000)**.

Plant science is also utilizing RNAi methodologies to inactivate unhealthy substances. Recently, theobromine synthase of coffee plant was knockdown with hairpin construct to facilitate decaffeinated coffee plants **(Ogita et al., 2003)**. Additionally, some plant endotoxins are also being targeted by anti-sense technology to block their synthesis.

Drug screening and development may also adopt RNAi technology to identify and suppress genes that confer drug resistance to a particular disease. RNAi has also been implicated in silencing the mutant allele of defective genes whose product may harms normal physiological status of an individual. It may have a tremendous impact for those organisms that are not amenable to the knockout strategy **(Moss 2003)**.

In cell culture lines, siRNAs have been shown useful in blocking infection by human immune deficiency virus, polio virus and hepatitis C virus **(McManus and Sharp, 2002)**. Similarly, genes of respiratory disease causing RNA virus- respiratory syncytial virus were also silenced successfully using anti-sense technology **(Bitko and Barik, 2001)**. siRNA treatment has also been documented to reduce expression of BCR-ABL oncoprotein in leukemia and lymphoma cell lines, leading to apoptosis of these cells **(Wilda et al., 2002)**. siRNA based therapy seems to have great potentials to combat several dealy diseases like carcinoma caused by over-expression of oncogenes formed by point mitation or chromosomal translocation **(Tuschl and Borkhardt, 2002)**.

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5. CONCLUSION

RNAi is an emerging technique in the field of molecular biology to silence genes of human interest. It has great potentials in the field of drug designing and therapeutics to combat deadly diseases including AIDS and cancers. Several tremendous powers of RNAi technology in laboratory have been revealed but further reliable advancements in practical usage, delivery system of dsRNAs and maintaining its stability in cellular environment are yet to be achieved.

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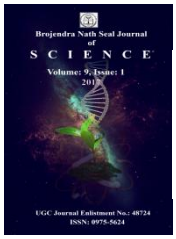

Brojendra Nath Seal Journal of SCIENCE

Research Article

1α, 25-DIHYDROXYVITAMIN D_3 INHIBITS DIETHYLNITROSAMINE-INDUCED HEPATOCELLULAR PRENEOPLASTIC TRANSFORMATION IN SPRAGUE-DAWLEY RATS

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A B S T R A C T

The prospect that a high intake of certain vitamins, antioxidants and dietary micronutrients may confer protection against carcinogenesis has drawn special attention during the last decade. The biologically active metabolite and hormonal form of Vitamin D_3, 1α, 25-dihydroxyvitamin D_3 [1,25$(OH)_2D_3$] has been found to posses, besides calcium homeostasis, several potential activities with regard to anticarcinogenicity and chemoprevention; these are free radical trapping, immune stimulation, inhibition of nitrosamine formation, influence on metabolic activation of carcinogens and regulation of cellular growth, differentiation and cell death. In the present study, attempts have been made to investigate the chemopreventive effect of 1α, 25-dihydroxyvitamin D_3 in a defined model of two-stage experimental hepatocarcinogenesis in male Sprague-Dawley rats. Morphology and morphometric analysis of preneoplastic hepatocellular lesions were monitored throughout the study as an end-point biomarker. Antioxidant defence system, including glutathione (GSH), glutathione-S-transferase (GST), and manganese-dependent superoxide dismutase (Mn-SOD) activities followed by generation of single-stranded DNAs (SS-DNAs) and DNA single-strand breaks (SSBs) in rat liver were evaluated to ascertain the chemopreventive efficacy of this metabolite. Hepatocarcinogenesis was initiated by a single, necrogenic, intraperitoneal (i.p.) injection of diethylnitrosamine (DEN) at a dose of 200 mg / kg body weight followed by administration of phenobarbital (PB) as a carcinogenic promoter, 0.05% in basal diet, 5 days a week, till the end of the experiment. Treatment of 1α, 25-dihydroxyvitamin D_3 was given at a dose of 0.3 µg / 100 µl in propylene glycol, *per os*, twice a week either in the initiation phase or in the promotion phase of carcinogenesis or in a long-term continuous regimen. Results showed that, 1α, 25-dihydroxyvitamin D_3 treatment throughout the experiment reduced nodular incidence (55.67%), total number and multiplicity (79.83%) and altered the size of visible persistent nodules (PNs) (≤1 mm; 69.86%) in DEN+PB -treated rats when compared to the carcinogen control. Also, 1α, 25-dihydroxyvitamin D_3 treatment restored the levels of hepatic GSH ($P<0.02$), GST ($P<0.001$) and Mn-SOD ($P<0.001$) which were otherwise altered in carcinogen control. Furthermore, in a short-term regimen, 1α, 25-dihydroxyvitamin D_3 significantly abated ($P<0.001$) the generation of SS-DNAs along with a profound decrease (52.17%; $P<0.01$) in the number of SSBs/DNA unit when compared to DEN control. Data presented in this report indicate that continuous supplementation with 1α, 25-dihydroxyvitamin D_3 as a chemopreventive agent suppresses hepatocellular preneoplastic transformation in rats.

Keywords: *1α, 25-dihydroxyvitamin D_3, Hepatocarcinogenesis, Diethylnitrosamine, Preneoplastic foci, GSH, GST, Mn-SOD, DNA strand-breaks.*

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1. INTRODUCTION

In recent years, cancer chemoprevention strategies involving natural, synthetic, or biological/phytochemical/herbal substances and molecules to reverse, suppress, or prevent the development and progression of malignant diseases hold great promise in cancer research [Poppel and Berg 1997; Davis and Wu, 2012]. Although, the clinical use of cytotoxic drugs has had a significant impact on neoplastic diseases, however, their therapeutic effectiveness is limited due to their narrow therapeutic index and the onset of chemoresistance. In this scenario, a consistent body of investigation provides evidence that Vitamin D_3, in addition to its well-known involvement in calcium homeostasis, appears to be potentially effective in suppressing malignant transformation and in limiting the progression of various types of human tumours through modulation of cellular proliferation, differentiation, apoptosis, and angiogenesis [Ingraham et al. 2008]. These anticancer properties have been attributed primarily to 1α, 25-dihydroxyvitamin D_3 [1,25$(OH)_2D_3$] (calcitriol), the hormonal form and the active metabolite of Vitamin D_3 [Ali and Vaidya 2007].

Experimental hepatocarcinogenesis can be induced by various chemical carcinogens, like diethylnitrosamine (DEN), 2-acetylaminofluorene (2-AAF), aflatoxin B1 etc. DEN is a potent hepatocarcinogen in rats influencing the initiation stage of carcinogenesis during a period of enhanced cell proliferation accompanied by hepatocellular necrosis and forming DNA-carcinogen adducts, inducing DNA strand-breaks and in turn hepatocellular carcinomas (HCCs) without cirrhosis through the development of putative preneoplastic focal lesions [Farber and Cameron 1980]. Chronic administration of a promoting agent, such as phenobarbital (PB) has many effects on the liver, including development of hyperplasia and hypertrophy without increasing cell death and has been shown to stimulate cell proliferation in focal relative to non-focal areas of carcinogen-challenged tissues [Goldsworthy and Pitot 1985; Kolja 1996]. The DEN-PB rat model of two-stage experimental hepatocarcinogenesis is so well defined that it makes itself a unique tool for studying mechanisms of cell growth, differentiation and cell death [Farber 1980].

Exposure to carcinogenic insults results in depletion of tissue antioxidants generating huge amounts of reactive oxygen species (ROS) that may in turn interfere with apoptotic pathways and trigger oncogene activation leading to increased cell proliferation, altered cellular biochemistry, and molecular lesions, all of which ultimately lead to the transformation of a

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normal cell to a malignant phenotype [Duthie 1996]. Cellular antioxidant defense systems, such as superoxide dismutase (Mn-SOD), catalase, glutathione (GSH), glutathione-S-transferase (GST) etc. act against the detrimental effects of ROS. A shift in equilibrium between oxidative stress and antioxidative defense in favour of oxidative stress thus plays a pivotal role in the induction and development of various pathological conditions including neoplasia. GSH functions in the synthesis of important macromolecules and in the protection against superoxide-anion free radical (O_2^-) by the GSSG-GSH system. GST catalyzes the reaction of nucleophilic Cys-thiol-(SH) group of GSH with electrophiles, including activated carcinogens, to form less toxic conjugates which are thereby readily eliminated from the system [Chasseaud 1979]. Besides cellular and biochemical changes, cellular exposure to chemical carcinogens results in a variety of chromosomal and DNA damages which are considered as potential markers for chemical carcinogenesis. These include sister-chromatid exchanges, micronucleus formation, several types of chromosomal aberrations, and DNA lesions caused by base-alterations, disruption of the sugar-phosphate backbone, DNA-DNA as well as DNA-protein cross-links (DPCs), single-strand breaks (SSBs) and double-strand breaks (DSBs) [Grover and Fisher 1971; Ward 1988].

With this background, the present study was designed with the following objectives: first, to investigate the antitumorigenic efficacy of 1α, 25-dihydroxyvitamin D_3 by monitoring hepatic nodulogenesis, a surrogate end-point biomarker in an *in vivo* two-stage model of chemical carcinogenesis; secondly, to study the biochemical antioxidant system; and thirdly, to estimate the generation of single-stranded DNAs (SS-DNAs) and SSBs; so as to deduce a possible correlation between Mn-SOD, GSH or GST and DNA damage following DEN challenge in the presence or absence of this vitamin, in order to ascertain the underlying biochemical basis of chemopreventive potential of 1α, 25-dihydroxyvitamin D_3 during DEN-initiated and PB-promoted rat hepatocarcinogenesis.

2. MATERIALS AND METHODS

2.1. Materials and Maintenance of Animals

All the reagents and biochemicals, unless otherwise mentioned were obtained from Sigma Chemicals Co. (St. Louis, MO), USA and E. Merck, (Dermstadlt) Germany. Male Sprague-Dawley rats obtained from the Indian Institute of Chemical Biology (CSIR), Kolkata, India weighing 80-100 gm at the beginning of the experiments were used throughout the study. The

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animals were acclimatized to standard laboratory conditions (temperature 24±1 ^{0}C, relative humidity 55±5 % and a 12 hour photoperiod) in Tarson Cages (four to five rats per cage) for 1 week before the commencement of the experiment. During the entire period of study, the rats were supplied with a semi-purified basal diet (Lipton India Ltd., Mumbai, India) and water ad libitum. The recommendations of Jadavpur University's "Institutional Animal Ethics Committee" ["Committee for the Purpose of Control and Supervision of Experiment on Animals" (CPCSEA Regn. No. 0367/01/C/CPCSEA) INDIA] for the care and use of laboratory animals were strictly followed throughout the study.

2.2. Experimental Regimen

Rats were randomly divided into eight experimental groups [Bishayee and Chatterjee 1995]. Groups A, B, C and D rats were the DEN+PB -treated groups that received a single, necrogenic, intraperitoneal (i.p.) injection of DEN at a dose of 200 mg / kg b.wt. at 9 weeks of age i.e. at week 4 of experimentation. After a brief recovery period of 3 weeks, all the DEN-treated rats were given PB at a dose of 0.05% in basal diet, 5 days a week, for the remainder of the experimental protocol (i.e. week 20). Group A was the carcinogen control, whereas, group a rats were the untreated vehicle control for DEN and 1α, 25-dihydroxyvitamin D_3 that received normal saline once and propylene glycol, twice a week, for 20 consecutive weeks. 1α, 25-dihydroxyvitamin D_3 at a concentration of 0.3 μg / 100 μl in propylene glycol, *per os*, twice a week was given to the rats of all groups except groups A and a [Sardar et al. 1996]. Group B rats received 1α, 25-dihydroxyvitamin D_3 treatment at the same dose during the entire length of the study, i.e. for 20 consecutive weeks, starting the treatment 4 weeks before initiation with DEN (long-term continuous study). Treatment of 1α, 25-dihydroxyvitamin D_3 in group C rats was started 4 weeks prior to DEN injection (at 0 week) and stopped at week 4 on the day of DEN administration (initiation study). In group D rats, 1α, 25-dihydroxyvitamin D_3 treatment at the same dose mentioned above was started 1 week after 'initiation' with DEN i.e. at week 5 and was continued thereafter till the completion of the experiment, i.e. a total of 15 successive weeks (promotion study). The rats from groups b, c, and d served as 1α, 25-dihydroxyvitamin D_3 controls for groups B, C, and D, respectively, and were provided with 1α, 25-dihydroxyvitamin D_3 for 20, 4, and 15 consecutive weeks, respectively. Daily food and water intakes were noted and the body weights of the animals from each group were recorded every second day. All the treatments were withdrawn after week 20 and rats were sacrificed by decapitation under proper light

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ether anaesthesia after week 21 to carry out experimentations. All the animals were fasted over night before sacrifice. For DNA strand-breaks study, rats were divided into four groups (A-D) with 20 rats in each group. In group C (DEN control) and D (1α, 25-dihydroxyvitamin D_3 + DEN treatment), hepatocarcinogenesis was initiated by a single, i.p. injection of DEN at a dose of 200 mg / kg body weight in 0.9% normal saline at week 4. Group A rats served as the untreated vehicle control. Group B (1α, 25-dihydroxyvitamin D_3 control) and D rats received 1α, 25-dihydroxyvitamin D_3 at the same dose regimen of morphometric analysis for 4 consecutive weeks prior to DEN injection. All the rats were sacrificed 18-20 hours after DEN injection at week 4; livers were promptly excised and hepatic DNA was isolated.

2.3. Morphology and Morphometry of Liver Tissue

After the rats were sacrificed, their livers were promptly excised, blotted, weighed and then examined macroscopically on the surface as well as in 3 mm cross sections for gross visible persistent nodules (PNs), which represented focal proliferating hepatic lesions with a low tendency to spontaneous regression [Farber 1984]. The PNs were easily identified from the reddish-brown non-nodular surrounding parenchyma (NNSP) by their greyish-white colour and short demarcation and the plates of nodules were discontinuous with those of the adjacent liver tissue. The PNs that approximated spheres were measured in two perpendicular directions to the nearest mm to obtain an average diameter of each nodule. The PNs were divided into three categories, in accordance with their respective diameter and total area of liver parenchyma occupied, namely, ≥3, <3 – >1 and ≤1 mm [Moreno et al. 1991].

2.4. Enzyme Assays

2.4.1. Preparation of Hepatic Cytosolic Fraction

Livers from different group of rats were quickly excised, washed with chilled 0.9% NaCl, blotted and weighed dry. All subsequent operations were carried out at 0-4^{o}C. The livers were separately homogenized in ice-cold 0.154 M KCl (pH 7.4) by using a precooled Potter-Elvehjem Teflon : glass homogenizer for 1 min to make a 10% w/v tissue homogenate. The homogenate was centrifuged at 9,000 g for 20 min and the supernatant was again centrifuged at 100,000 g for 1 hour in a Sorvall OTD-50B ultracentrifuge at 4^{o}C. The supernatant obtained through this second centrifugation from the cytosolic fraction was kept frozen at -20^{o}C until assayed for GSH, GST and SOD.

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2.4.2. Estimation of GSH

Hepatic GSH level was quantified by the method of Ellman [1959]. In short, 1 ml of cytosol was mixed with 1 ml of 4% 5-sulfosalicylic acid and the mixture was centrifuged at 1,5000 g for 15 min. The supernatant (1 ml) was allowed to react with 9 ml of 0.1 M 5,5'-dithio-bis-(2-nitrobenzoic acid) in 0.1 M phosphate buffer (pH 8.0). The resultant solution was kept at room temperature for 10 min and read at 412 nm by a Hitachi U-2000 spectrophotometer.

2.4.3. Assay of GST Activity

The GST activity of hepatic cytosol was determined by an adaptation of the method of Habig et al. [1974] using 1-chloro-2,4-dinitrobenzene (CDNB) and GSH as substrates. The reaction mixture (1 ml) consisted of 0.1 M potassium phosphate buffer (pH 6.5), 1 mM CDNB and a suitable amount of cytosol (1.2-1.6 mg protein/ml). The reaction mixture was incubated at 37^{o}C for 5 min and the reaction was initiated by the addition of CDNB. The increase in optical density at 340 nm was measured spectrophotometrically.

2.4.4. Estimation of Mn-SOD Activity

The activity of Mn-SOD was measured as per the method described by Beyer and Fridovich [1987]. The assay conditions were 50 mM potassium phosphate, 0.1 mM EDTA, 50 μM xanthine, 10 μM ferricytochrome c, 6 nM xanthine oxidase and cytosolic fraction in a total volume of 3.0 ml at pH 7.8 and 25^{o}C to yield absorbance at 550 nm. One unit of SOD activity is defined as the amount that causes 50% inhibition of the initial rate of reduction of the cytochrome under the conditions specified.

2.5. Isolation and Assay of DNA Unwinding

DNA was isolated from the rat liver by a modification of the published criteria [Gupta 1984]. After isolation, the purity of DNA solution was checked spectrophotometrically by determining the ratios of absorbance at A_{260} / A_{280} *and* A_{260} / A_{230}. The solution containing the purified DNA was then stored at -20 ^{0} C.

The principle of Fluorimetric Analysis of DNA unwinding (FADU) is that the fluorescent dye ethidium bromide (EtBr) binds selectively to double-stranded DNA (DS-DNA) in the presence of single-stranded DNA (SS-DNA) when short duplex regions in SS-DNA

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molecules are destabilized by alkali treatment [Morgan and Pullyblank 1974; Birnboin and Jevcak 1981].

After isolation of DNA from each experimental and control group, the DNA solution was divided equally among three sets of tubes. The contribution to fluorescence by components other than DS-DNA (including free dye) is estimated from a blank sample (B) in which the DNA sample is first sonicated highly and then treated with alkali under conditions, which cause complete unwinding of low molecular weight DS-DNA. A second sample is used for estimating the total fluorescence (T), i.e. fluorescence due to the presence of DS-DNA with contaminants. The difference (T-B) provides an estimate of the amount of DS-DNA in the DNA pool. A third sample (P) is exposed to alkaline conditions sufficient to permit partial unwinding of the DNA, the degree of unwinding being related to the size of DNA. The fluorescence of the sample less than the fluorescence of the blank (P-B) provides an estimate of the amount of DS-DNA remaining. Percent D is given by the equation:

$$\text{Percent D (DS-DNA \%)} = (P-B) / (T-B) \times 100.$$

2.5.1. Estimation of DNA Single-Strand Breaks (SSBs)

It is assumed that the distribution of SSBs in the DNA population follows a simple Poisson's Law. Under this circumstance, it is possible to make an approximate estimate of the average number of single-strand breaks (n) per DNA fragment from the following equation [Basak 1996]:

$$e^{-n} = D / S + D$$

S = percentage DNA that remains single-stranded after alkali treatment, D = percentage remaining as DS-DNA. D/S+D represents the fraction (f_o) of the molecules without strand-breaks. The values of 'n' corresponding to different DNA solutions isolated from different groups were then estimated.

2.6 Statistical Analysis

Data were analyzed statistically for differences between the means using Student's t-test and values of $p<0.01$ were taken to imply statistical significance. Percent inhibition was obtained by using the formula [(mean control - mean treatment) / mean control] x 100.

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3. RESULTS

During the entire period of study, no differences in food and water consumption were observed among the various groups of animals. Food and water intakes were 10.7-12.8 gm 100 g^{-1} day^{-1} and 8-10 ml / day / rat respectively for all rat groups.

