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FACULTY OF ENGINEERING AND COLLEGE OF COMPUTING SCIENCES & IT
TEERTHANKER MAHAVEER UNIVERSITY
MORADABAD, UTTAR PRADESH

# About the Journal

TMU Journal of Basic & Applied Chemistry (TJBAC), is a prominent source to spread worldwide promotion of systematic research awareness across INDIA in various field of chemistry. This is an international scientific peer reviewed, open access journal, dedicated in publishing original research from pure chemistry, applied chemistry and focusing on wide range of applications. This journal covers: analytical/ inorganic, organic/ industrial, and physical theoretical/experimental chemistry as well as new interdisciplinary fields such as material science, spectroscopy, biological, medicinal, and environmental chemistry. The original research papers and short communications are published in "**TMU Journal of Basic & Applied Chemistry**" and is issued yearly. It has high profile editorial standards, with leading editors involved in the current research fields, get knowledgeable peer reviews and publishing decisions. Manuscripts published in the Journal should not be reproduced without a written permission from the Editor-in-Chief.

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# Teerthanker Mahaveer University

Teerthanker Mahaveer University was established by an 'Act' (No. 30) of 2008 of the Government of Uttar Pradesh and has been approved by the University Grants Commission (UGC) vide letter No. F. 9-31/2008(CPP-1) dated October, 2008. The University is located on National Highway-24, barely 144 Km from New Delhi.

The University stands committed to the ideals of Lord Mahaveer – Right Philosophy, Right Knowledge, and Right Conduct – in all the spheres of activity and aspire to be recognized as the ultimate destination for world class education.

The multi-disciplinary University offers career oriented courses at all levels, i.e., UG, PG and Doctoral degrees across diverse streams, namely, Medical, Dental, Pharmacy, Nursing, Paramedical Sciences, Physiotherapy, Hospital Administration, Education, Physical Education, Engineering, Architecture, Polytechnic, Management, Law, Journalism, Fine Arts, Jain Studies, and Agriculture Science to meet rising aspirations of the youth.

## Faculty of Engineering & Computing Sciences

The College of Engineering has emerged as a hub for academic excellence in engineering training. The college contributes to quality education in all major disciplines of engineering and technical education and helps meet the needs of industry for trained technical manpower with practical experience and sound theoretical knowledge.

The college was established by the university with the aim of providing relevant, essential, upgraded education to the young aspirants in the field of computer science and engineering, including computer applications. In recent times and the years to come there will be increasing demand of skilled manpower in the domain of Computer Science and Engineering because of the 'Digital India' mission, projected around the globe by Government of India.

**TMU Journal of Basic & Applied Chemistry** is a **peer-reviewed** and multidisciplinary **journal** that publishes original research, case studies, & review articles of all major branches of Chemistry. The Journal does not charge for publishing the manuscript. The papers contained in the journal carry the opinion and views of the contributors and not necessarily of the editorial Board. The editorial Board as such shall not be responsible for the authenticity and legality concerned regarding the submission made in this journal. The author shall be responsible for authenticity of the published research papers.