3.1. Effect of 1α, 25-dihydroxyvitamin D_3 on the Number and Size Distribution of Visible Hyperplastic Nodules in Rat Liver Treated with DEN+PB

There were no visible hyperplastic nodules in the livers of untreated vehicle control (group a) as well as in the 1α, 25-dihydroxyvitamin D_3 control (groups b, c and d) groups. There was 100% nodular incidence in DEN control rats. Supplementation of 1α, 25-dihydroxyvitamin D_3 decreased the nodular incidence in all the DEN+PB -treated groups but the inhibition was maximum (55.67%) in group B that received 1α, 25-dihydroxyvitamin D_3 for 20 successive weeks. There was also a decrement in the total number of nodules in all the carcinogen-treated rats but the reduction was most pronounced in groups B and C. The largest-sized nodules (≥3 mm) comprised 43.17% of the nodules detected in DEN+PB control rats whereas there were no nodules of this size in Group B. In the 1α, 25-dihydroxyvitamin D_3 -treated rats, the percentage of nodules (≤1 mm) was increased compared to Group A (69.86% in group B compared with 19.88% in group A). Also, the nodule multiplicity was decreased significantly in all the DEN-treated groups when compared to the DEN+PB counterpart. The percentage inhibition of nodule multiplicity was also maximum (79.83%) in group B rats than in groups C and D when compared to group A.

3.2. Effect of 1α, 25-dihydroxyvitamin D_3 Treatment on Hepato-cytosolic GSH, GST and Mn-SOD Activities upon DEN+PB Challenge

It is evident that, DEN+PB challenge to group A rats significantly suppressed the levels of GSH ($P<0.01$) and GST ($P<0.001$) when compared to the vehicle control (group a). On the contrary, 1α, 25-dihydroxyvitamin D_3 treatment to all the carcinogen-challenged rats (groups B, C, and D) increased the levels of both GSH and GST, although the results were significant in groups B ($P<0.02$ and $P<0.001$, respectively) and C ($P<0.05$ and $P<0.02$, respectively) as compared to the carcinogen counterpart. On the other hand, there was a significant increase ($P<0.001$) in the level of Mn-SOD in DEN control rats (group A) when compared to the normal counterpart (group a). However, treatment with 1α, 25-dihydroxyvitamin D_3

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successively reduced the elevated levels of the enzyme but the results were significant in groups B ($P<0.001$) and C ($P<0.001$).

3.3. Effect of 1α, 25-dihydroxyvitamin D_3 on the Generation of SS-DNAs and SSBs in Rat Liver 18-20 Hours Post DEN Injection

The percentage of double-stranded DNA (DS-DNA) and single-stranded DNA (SS-DNA) in rat livers of groups A (96.46% and 3.54% respectively) and B (94.93% and 5.07%) suggests that 1α, 25-dihydroxyvitamin D_3 treatment had no side effects *in vivo*. A significant rise ($P<0.001$) in the total percentage (69.58%) of hepatic SS-DNAs could be observed in group C rats when compared with the normal vehicle control group (group A). The percentage of native DS-DNA in group C rats was found to be more than 3 fold less (30.42%) than in normal control rats, where as the total aberrant single-stranded regions in group C rats were almost 23 fold higher than that of group A control. This explains that the potent hepatocarcinogen DEN exerts a direct genotoxic effect on DNA. Treatment with 1α, 25-dihydroxyvitamin D_3 in group D rats strictly abated ($P<0.001$) the generation of SS-DNAs following DEN insult when compared to the DEN control (Group C). Moreover, the native DS-DNA (60.49%) in group D rats was almost 2 fold higher than in group C rats. Furthermore, a significant increase ($P<0.001$) in the average number of SSBs/DNA fragment following DEN challenge was observed in group C rats when compared with group A. 1α, 25-dihydroxyvitamin D_3 treatment in group D rats showed a significant decrease (52.17%; $P<0.01$) in the number of SSBs/DNA when compared to DEN control.

4. DISCUSSION

Epidemiological studies have suggested that supplementation of natural antioxidants, micronutrients and macronutrients may retard or halt oxidative damage leading to disease progression [Maxwell 1995; Fenech and Ferguson 2001]. The results of the present investigation clearly demonstrate that supplementation of active metabolite of Vitamin D_3, 1α, 25-dihydroxyvitamin D_3 (0.3 μg / 100 μl in propylene glycol) during the entire experiment, before initiation and during promotion, greatly reduced nodular incidence, multiplicity and size of visible PNs and DNA strand-breaks and restored hepatic antioxidant system in this particular two-stage model of chemical hepatocarcinogenesis in rats. Long-term continuous treatment with 1α, 25-dihydroxyvitamin D_3 elicited a greater protection in

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terms of magnitude of preneoplasia than exposure at either the initiation or promotion phase alone.

Studies on the cellular changes that precede the development of liver cancer in animals exposed to chemicals / hepatocarcinogens have focussed on a series of microscopic lesions called "hyperplastic foci" and "nodules" which have been designated "preneoplastic" or "premalignant" [Farber and Sarma 1987]. Oral supplementation of 1α, 25-dihydroxyvitamin D_3, especially during the entire period of study, resulted in fewer rats developing visible PNs and a smaller number of nodules per nodule-bearing rat liver than those observed in DEN control rats. Another striking observation of the study was the 1α, 25-dihydroxyvitamin D_3-mediated inhibition of PNs greater than 3 mm in size. In view of this, inhibition of nodule incidence and enhancement of their regression by 1α, 25-dihydroxyvitamin D_3 treatment as observed herein may be important for cancer chemoprevention.

Mn-SOD forms one of the primary enzymic defence systems and an efficient *in vivo* strategy to combat oxidative stress through the dismutation of superoxide radicals. The enhanced oxygen-tension due to accumulation of ROS in precancerous cells acts as a signal for Mn-SOD induction [Skrzydlewska 2001]. On the other hand**,** the intracellular redox balance of mammalian cells is maintained by homeostatic mechanism that links small pools of coenzymes and cofactors to a large redox buffer (i.e. thiol system). Most of the extracellular and intracellular thiols are represented by the non-protein tripeptide GSH which plays an important role in the detoxification of organic xenobiotics, including several chemical carcinogens [Chasseaud 1979]. Because of high nucleophilicity of GSH Cys-thiol-sulfur atom, it seems reasonable to postulate that, this tripeptide may act as a scavenger of electrophilic species generated by the metabolic activation of a number of carcinogens, thus eliminating and thereby reducing the concentration of these species available for binding with cellular macromolecules. Thus, GSH can influence the DNA adduction ability and mutagenicity of nitrosamines and other carcinogens [Peraino 1981]. GSTs, a family of multifunctional proteins which act as binding proteins and also as enzymes in detoxification processes, catalyze the reaction of compounds with the thiol group of GSH, thus neutralize their electrophilic sites and render the product more water soluble [Habig et al. 1974]. Results of the present study showed a significant decrease in hepatic GST activity towards CDNB with a concurrent depletion of GSH level in liver following DEN challenge. DEN-mediated depletion of GSH as noted in this study might be related to the failure of the system to combat oxidative stress generated by accumulation of high amount of toxic metabolites and

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ROS in the host. This may enhance the covalent binding of DEN-derived reactive alkylating species to cellular DNA and other macromolecules. This in turn may be related to the initiation of carcinogenesis with the enhancement of hepatocellular lesions and DNA damage *in vivo* followed by subsequent steps of promotion and progression leading to neoplasia.

Several naturally occurring products and dietary micronutrients are known to induce hepatic GSH and GST activity which has been correlated with their anticarcinogenic actions. 1α, 25-dihydroxyvitamin D_3 -mediated induction of a steady high level of GST activity together with maintenance of GSH content towards near normalization during the entire length of the study may lead to an enhanced carcinogen elimination as well as reduction of DNA-carcinogen adduct formation thereby limiting the expression of preneoplastic phenotype. Elimination of ROS from the system may therefore be related to the 1α, 25-dihydroxyvitamin D_3 -mediated lowering in the level of Mn-SOD activity toward normalization. All these events may be considered as one of the underlying biochemical mechanisms of the antihepatocarcinogenic effect of 1α, 25-dihydroxyvitamin D_3.

There was a substantial decrease in the number of SSBs ($P<0.01$) which may provide the basis for anticlastogenic and antigenotoxic actions of 1α, 25-dihydroxyvitamin D_3. A strong inverse relationship was observed between the generation of SS-DNAs / SSBs and hepatic levels of GSH / GST following DEN insult. The findings presented herein thus suggest that induction of GSH and GST by 1α, 25-dihydroxyvitamin D_3 before and after carcinogenic insults plays important role in detoxification of DEN metabolites and in limiting DNA damage thereby. It is well known that DNA strand-breaks responsible for chromosomal aberrations are generated from DNA base-lesions induced by most chemical carcinogens. These DNA base-lesions are generally repaired by the excision-repair system [Friedberg et al. 1979]**.** It is assumed that the beneficial *in vivo* effect of 1α, 25-dihydroxyvitamin D_3 may be exerted through its effect on excision-repair activity. *In vitro,* 1α, 25-dihydroxyvitamin D_3 delays the cell cycle and can thus prolong the DNA repair mechanism [Liu et al. 1996; Wang et al. 1996].

In conclusion, data presented in this report indicate that antioxidant vitamin 1α, 25-dihydroxyvitamin D_3 has the potential in suppressing nodulogenesis and progression of premalignant lesions in rat liver. Chemoprotective effect of 1α, 25-dihydroxyvitamin D_3 was further evident through its role in attenuating DEN-induced DNA strand-breaks through the restoration of cellular antioxidant defence system. It is concluded that, 1α, 25-

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dihydroxyvitamin D_3 is chemopreventive against DEN-induced hepatocellular preneoplastic transformation in rats.

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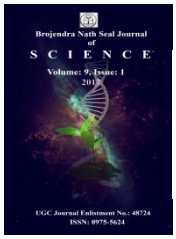

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Review Article

PARKINSON'S DISEASE: CAUSE TO CURE, A JOURNEY OF 200 YEARS

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A B S T R A C T

Parkinson's disease (PD) is referred to a group of conditions that is commonly known as "motor system disorders". This kind of disorder is a result of the loss of dopamine producing neurons in the central nervous system (CNS). The four primary symptoms of PD are tremor, or trembling in hands, arms, legs, jaw, and face; rigidity, or stiffness of the limbs and trunk; bradykinesia, or slowness of movement; and postural instability, or impaired balance and coordination. With advancement of age, the symptoms become more pronounced and the patients face increasing difficulty in various motor movements like talking, walking, etc. Progression of the disease often leads to the development and appearance of several other symptoms like depression, emotional changes, difficulty in swallowing, chewing, and speaking, urinary problems or constipation, skin problems, and sleep disruptions. However the diagnosis of PD is largely based on medical history and neurological examinations due to lack of specific laboratory blood tests. There is no cure for PD. Temporary relief may be provided to the patients through different modes of treatment of which L-DOPA is used maximally. Besides levodopa, there are other procedures which also provide temporary relief and increased life-expectancy but permanent cure is yet to be discovered.

Keywords: *Parkinson's disease, Levodopa, neurodegenerative disorder, motor system disorder*

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1. INTRODUCTION

In the past two centuries there have been several eminent personalities in the history of the world who have been afflicted with the "shaking palsy". Adolf Hitler (German dictator), Muhammad Ali (American boxer), and George Bush (former US President) are among the few who have been inflicted with the disease. The "shaking palsy", now better known as

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Parkinson's disease (PD) is a long-term neurodegenerative disorder of the central nervous system (CNS) affecting the functional status of the motor system. It is the second most important neurodegenerative disease following Alzheimer's disease (Campenhausen *et al*. 2005). Being a movement disorder, PD is generally characterized by rigidity, resting tremor and bradykinesia (Campenhausen *et al*. 2005; Zou *et al*. 2015).

The disease has been named after James Parkinson (1755–1824), who was the first to describe the clinical entity of the disease exactly 200 years ago in 1817, as "paralysis agitans" in his "Assay on the Shaking Palsy" (Muangpaisan *et al*. 2009). He had described the disease by studying a handful of patients who had a singular association of tremor at rest, slowness (bradykinesia) of voluntary movements or, in some cases a complete absence of voluntary movements (akinesia) alongwith stooped posture and festinating gait. In the present scenario, PD has more than 30 distinct features and as such the term "Parkinsonism" is used to label any clinical condition with bradykinesia or akinesia and at least one of the following signs: muscle rigidity, resting tremor or postural instability (Przedborski 2017).

The prevalence of PD ranges from 41 in every 100,000 in the age group of 40 plus population to 1900 in every 100,000 in the 80 plus age group. Prevalence of PD is more in males (1729 per 100,000, >65 years) than in females (1644 per 100,000), with a peak prevalence in the age group of ≥90 years (4633 cases per 100,000), and a mean prevalence of 1680 per 100,000 in people over 65 years of age (Riedel *et al*. 2016; Sveinbjornsdottir 2016; Cacabelos 2017). The risk factors for PD are summarized in Table 1.

Table 1: *The risk factors for Parkinson's Disease*

Non-modifiable risk factors	**Modifiable risk factors**	
	Increased risk	**Possible decreased risk**
• Age (mean age 65 yr) • Sex (M:F = 1.5:1.0) • Genetics (10% of cases) LRRK2 mutation (most common) Glucocerebrosidase gene mutation Parkin mutation (juvenile onset)	• Industrial exposure •Heavy metals (i.e., manganese, lead, copper) •Pesticides (i.e., rotenone, paraquat) •Obstructive sleep apnea (maybe in women)	•Smoking •Caffeine

2. ETIOLOGY OF PARKINSON'S DISEASE

Initial studies have not revealed much about the anatomical changes in the brain of PD patients. However, Blocq and Marinescu pointed that a left-sided 5 Hz resting tremor in a 38-year-old patient was reminiscent of the symptoms of PD. They further noted that the probable reason for the condition may be a tuberculous granuloma of the right cerebral peduncle that impinged on the ipsilateral substantia nigra (SN) (Blocq *et al*. 1893). This lead to a

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proposition that the probable sight of lesion in the PD may be substantia nigra (Brissaud 1899).

The neuropathology of PD is mainly characterized by a selective loss of dopaminergic neurons in the substantia nigra pars compacta and Lewy body deposition with widespread involvement of other CNS structures and peripheral tissues (Sveinbjornsdottir 2016). The neurons of SN contain copious amounts of neuromelanin. The loss of these neurons alongwith the microscopic loss of neurons associated with gliosis and Lewy bodies have been said to be the key cause of PD (Marsden 1983).

The Lewy bodies are spherical eosinophilic intraneuronal inclusions were originally reported in the dorsal nucleus of the vagus nerve and the substantia innominate but there presence was not found in SN (Lewy 1913; Marsden 1983). Thus it was proposed that SN was not the site of PD initiation. This controversy remained a topic of debate for a long time until the discovery and elucidation of the dopaminergic nigrostriatal pathway. With advancement of techniques, detailed neuropathological studies revealed that within the SN exists a subregion, the pars compacta (SNpc) (Hassler 1938; Greenfield and Bosanquet 1953), that is disproportionately affected by PD with the loss of pigmented neurons being more than the unpigmented ones (Hirsch *et al.* 1988). Based on pathologic studies, there is a stepwise degeneration of neurons over many years, with each affected site corresponding to specific symptomatology in Parkinson disease (Rizek *et al*. 2016) (Table 2).

Table 2: *Braak staging of Lewy body deposition (Rizek et al., 2016)*

Stage	**Sites affected by Lewy bodies**	**Major symptoms**
I	Dorsal motor nucleus of the vagus nerve and olfactory tract	Constipation, anosmia
II	Locus coeruleus and subcoeruleus complex	Sleep and mood dysfunction
III	Substantia nigra	Motor symptoms of Parkinson disease
IV-VI	Cortical involvement	Dementia, psychosis

Dopamine signalling had been proposed to play a crucial role in basal ganglia in motor control (Przedborski 2017). Hence PD being a motor disorder, it was easily proposed that this dopaminergic system must have been compromised in the patients. Simultaneously, two research studies revealed that there was substantial deficiency of dopamine in both the striatum as well as SN of patients dying with PD (Sano 1960; Ehringer and Hornykiewicz 1960). Direct and indirect pathways of the basal ganglia motor circuits in health and parkinsonism is represented in Figure 1.

Further investigations revealed mutations in the mitochondrial genes, specifically of complex I of electron transport chain leads to development of PD. Certain polymorphisms have also been found to enhance the probability of the disease in an individual. Mitochondria is of maternal origin, hence this mitochondrial cytopathy hypothesis predicts that PD may be maternally inherited (Wooten *et al*. 1997; Swerdlow *et al*. 1998; Kosel *et al*. 1998; van der

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Walt *et al*. 2003; Bender *et al*. 2006; Kraytsberg *et al*. 2006). In some studies, it was revealed that loss-of-function mutations in PARK2 gene that encodes parkin. Parkin participates in the macro-autophagy of defective mitochondria in a process that is dependent on the mitochondrial serine/threonine protein kinase PINK1. Mutations in PARK2 have been shown to cause early onset of PD. PINK1 mutations, similarly to those found in PARK2, are linked to a recessive form of PD that is probably caused by a loss of gene function (Kitada *et al*. 1998; Mizuno *et al*. 2001; Goldberg *et al*. 2003; Valente *et al*. 2004). Various lifestyle factors like consumption of excess coffee, cigarette smoking (Herner *et al*. 2002), exposure to herbicides and pesticides (Tanner *et al*. 2002) have also been linked to PD.

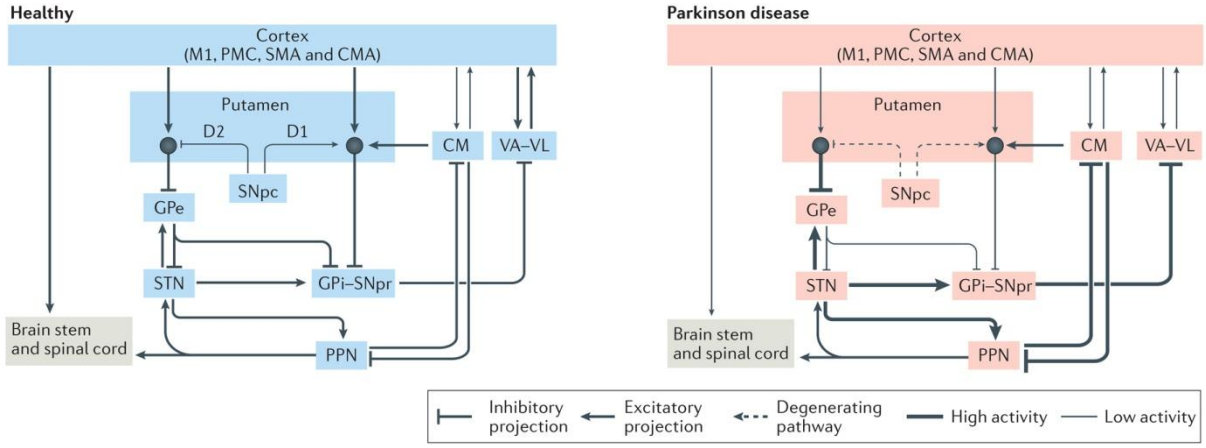

Fig. 1: *Direct and indirect pathways of the basal ganglia motor circuits in health and parkinsonism. Under healthy conditions, substantia nigra pars compacta (SNpc) dopaminergic neurons activate the D1 dopamine receptor-expressing striatal projecting neurons of the direct pathway and inhibit the D2-expressing striatal projecting neurons of the indirect pathway. Once activated by the cortex and the SNpc, the direct pathway inhibits the globus pallidus internal segment (GPi)–substantia nigra pars reticulata (SNpr). Once the indirect pathway is activated by the cortex (and to a lesser extent inhibited by the SNpc), it inhibits the globus pallidus external segment (GPe), which inhibits the subthalamic nucleus (STN) and the GPi–SNpr. These inputs to the GPi–SNpr together cause a net decrease in inhibition to the thalamus. As the thalamus activates the motor cortex itself it can be concluded that an increase in activity in the SNpc may promote motor activity. However, in Parkinson disease, degeneration of the SNpc will decrease the activation of the direct pathway and the inhibition of the indirect pathway. This striatal imbalance will cause an increase in STN-mediated activation and a decrease in GPe-mediated inhibition of the GPi–SNpr, which, in turn, will exert a much stronger inhibition of the thalamus, resulting in a lower activation of the motor cortex. Thus, the loss of SNpc input to the striatum leads to a decrease in motor activity. CM, centromedian nucleus; CMA, cingulate motor area; M1, primary motor cortex; PMC, premotor cortex; PPN, pedunculopontine nucleus; SMA, supplementary motor area; VA–VL, ventral anterior–ventral lateral nucleus.*

[taken from Przedborski 2017]

There are various pathogenic mechanisms which have been proposed to be involved in PD (Figure 2). Among the various other mechanisms one of the most important one is the quality control mechanisms for proteins and organelles, such as the mitochondria. When such mechanisms become defective, advancement towards PD is initiated. Overloading the ubiquitin-proteasome and lysosomal degradation pathways hampers the cellular machinery to

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detect and degrade undesired proteins. Protein misfolding may be a result of gene mutations or post-translational modifications induced by ROS (reactive oxygen species). ROS directly contributes to neurodegeneration, and can be generated through the oxidation of dopamine, by environmental toxins that behave similarly to 6-hydroxydopamine (6-OHDA), and by mitochondrial repair defects. Several other mutant and modified proteins, such as parkin and PINK1 have altered functionality due to the mutations. Defects in the function of one or both of these proteins alter the mitochondrial turnover, thus leading to the inability of the cellular machinery to detect and degrade dysfunctional mitochondria. This accumulation of unwanted proteins and mitochondria are often the reason behind neurodegeneration. Two well-known neurotoxins, 1-methyl-4 phenyl-1,2,5,6-tetrahydropyridine (MPTP) and rotenone affect mitochondrial respiration which often leads to increased ROS generation and decreased ATP production. This causes potentially pathogenic cellular oxidative stress and an energy crisis. All these changes often lead to an alteration in the milieu of the neurons and cause even neighbouring glial cells like microglia and astrocytes to adopt a pro-inflammatory phenotype, give rise to more stress in the tissue and hence enhance neurodegenerative processes (Przedborski 2017).

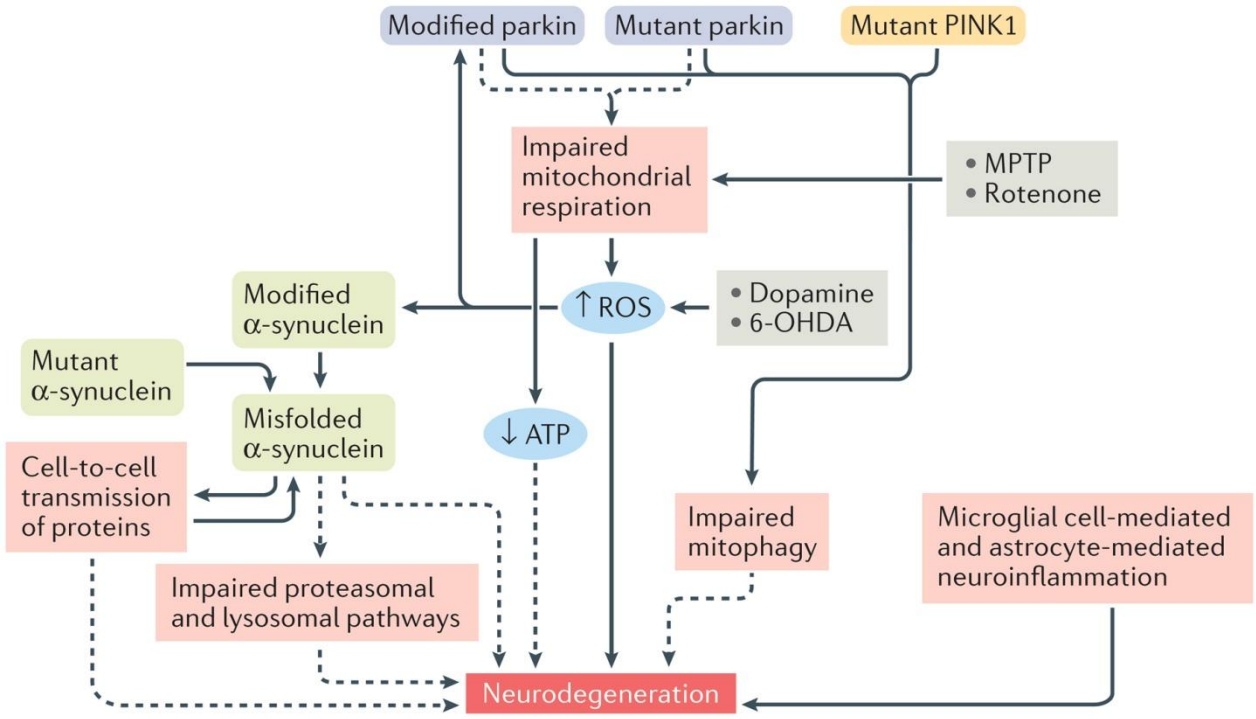

Fig. 2: *Potential pathogenic mechanisms involved in Parkinson disease. [taken from Przedborski 2017].*

Parkinson's disease is thus a form of multi systemic α-synucleinopathy (due to an abnormal accumulation of alpha-synuclein protein in the brain) with Lewy bodies deposited in the midbrain. This neuropathological phenotype may be briefly described to include (i) genomic factors; (ii) epigenetic changes; (iii) toxic factors; (iv) oxidative stress anomalies; (v) neuroimmune/neuroinflammatory reactions; (vi) hypoxic-ischemic conditions; (vii) metabolic deficiencies; and (viii) ubiquitin–proteasome system dysfunction (Toledo *et al*. 2013; Lill

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2016; Rokad *et al*. 2016; Wen *et al*. 2016; Nussbaum *et al*. 2017; Cacabelos *et al*. 2017; Irwin *et al*. 2017). All these conditions often lead to protein misfolding and aggregation and premature neuronal death. Recent evidence also suggests that PD might be a prion-like disease (Xie *et al*. 2017). Telomere shortening as a result of the inability to fully replicate the ends of linear chromosomes is one of the hallmarks of aging which might also contribute to PD pathology (Olanow and Brundin 2013).

3. CLINICAL MANIFESTATIONS

The major clinical symptoms of PD include motor manifestations like resting tremor, hypophonia (soft voice), micrographia (small handwriting), rigidity, bradykinesia (slowness of movement) and non-motor symptoms like constipation, disorders of rapid eye movement sleep behaviour, depression and olfactory impairment (Gibb and Lees 1988). The various criteria for diagnosis of PD (Rizek *et al*. 2016) are given in Table 3.

Table 3: *Diagnostic Criteria for PD (Rizek et al., 2016)*

Bradykinesia and at least any one of the following features	**At least three of the following supportive (prospective) features**
1.Rigidity 2.Resting Tremor 3.Postural instability not caused by primary visual, vestibular, cerebellar or proprioceptive dysfunction	1.Unilateral onset 2.Persistent asymmetry primarily affecting the side of onset 3.Resting tremor (hand, leg or jaw; low frequency (4–5 Hz), asymmetric, disappears with action) 4. Excellent response to levodopa (70%–100%) 5. Progressive disorder 6. Severe levodopa-induced chorea (dyskinesias) 7. Levodopa response for five years or more 8. Clinical course of 10 years or more

PD can be classified into early-onset and late-onset disease. Patients with early-onset of the disease have less gait disturbance as a symptom, but have more pronounced rigidity and bradykinesia than those with late-onset disease. Patients with early-onset disease have a slower disease progression than delayed onset (Gibb and Less 1988; Gomez *et al*. 1997; Ferguson *et al*. 2016). The early and late motor and non-motor features of PD is summarized in Figure 3. (15).

4. TREATMENT

Parkinson's disease does not have any cure. But there are several treatment procedures that improve the condition in patients and their life-expectancy.

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The symptomatic therapy for the motor symptoms of PD includes dopaminergic medications.

Early motor features	Late motor features (usually develop 5–10 yr after disease onset)
• Difficulty turning in bed • Frozen shoulder • Stiffness, numbness or pain in limb • Micrographia • Difficulty with fine finger movements (bradykinesia) • Tremor of hand, jaw, foot • Decreased facial expression • Decreased arm swing, dragging a leg • Soft voice	• Motor fluctuations •Dyskinesia (complication of dopaminergic treatment, more so with levodopa); typically choreiform, involving the neck, head, limbs and trunk • Gait freezing • Falls
Early nonmotor features (may precede the diagnosis)	**Late nonmotor features**
• Constipation (30%) • REM sleep behaviour disorder (50%, often preceding the diagnosis by median of 14 yr) • Depression occurs with a prevalence of 35% in Parkinson disease, and 10%–15% will have depression at the time of diagnosis • Olfaction impairment (most consistent nonmotor feature predicting Parkinson disease); up to 97% of patients	• Dysphagia (50% at 15 yr) • Neuropsychiatric symptoms (50% at 15 yr) including hallucinations, sleep disturbance and dementia • Autonomic disturbances (70%–80%) including sweating, orthostasis, sialorrhea and urinary dysfunction • Seborrheic dermatitis (usually involving the forehead, with flaky oily skin)

Fig. 3: *Early and late motor and non-motor features in patients with Parkinson disease [taken from Rizek et al. 2016].*

Treatment with L-DOPA elevated the status of motor functions in PD patients. However, most of the patients who were treated with L-DOPA chronically were found to develop dyskinesia and hallucinations. These effects were at least partly attributed to the non-physiological pulsatile striatal receptor stimulation as was caused by the intermittent oral administration of L-DOPA (Olanow *et al*. 2006). Such a condition gave rise to the development of various modifications like change in route of drug delivery, new formulations, which would further strengthen the treatments with L-DOPA with increased effectiveness and decreased side-effects. As because patients with early-onset disease are more likely to develop levodopa-induced dyskinesia, dopamine agonists are often given as an initial treatment. But this advantage of dopamine agonists over levodopa is short-lived (Connoly and Lange 2014). Anticholinergics, such as trihexyphenidyl, may be used in patients with early-onset Parkinson disease and severe tremor, however, it is not used a first choice on account of its limited efficiency and propensity for neuropsychiatric adverse effects (Postuma *et al*. 2015). It may be noted here that any drug used as an Antiparkinsonian medication should not be withdrawn abruptly so to avoid acute akinesia or neuroleptic malignant syndrome. To avoid the risk of dopamine agonist induced withdrawal symptoms, they should not be discontinued suddenly (Nirenberg 2013; Pondal *et al*. 2013; Solla *et al*. 2015).

Psychotropics that are used as a treatment for depression in PD include tricyclic antidepressants (TCAs), tricyclic-related drugs (trazodone), selective serotonin reuptake inhibitors (SSRIs), the serotonin and noradrenaline re-uptake inhibitor (SNRI) venlafaxine,

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the selective noradrenaline re-uptake inhibitor reboxetine, and the pre-synaptic alpha-2 adrenoreceptor antagonist mirtazapine (Aarsland *et al*. 2009). Besides these several other techniques have evolved, which have been used in treatment of PD (Farzanehar 2016), are summarized in Figure 4.

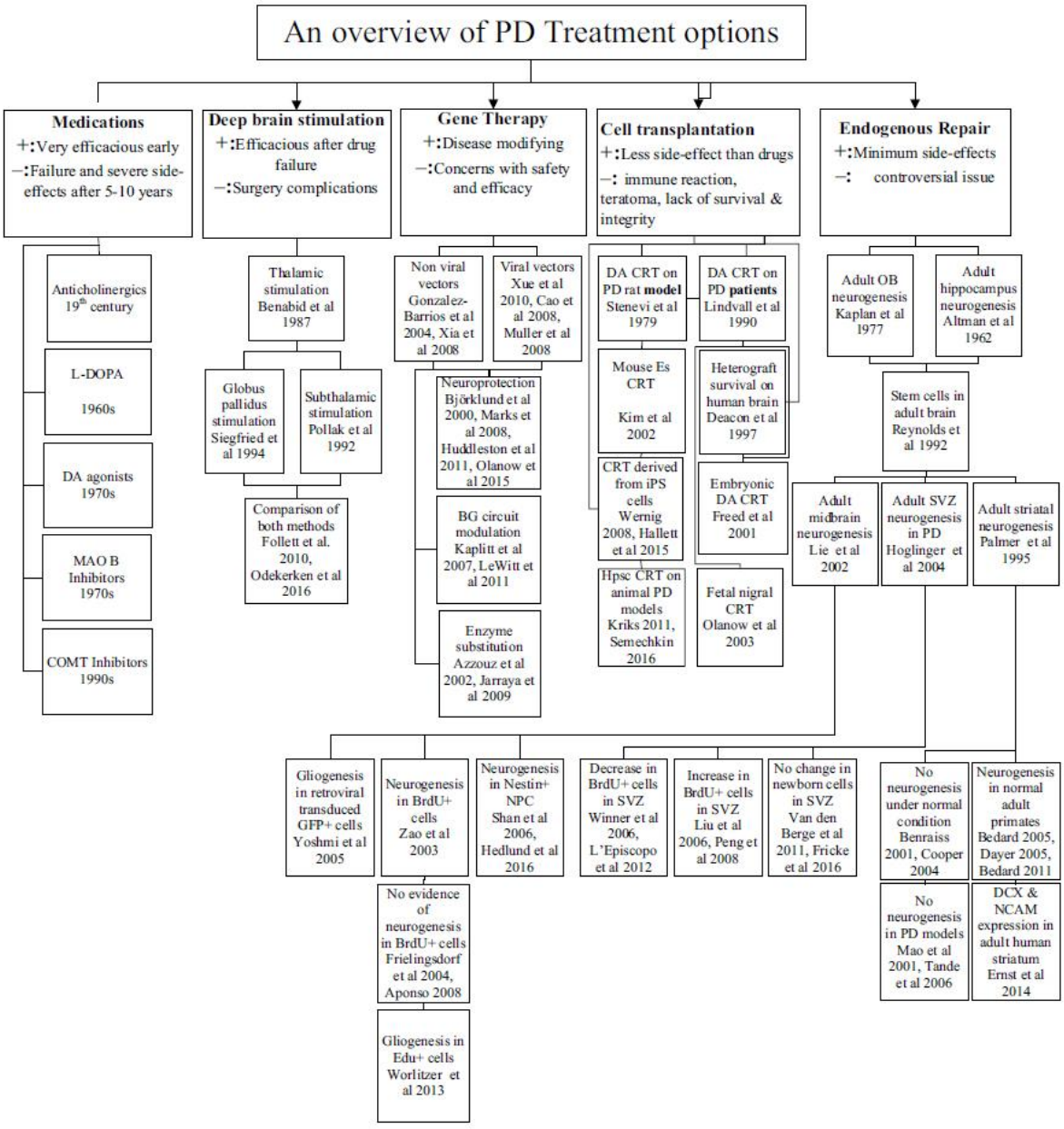

Fig. 4: *Therapeutic options of PD. L-DOPA: L-3,4- dihydroxyphenylalanine. DA: Dopamine, MAO: Monoamine oxidase, COMT: catechol-O-methyl transferase, CRT: cell replacement therapy, iPS: induced pluripotent stem cell, Hpsc: human pluripotent stem cell, OB: olfactory bulb, SVZ: subventricular zone, NPC: neural precursor cell, BG: basal ganglia (Farzanehar 2016).*

5. DRUGS TO BE AVOIDED

There are some drugs which under their normal course of action block dopamine receptors. This may result in development of PD or substantially worsen motor symptoms in patients with PD and may lead to neuroleptic malignant syndrome. Such drugs include

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neuroleptics, such as haloperidol, thioridazine, chlorpromazine, promethazine, fluphenazine, risperidone and olanzapine; antiemetics, such as prochlorperazine and metoclopramide; tetrabenazine; and antihypertensives, such as methyldopa (Orti-Pareja *et al*. 1999; Burkhard 2014). Meperidine should be avoided in those receiving monoamine oxidase B inhibitors (Nicholson *et al*. 2002). Hence use of such drugs and chemicals must be avoided to prevent development of PD.

In its two hundred years of history from identification to prevention and cure, there have been numerous discoveries relating to Parkinson's disease. However, there has been no discovery related to complete cure of PD. Research has been going on as to prevent and/or cure Parkinson's Disease. The discoveries so far from its first identification to the present day are represented in Figure 5.

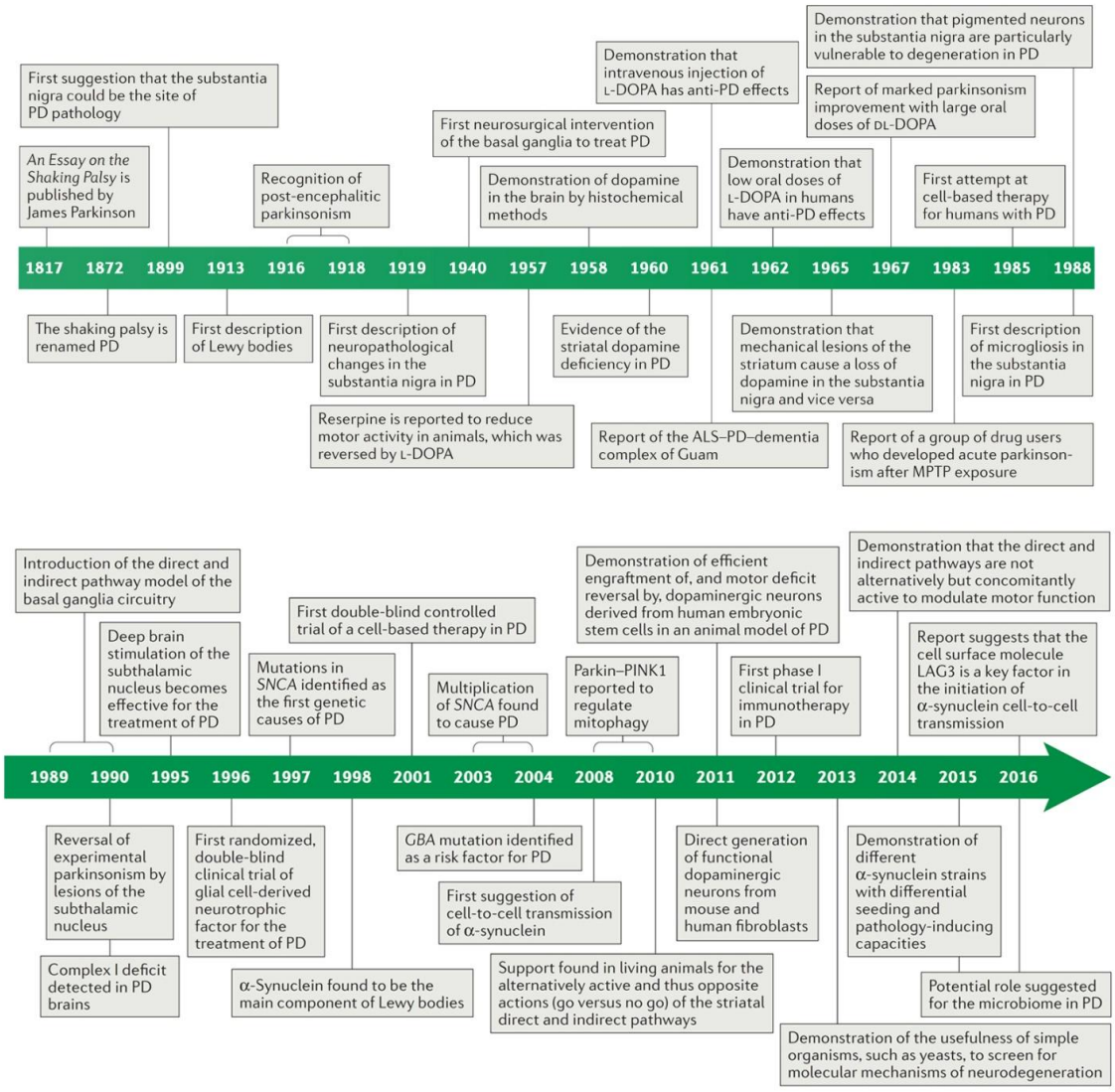

Fig. 5: *The various milestones in the 200 years of Parkinson's disease and related research (Przedborski 2017).*

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6. CONCLUSION

PD is a complex disease that has both environmental basis as well as genetic cause. The several multidirectional studies conducted so far have been able to provide a better platform to understand not only the underlying mechanisms but also the phenotypical heterogeneity. This has helped to treat the various symptoms and give a better life to the patient with a temporary relief. However, the disease itself affects an individual long before the manifestation of the first symptoms and thus is often modulated by various environmental factors that may give rise to further complications. Thus despite the various major discoveries and breakthroughs in the context of PD, its pathogenesis and treatment, a completely effective treatment are yet to be established. Hence, still there is a lot more into the cloud than the clearing, to be cleared out very soon, relating to the permanent cure and prevention for PD.