## CHIEF PATRON

**Shri Suresh Jain**
Chancellor,
TMU, Moradabad

I am extremely glad and feeling inner happiness for the release of vol-3, 2023 of **TMU Journal of Basic & Applied Chemistry**, an International Journal of Chemistry, Faculty of Engineering and Computing Sciences, Teerthanker Mahaveer University, Moradabad in the Month of January-December, 2023. I express my feelings that the World is growing very fast and creative researches have changed the entire Technology in the field of Engineering, Medical Sciences, Computing Sciences and variety of industrial products. This is true that research in any discipline is not one day job but it needs consistent and continuous efforts to do constructive work for the benefit of mankind. In the present Scenario the scientists all over the World have achieved wonderful Technology to make impossible task to possible through research only. Just see the defense technology, in medical the robotic surgery, in Engineering heavy duty working Machines, variety of Batteries, IOT, and Fuels etc. The dream of this University has achieved a lot, it was completed in the year 2008 and since that day the teaching /research standard is getting advancement, and an ambitious to enhance research interest among the faculty members to grow vertically and horizontally for bright and successful endeavor in the department of chemistry. This is true that any institution is recognized by research work, quality publications and patents which are usable by industries and not by colossal and huge towers. The faculty members may spare one /two hours per day for research. Everyone must have determination, confidence and research interest to produce quality research work. Now I express my happiness to publish this journal on regular basis. I am sure that readers of this message will take it very positive to move ahead among the best researchers. I trust that FOE & CS will definitely bring revolution through quality research work to give a good name and fame to Teerthanker Mahaveer University in India and abroad as prestigious institute in academics and research. My heartiest felicitation to Director and Principal of FOECS, Editor- in- Chief, Associate Editors , advisory committee to release this Journal continuously for the extreme satisfaction of research students, researchers and scientists.

## CHIEF PATRON

**Shri Manish Jain**
Group Vice Chairman,
TMU, Moradabad

I take this opportunity to rejoice along with critical faculties and students, Faculty of Engineering and Computing Sciences for the smooth and efficient functioning of the college under the vigilant supervision of Professor R.K. Dwivedi, Director and principal, TMU, Moradabad. I am feeling immense pleasure that FOE&CS is publishing vol.-3, 2023 of **TMU Journal of Basic & Applied Chemistry**, to boost the research environment in the college. I advice the learned faculties that develop addiction to perform research activities in your respective field. You may feel that it is a difficult task but this will add in your profile as an excellent researcher. This will be beneficial for the students also to show them right path for their professional and prosperous life in endeavor. Keep it up in doing constructive work to elevate the academic and research standard of this unique Teerthanker Mahaveer University, Moradabad. Though this university young in years, Second to none in this area as most popular interdisciplinary University. I am sure that fragrance of quality education, research potential, variety of courses offered, is spreading through cooperation and perseverance.

## CHIEF PATRON

**Shri Akshat Jain**
Executive Director
TMU, Moradabad

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I personally feel that hard work never goes astray. The conferences, webinars and seminars, special talks play an important role in creating congenial research environment in the department and ultimately in the University. It gives reflection of learned faculty serving in the department. I am highly excited to congratulate the organizing team of the department of Chemistry, versatile and eminent scholar Professor R. K. Dwivedi, Director and Principal , Faculty of Engineering and Computing Sciences, TMU , for releasing vol.-3, 2023, "**TMU Journal of basic & applied Chemistry**" . This is a challenging work for all the researchers to accept the demand of present scenario of research. In my opinion the Journal will provide National platform for academicians, researchers and scientists coming from various National Institutes/ Universities and Research Laboratories to present break through facts, research findings and innovations in the field of Chemistry. I am sure that this Journal shall bring valuable exchange of ideas among participants. I would like to express my appreciation to the organizing team for their hard work and restless efforts.
I extend my best wishes for grand success of this Journal.

# PATRON

**Prof. Raghuvir Singh**
Vice Chancellor,
TMU, Moradabad

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I am very happy to announce the release of TMU Journal , The **TMU Journal of Basic & Applied Chemistry” vol.3 , 2023** broadening the scope and coverage among researchers in the entire Indian Universities. I personally believe that University education system, particularly technical education, requires a platform to encourage budding researchers for publishing their research output in the form of journal articles. TMU is largest Technological Universities in the country with a very large pool of faculty, research scholars, and post graduate and graduate students. As such the University would like to create a platform for its fraternity for publishing their research works by instituting a high quality technical journal covering all branches of Engineering and allied fields.

No doubt publication of the journal is expected to be beneficial for the University in many ways — it brings scholarly recognition to the University; it would also contribute for the career development of faculty and researchers through their participation in the creation and sharing of new innovations, research and development. These new ideas, research and development activities finally translate into the overall development of the community and society at large. These scholarly publications will be a medium for academic and scientific discussions and enrichment of research areas. Though there is a long list of advantages that an academic journal can offer to research community, primarily for a researcher an academic journal is a credible and authoritative source of information and offer platform and evidence for their research output.