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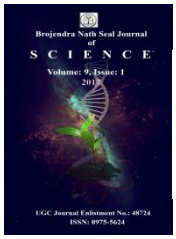

Brojendra Nath Seal Journal of SCIENCE

Research Article

PHYTOCHEMICAL ANALYSIS OF TWO MEDICINAL PLANTS OF NORTH BENGAL

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A B S T R A C T

Medicinal plants have been used as a source of remedies since ancient times in India. Traditional medicine systems consist of large numbers of plants with medicinal and pharmacological importance. Rouvolfia Serpentina and Moringa Olifera are two such important medicinal plants traditionally used in India for their immense therapeutic properties. In this present study plants leaf extracts are screened for the presence of major phytochemical groups which are plants primary and secondary metabolites and known for their therapeutic values. These compounds are reported to have antiaging, anticarcinogen, antiinflammation, antiatherosclerosis, cardiovascular protective and antimicrobial activities. Qualitative analysis showed the presence of metabolites such as glycosides, phenolic compounds, alkaloids, flabinoids, tannins, saponins, steroids for both the plants ensuring their potentiality as therapeutic agent.

***Key Words**: Rouvolfia Serpentina, Moringa Olifera, medicinal plants, therapeutic properties, phytochemical*

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1. INTRODUCTION

The use of herbal medicine for the treatment of diseases and infections is as old as mankind. The World Health Organization supports the use of traditional medicine provided they are proven to be efficacious and safe (WHO, 1985). In the last few decades there has been an exponential growth in the field of herbal medicine. It is getting popularized in developing and developed countries owing to its natural origin, lesser side effect and cost

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effective qualities (Report of seminar on Herbal Drug, 2001). Medicinal plants have been used as a source of remedies against many pathological conditions since ancient times in India. Traditional medicine systems consist of large numbers of plants with medicinal and pharmacological importance and hence represent an invaluable reservoir of new bioactive molecules.

The plant kingdom is a treasure house of potential therapeutic compounds and in the recent years there has been an increasing awareness about the importance of these compounds of medicinal plants and uses them as therapeutic agents because compounds from the plants are easily available, less expensive, safe, and efficient and proven to have side effects. Recently some plants have been selected for examination and proven therapeutically effective new drugs such as anticancer drugs (Dewick 1996), antimicrobial drugs (Phillipson and Wright 1996), antihepatotoxic compounds. Some organic compounds from medicinal plants which are by primary or rather secondary metabolites provide definite physiological action on the human body. These bioactive substances include tannins, alkaloids, carbohydrates, protein, glycosides terpenoids, steroids and flavonoids (Mann 1978; Edoga et al. 2005). They are widely used in the human therapy, as well as veterinary, agriculture, scientific research and many other different areas of human interest (Vasu et al. 2009). A large number of phytochemicals also have been shown to have inhibitory effects on all types of microorganisms in vitro and in animal models (Cowan 1999).

Among The secondary plant metabolites, phenol compounds such as flavonoid, phenolic acids, tocopherols etc are most ubiquitous groups of (Singh et al. 2007). Studies revealed that plant rich in phenolic compounds possess biological properties such as antiapoptotic, antiaging, anticarcinogen, antiinflammation, antiatherosclerosis, cardiovascular protection and improvement of endothelial function, as well as inhibition of angiogenesis cell proliferation activities antioxidant properties and (Brown and Rice-Evans 1998; Krings and Berger 2001; Han et al. 2007; Ali et al. 2008). In response to microbial infection plants synthesize a hydroxylated phenolic substance, flavonoids having activities against wide array of microorganisms in vitro, which may be due to their ability to complex with extracellular and soluble proteins and to complex with bacterial cell wall (Marjorie. 1996). Another metabolite, tannins interfere with protein synthesis by binding with proline rich protein. The plant extracts containing saponins, have anti inflammatory (Just et al. 1998) hemolytic (Okwu 2004) activities. Studies show that, Glycosides lower the blood pressure (Nyarko and Addy 1990). Steroids are very important compounds, having relationship with sex hormones (Okwu 2001).They also have antibacterial activities (Raquel 2007). Alkaloids have been used for centuries for their medicinal value. They have cytotoxic (Nobori et al. 1994), analgesic antispasmodic and antibacterial (Stray, 1998; Okwu and Okwu 2004) properties. The mechanism of action of some phytochemicals are shown below (Table 1)

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Table 1: *Mechanism of action of some phytochemicals (Tiwari et al. 2011)*

Phytochemicals	Activity	Mechanism of action
Quinones	Antimicrobial	Binds to adhesins, complex with cell wall, inactivates enzymes
Flavonoids	Antimicrobial Antidiarrhoeal	Complex with cell wall, binds to adhesins Inhibits release of autocoids and prostaglandins, Inhibits contractions caused by spasmogens, Stimulates normalization of the deranged water transport across the mucosal cells, Inhibits GI release of acetylcholine
Polyphenols and Tannins	Antimicrobial Antidiarrhoeal Anthelmintic	Binds to adhesins, enzyme inhibition, substrate deprivation, complex with cell wall, membrane disruption, metal ion complexation Makes intestinal mucosa more resistant and reduces secretion, stimulates normalization of deranged water transport across the mucosal cells and reduction of the intestinal transit, blocks the binding of B subunit of heat-labile enterotoxin to GM1, resulting in the suppression of heat-labile enterotoxin-induced diarrhea, astringent action Increases supply of digestible proteins by animals by forming protein complexes in rumen, interferes with energy generation by uncoupling oxidative phosphorylation, causes a decrease in G.I. metabolism
Phytochemicals	**Activity**	**Mechanism of action**
Coumarins	Antiviral	Interaction with eukaryotic DNA
Terpenoids and essential oils	Antimicrobial Antidiarrhoeal	Membrane disruption Inhibits release of autocoids and

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		prostaglandins
Alkaloids	Antimicrobial Antidiarrhoeal Anthelmintic	Intercalates into cell wall and DNA of parasites Inhibits release of autocoids and prostaglandins Possess anti-oxidating effects, thus reduces nitrate generation which is useful for protein synthesis, suppresses transfer of sucrose from stomach to small intestine, diminishing the support of glucose to the helminthes, acts on CNS causing paralysis
Lectins and Polypeptides	Antiviral	Blocks viral fusion or adsorption, forms disulfide bridges
Glycosides	Antidiarrhoeal	Inhibits release of autocoids and prostaglandins
Saponins	Antidiarrhoeal Anticancer Anthelmintic	Inhibits histamine release in vitro Possesses membrane permeabilizing properties Leads to vacuolization and disintegration of teguments
Steroids	Antidiarrhoeal	Enhance intestinal absorption of Na+ and water

Plant products having phytomedicinal properties, can be derived from barks, leaves, flowers, roots, fruits, seeds of the plant (Criagg and David 2001). So for synthesis of complex chemical substances, knowledge of the chemical constituents of plants is essential (Mojab et al. 2003; Parekh and Chanda 2007; Parekh and Chanda 2008).

The present study investigates the fundamental scientific basis for the use of Rouvolfia Serpentina and Moringa Olifera plants leaf as therapeutic agent by defining the presence of crude phytochemical constituents .

2. MATERIALS AND METHODS

2.1. Collection of plant materials

The leaves of the plants were collected from different uncultivated farmlands of Jalpaiguri District, West Bengal. The sample leaves of two plants were identified by the authors. The leaves were air-dried and ground into uniform powder using a REMI Mixer grinder machine and kept in air tight container. The aqueous extract of each sample was

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prepared by soaking 100 g of dried powdered samples in 200 ml of distilled water for 12 h. The extracts were filtered using Whatman filter paper No 42 (125 mm).

2.2. Phytochemical screening

Chemical tests were carried out on the aqueous extract and on the powdered specimens using standard procedures as described by Sofowara (1993), Trease and Evans (1989) and Harborne (1973) to identify the constituents phytochemicals.

2.3. Test for tannins

About 0.5 g of the dried powdered samples was boiled in 20 ml of water in a test tube and then filtered. A few drops of 0.1% ferric chloride was added and observed for brownish green or a blue-black coloration.

2.4. Test for phlobatannins

Deposition of a red precipitate when an aqueous extract of each plant sample was boiled with 1% aqueous hydrochloric acid was taken as evidence for the presence of phlobatannins.

2.5. Test for saponin

About 2 g of the powdered sample was boiled in 20 ml of distilled water in a water bath and filtered. 10ml of the filtrate was mixed with 5 ml of distilled water and shaken vigorously for a stable persistent froth. The frothing was mixed with 3 drops of olive oil and shaken vigorously, then observed for the formation of emulsion.

2.6. Test for flavonoids

5 ml of dilute ammonia solution were added to a portion of the aqueous filtrate of each plant extract followed by addition of concentrated H_2S0_4. A yellow coloration observed in each extract indicated the presence of flavonoids. The yellow coloration disappeared on standing. Few drops of 1% aluminium solution were added to a portion of each filtrate. A yellow coloration was observed indicating the presence of flavonoids. A portion of the powdered plant sample was in each case heated with 10 ml of ethyl acetate over a steam bath for 3 min. The mixture was filtered and 4 ml of the filtrate was shaken with 1 ml of dilute ammonia solution. A yellow coloration was observed indicating a positive test for flavonoids.

2.7. Test for steriods and terpenoids

Libermann Burchard's test

Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of acetic anhydride, boiled and cooled. Conc. sulphuric acid was added to the solution. Formation of brown ring at the junction and green upper layer indicates the presence of phytosterols and formation of deep red colour indicates the presence of triterpenoids.

2.8. Test for cardiac glycosides (Keller-Killani test)

Five ml of each extracts was treated with 2 ml of glacial acetic acid containing one drop of ferric chloride solution. This was underlayed with 1 ml of concentrated sulphuric acid. A brown ring of the interface indicates a deoxysugar characteristic of cardenolides. A violet

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ring may appear below the brown ring, while in the acetic acid layer, a greenish ring may form just gradually throughout thin layer.

2.9. Detection of alkaloids

Extracts were dissolved individually in dilute Hydrochloric acid and filtered.

***2.9.1. Mayer's Test*:** Filtrates were treated with Mayer's reagent (potassium mercuric iodide). Formation of a yellow colour precipitate indicates the presence of alkaloids.

***2.9.2. Wagner's Test*:** Filtrates were treated with Wagner's reagent (Iodine in Potassium Iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

***2.9.3. Hager's Test*:** Filtrates were treated with Hager's reagent (saturated picric acid solution). Presence of alkaloids confirmed by the formation of yellow colored precipitate.

2.10. Detection of carbohydrates

Extracts were dissolved individually in 5 ml distilled water and filtered. The filtrates were used to test for the presence of carbohydrates.

***2.10.1. Molisch's Test*:** Filtrates were treated with 2 drops of alcoholic α-naphthol solution in a test tube. Formation of the violet ring at the junction indicates the presence of Carbohydrates.

***2.10.2. Benedict's Test*:** Filtrates were treated with Benedict's reagent and heated gently. Orange red precipitate indicates the presence of reducing sugars.

***2.10.3. Fehling's Test*:** Filtrates were hydrolysed with dilute HCl, neutralized with alkali and heated with Fehling's A & B solutions. Formation of red precipitate indicates the presence of reducing sugars.

2.11. Detection of organic acids

2.11.1. *Oxalic acid test*: To the test solution few drops of 1% $KMnO_4$ and dilute H_2SO_4 is added, if the colour disappears, shows the presence of organic acid.

2.11.2. *Malic acid test*: To the test solution 2-3 drops of 40% $FeCl_3$ is added, appearance of yellowish colour proves the presence of organic acid.

3. RESULT

The leaf extract and the dried powder of leaf of Rouvolfia Serpentina and Moringa Olifera showed the presence of tannin, phlobatannin, saponin, flavonoids, sterols, alkaloids, carbohydrate, protein and organic acids. Both the leaf extract tested negative for the presence of triterpinoids, while only the leaf extract of Rouvolfia Serpentina tested negative for the presence of cardiac glycosides. The phytochemical constituents of Rouvolfia Serpentina and Moringa Olifera are represented in the following table (Table 2).

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***Table 2**: Phytochemical constituents of Rouvolfia Serpentina and Moringa Olifera*

Sl. no.	Phytoconstituents	Rouvolfia Serpentina	Moringa Olifera
1.	Alkaloids	++	+
2.	Flavonoids	+	+
3.	Tannin	+	+
4.	phlobatannin	++	++
5.	Saponin	+	++
6.	Steroid	+	++
7.	Triterpinoid	-	-
8.	Cardiac Glycoside	-	++
9.	Organic acid	+	+
10.	Carbohydrate	+	+
11.	Protein	+	+

4. DISCUSSION

The result obtained in this study suggests that the selected plants leaves are source of many phytochemical compounds and bioactive constituents and these plants are proving to be an increasingly valuable reservoir of bioactive compounds of substantial medicinal merit. They are highly recommended for further quantitative analysis of phytochemicals present and their potentiality as therapeutic agent.

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Research Article

ANTHROPOMETRIC PROFILE OF DISTRICT LEVEL JUNIOR VOLLEYBALL PLAYERS IN COOCH BEHAR, WEST BENGAL

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A B S T R A C T

The purpose of this study was to analyse the anthropometric variables of volleyball players in Cooch Behar district and also to generate a regional reference standard. The analysed samples include 10 male and 9 female junior level volleyball players along with 11 male and 14 female sedentary controls. The height (P>0.05), body mass (P>0.001) and body fat % (P>0.001) were significantly varied between female sportspersons and their sedentary counterparts, though such differences were not found in the male subset. This investigation also exhibited the different anthropometric aspects to achieve better performance in the game. In a nut shell, the present data will serve as a regional anthropometric reference standard and will provide the first-hand impression on the body fat composition of the investigated population.

Keywords: *Anthropometry, Volleyball, Body fat %, Physical fitness, BMI, Koch Rajbongshi community*

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1. INTRODUCTION

The prerequisites of a successful sportsperson are the anthropometric features which improve with proper training schedule. The anthropometric parameters are the indicators of growth and it depends on gender, age, ethnicity, nutritional status [Fagard *et al*. 1991]. Physical exercise schedule and training regime of an athlete may alter the anthropometric measurements and improve the skill for achieving better performance.

Aerobic fitness, speed, strength are the basic requirements for a team sports like volleyball along with technical skill [Roque *et al*, 2001]. General endurance training helps to meet the excess oxygen need during the match by increasing heart rate. Several types of speed are

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required during the match, like technical speed, first-step quickness and transition quickness. Fundamental drills in the training schedule are accomplished for the need of basic speed skills [Roque *et al*, 2001]. These training regimes may influence the anthropometric parameters of the growing group of players. Therefore, evaluation of linear anthropometric parameters along with body composition intimates the major structural modules of body which are prerequisite in the game to attain excellence [McArdle *et al*, 1986].

Previous research showed the specific need of body composition and anthropometric profile in volleyball players. Major investigations in this field were conducted only in the developed countries like UK, Italy, and USA. In Indian context, standard data is still lacking on such parameters of volleyball players. Recently some information is gathered by a Maharastra-based research group [Taware et al, 2013]. But, only a single study was found on senior (20-24 years) male volleyball players of West Bengal [Bandyopadhyay, 2007], which indicate the poor research interest in this area. Though Cooch Behar district is a tribal belt of West Bengal, the District Sports Association (DSA), Cooch Behar gives ample facility for the improvement of the game. But paucity of anthropometric research in this field is one of the hindrances in the proper development of players in this region. Thus, the aim of this study is to evaluate the anthropometric measurements and body composition of district level junior volleyball players of Cooch Behar.

2. METHODS AND MATERIALS

The study was carried out at Netaji Indoor Stadium in District Sports Association (DSA), Cooch Behar and Community Hall, Old Post Office para, Cooch Behar after taking the ethical permission from DSA, Cooch Behar.

2.1.Subjects

Ten male and nine female junior (14-19 years) volleyball players from DSA, Cooch Behar were investigated in this study. The control group (10 male and 14 female) were selected randomly from the nearby locality keeping in mind that the persons are sedentary worker of same age group and not involved in any sort of endurance or fitness training. Volleyball players were selected on the basis of minimum one year continuous volleyball training and non-participation in any other sports. The consent was taken from all the subjects.

2.2. Procedure

Stature of the subjects was measured by the traditional anthropometric rods. Certain methodical rules were followed during the measurement to avoid technical variations:

- Subjects were asked to wear thin shocks during the measurements.
- Subjects stood on a flat surface which was at a right angle to the vertical wall.
- Weight of a subject was distributed evenly on both feet and the head was positioned in horizontal plane.

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- Subjects were asked to place the heels together and were also requested to touch both heels to the base of a vertical wall. The scapula and buttock were in contact with the vertical wall.
- The movable head stylus was brought onto the most superior point of the head with sufficient pressure to compress the hair.

The weight of the subjects was taken by analog weighing machine. As the subjects placed the heels together, their weight was distributed evenly on both feet.

The body fat % was measured by automated body fat monitor (Omron, Model No. HBF-306). This monitor measures the body fat percentage by bioelectrical impedance method. The body fat percentage were determined by following formula-

Body fat percentage= {Body fat mass (Kg) / Body weight (Kg)} x 100

The following specification was followed during the measurement:

- Subjects were asked to stand in erect position.
- The monitor was kept at the chest level with the both hands stretching outward.
- Palms of the subjects were completely dry and they were asked to grip the electrodes at proper places.

This body fat % monitor also determines the Body Mass Index (BMI). BMI were calculated by the following formula [Meltzer *et al*., 1988]:

BMI (Kg/m^2) = (Body mass in Kg)/ (Stature in Meters)^2

From the measured parameters a clear idea was obtained about the body composition and physics of the subjects.

2.3. Statistical analysis

Students' t-test analysis was used to interpret the difference in anthropometric parameters between trained and non-trained subjects as the investigated sample sizes were small and groups were distributed normally [Das *et al*., 2003]. Means and standard deviations were also calculated.

3. RESULTS

The anthropometric parameters are compared between sedentary females and female volleyball players of the same age groups. The mean of each parameter along with their standard deviation (SD) of the female sub-sets are summarized in Table 1. Data of male sub-set are presented in Table 2.

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Table 1: *Anthropometric parameters of sedentary females and female volleyball players*

Parameter	Category	Mean ± SD
Age (Years)	Sedentary Females	16.7 ± 4.1
	Female Volleyball Players	16.6 ± 1.5
Height (cm)	Sedentary Females	149.2 ± 4.9
	Female Volleyball Players	159.2 ± 4.5 *
Weight (Kg)	Sedentary Females	62.0 ± 6.9
	Female Volleyball Players	45.0 ± 5.0 **
Body Fat %	Sedentary Females	28.6 ± 3.5
	Female Volleyball Players	20.8 ± 3.4 **

**P>0.05, **P>0.001 (when compared by t-test)*

Table 2: *Anthropometric parameters of sedentary males and male volleyball players*

Parameter	Category	Mean ± SD
Age (Years)	Sedentary males	17.1 ± 2.7
	Male Volleyball Players	17.1 ± 2.1
Height (cm)	Sedentary males	165.5 ± 3.9
	Male Volleyball Players	166.9 ± 6.6
Weight (Kg)	Sedentary males	59.6 ± 8.5
	Male Volleyball Players	54.0 ± 9.9
Body Fat %	Sedentary males	19.0 ± 6.6
	Male Volleyball Players	16.9 ± 3.1

The results indicate that the stature of the female volleyball players were significantly ($P<0.05$) differ from the sedentary counterpart, whereas no significant difference in height was found in the male sub-set. The average body weight of sedentary girls were too much high than that of the trained players. Along with the body weight, the body fat percentage were differ significantly at $P<0.001$ level between the trained and non-trained female groups. These results were also reflected in the high BMI of the sedentary females (data not shown).The basic anthropometric parameters (height, weight and body fat %) are not significantly differ between the athletes and non-athletes males in this investigation.

4. DISCUSSION

In Indian scenario, the average height of 14-19 years girls ranges between 158cm to 163cm, whereas for the boys the range is from 163cm-176cm. The average height of sedentary males of the same age group in our data set falls within the range, but that of sedentary girls are lower than the standard Indian measures. In this study most of the subjects were from local Koch Rajbongshi Community and the ethnicity shows impact on genetic

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variation which may cause the phenotypic deviation. On the other hand, the mean stature of female volleyball players was significantly (P>0.05) varied from the sedentary counterparts. The long-term endurance training may help to achieve the extra height which is useful for attaining good jumping reach [Bandyopadhyay, 2007]. The taller stature is a favourable measure for the game. The physical variations of players are taken into account to set the playing position of them during the match. Generally the hitters, blockers and opposites are participated in blocking and spiking and they are comparatively taller than the setters and liberos, who are not involved in blocking and spiking activity [Gualdi-Russo *et al.,* 2001; Marques *et al.,* 2009; Sheppard *et al*., 2009; Fattahi *et al*., 2012]. In case of the male sub-set, the variations in height between the sedentary and volleyball players are not too much significant. Most of the teenage boys are involved in some kinds of pleasure games daily and the physical exercise during these games may affect the height positively and also help them to build their body.

The work-rate profile of a player during the game depends on the playing position which is highly correlated with the anthropometric parameters [Rienzi *et al.*, 2000]. The lower body mass of the volleyball players may be beneficial for them to attain good jumping height. In the present study, the female sportspersons were showed significantly lower (P>0.001) body weight than the sedentary counterpart. However, the average body weight of control and players of male subset is lower than the international standard, which is helpful to achieve the good jumping height easily [Duncan *et al.*, 2006; Gualdi-Russo *et al.*, 2001; Calbet *et al.*, 1999].

Body fat % is a major contributor of physical fitness and performance in the game like volleyball, where explosive strength of lower limbs is required for good jump height. The fat free mass is the important provider of power for the high intensity activity during the game [Mala *et al.*, 2015]. Only few studies were published regarding body composition variables of female volleyball players. In present study, the significant difference (P>0.001) in body fat % between players and sedentary females indicate that the build of sportspersons satisfy the prerequisite parameter for good performance. The fat % of male volleyball players at elite level should be within 6-15% [Wilmore *et al.*, 1999] and present data also accords with that proposal. This lower fat content is an advantage for better performance as it enhances the energy output and also the cardiovascular fitness [Bandyopadhyay *et al.*, 2003; Chatterjee *et al.*, 2005].

The results of present study intimated that the lower free fat mass along with higher stature among the female sportspersons provide a positive impact on their performance though the data of male sub-set requires further analysis. Extensive research is required to detect the impact of morphological characteristics on the specific positional enactment. Moreover, the present investigational data will serve as a regional reference standard for the anthropometric parameters of Cooch Behar district volleyball players, both male and female.

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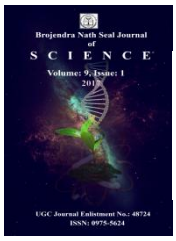

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Research Article

A CHECK LIST OF WILD TREES OF COOCH BEHAR, WEST BENGAL, INDIA

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A B S T R A C T

Cooch Behar is a district of West Bengal, India and is situated on its extreme north-eastern part. It is located in between 25°57′47″ N to 26°36′2″ N latitudes and 89°54′35″ E to 88°47′44″ E longitudes. It is a deforested area and its vegetation is similar with that of Duars, but plant diversity is not so rich. Most tree species in this area are exotic and planted for beautification. Wild plant species found in this region are under threat of increasing human population. In this floristic study, 58 species of tree, under 43 genera and 29 families are found to grow wild or semi-wild condition in this area. In this present work these plants are enumerated by their botanical names, common name(s) along with ecological status.

Key words: *Cooch Behar, ecological status, floristic study, semi-wild*

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1. INTRODUCTION

Cooch Behar is a District of West Bengal, India and situated on its extreme north-eastern part. It is located in between 25°57′47″ N to 26°36′2″ N latitudes and 89°54′35″ E to 88°47′44″ E longitudes. Total area of the district is 3387 square kilometers (http://coochbehar.gov.in/HTMfiles/CoB_inWB.html).

The District Cooch Behar is bounded in east with Kokrajhar and Dhubri Districts of Assam, on the west with Jalpaiguri District, on the north with Alipurduar and Jalpaiguri Districts of West Bengal and on the south with Rangpur District of Bangladesh.

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The District is a deforested area with floristic composition comparable to that of Duars, but not so rich in plant diversity. Most tree species in this area are exotic and planted for beautification. Wild plant species found in this region are under threat of increasing human population.

2. MATERIALS AND METHODS

The investigation on the trees of Cooch Behar is conducted during 2012-2016, on the seasonal basis following floristic, phenological and community studies through sampling method throughout the area. Trees of Euphorbiaceae *s. l.* of Cooch Behar district are studied before this work and 9 wild and planted trees of this family have been reported (De, 2016). Along with this field survey, study of herbarium specimens, Museum materials and literatures were also done in the same time period. Plant specimens were identified following available literatures (i. e. Haines, 1921-1925; Hooker, 1890; Mooney, 1948; Prain, 1903). Nomenclature of plant taxa has been verified from literature and available online (i. e. http://www.theplantlist.org/tpl/record/kew). Common names of plats are collected from field and also from various literatures and online (i. e. Haines, 1921-1925; Hooker, 1872-1897; Mooney, 1948; Prain, 1903).

57 wild or semi-wild tree species, under 42 genera and 29 families are found in this field study. Plant families are arranged according to the system of Cronquist (1981) with some necessary modification of nomenclature, and plant species are arranged according to Hooker, 1872-1897; by their botanical name with common synonym/s, common name(s), and ecological status and necessary notes if needed.

List of abbreviations: B – Bangla; E – English; R – Rajbansi; *s.l.* – *sensu lato*; Syn. – Synonym.

3. RESULT AND DISCUSSION

During the survey 57 wild or semi-wild tree species have been observed and recorded, under 42 genera and 29 families, in the Cooch Behar District. The detailed enumeration of the species is discussed below:

Annonaceae

1. *Polyalthia suberosa* (Roxb.) Thwaites Syn. *Uvaria suberosa* Roxb..
Common name: Barha chāli (B).
Not common.

Lauraceae

2. *Litsea glutinosa* (Lour.) Robinson Syn. *L. chinensis* Lam., *L. sebifera* Pers., *Sebifera glutinosa* Lour.
Common names: Kukurchitā, Ledā, Piplās (B); Indian laurel, Tallow laurel (E); Bijlighantā, Khārhājurhā (R).

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Not common.
3. *Litsea monopetala* (Roxb.) Pers. Syn. *L. polyantha* Juss.
Common name: Barha kukurchita, Sowālu (B).
Frequent, mostly planted for *mugā* cultivation.
4. *Machilus gamblei* King ex Hook. f. Syn. *Machilus bombycina* King ex Hook., *Persea bombycina* (King ex Hook. f.) Kosterm.
Common name: Som (B).
Frequent, mostly planted for *mugā* cultivation.

Ulmaceae

5. *Trema orientalis* (L.) Blume Syn. *Celtis orientalis* L.
Common names: Jiban (B); Indian charcoal tree, Indian nettle (E); Jigni, Jhikni (R).
Frquent.

Moraceae

6. *Streblus asper* Lour.
Common name: Sheorhā (B); Siamese rough bush (E).
Common, wild or planted for hedge.
7. *Artocarpus lakoocha* Roxb.
Common name: Dāwā (B); Monkey jack (E).
8. *Ficus benhgalensis* L.
Common name: Bat (B); Banyan tree (E).
Two forms are found : fruits red and fruits yellow (similar to that of *Ficus mysorensis* Heyne).
9. *Ficus rumphii* Blume.
Common names: Gāi ashwattha, Gayā ashwattha (B).
More frequent than *F. religiosa*.
10. *Ficus religiosa* L.
Common names: Ashwattha, Pipul (B); Peepul, Bo-tree (E).
11. *Ficus virens* Aiton
Common name: Pākurh (B); White fig (E).
Less frequent.
12. *Ficus hispida* L. *f.* Syn. *F. oppositifolia* Willd.
Common names: Dumur, Kāk dumur (B); Devil fig, Hairy fig, Opposite-leaved fig-tree, Rough-leaved fig (E); Khoskā (R).
13. *Ficus semicordata* Buch.-Ham. ex Sm. Syn. *F. conglomerata* Roxb., *F. cunia* Buch.-Ham. ex Roxb.
Common names: Drooping Fig (E).
Rare.
14. *Ficus racemosa* L. Syn. *F. glomerata* Roxb.
Common names: Jag dumur, Jagya dumur (B); Cluster fig, Wild fig (E).

Dilleniaceae

15. *Dillenia indica* L.
Common names: Chāltā (B); Elephant apple (E); Pānchkol, Pānchkhol (R).

Dipterocarpaceae

16. *Shorea robusta* Gaertn. *f.*

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Common name: Shāl (B); Sal (E).
Rare, and highly vulnerable.

Elaeocarpaceae

17. *Elaeocarpus ganitrus* Roxb. ex G.Don
Common names: Rudraksha (B).
Rare, may be planted but wild in neighboring districts.

Sterculiaceae

18. *Sterculia villosa* Roxb.
Common names: Odlā, Odāl (B); Elephant rope tree, Hairy sterculia (E).

Bombacaceae

19. *Bombax ceiba* L. Syn. *B. ceiba* Burm. f., *B. malabaricum* DC., Salmalia malabarica (DC.) Schott & Endl
Common name: Simul (B); Red silk-cotton tree, Silk-cotton tree (E).
Three forms are found: flowers red, mauve, and yellow.

Flacourtiaceae

20. *Flacourtia jangomas* (Lour.) Raeusch. Syn. *Flacourtia cataphracta* Roxb. ex Willd.
Common names: Pāniyāl, Pāniyālā (B); Coffe plum, Indian cherry, Indian plum (E).
Rare, and highly vulnerable.
21. *Flacourtia indica* (Burm. f.) Merr.
Common name: Baichi (B); Governor's plum, Madagascar plum (E).
Not Common.

Ebenaceae

22. *Diospyros racemosa* Roxb. Syn. *D. toposia* Buch.-Ham.
Common name: Tapsi (B).
Not Common.

Caesalpiniaceae

23. *Cassia fistula* L.
Common names: Bandarlathi (B); Indian laburnum (E); Barha henās (R).
24. *Tamarindus indica* L.
Common name: Tentul (B); Tamarind (E).

Myrtaceae

25. *Syzygium fruticosum* DC. Syn. *Eugenia fruticosa* (DC.) Roxb.
Common name: Khudi jām (B).
Frequent.
26. *Syzygium cumini* (L.) Skeels Syn. *Eugenia jambolana* Lam., *E. obtusifolia* Roxb.
Common names: Jām, Kālo jām (B); Black berry, Indian black berry, Black plum (E).
Less frequent.

Combretaceae

27. *Terminalia bellirica* (Gaertn.) Roxb.
Common names: Baherhā, Bayrhā (B); The beleric myrabolan (E).
Less frequent.
28. *Terminalia citrina* Roxb. ex Fleming
Common names: Haritaki, Harra, Hattuki (B).
29. *Terminalia arjuna* (Roxb. ex DC.) Wight & Arn.

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Common name: Arjun (B); White murdah, White winged myrabolan (E).
30. *Terminalia myriocarpa* Van Heurck & Müll.Arg.
Common names: Pānisāj (B); East Indian almond (E).
Less frequent.

Alangiaceae

31. *Alangium chinense* (Lour.) Harms Syn. *Marlea begoniifolia* Roxb. Frequent.

Phyllanthaceae (Euphorbiaceae *s.l.*)

32. *Phyllanthus acidus* (L.) Skeels Syn. *Cicca disticha* L., *C. acida* (L.) Merr.
Common name: Noarh (B); Star Gooseberry (E); Harhbarai (R).
Less frequent.
33. *Glochidion sphaerogynum* (Mull.Arg.) Kurz.
Less frequent.
34. *Bischofia javanica* Blume.
Common names: Kāinjal (B); Bishop wood (E).
Fequent and abundant.
35. *Baccaurea ramiflora* Lour. Syn. *B. sapida* (Roxb.) Müll.Arg., *Pierardia sapida* Roxb.
Common names: Latkā, Natko, Natkol, Notkol (B); Burmese grape (E).
Mostly planted.

Euphorbiaceae

36. *Mallotus nudiflorus* (L.) Kulju & Welzen Syn. *Trewia nudiflora* L.
Common name: Ban Gāmāri, Pituli (B); False white teak (E); Bhelli, Bheliyā, Petkurhā (R).
37. *Mallotus roxburghianus* Müll. Arg. Syn. *Rottlera peltata* Roxb.
Common name: Thoskā (B)
38. *Mallotus philippensis* (Lam.) Müll. Arg. Syn. *Rottlera tinctoria* Roxb.
Common name: Kamalāgunrhi (B). Kamala tree (E).

Rhamnaceae

39. *Ziziphus jujuba* Mill. Syn. *Z. mauritiana* Lam.
Common names: Barai, Kul (B).

Anacardiaceae

40. *Mangifera indica* L.
Common name: Ām (B); Mango (E).
41. *Lannea coromandelica* (Houtt.) Merr. Syn. *Odina wodier* Roxb.
Common name: Jeol (B); Jikā, Jigā, Jingā (B, R); Indian ash tree (E).
42. *Spondias pinnta* (L.*f*.) Kurz. Syn. *S. acuminata* Roxb.
Common name: Āmrhā (B); Hog-plum, Indian hog-plum, Wild mango, Bile tree (E).

Meliaceae

43. *Azadirachta indica* A.Juss. Syn. *Melia azadirachta* L.
Common name: Nim (B); Margosa tree, Neem, Indian lilac (E).
44. *Aphanamixis polystachya* (Wall.) R.Parker Syn. *Amoora rohituka* (Roxb.) Wight & Arn., *Andersonia rohituka* Roxb.
Common name: Lāli, Reshmi lāli (B).

Rutaceae

45. *Aegle marmelos* (L.) Corrêa. Syn. *Crateva marmelos* L.
Common name: Bel (B); Wood apple, Bengal quince (E).

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Araliaceae

46. *Heteropanax fragrans* (Roxb.) Seem. Syn. *Aralia fragrans* (Roxb.) G.Don., *Panax fragrans* Roxb.

Common name: Fragrant aralia (E).

Rare, and highly vulnerable.

Apocynaceae

47. *Alstonia scholaris* (L.) R.Br. Syn. *Echites scholaris* L.

Common names: Chāitan, Chhātim (B); Davil's tree, Dita bark tree (E).

48. *Holarrhena pubescens* (Buch.-Ham.) Wall. *ex* G. Don. Syn. *H. antidysenterica* (Roth) Wall. ex A.DC., *Echites antidysentericus* Roth

Common name: Kurchi, Kutrāj (B); Conessi bark, Easter tree, Ivory tree (E).

Boraginaceae (Ehretiaceae**)**

49. *Ehretia acuminata* R.Br. Syn. *E. serrata* Roxb.

Common name: Kāth guyā (B); Brown cedar, Koda tree (E).

Most frequent.

Verbenaceae

50. *Premna bengalensis* C.B.Clarke

Common names: Dholli, Douli (B).

51. *Premna mollissima* Roth Syn. *Premna latifolia* Roxb., *Premna mucronata* Roxb.

Common name: Ganiyari (B); Dusky fire-band teak (E).

Bignoniaceae

52. *Oroxylum indicum* (L.) Benth. ex Kurz Syn. *Bignonia indica* L.

Common name: Sonā, Shonā (B); Surimālā (R); Indian trumpet flower (E).

Most frequent.

Rubiaceae

53. *Neolamarckia cadamba* (Rox.) Bosser Syn. *Nauclea cadamba* Roxb.; *Anthocephalus cadamba* (Roxb.) Miq.

Common name: Kadam (B); Indian Amboina tree, Wild cinchona (E).

54. *Tetrameles nudiflora* R.Br.

Common name: Mayna (B); False hemp tree (E).

Not common.

Arecaceae

55. *Phoenix sylvestris* (L.) Roxb.

Common name: Khejur (B); Indian date palm (E).

Not common.

56. *Borassus flabellifer* L. Syn. *B. flabelliformis* L., *B. flabelliformis* Roxb.

Common name: Tāl (B); The Palmyra palm, Toddy palm (E).

Not common.

57. *Caryota urens* L.

Common names: Tālsupāri (B); Chā guyā, Chāu (B, R); Fishtail palm (E).

Frequent.

Pandanaceae

58. *Pandanus furcatus* Roxb. Syn. *P. nepalensis* H.St.John

Common name: Ban Ānāras (B).

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4. CONCLUSION

In this floristic study, 58 species of tree, under 43 genera and 29 families are found to grow wild or semi-wild condition in this area. Moraceae is the largest family containing 9 species, followed by Euphorbiaceae *s. l.* (Euphorbiaceae and Phyllanthaceae) containing 7 species. Table 1 depicted the number of species under each family. *Ficus* is the largest genus containing 7 species, followed by *Terminalia* and *Mallotus* containing 4 and 3 species respectively.

Table 1: *No. of species of each family*

Sl. No.	Family	No. of species	Sl. No.	Family	No. of species
1	Alangiaceae	1	16	Euphorbiaceae	3
2	Anacardiaceae	3	17	Flacourtiaceae	2
3	Annonaceae	1	18	Lauraceae	3
4	Apocynaceae	2	19	Meliaceae	2
5	Araliaceae	1	20	Moraceae	9
6	Arecaceae	3	21	Myrtaceae	2
7	Bignoniaceae	1	22	Pandanaceae	1
8	Bombacaceae	1	23	Phyllanthaceae	4
9	Boraginaceae	1	24	Rhamnaceae	1
10	Caesalpiniaceae	2	25	Rubiaceae	2
11	Combretaceae	4	26	Rutaceae	1
12	Dilleniaceae	1	27	Sterculiaceae	1
13	Dipterocarpaceae	1	28	Ulmaceae	1
14	Ebenaceae	1	29	Verbenaceae	2
15	Elaeocarpaceae	1			

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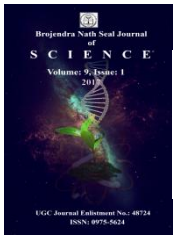

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Review Article

HIMALAYAN MAIDENHAIR FERN – AN OVERVIEW

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A B S T R A C T

The knowledge of the use of medicinal plants has been acquired through the centuries by observing the nature and such plants are still valuable for human health care programme. Himalayan maidenhair (*Adiantum venustum* D.Don; Family: Pteridaceae), popularly known as 'Hansraj' or 'Hanspad', employed as an ingredient in several Ayurvedic and Unani system of medicine. The species possesses immense therapeutic as well as other potential uses and frequently grown as a decorative plant because of its delicate fronds. An overview is conducted on *A. venustum* with an objective to provide information on the essential aspects for further exploration in human benefits.