I suggest and appeal the students, faculties to strengthen the quality of the Journal by performing quality research reviews, research papers.

Congratulations to Professor R.K. Dwivedi, Director and Principal , FOE & CS , Editor-in- Chief, Associate Editors, section Editors and Advisory committee to motivate a positive environment of research in the college..

# PATRON

**Prof. (Dr.) R. K. Dwivedi**

Principal & Director, FOE &
CS, TMU, Moradabad

I take this opportunity to share my views for the smooth working of the Faculty of Engineering & Computing Sciences, Teerthanker Mahaveer University, Moradabad. Firstly I congratulate to team of learned persons in publishing the vol-3, 2023 of **TMU Journal of Basic & Applied Chemistry**. This is an excellent approach to publish Reviews, research Papers, on regular basis in the field of Chemistry. I always say, nature does not thrust potentials and accomplishments upon mankind. We are endowed with insipient powers and latent forces. This is our duty to develop them so as to master himself. To my mind, Faculty of Engineering & Computing Sciences is not just a building made of bricks, mortar and concrete , but It is a noble centre of education that help in building character, empowering minds and imparting rich and rewarding experience that last life time. Ultimately, this lead to realization of all cherished dreams. Try to know your potential yourself otherwise you will not value your time. My aim of life is, live with enthusiasm to go higher and higher and contribute for the welfare of the society. I express my heartiest gratitude and thanks to His eminence Shri Suresh Jain, Chancellor, Shri Manish Jain, Group Vice Chairman, most respected Vice Chancellor Prof. (Dr) Raghuvir Singh, the Editor-in-chief, Associate Editors, Section Editors, Members of advisory committee for their untired efforts to bring this issue in magnificent form.

# TMU
# Journal of Basic & Applied Chemistry

## Volume-3, January-December, 2023

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*Original Article*

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*TMU Journal of Basic & Applied Chemistry*
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# Sunlight-induced photocatalytic degradation of rhodamine B dye by $Bi_2MoO_6$ microspheres

**Abstract**

Removal of dyes from water bodies is a significant concern throughout the world. In this study, $Bi_2MoO_6$ microspheres were synthesized by a hydrothermal synthetic route at 180°C, and it is effectively characterized by various techniques. The XRD peaks confirmed the orthorhombic planes of $Bi_2MoO_6$. The microsphere-like morphology was revealed by FESEM and HRTEM. The photocatalytic activity of the $Bi_2MoO_6$ microsphere is tested against the degradation of rhodamine B under natural sunlight irradiation. About 90 % degradation of rhodamine B is observed in 90 min with the photocatalytic degradation rate of 0.028 $min^{-1}$. Results confirmed that the $Bi_2MoO_6$ microsphere could facilitate 90% degradation of RhB dye and followed the first-order kinetic model.

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**Keywords:**

$Bi_2MoO_6$; solar photocatalyst; rhodamine B;, photocatalysis

## Introduction

Organic dyes in aquatic environments are a significant pollutant due to their extensive usage in textile and other fabric industries (Homem and Santos, 2011; Qin et al., 2021; Rivera-Utrilla et al., 2013). Many water sources are polluted by residual dyes, which enter directly into the aquatic environment through various means like dye industries, textile industries, etc. (Dinh et al., 2017; Michael et al., 2013). Rhodamine B dye is a widely used cationic dye found in its application in coloring fabrics. Rhodamine B is water-soluble, stable in an aquatic environment, non-biodegradable, and cancer-causing in nature, which makes it harmful to humans and living species of aquatic ecosystems (Kumar et al., 2022a; Kumar and Dutta, 2022a; Kumar and Kumar, 2022; Mukherjee and Vellenki, 2022).

However, these residual dyes are not quickly metabolized, so they can easily pollute groundwater and surface water, causing harmful diseases in animals and humans (Bisht et al., 2022; Kumar et al., 2022b; Kumar and Dutta, 2022b). Due to this, several methods have been developed for wastewater remediation. Out of these techniques, semiconductor-based photocatalysts are widely utilized for the photocatalytic removal of various water pollutants (Akbari et al., 2021; Calvete et al., 2019; Durán-Álvarez et al., 2016). To date, ZnO and $TiO_2$ nanoparticles are the most commonly used photocatalysts for degrading organic dyes, but they require UV light for photoexcitation as their band gap is large (Nenavathu et al., 2013; Schneider et al., 2014). Recently, bismuth-based photocatalysts have been the most promising and new class of photocatalysts used in wastewater treatment over the last few decades. Their applications cover several areas such as water-splitting, $NH_3$ production from $N_2$, reduction of $CO_2$, and degradation of water pollutants through heterogeneous photocatalysis.Thebandstructure of these materials provides them with a suitable band gap for visible light-activeand a well-distributed valence band in favor of recombination charge, enabling them to act as potential photocatalytic materials for wastewater treatment overmetal oxides. Bismuth-based multi-component oxides are usually identified as stoichiometric hybrid oxides of $Bi_2O_3$ and metal oxides like $TiO_2$, $V_2O_5$, $Mo_2O_3$, $W_2O_3$, etc. The Aurivillius layered structure is generally determined by $[Bi_2O_2]^{2+}$ layers combined with metal oxide layers along the c-axis. The $Bi_2MoO_6$ (n = 1) is the simplest member of the Aurivillius family, which is a promising candidate for the photocatalytic degradation of inorganic and organic pollutants, under solar-light illumination (Das et al., 2018). In this work, we have reported the synthesis of $Bi_2MoO_6$ microsphere as a solar photocatalyst, and its photocatalytic activity was tested on RhB dye degradation under solar light irradiation.

## Experimental Section

4 mmol bismuth nitrate pentahydrate was mixed in 20 mL of ethylene glycol, and 4 mmol sodium molybdate dihydrate was dissolved in 30 mL of ethyl alcohol. After stirring both the solutions for 30 min separately, the sodium molybdate dihydrate solution was added slowly into the bismuth nitrate pentahydrate solution with continuous magnetic stirring. After 45 min of constant stirring, the mixture was poured into a Teflon-lined stainless-steel autoclave and heated under a controlled temperature of 180 °C for 24 h. The finally prepared precipitates were washed with DI water and $C_2H_5OH$ and separated by centrifugation at 10000 RPM for 20 min, and the white product finally obtained was dried in an oven at 50 °C.

### Methodology for photocatalytic experiment

The photocatalytic performance of the $Bi_2MoO_6$ photocatalyst was determined by observing the degradation of RhB dye (10 mg/L) solutions under exposure to natural sunlight radiation. Typically, 100 mL aqueous solution of 10 ppm RhB dye is taken into a 500 mL beaker, followed by the addition of 80 mg of $Bi_2MoO_6$ photocatalysts into it, which was then subjected to continuous stirring for 60 min under the dark condition. After 60 min of dark study, the beaker was kept under sunlight. 2 mL aliquot was taken from the beaker at certain intervals. The change in concentration of the RhB molecule was recorded by UV-vis spectrophotometer (UV-1800, Shimadzu, Japan) at absorbance $\lambda = 553$ nm.

## RESULTS AND DISCUSSIONS

### Characterization of $Bi_2MoO_6$

### XRD analysis

The XRD spectra of pristine $Bi_2MoO_6$ was investigated by Bruker AXS advanced diffractometer with a scan range of 1 $min^{-1}$ using graphite monochromatized Cu Kα radiation (1.5418 Å) operated at 40 kilovolts. The XRD peaks for $Bi_2MoO_6$ were detected at $2\theta = 11.1°$, 28.5°, 32.9°, 36.2°, 47.2°, 55.6°, 58.4°, which are matched to (020), (131), (002), (151), (062), (133), and (262) orthorhombic planes of $Bi_2MoO_6$ (JCPDS Card No.- 21 1272) (Figure.1). The lattice parameters are calculated to be as $a = 5.42$ Å, $b = 16.32$ Å, and $c = 5.42$ Å, with the average crystallite size of 14.10 nm.