Keywords: *Adiantum venustum, Pteridaceae, Pteridophyte, Ethnobotany*

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1. INTRODUCTION

Moving from ancient times to the present, humans have been dependent directly or indirectly upon the plants as an important source of food, medicines and for many other necessities. Over 60 % of all pharmaceuticals are plant based (Jain *et al.* 2007) and are increasingly substituting chemical and synthetic medicine (Heber 2004). As a group of plants, ferns have been used by different tribal communities and folklore for their livelihoods. Though a lot of studies focusing on the medicinal properties of plants, especially angiosperms, have been taken place, unfortunately limited amount of studies have been done to explore the medicinal potentialities of the ferns. The medicinal importances of ferns are mentioned as early as 300 B.C. by the Greek Philosopher Theophrastus (Corne 1924) and by

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his Indian contemporaries Sushrut and Charak. Among the medicinal plants mentioned in old Indian literature, two are definitely ferns, of which the drug called Hanspad or Hansraj, seems to be some species of *Adiantum*, and one of them is most probably *A. venustum* D.Don (Puri 1970). *A. venustum* (Family: Pteridaceae; english name: Himalayan maidenhair fern, evergreen maidenhair, hardy maidenhair; common name: hansraj, hanspadi, maiden hair fern, damtuli - Chauhan 1999), a deciduous fern with delicate foliage on black stalks, is one of such plant in folk medicine that has been used to cure various disease conditions. The species possesses many therapeutic as well as other unexplored potentials which need to be explored. With a view to it, an overview on *A. venustum* is conducted providing adequate information which may motivate the researchers for future exploration of the species in human benefits.

2. SYNONYMS

Adiantum venustum var. *wuliangense* Ching & Y.X.Lin, *A. venustum* var. *smithianum* C. Chr., *A. venustum* var. *venustum*, *A. venustum* var. *breviserratum* Ching (The Plant List 2013; Roskov *et al.* 2017).

3. DISTRIBUTION

The species is native to China and India and one of the commonest ferns of the Western Himalayas between 1500-3000 m. In India, it is found in Himachal Pradesh, Uttarakhand, West Bengal, Sikkim, Assam, Arunachal Pradesh and Meghalaya. It also occurs in Myanmar, Tibet, Pakistan, Nepal, Afghanistan, Bhutan, Canada, United Kingdom (Global Biodiversity Information Facility; website: http://www.gbif.org/species/7335278; Mehra 1964; Tiwari et al. 2013; Mir *et al.* 2015).

4. HABITAT AND PLANT DESCRIPTION

This species typically grows in moist shady humus rich but well-drained soils, rock crevices, forest slopes, water channels, nalahs, natural spring and village bawlies (Chauhan 1999; Burrell 2002). Rhizome: long-creeping, branching, scales dark brown; frond: deciduous, monomorphic, stipe dark purplish to nearly black in colour, grooved above, scaly at base, glabrous in upper portion; blade: 3-pinnate at the base, triangular, with a terminal pinna, membranaceous, glabrous; pinnae: 5 to 7 pair, lanceolate, anadromous in plan, alternate, lowest pair the longest; pinnules 4-5 pair, wedge-shaped, alternate, regularly toothed; margins fertile lobed, sterile toothed; veins free, forking; sori: sporangia sub-marginal with false indusium, inrolled margins, oblong at the ends of pinnules; sporangia stalked, 17-22 celled annulus, spores light brown (Mir *et al.* 2015).

5. PHYTOCHEMICAL CONSTITUENTS

3-filicene, adiantone, 21-hydroxy-adiantone (Zaman *et al.* 1966), kaempferol glucoside, quercetin-3-O-glucoside, leucopelargonidin (Rangaswami and Iyer 1967, Asolkar *et al.* 1992), adiantulanosterol, adiantulanostene (Chopra *et al.* 1997; Alam *et al.* 2000; Chopra *et al.* 2000; Chopra *et al.* 2001), α-carotene monoepoxide (Rangaswami and Iyer 1967), fern-9(11)-en-25-oic acid (Banerjee *et al.* 1991).

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6. TRADITIONAL USES AS FOLK MEDICINE

The species possesses immense medicinal value. It is one of such plants in folk medicine that has been used for the management of various disease conditions. Various part of the plant is used in different parts of the world by different local and tribal people. The fronds/ leaves are used as astringent, diuretic, expectorant, tonic and emetic (Vasudeva 1999; Sher *et al.* 2011; Haq 2012; Rashid 2012). The decoction of fronds is given in fever also used in the treatment of headaches and scorpion stings (Singh and Kachroo 1976; Chopra *et al.* 1986; Vasudeva 1999; Upreti *et al.* 2009; Kumari *et al.* 2011; Haq 2012). Powder of leaves with luck water twice a day is useful against Nephrolithiasis and largely used by the villagers of Pauri, Garhwal, Uttarakhand (Khajuria and Bisht 2017). Leaves along with pepper and honey are used to reduce fever and in catarrhal affections, respectively (Awan et al. 2011). A paste made from rhizomes is used to treat cuts and wounds (Samant *et al.* 1998; Manandhar 2002; Kholia and Punetha 2005; Haq 2012). The extract or decoction from the rhizome and leaves can be used to treat diabetes, liver problems, renal and gall bladder stone (Bisht and Khajuria 2014; Joseph and Thomas 2015). It was also observed from Ayurvedic literature and ethno-botanical studies that the plant is very useful in treating jaundice, nasal catarrh, chest infection, urinary problems, blood loss, bone weakness, hair loss, dandruff, headache, opthalmia, hydrophobia, fever and body muscular pains and chilblain (Kirtikar and Basu 1935; Natkarni 1976; Ambarta 1986; Mannan *et al.* 2008; Lone *et al.* 2015). The plant is also used in combination with other plant species as expectorant, hypothermic, diuretic and in stomach ache (Haq 2012).

7. ANTICANCER ACTIVITY

Viral *et al.* (2011) carried out preliminary phytochemical screening and anticancer evaluation of *A. venustum* against Ehrlich Ascites Carcinoma in Swiss albino mice. The ethanolic extract of the plant possesses significant anticancer and antioxidant activity due to the presence of terpenoids and flavonoids.

8. ANTI-INFLAMMATORY ACTIVITY

Hussain *et al.* (2008) showed analgesic and anti-inflammatory activity of the crude extract with a standard synthetic drug paracetamol (150 mg/kg) and Diclofenac sodium (10 mg/kg), respectively. A good analgesic activity was seen with (100 mg/kg crude extract) when compared with other dose levels (50 mg/kg). Anti-inflammatory study at two dose levels (tested in rats), exhibited significant anti-inflammatory activity with maximum percentage (71.15 %) of inhibition of inflammation recorded with 100 mg/kg of plant extract.

9. ANTIVIRAL ACTIVITY

Pandey and Bhargava (1980) reported that the leaf and fronds extract of the species inhibit the formation of local lesions effectively on *Chenopodium amaranticolor* by cucumber mosaic virus.

10. ANTIFUNGAL AND ANTIBACTERIAL ACTIVITIES

Singh *et al.* (2007) tested antimicrobial activity of the methanolic extract of four important species of *Adiantum* against five gram positive, six gram negative (including multiresistant

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Staphylococcus aureus) bacteria and eight fungal strains using standard microdilution assay and the maximum activity was exhibited by *A. venustum* among the four, and the activity could be related to considerable amount of phenolics. Tapwal *et al.* (2011) investigated *in vitro* antifungal activity of aqueous extract of *A. venustum* along with another pteridophyte *Polystichum squarrosum* and three weeds/ medicinal plants against *Alternaria solani*, *A. zinniae*, *Curvularia lunata*, *Rhizoctonia solani* and *Fusarium oxysporum* at different concentrations and the aqueous extract of *A. venustum* showed moderate to low inhibitory effect against all the pathogens and more efficient as compared to *Polystichum*.

11. CONCLUSION

A comprehensive overview on *A. venustum* is presented in the text with an objective of providing adequate references to present and future researchers for profitable utilization of the plant species, and human welfare from the natural habitat.

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Research Article

PHYSIOGRAPHICAL CHARACTERISTICS OF THE SIKKIM HIMALAYA ALONG WITH ITS CHANGING CONFIGURATION AND IDENTIFICATION OF GEOMORPHIC UNITS

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A B S T R A C T

The Sikkim Himalaya is a tiny but unique segment of the entire Himalayan system. The ridges and spurs lying in this segment mostly belong to the Great and Middle Himalayas with altitudes varying from two to eight thousand metres. The rugged mountains together with extremely dissected valleys of the tract exhibit their evolution through vigorous weathering and erosion processes in one hand. On the other hand faults and thrusts of different sizes along with cascades and terraces of different volumes (both of fluvial and glacial types) show structural instability of the region too. The neo-tectonic upliftments of the terrane have made the landscape much more attractive to the explorers as well as earth scientists. Hence the present paper is trying to attempt for identification of geomorphic units of the whole region (in a meso-level study) which must be a guide-base for the future researchers.

Keywords: *Thrust, Terrane, Strath, Tectonic disturbance, Terrain, Morpho-climatic region, Deglaciation, Glaciofluvial, Periglacial, Massif, Isostasy, Shastrugi, Sichelwannen, Thalweg.*

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1. LOCATION AND AREA

Sikkim is located to the north of West Bengal and is bounded by Nepal, Tibet (China) and Bhutan in its other sides. Administratively the state is divided into four districts – North, West, South and East Sikkim. All the districts are totally adorned with picturesque mountains and their associated ridges. In no part is found a plain except the narrow strips of terraces along the deep glens. The boundaries of the state are well demarcated by natural elements: west, north and east running along the watershed of the great Tista basin; whereas the south following the courses of the rivers Rammam-Baro Rangit and Rangpo-Rishi khola. The latitudinal extension of tract is 27° 01′N to 28° 08′N, while its longitudinal confinement lies

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in between 88° 01′E and 88° 55′E. Maximum length from north to south is 112 kilometres, while the same from west to east is only 84 kilometres. Total area of the region is 7096 square kilometres, though the surface area seems to be much larger on account of its wavy, extremely dissected topography netted with ridges and valleys of irregular shape and size. The highest point of the state is represented by the eastern part of North Kangchendzonga peak (8586 m). The elevation rapidly decreases towards south-east and descends below 400 metre contour at Melli - the southernmost point of the terrain.

2. STRUCTURAL BACKGROUND:

The beautiful landforms of the Sikkim Himalaya are resting upon such a geological structure which is one of the most complicated structures not only in the Himalayan Ranges but also in the world. In general the region comprises a series of thrusts the planes of which are inclined from north to south. The angle of the thrusts decreases also from north to south: more than 30° near Chomoyummo to less than 10° around Jorethang and Rangpo. The faults along the Tista valley divide the thrusted blocks into two main groups: in the west Jongsong-Kangchendzonga-Kabru-Singalila; and in the east Gurudongmar-Dongkiya-Chola Ranges. The blocks lying in the western part are more massive and elevated than those located in the eastern part.

The first map of geological characteristics of the Sikkim Himalaya, though in incomplete form, was prepared by W. S. Sherwill in 1854. In 1874, F. R. Mallet, a geologist of G. S. I., published a coloured map of the region with his report on mineral resources which are found locally. In 1878, the Tista valley was traversed by L. V. Loczy who described in details the thrusts and other types of faults found in that segment. Following his account, E. Suess, the Austrian expert on the Alpine structure, explained elaborately the nature of the strata in his famous book ‘Das Antlitz der Erde’ brought out during 1883-88. Here he first pointed out the ‘Nappe’ structure of the Singalila and Dongkiya Ranges. Advancement of the concept regarding Nappism of the Ranges lying in south-west and south-eastern sections of Sikkim as well as the high thrusting in the northern mountains went on by the explorers of the 20th century. F. Smythe and E. E. Shipton identified the fossiliferrous rock beds in the Jongsong peak during their expedition in 1930. The nature of thrusts enclosing the Great Himalaya extending from Kangchendzonga to Pauhunri was clearly described by S.S. Roy in early 1980’s. Recently, especially during the last three decades, many Indian geologists along with the scholars from different Universities studied the region in detailed. They unveiled almost all the complicacies in the structure of the mountains and valleys through their micro-level studies and explained them much more scientifically.

Although the width of the entire Himalayan mountain chain is the narrowest in Sikkim-Darjiling region, the pair of Main Central Thrusts can easily be identified here: the first one running along the southern precipices of Kabru-Simvo-Siniolchu-Gurudongmar mountains, and the second running below the straths of the rivers Rammam-Baro Rangit and Rangpo. The Ranges lying in between these two great thrusts may be grouped as the part of the Middle Himalaya. The Lesser Himalaya is exclusively located in the south of the southern Main Central Thrust and comprises the ridges of Darjiling district, West Bengal. The Great

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Himalaya masters up the loftiest parts of the system and includes all the mountains lying to the north of the northern Main Central Thrust. Almost all portions of the Middle and Great Himalayas are composed either of Archaean gneiss and schists or of felsic igneous rocks originated in Upper Tertiary period except the extreme southern belt where some sedimentary facies, though very much squeezed and partly metamorphosed, seem to be exposed by prolonged denudation.

The Northern Boundary Fault marks the northern limit of the Great Himalaya. It continues from the Nepal gap in the west to Chholamu lake area in the north-east. Two main headstreams of the river Tista, the Lhonak chhu and Lachen chhu have set up their valleys along this Fault. The mountains lying beyond the Fault may be grouped into the Trans-Himalayan Range. Jongsong and Chomoyummo mountains are two important units of this system. They are composed of fossiliferous sedimentary rocks showing from Lower to Upper Tertiary formations.

3. EVOLUTION OF LANDFORMS:

The evolution of landforms in the Sikkim Himalaya is controlled strongly by the local tectonic movements as well as past and present climatic conditions prevailing over the tract. Since the mountains are located on the colliding plate margin (Indian–Tibetan plates) and are rising rapidly (10 to 12 mm per year) they are very fragile in nature. Moreover the terrain is influenced heavily by the oscillating winds in different seasons. In fact the region experiences the chill effects of the North-Eastern Trade blowing from the Tibetan Highland from October to May, while it bears the moist attack of the South-West Monsoon from June to September. Total amount of precipitation caused by these two winds is much more than any other part of the Middle or Great Himalayas. Thus the denudation processes are also vigorous over the mountains. According to Strakhov's categorization of morpho-climatic region the land belongs to 'Ta' zone. Characteristically the tract is very much rugged and the landforms produced here are changing quickly. The variation in denudation processes and their intensities have been increased during the Holocene epoch, especially after the deglaciation of the Pleistocene ice sheets spread over the mountains. As a consequence the rates of slope retreat across the mountain faces and the valley deepening in between have enhanced enormously in the last few millenniums.

Until 4000 years before present the entire region was covered with the last phase of Pleistocene ice sheets showing little or no sculpturing over its landforms. The sheets began to retreat thereafter and, astonishingly with rapid pace, leaving some major and numerous minor glaciers. The latter ones retreated in the last millennium - the snouts of the major glaciers rose above 5000 metres in the eighteen century while the minor ice-flows became extinct. At present the summit sections of the lofty mountains situated above 6000 m are only covered with permanent ice caps. Maximum portions of the terrain are now exposed either for glaciofluvial or fluvial processes. A little belt lying in between the Great and Trans Himalayas, especially along the upper sections of the Lhonak and Lachen chhu, show some effects of aeolian process. While the extreme south- eastern part, along the gentler slopes of the Chola Range, exhibits some accumulations of periglacial deposit.

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4. REGIONAL CONTRAST IN GEOMORPHOLOGICAL FEATURES:

The geomorphology of the Sikkim Himalaya was observed and described part by part by many explorers in the 19th and 20th centuries. In 1848-49 J. D. Hooker, the famous naturalist, traversed large part of western and northern sectors and presented a vivid account of landform characteristics of the districts. J. C. White examined the local physiography in more detail through his journeys across the Ranges of the entire state during his prolonged service-period as the British Political agent in Sikkim (1887-1908). He is the first person who surveyed and marked the northern limit of the Tista basin. The magnificent landscapes of the massif Kangchendzonga and its surrounding mountains were further analysed by D. W. Freshfield during an expedition of an enthusiastic team led by him in 1899. His book 'Round Kangchenjunga', well illustrated with many maps and photographs, provides valuable information of the region regarding differentiated terrain as well as condition of glacial fields during that time. In 1950's M. K. Bandyopadhyay, an eminent Indian geomorphologist observed the landforms of North Sikkim. He explained them first in the view of geomorphological science. In late 1970's S. C. Mukhopadhyay studied the Tista basin as a whole and published his research-works in an encyclopaedic book 'The Tista Basin'. Since 1980's many other Indian geomorphologists have been selecting different parts of the tract for their researches. Their theses elucidate more the alteration of physiographical constituents of the areas in relation to recent environmental changes. The local expedition-teams also give us valuable information on changing nature of the surface configuration lying in high altitudinal segments.

In respect of altitude, shape and size the landforms in the region show spectacular but perplexed figures sometimes varying within a very short distance. Like other parts of the Himalayan mountain system the chain of the Great Himalaya of this state rises high enough to its neighbouring ridges. The massif of Kangchendzonga peaks stands at its westernmost point but shares a heavy isostasy being deep rooted (about 80 km) with extensive base (over 100 sq. km) composed of compact granite-gneissic rocks. Sedimentary formation is found over 8000m with a negligible slice (250 m) of yellow sandstone. Three out of five peaks, North (the highest, 8586 m, as stated earlier), Central (8482 m) and South (8494 m) stand along the international boundary between Nepal and Sikkim. Other two, North-western peak, also known as Yalung Kang (8505 m) and the most western one Kangbachen (7903 m), are exclusively located in Nepal territory. The great North Kangchendzonga peak is saluted by a series of mountains each of which has a stupendous mass though seem to be humble in size on account of their nearby king. From close to distant location from the king running towards north the peaks of these mountains are Twin (7117 m), Tent (7343 m), Pyramid or Phatibara (7123 m) and Lango (6920 m). Some famous glaciers are found at their eastern face, e.g. Zemu at North and Central Khangchendzonga, Green lake glacier at Twin, and Lhonak at Lango. All of the glaciers have been retreating rapidly for the last two centuries.

From central part of Kangchendzonga stretches another line of Generals standing across a high jagged Range with varying width of 5 to 15 km. They are relatively slender in size but much magnificent in shape. From west to east (slightly swinging north-easterly) they are Simvo (6812 m), Siniolchu (6888 m), Lama Anden (6116 m), Kangchengyao (6889 m),

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Gurudongmar (6715 m) and Pauhunri (7125 m). All of them are ice-covered though the volume of their glaciers is less than that of the northern mountains. The Cervino-type peak Siniolchu represents the maximum gradient along its free-faces (more than 75°) and is said by the explorers 'the gracest mountain in the world'. After Lama Anden the Range has been shifted northward by a Transverse Fault through which passes the Lachen chhu. The stream is the main source of the mighty river Tista and is originated from the glacier Kang tse lying at northern face of Pauhunri. The valley of the stream is wide and shallow with very slender thalweg in its upper section situated over a thick moraine-belt, but becomes narrow and deep, rocky gorge just entering into the aforesaid Fault. From Kangchengyao a klippen type ridge, Tsen-gui Kang, extends southward for about 40 km parallel to that Fault. Its altitude reaches maximum at the spire Chombu (6362 m) and terminates abruptly at Chungthang (1790 m) - the confluence point of the torrents Lachen chhu and Lachung chhu, and the starting point of the river Tista.

In front of the southern precipice of South Kangchendzonga peak a large brigade of mountains are standing from south-south- west to south- south-east. They are badly dissected by vigorous attacks of sub-aerial erosional activities. In Sikkimese territory the main guards are Talung (6529 m), Kabru group (North peak -7338 m), Rathong (6678 m), Koktang (6147 m) and Pandim (6691 m). The glaciers lying at their bases are small in volume and flow down enough below the permanent snow-line (occasionally reaching 4200 m). Except Talung, all of them lie at the head of the river Baro Rangit which is the main right hand tributary of the river Tista. There are many conjectures regarding its age and valley formation. According to recent geological explorations along with geomorphological observations it may be concluded that the river originated sometime in between the last two Pleistocene ice ages and initially was a sluggish subsequent stream of the river Rammam (west of Jorethang lies the confluence point of the two). The latter is much older in age (Oligocene), directed by the lineation of Main Central Thrust and was a larger tributary of the Tista in many interglacial times. The glaciers situated over the south-eastern slopes of Talung and South Kangchendzonga, however, follow a common easterly direction –another example of a structurally controlled valley but bedded over higher altitudes. Residuals of glacial terraces along the valley indicate the elevation of the former glacial valleys developed in different phases of the Pleistocene glaciation. The river Talung chhu carving this valley joins the Tista near Mongan, the headquarters of North Sikkim district. The water-parting between the Talung chhu and Baro Rangit is represented by a series of high ridges crowned with some lofty crags the altitudes of which vary from 5500 m to 5800 m. Narsing peak (5840 m) is the highest amongst them revealing a mass resistant to erosion because of its pure gneissic structure with complex tight folds.

The western side of the Baro Rangit basin is bounded by the Singalila Range – a spectacular nappe uprooted from the Kangchendzonga-Ratong-Kabru mountain group. It stretches from Kang peak (5580 m) for about 40 km and crosses the southern Main Central Thrust to the south of Melido or Singalila peak (3685 m). Due to its fragile structure the summit line is very much undulating: the sharp rock pinnacles are projected at the end of synclinorium while round headed crags are situated on its stable central portion. Sub-aerial erosion has

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obviously been increasing the ruggedness of crest-line since the retreat of Pleistocene ice-covers.

From Pauhunri emanates a large thrust, Dongkiya Range which strides southward for about 50 km. It is separated from Tsen-gui kang by a fracturing belt of the Lachung chhu valley and leans over the Chola Range just north of Cho la (4435 m). The altitude of this Range decreases from 6500 m in the north to 4400 m at its southern end. No permanent glacier is present along its central and southern parts, though huge amount of snowfall occurs during the prolonged cool period: from late September to June. Consequently glaciofluvial landforms such as proglacial channels with sandur valleys and kame terraces are very much common in the region. The stream Rate chhu originates near Cho la which makes the boundary between North and East Sikkim, and ultimately plunges into the river Tista near Dikchu. The Range Chola extends further south for 20 km along the eastern boundary of East Sikkim and acts as the water-divide between Rangpo-De chhu valleys lying in the district and Ammo chhu in Tibet. Nathu La (4310 m) and Jelep La (4270 m) are two famous passes across this Range. Rangpo with its numerous tributaries drains more than half of the East district and joins the Tista near Rangpo town - the main gateway of the state Sikkim. On the contrary, the De chhu excavates a narrow valley in south-eastern portion of the area, cuts deeply the last tip of Chola Range and ultimately flows southward through a glen to mark the boundary between Darjiling district and Bhutan. After meeting its left bank tributary, the Ne chhu, the river is renamed as Jaldhaka.

The mountains along the northern boundary of Sikkim and beyond Chorten Nyima La (5685 m) belong to Trans Himalayan system. Jongsong (7462 m) peak is the highest among them. All of them including the subdued ridges on the north of the upper Lachen valley are carved both by glacier and wind resulting round-headed, grooved and fragile landforms partly due to soft sedimentary structure but mostly by the effects of arctic to sub-arctic climates prevailed over the section. The permanent ice-cover (shastrugi-like icy coverage) over the upper Lhonak valley has diminished during the last hundred years. It is now characterised by different types of friction cracks and sichelwannens. Chomoyummo (6829 m) is the second highest in the northern mountain belt whose projected mass Chuma kang ridge compels the Lhonak chhu to flow south-easterly direction before plunging down into the Lachen chhu (just north of Lachen town).

Regular tectonic disturbance as well as intensive glacial action causes numerous excavations in the surface topography of the state. Most of them represent enchanting lakes (more than tens of hectare in areas) – fed either by glacier or by rains. Gurudongmar (5200 m) and Chholamu (5100 m) are two such glacier-fed lakes lying at the head of the Lachen Chhu valley. Their depths are decreasing constantly by the depositional work of the southlying glaciers. Green lake (4600 m), at the confluence of the snouts of Zemu and Green lake glacier, has been transformed recently into a boulder-strewn bog for the same reason. There are many tarns at the base of Chola Range amongst which Tsomgo (3800 m) and Kupup (4000 m) are frequently visited by the tourists. The first one is at the head of the Lungze Chhu and is in very distressed condition in effect of increasing anthropogenic activities. The second is the main source of the De chhu showing relatively better environs. Human

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construction is absent here till now most probably for its harsh climatic condition. A number of medium sized tarns are found in the upper portion of the Baro Rangit valley. These are located in different altitudes – from 1700 m to 5000 m. Most of these are inaccessible to general tourists and, hence, are free from human interferences. The lakes will, however, be filled up slowly by natural processes of mass-wasting from the surrounding mountains and deposition of those borne materials under the lake water.

5. GEOMORPHIC UNITS

Geomorphic Unit	Litho-stratigraphical characteristics	Landform variation
1. Summit section of the Great and Trans- Himalayas (above 6000m).	1.Gigantic thrusts mainly composed of Archaean gneiss and schists in Great Himalaya with thin layer of limestone over 8000 m on Kangchendzonga massif; closed folds occurring in Trans- Himalaya having fossiliferous sedimentary formations of Tertiary period.	1. Highly rugged summits permanently covered with ice and glaciers; cirques with high, steep headwall, jagged arêtes, and medium to long glacial terraces generally adorned with ice cornices and seracs (absent in eastern part).
2. Upper part of the Lhonak basin	2. Series of small to medium Transverse faults offsetting the Northern Boundary Fault; surface rocks are Archaean gneiss, milonite and schists with intrusions of pegmatite of later ages; limestone, flagstone and other Tertiary sedimentary rocks found along northern ridges.	2. Wide glacial valleys with hanging ones on both sides of the trunk streams, bedrocks are marked by rock pedestals, friction cracks and sichelwannens.
3.Upper part of the Lachen chhu valley	3. Northern Boundary Fault is concealed beneath the thick layer of Pleistocene till deposits; northern subdued ridges are composed of fossiliferous shale, sandstone and greywacke; black limestone noticed on eastern hill slopes.	3. Shallow and thin thalweg rolling down through a wide glacial valley of the last Ice ages flanked with high trains of lateral moraines; scattered erratic boulders over smooth layer of ground moraines; all features are being modified by strong wind action.
4.Tsen-gui kang ridge	4. Extended thrust	4. Badly weathered ridge

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including the gorge of lower Lachen chhu	composed of Archaean gneiss and schists showing crumpling and fracturing cross-sections; often found granitized rocks; mineralization of rocks with high concentration of feldspathoids.	festooned with rock streams and debris flows; narrow V-shaped valley flanked with frost-shattered rock debris; in-valley section sometimes clogged with drumline-type mounds of tills.
5. Lower Lhonak basin with Zemu valley	5. Deeply faulted area; rock benches high above the valleys are very common which are the result of neo-tectonic upliftments.	5. Summit section of the water divides is featured by frost- shattered rocks; ridge slopes show striations caused by paleo-glacial abrasion; lower valleys are skirted with kame terraces though discontinuous due to vigorous attack of sub-aerial erosion.
6. The Lachung basin	6. Series of small faults and ruptures in Archean bedrocks; Hot springs are present at short distances.	6. Wide 'U'-shaped valley borne with palaeo-glacial landforms like broken cirques, curtailed arêtes and shortened rock pinnacles; deep ravines in upper part but shallow meandering valleys in lower part with slender pro-glacial channels.
7. Dongkiya and North Chola Range	7. Massive thrusts with Archean gneiss and schists; often exposed milonite, migmatite and other types of metamorphic rocks of Late Proterozoic to Cainozoic eras in deep valleys; intrusion of granite, pegmatite and syenite is found in axial part.	7. Badly weathered crests with highly dissected slopes due to the down-cutting action of innumerable rivulets; kame terraces along valley sides; erratic boulders at the valley-bottoms.
8. South Chola Range with De chhu basin	8. Low-angled thrusts composed of Archean gneiss with intrusions of granitoid,	8. Rounded crest-line with occasional sharp pinnacles; hill-slopes and valley-floors

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	grano-diorite and peridotite at the fault planes.	are adorned with patterned rocks caused by periglacial action.
9. The Tista basin including Rongni chhu and Rangpo valleys	9. A deep Transverse fault acts as the link of the Main Central Thrusts; minor faults offsetting the former; complicated plunging folds along the west-lying water divide; inverted strata of Palaeozoic Era (phyllite, schists) to late Tertiary period (sandstone, conglomerate etc.) are exposed in lower valley sections.	9. Multi-terraced valleys formed by neo-tectonic movements; wide meandering channels guided by interlocking spurs; hill slopes are receding rapidly due to differential denudation processes. Wider valley-floor of the Tista with huge bed-load deposition after crossing 450 m contour.
10. The basin of Talung chhu	10. Northern Main Central Thrust running below the valley of the Trunk stream; minor faults guide the tributaries; hornblende-gneiss, syenite and coarse granite occur in the valley-walls.	10. Structurally controlled rectangular pattern of drainage system headed with cirques; narrow deep stream-valleys skirted with gently sloping glacial terraces; shifting tendency of the Trunk valley towards south resulting asymmetrical profiles throughout the length.
11. Singalila Range	11. Typical nappe started from Northern Main Central Thrust, broken at places by parallel Transverse faults; partly metamorphosed quartzites and other Permian –Carboniferous rocks are overlain by Archaean granite-gneissic structure.	11. Badly weathered summit section with a series of rock pinnacles; projected spurs are truncated by the lateral erosion of the river Baro Rangit and its preceding glaciers.
12. The basin of Baro Rangit	12.Complicated net of faults (medium to small scales) in Archean strata; younger series are exposed at the valley bottoms and around	12. Ideal dendritic pattern of drainage system developed with innumerable rivulets and springs; incised meandering course found in

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	Namchi area; hot springs are found at the convergent plane of faults (little north of Jorethang), garnet and calcite are abundant in granites; augen-gneiss found in upper layer of the strata.	the main valley with picturesque depositional features at its base.

6. CONCLUDING REMARKS:

Although the region under study provides many examples of past glacial covers all over the tract fluvial processes are dominant at present. The river valleys are widening with continuous receding of cascades and terraces. The evolution of landform is, however, interrupted frequently by neo-tectonic movements. Rupturing in rock strata, creation or collapse of caves, springs (hot and normal), retreat of hill slopes, sharpening of water divides, avalanches (rock and snow), and frequent change in stream thalwegs are common phenomena found in every part of the terrain. The effect of Global warming is diminishing the glaciers over the mountain tops (especially between 5500 m and 6000 m elevations) as well as the periglacial features in De chhu basin. In short, the Sikkim Himalaya is an ideal example having a large variety of geomorphic settings across the entire Himalayan system.

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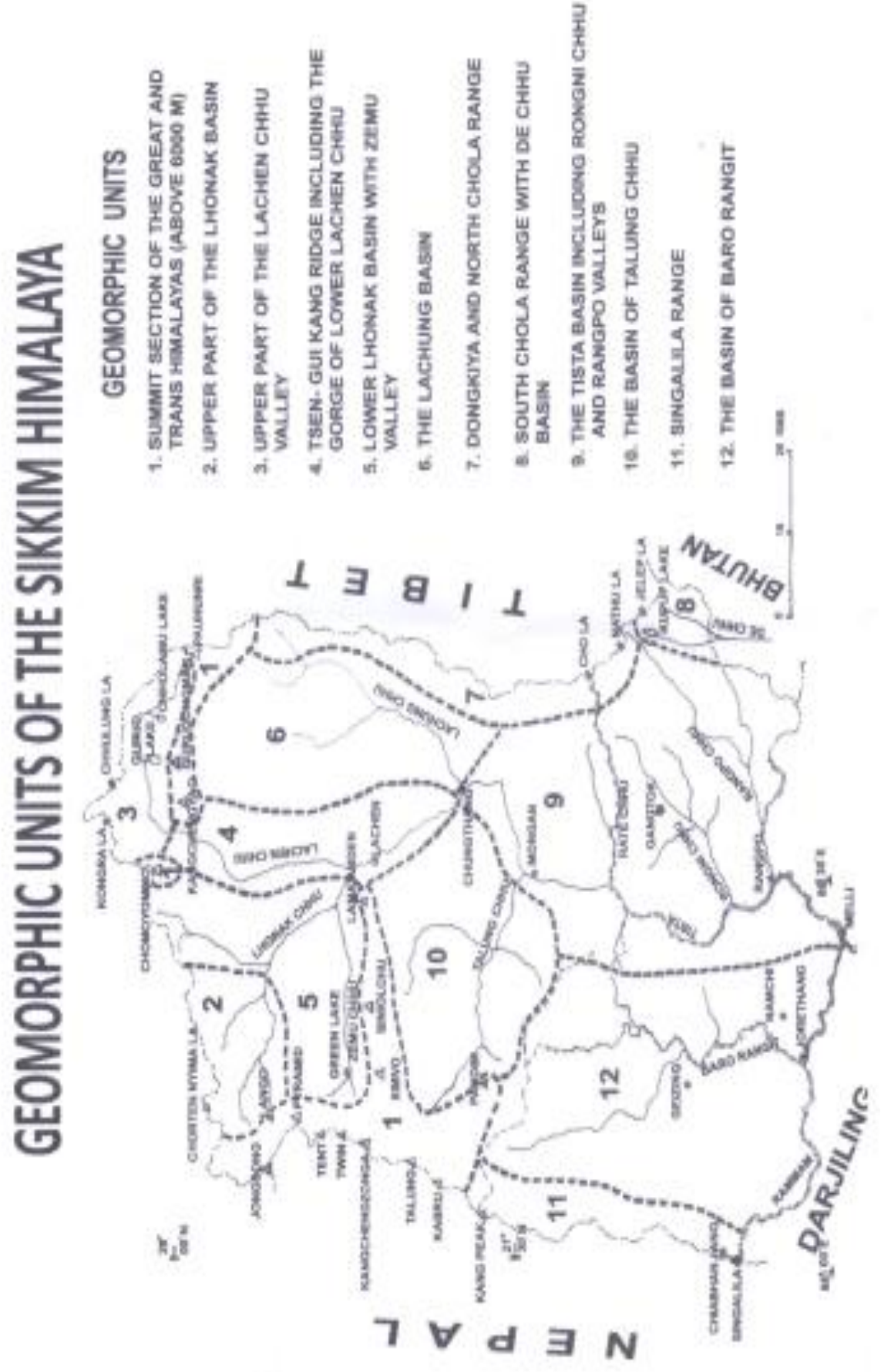

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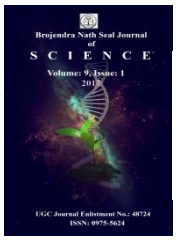

Brojendra Nath Seal Journal of SCIENCE

Research Article

MEASUREMENTS OF TOURIST ATTRACTIVENESS USING PROBABILISTIC TOURISM MODEL: A CASE STUDY ON MANALI

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A B S T R A C T

Models are prepared to understand the complex interrelation among different attributes in nature. Mathematical models use variables, parameters and equations to represent these highly complex relations. Probabilistic travel models aim to understand the complex tourists' behavior towards the tourist spots based on their attractiveness and identify the factors contributing decision making of the tourists. Manali is a famous hill station located in Himachal Pradesh in lap of the Himalayas. It is one of India's busiest travel destinations where people come to visit from every corner of the world. There're many a places to which one day trip can be organized by staying in Manali. These particular tourist spots and their attractiveness have been aimed to be identified in this paper by means of Probabilistic Tourism Model.

Keywords: *Tourist attractiveness, Tourism Attitude, Probabilistic Tourism Model*

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1. INTRODUCTION

The word 'tourism' was first used in 1811 and it has come from the word 'tour'. Tourism has been defined as "the temporary, short term movement of people to destinations outside the places where they normally live and work and their activities during the stay at each destination. It includes movements for all purposes" (Tourism Society of England). In 1994, United Nations (UN) identified three forms of tourism- a>Domestic (residents of the country travelling within), b> Inbound (non-residents travelling in a given country), c> Outbound (residents of one country travelling to another country).

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With the spurt of tourism in last few decades there has been phenomenal growth in tourism research. Within the period 1960-2002, 420 number of studies related to the topic of tourism were published (Li et al, 2005). Being one of the important topics in tourism research, tourism demand modeling and forecasting has attracted much attention. Within the year 2002-2006, there have been 119 publications based on tourist demand forecasting studies (Li and Song, 2007). The methods used in these studies can broadly be divided in two categories- quantitative and qualitative. Tourist arrival variable has been the most popular measure of tourist demand over the past few years. The quantitative measures followed non causal time series models and causal econometric approaches. Time series techniques have mostly been used to model the demand of tourism. Econometric models, on the other hand, analyze the causal relationship between tourist demand and its influencing factors. But they fell a little short of suggesting targeted measures to promote tourism in individual tourist attractions in a tourism destination. A little different from both of these approaches, probabilistic tourism model try to calculate the attractiveness of the tourist spots, how it is influenced by the related variables and how it influences tourism development plans in a region.

Manali, a small town in Himachal Pradesh, located at an altitude of 2050 m. in the picturesque valley of river Beas is one of India's most favoured travel destinations. Lofty mountain peaks, bubbling rivers, greeneries everywhere make Manali a paradise of nature where colonial heritage meets ancient tribal culture. There are many a places to visit within the town and away from it, making it a favourite holiday destination among tourists all over the world. In this study, an attempt has been made to perceive the travel preferences of the tourists in and around the town of Manali.

2. STUDY AREA

Himachal Pradesh is a state in Northern India and was anciently known as 'Dev Bhoomi' (the abode of gods). The literal meaning of Himachal Pradesh is 'Region of Snowy Mountains' and the state mostly lies in the middle of Dhauladhar Range of the Great Himalayas. While a large part of the state experiences prolonged winter snowfall, some other stretches deal with cold desert climate. The state is drained by the Chenab, the Ravi, the Beas, the Sutlej and the Yamuna. 66.52% of the state is covered by forest areas (Forest Survey of India, 2003). Such a kind of natural bliss coupled with ancient cultural traits and colonial heritage have made Himachal Pradesh one of the topmost tourist destinations in India. The popular tourist destinations in the state are- Shimla, Kullu Valley, Manali, Dharamsala, Dalhousie, Chamba, Lahaul and Spiti Valley etc.