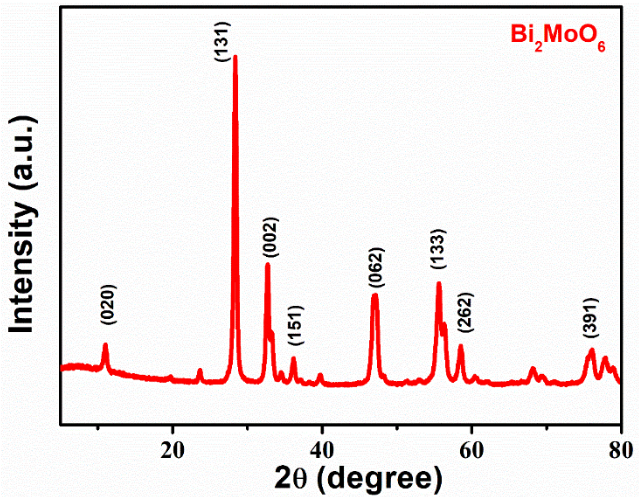

**Figure.1** XRD patterns of as-synthesized $Bi_2MoO_6$ microspheres

### Morphology of $Bi_2MoO_6$

The surface morphology of the $Bi_2MoO_6$ photocatalyst was investigated by electron microscopy. The FE-SEM image of $Bi_2MoO_6$ microspheres was recorded by Zeiss FESEM, Ultra-plus55 shows agglomeration of nanospikes-like structures (Figure. 2a). Similarly, the morphology of the $Bi_2MoO_6$ microsphere was better displayed from the HRTEM images (Figure. 2b) are recorded on a JEM-3200FS, JEOL transmission electron microscope.

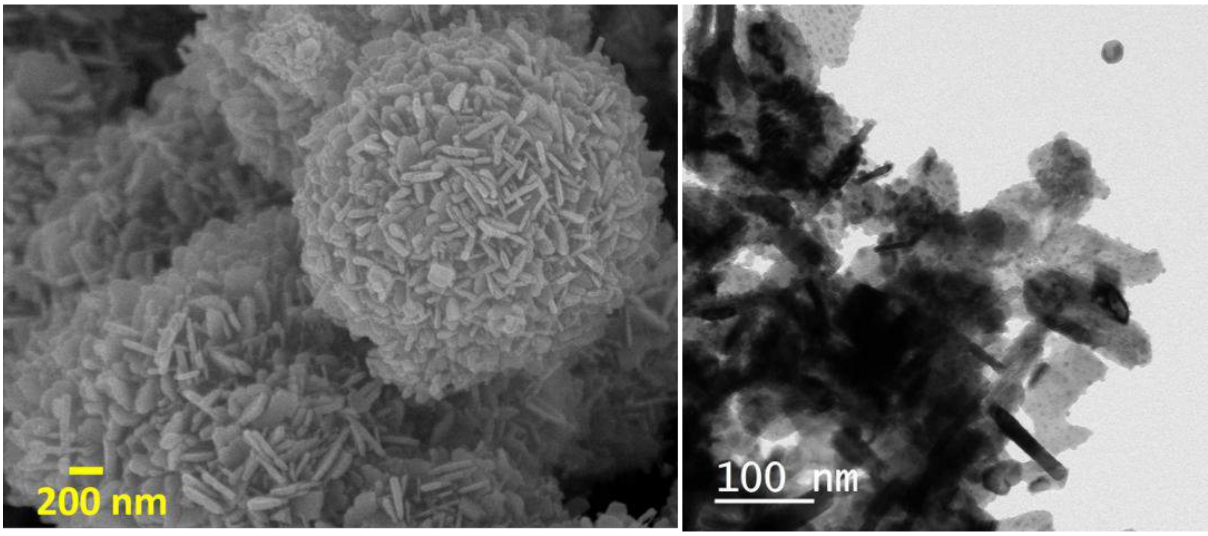

**Figure.2** a) FE-SEM image of $Bi_2MoO_6$ microspheres; b) HR-TEM image of $Bi_2MoO_6$ microspheres

### Photocatalytic activity

The sunlight-mediated photocatalytic degradation of RhB dye (10 mg/L) by the $Bi_2MoO_6$ microsphere is shown as a curve of $C_t/C_0$ vs. (t) time (Figure. 3). In the dark experiment firstly, the change in concentration of RhB dye was determined by the dark experiment. About 16% of RhB dye was adsorbed on $Bi_2MoO_6$ microspheres (Figure. 3a). The self-decomposition investigation of rhodamine B shows negligible results. The $Bi_2MoO_6$ microspheres show the photocatalytic performance of about 90 % rhodamine B dye degradation after 90 min of sunlight exposure. The degradation kinetics of rhodamine B was modelled by a 1st-order kinetics model. The 1st order kinetics equation is:

$$\ln(C_0/C_t) = kt \qquad (2)$$

Where $C_0$ is the initial dye concentration of dye, and $C_t$ is the dye concentration at any time, whereas k ($min^{-1}$) is the 1st-order kinetic rate constant for RhB dye photocatalytic degradation. The photocatalytic rate constant of pristine $Bi_2MoO_6$ (k= 0.028 $min^{-1}$) (Fig. 3b).

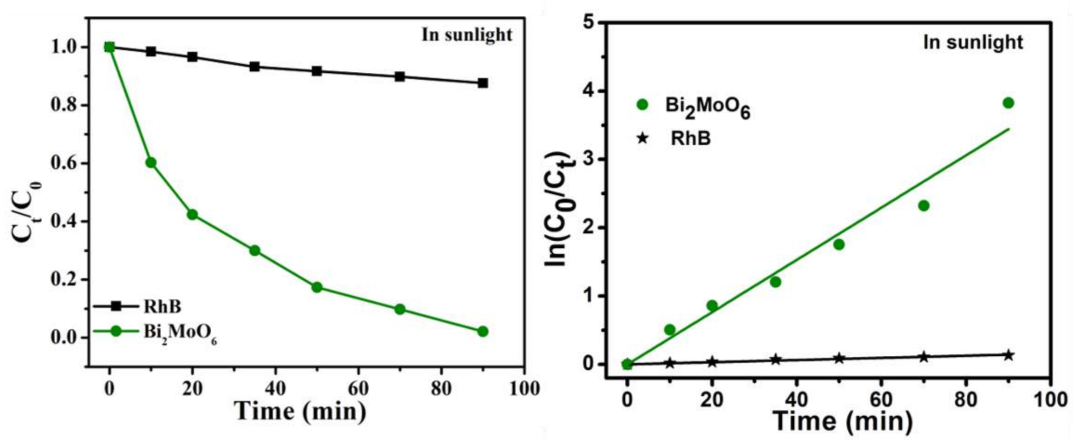

**Figure. 3** a)Degradation profile (b) Corresponding 1st order kinetics curves

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# Yttria-zirconia based Lewis acid catalysed acylation of activated aromatic compounds

**Abstract**

The heterogeneous Yttria- zirconia based Lewis acid serves an efficient catalyst for regioselective acylation of diverse range of activated aromatics including heteroaromatic such as thiophene. Phenols were acylated at the aryl position, and no O-acylated product was obtained. In acylation of acetanilide, no transacylated product was obtained. The main advantage of this catalyst is its recovery and repeated reuse for several times.