Among these, Manali located at an altitude of 2050 m. in the Kullu District of Himachal Pradesh has been selected as the study area in this paper. Surrounded by the Himalaya and Zanskar mountain ranges bounded by the majestic Beas and Manal Su rivers; Manali is a hill town covered by ample natural vegetation dotted with fruit orchards. The place gets its name from the ancient saint of Hindu texts, 'Manu' who is said to have engendered the modern world after a catastrophic event destroying the old world order. Those texts say that Manu started the process of recreation from this place in lap of the Himalayas and hence the name 'Manali'. The place is also associated with 'Devi Hadimba' and her son 'Ghatothkach' from

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the epic of 'Mahabharat'. With such kind of myths and local tribal culture, Manali also has a colonial heritage.

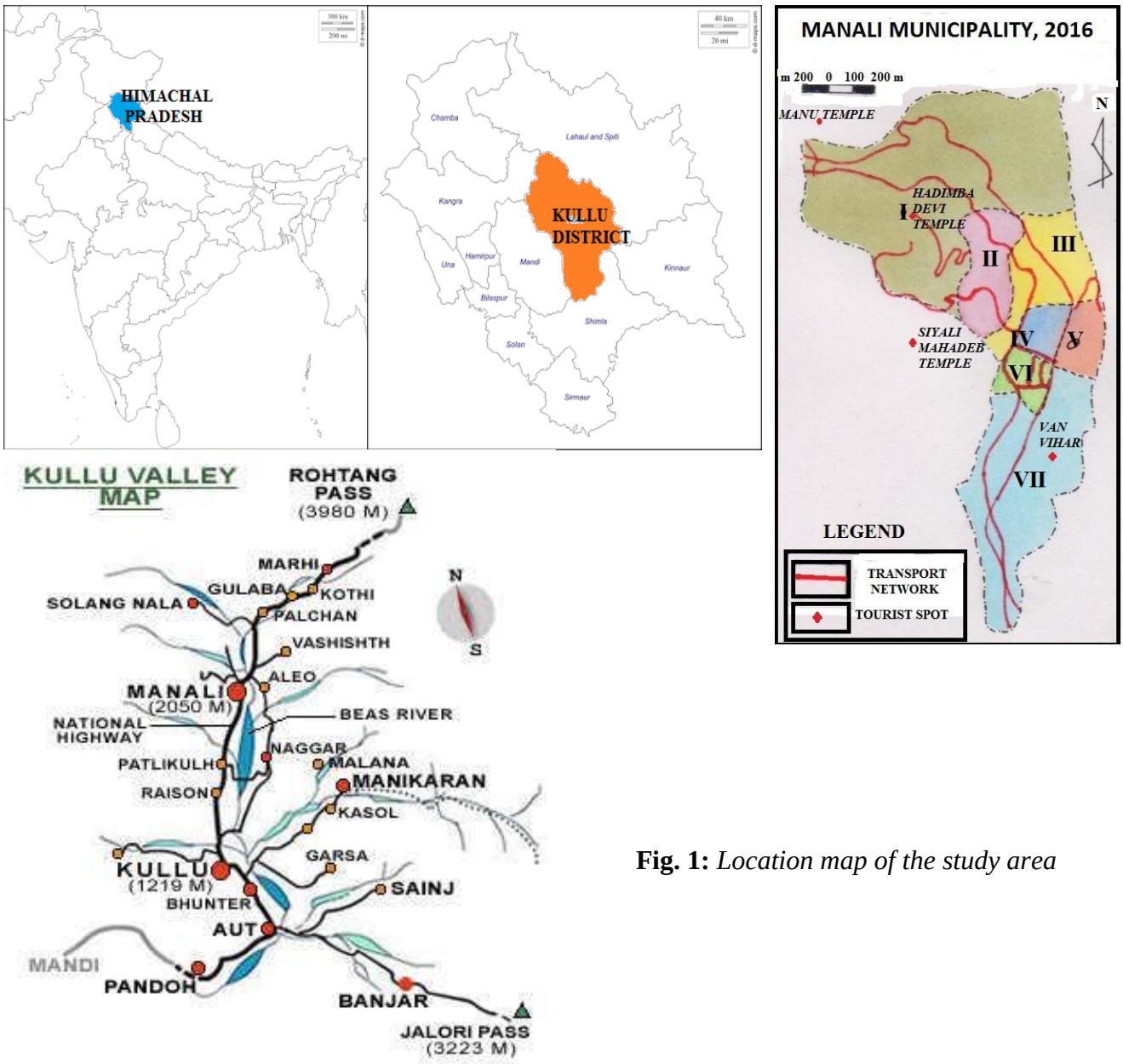

Fig. 1: *Location map of the study area*

In the British period, the town developed as a summer gateway of the governors, officials and the Maharajas of the princely states. To match with the global standards, some private initiatives have recently been taken to utilize the natural terrain to develop adventure tourism. All these factors have led to the growth of different kinds of tourist spots in and around the town of Manali. Some tourists stay in Manali for 3-4 days, visit those places and return back, while others use Manali as a halt and prepare for journey to Leh and Ladakh in Jammu & Kashmir. These have attracted increasing number of domestic and foreign tourists in Manali, from 21,14,584 in 2008 to 34,23,931 in 2015 (Fig. 2). Manali is well connected by roads with Delhi, Shimla, Chandigarh, Dehradun etc. Nearest convenient railheads are Kalka, Chandigarh and Pathankot; while nearest airport, Bhunter is some 50 km away from Manali.

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The tourist spots in and around Manali that can be visited in a day's trip are listed below in Table 1.

Table 1: *Classification of tourist attractions of Manali and its surroundings*

Natural Sight Seeing	Religious and Cultural	Recreational
1.Van Bihar 2.Rahala Waterfalls 3.Rohtang Pass 4.Kais Wildlife Sanctuary 5.Jana Waterfalls 6.Nehru Kund 7.Kasol Valley	1.Hadimba Temple 2.Siyali Mahadeb Temple 3.Vashistha Temple and Hot spring 4.Tibetan Monastery 5.Manu Temple 6.Naggar Castle 7.Jagatsukh Temple 8.Manikaran Temple and Hot spring	1.Marhi 2.Kullu Town 3.Rafting Point in the Beas 4.Himalaya Fish Farm 5.Solang Valley 6.Gulaba Camp

3. OBJECTIVES

The following objectives have been set for the study-

1. To assess the tourism infrastructure in Manali Town.
2. To find out tourists' interest to visit a particular spot and their perception regarding it.
3. To develop Probabilistic Tourism Model based on the physical distance of different tourist spots from Manali and the perception of the tourists.

4. Methodology: Sample Design, Data Collection and adoption of Statistical Techniques

The study is based on primary survey and it has been supplemented by secondary information wherever required. A questionnaire survey was conducted among local people, tour operators, hotels and both domestic and foreign tourists during September, 2016. From this survey, 21 most favoured tourist spots have been identified to which they visit while staying at Manali.

Table 2: *Sample Size of the Study*

Place	Local people	Hotels/ Resorts	Tourists		Tour and Travel Operators
			Domestic	Foreign	
Manali	371	83	128	45	4

Source: primary data

The proportion of tourists, out of every 10, visiting each place and how they rate an individual place, from Poor to Excellent, were tried to be discovered. Necessary secondary information was collected from Manali Municipal Office, Tourist Information Centre, local Tour and Taxi operators. Thus both quantitative and qualitative measures have been attempted to calculate the attractiveness of all the spots. Simple and standard statistical techniques have been applied to infer the facts.

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To quantify the qualitative data of tourists' perception regarding each and every spot, a Likert scale has been developed. The tourists' rating of 'Poor' to 'Excellent' has been assigned values between 0 and 10. Now **Attractiveness of individual tourist spot (Sj)** is measured using a combined average of tourists' interest about a place 'j' and how the tourists rate the place 'j'.

Sj= (No. of tourists out of every 10, visiting a place +Tourists' rating by Likert -scale) / 2

…….. [1]

Now to measure the impact of distance of each spot from Manali, a **Utility Variable of Tourism Product (Uj)** is calculated using following formula-

Uj= Sj / Distance (km) ……. [2]

At last it is attempted to develop the probabilistic tourism model. **Probabilistic Tourism Attitude (Pj)** is measured using the Utility Variable of Tourism Product (Uj). It is calculated by dividing the individual Utility Variable of Tourism Product (Uj) of a spot with the total Utility Variable of Tourism Product (Uj) of all the spots.

$Pj = Uj / \sum Uj$ ……. [3]

5. RESULTS AND DISCUSSIONS

1. Tourism Infrastructure in the town of Manali

Tourism infrastructure is a range of devices and institutions constituting material and organizational basis for tourism development. It comprises of four (4) basic elements: Accommodation, Food and Beverage Facilities, Accompanying and Communication Facilities (Panasuik A., 2007).

Table 3: *Types and Tariffs of the Hotels; Manali, September 2016*

Types of the Hotels			Room Tariffs (in Rupees)		
Regular	Resort	Home stay	AC	Non AC	Dormitory
207	21	21	2,000-5,000	500-5,000	500-2,000

Source: Tourist Information Centre, Manali and Field Survey

Manali, a popular travel destination for tourists all over the world, offers variety of cuisines in its restaurants and street side food joints. Manali is also a shopping destination for tourists. The goods range from apples, peaches and other dry fruits to shawl and other winter wears etc.

There are a number of tour and travel operators who organize tours in following circuits-

a. **Local Sight Seeing:** Hadimba Devi Temple, Siyali Mahadeb Temple, Vashistha Temple and Hot spring, Tibetan Monastery, Manu Temple, Van Bihar
b. **Manali-Rohtang-Manali:** Nehru Kund, Gulaba Camp, Rahala Waterfalls, Marhi, Rohtang Pass

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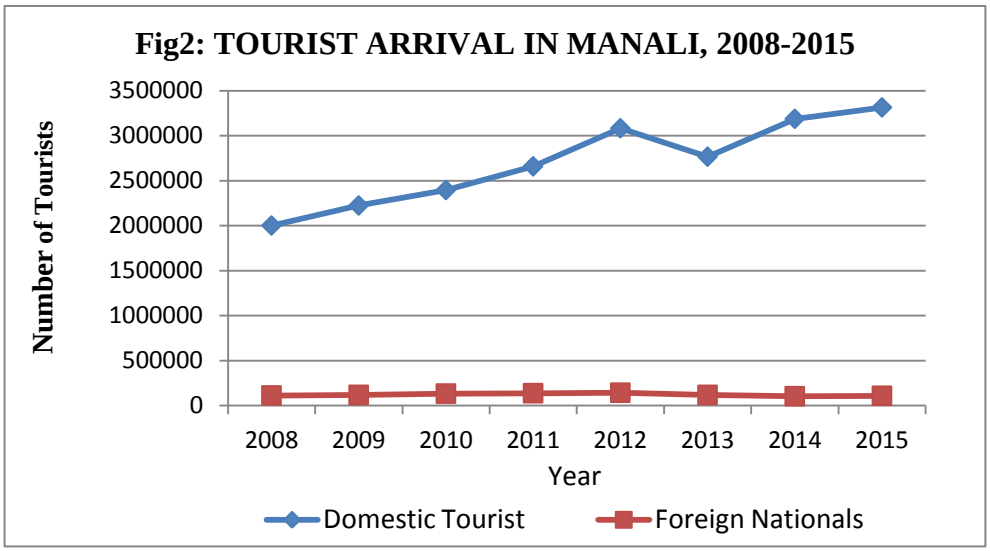
c. **Manali-Kullu-Naggar-Manali:** Kullu Town, Rafting Point in the Beas, Kais Wildlife Sanctuary, Naggar Castle, Jana Waterfalls, Jagatsukh Temple, Himalayan Fish Farm
d. **Manali-Manikaran-Manali:** Kasol Valley, Manikaran Temple and Hot spring
e. **Manali-Solang Valley-Manali:** A destination for adventure sports.

Latest attraction of Manali is its option of adventure tourism. Private tour operators organize varied kind of adventure sports, like- skiing, paragliding, river rafting etc.

All these have led to huge number of tourist arrivals in Manali town over the last few years.



Source: Tourism & Civil Aviation Office, Kullu

2. Probabilistic Tourism Model:

Probabilistic Tourism Model is a mathematical approach to understand the probability of tourists' footfall to any tourist location. The probability is measured on the basis of distance and attractiveness of the tourist spots. The Probabilistic Tourism Attitude thus found, helps to plan the tourism development. Spots closer to the place, where tourists stay, have higher Pj value as proximity and accessibility have strong influence on chance of tourists visiting a place. So the Pj gradually decreases for distant places. But Attractiveness (Sj) can be higher and lower for any tourist spot. Two nearby spots with high Pj values can have different tourist attractiveness (Sj) because tourists may rate them differently. While, a distant spot, with low Pj value, may offer high tourist attractiveness.

From Table 4 and Fig. 3, it can be observed that distance has a negative impact on probability of tourists visit. But tourist attractiveness is not much influenced by it. One of the tourists' favourite locations in Manali, Hadimba Devi Temple, comes high on both attractiveness and

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probability scale. While Van Vihar, the tourist spot located inside the town, have highest probability of tourists' footfall but falls short in terms of tourist attractiveness. Rohtang Pass, Manikaran etc. with some lower probability of tourists' visit, attract huge number of tourists in reality because of their high tourist attractiveness value. From the diagrams in fig3, it can be deduced that distance and probabilistic tourism attitude have a negative correlation, while distance has no considerable impact on tourist attractiveness, which again doesn't influence probabilistic tourism attitude much.

Table 4: *Probabilistic Tourism Model of Tourists in Manali*

Name of the Tourist Spot (j)	Dj in km	Tourists' Visiting(out of every 10)	Tourists' Rating in Likert Scale	Sj	Uj (Sj/Dj)	Pj (Uj/∑Uj)*100
1. Hadimba Devi Temple	1.6	9.6	6.6	8.1	5.063	12.093
2. Siyali Mahadeb Temple	1.8	7	4.9	5.95	3.306	7.896
3. Vashistha Temple and Hot spring	3.3	8.5	6.6	7.55	2.288	5.465
4. Van Vihar	0.4	5.3	4.7	5	12.500	29.859
5. Tibetan Monastery	0.5	5.9	6.2	6.05	12.100	28.903
6. Manu Temple	2.5	8.1	6.3	7.2	2.880	6.879
7. Nehru Kund	6	4.1	4.25	4.175	0.696	1.662
8. Gulaba Camp	20	6.7	4.2	5.45	0.273	0.651
9. Rahala Water falls	28	7.1	5.5	6.3	0.225	0.537
10. Marhi	35	7.9	4.3	6.1	0.174	0.416
11. Rohtang Pass	52	8.3	6.8	7.55	0.145	0.347
12. Kullu Town	41	8.2	5.5	6.85	0.167	0.399
13. Rafting Point in the Beas	39	3.7	5.9	4.8	0.123	0.294
14. Kais Wild life Sanctuary	42	5.5	4.3	4.9	0.117	0.279
15. Naggar Castle	22	6.3	6.2	6.25	0.284	0.679
16. Jagatsukh Temple	12	6.1	3.9	5	0.417	0.995
17. Jana Water falls	34	5.9	4.15	5.025	0.148	0.353
18. Himalayan fish farm	16	4.7	4.6	4.65	0.291	0.694
19. Kasol Valley	76	6.5	5.8	6.15	0.081	0.193
20. Manikaran Temple and Hot spring	80	7.2	6.25	6.725	0.084	0.201
21. Solang Valley	13	6.8	6.3	6.55	0.504	1.204
					∑Uj= 41.864	

Source: Field Survey

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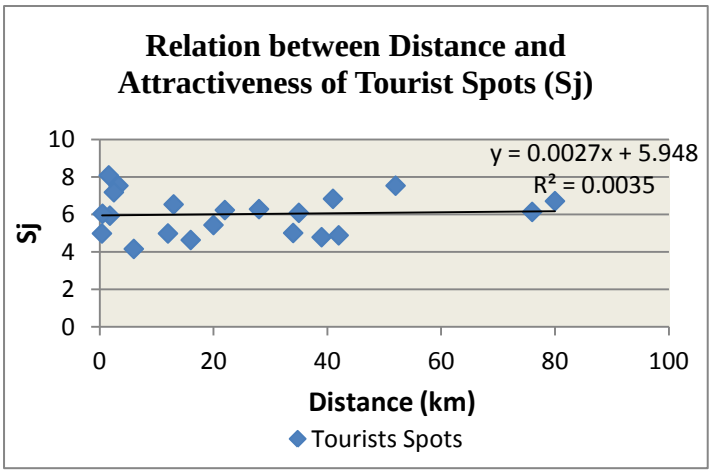

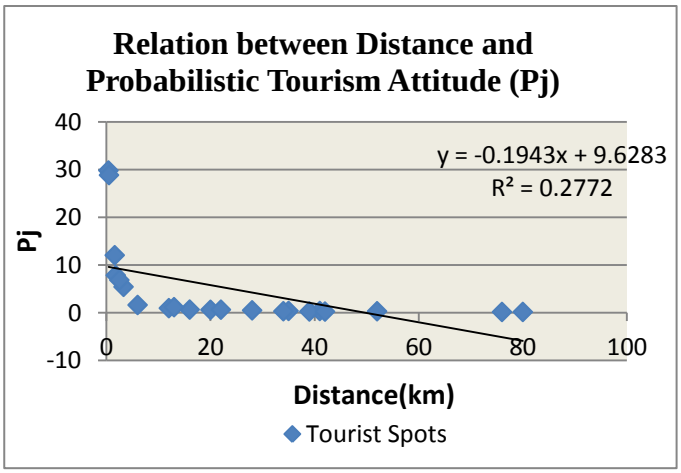

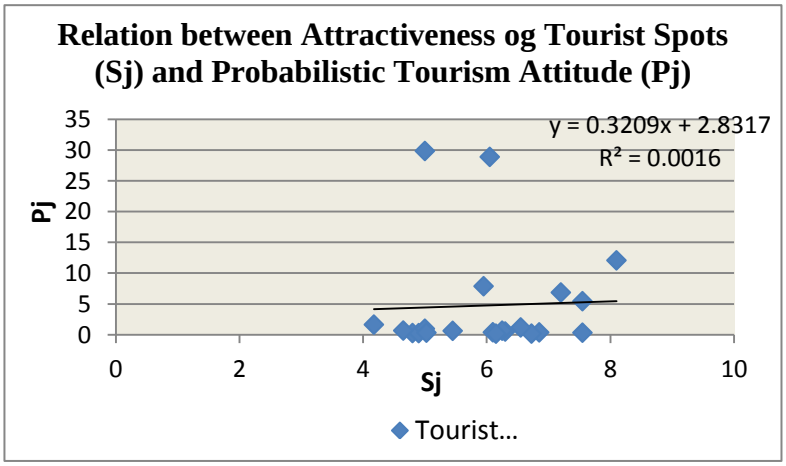

Fig 3: *Relationship among Distance, Attractiveness of tourist spots & Tourism Attitud*

3. CONCLUSION

Probabilistic Tourism Model can suggest measures to authorities and tour operators for development of tourism. The probabilistic tourism attitude (Pj) varies for different spots and plans should be different for their maintenance.

The places with both high attractiveness and probability values: Hadimba Devi Temple, Manu Temple; must be maintained thoroughly. More number of staffs should be involved in the management.

The places with high attractiveness but low probability; Naggar Castle, Manikaran Temple and Hot Spring; should be advertised more. The links, transport facilities etc., with those places must be improved. Authorities and tour operators should encourage more number of tourists to take the plight of long journey and enjoy the beauty of those spots.

The places, high on probability index but low on attractiveness, like Van Vihar, Siyali Mahadeb Temple; should be taken care of. Facilities, attractions of those spots must be improved and beautification works need to be done immediately.

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At last, there come those spots with both low attractiveness and low probability, e.g. Nehru Kund, Kais Wild Life Sanctuary. There is scope of maximum development. Authorities and operators can think of adding more number of attractions at those places, existing facilities must improve and beautification works need to be done.

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