**Keywords:** Yttria-zirconia; Lewis acid; Acylation; Friedel Craft acylation; Aromatic compounds.

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## Introduction

Friedal-Crafts acylation reaction (Heaney H., 1991; Sarvari MH and Sharghi H., 2004; Guena F. et al., 2008), is an important reaction in synthesis tool box for preparation of various aromatic ketones by $C-C$ bond creation and is generally performed employing acyl chlorides, carboxylic anhydride or carboxylic acids and an stoichiometric amount of acidic promoter. The use of stoichiometric amount of acidic promoter is known to produce gaseous effluents and mineral wastes. Catalysis by $FeCl_3$(Pearson DE and Buchler CA.,1972; Cornelis A., et al., 1990), $ZnCl_2$ (Naeimi H., et al., 2014; Paul S., et al., 2003)& zeolites(Sartori G and Maggi R, 2006; Bejblova M., et al., 2009) have been reported for the acylation of activated aromatics. Super acid(El-Sharkawy EA and Al-Shihry SS, 2010; SuryaPrakash GK, et al., 2015),&sulfonic acid (triflic acid)(Melero JA., et al., 2004; Tachrim ZP., et al., 2017) also catalyse the reaction, however the latter is associated with disadvantage such as extremely hygroscopic in nature and soluble in reaction media (Gramstad T and Haszeldine RN. 1957). Triflates of boron, aluminium and gallium(SuryaPrakash GK, et al., 2003) also catalyse the reaction, however, these catalyst are sensitive to hydrolysis. Triflic acid (Kawada A, et al., 1993 and 1994)bis(trifluoromethylsulfonyl)amide(Mikami K, et al., 1996) hafnium triflate(Mitsuhiro IH and Kobayashi

MS. 1995)bromopentacarbonylrhuthenium (I) (Hiroyuki K. and Koichi N. 1995), bismuth(III) trifluoromethanesulfonate(Balaguer AM., et al., 2014) were employed in the last decades. Unlike bismuth (III) triflate(Desmurs JR., et al., 1997), $SbCl_5$-$LiClO_4$ (Teruaki M., et al., 1992) & HZSM-5(Sreekumar R. and Padmakumar R. 2006; Boström Z and Holmberg K. 2013)was found to be water stable with high catalytic activity. A combination of $TiCl(OTf)_3$&TfOH,hydrated Zirconia (Nikoofar K. and Khademi Z. 2016; Patil ML., et al., 1997)were reported for the acylation of activated aromatics.

Recently gallium nono fluorobutanesulfonate (Matsuo J. et al., 2000) & yttribiumtris(per)fluoro alkanesulfonyl)methide (Barrett AGM. et al., 2000) are found to catalyseFriedal-Crafts acylation in good to moderate yield. As part of our continued interest in application of solid catalyst for different synthetic organic transformations, we have earlier reported yttria-zirconia Lewis acid as promising catalyst for the Diels-Alder reaction, transesterification of β-keto esters, acylation of alcohols, amines &thiols (Keshavaraja A., et al., 1995; Kumar P and Pandey RK. 2000; Kumar P. et al., 2001 and 2002; Pandey RK., et al. 2002)This promoted us to explore this catalyst for Friedal-Crafts acylation reactions, and herein we describe our findings on the yttria-zirconia Lewis acid catalysed Friedel-Crafts acylation of activated arenes.

## Experimental Section

Yttria- zirconia based catalyst was procured from the catalysis division of CSIR-NCL, Pune. It was synthesized and characterized as per the method published by us, (Keshavaraja A. et al. 1995).

### General experimental procedure for yttria-zirconia Lewis acid catalysed acylation of activated aromatic compounds

A slurry of activated aromatics (1eq), acid chloride or acid anhydride (5eq) &yttria-zirconia (10 mol%) were stirred at reflux temperature in acetonitrile (Table 1). The reaction was monitored by Thin Layer Chromatography. The removal of catalyst was done by filtration and filtrate quenched with 10% $NaHCO_3$solution & extracted with $CH_3COOC_2H_5$ (2x50mL) and dried over Sodium sulfate. The solvent was concentrated to give the corresponding acylated prouct as crude. The required product was obtained in pure form. using silica gel coloumn chromatography employing petroleum ether: EtOAc (95:5) as eluent.

**1-(4-Methoxy-phenyl)-ethanone (2a)**

**Yield:** 93%

**Yellow Oil**

**IR (Neat, $cm^{-1}$):** νmax 3487, 3334, 3100, 2950, 2840, 2550, 2410, 2070, 1950, 1673, 1600, 1508

**$^1$H NMR (200 MHz, $CDCl_3$):** δ 2.51 (s, 3H), 3.82 (s, 3H), 6.88 (d, 2H, *J* = 10Hz), 7.88 (d, 2H, *J* = 8 Hz)

**Mass:** 150 (M+), 136, 135, 120, 107, 92, 77, 64

**Analysis cacld for $C_9H_{10}O_2$ (150.17):** Found C, 71.81; H, 6.56{Required C, 71.98; H, 6.71}

**(4-Methoxy-phenyl)-phenyl-methanone (2b)**

**Yield:** 91% **Yellow oil.**

**IR (Neat, $cm^{-1}$):** νmax 3420, 3067, 3035, 2671, 2552, 1918, 1693, 1650, 1599.

**$^1$H NMR (200 MHz, $CDCl_3$):** δ 3.89 (s, 3H), 6.96 (d, 2H, *J* = 10Hz), 7.40–7.64 (m, 5H), 8.15 (d, 2H, *J* = 8Hz)

**Mass:** 212 (M+), 181, 169, 135, 122, 105, 92, 77

**Analysis cacld for $C_{14}H_{12}O_2$ (212.24):** Found C, 79.10; H, 5.76{Required C, 79.23; H, 5.70}

**(3-Benzoyl-4,6-dimethoxy-2-methylphenyl)-phenyl-methanone (2c)**

**Yield:** 87%

**Pale Yellow Oil**

**IR (Neat, cm$^{-1}$):** νmax 3454, 3019, 2910, 2900, 2850, 1665, 1588, 1464, 1449, 1323, 1280, 1245, 1215, 1174, 1122, 1085, 915

**1H NMR (200 MHz, CDCl$_3$):** δ 1.92 (s, 3H), 3.76 (s, 6H), 6.48 (s, 1H), 7.46 (t, 4H, *J* = 4 Hz), 7.60 (t, 2H, *J* = 4 Hz), 7.87 (d, 4H, *J* = 8 Hz)

**Mass:** 361(M++1), 360, 359, 343, 315, 289, 283, 267, 254, 240, 225, 211, 198, 181, 165, 152, 122, 105, 77

**Analysis cacld for $C_{23}H_{20}O_4$ (360.38):** Found C, 76.56; H, 5.51{Required C, 76.65; H, 5.59}

**1-(2, 4-Dimethoxy-6-methyl-phenyl-ethanone (2d)**

**Yield:** 89%

**Colorless oil**

**IR (Neat, cm$^{-1}$):** νmax 3449, 2933, 2843, 2395, 1752, 1690, 1602

**1H NMR (200 MHz, CDCl$_3$):** δ 2.25(s, 3H), 2.46 (s, 3H), 3.81 (s, 6H), 6.30 (s, 2H)

**Mass**: 194 (M+), 180, 179, 171, 164, 150, 136, 135, 128, 122, 121, 105, 99, 93, 91, 83, 77, 69, 65

**Analysis cacld for $C_{11}H_{14}O_3$ (194.22):** Found C, 67.89; H, 7.17{Required C, 68.02; H, 7.26}

**1-(2,4,6-Trimethoxy-phenyl)-ethanone (2e)**

**Yield:** 89%

**Colorless solid**

**M.P.:** 72-75°C

**IR (CHCl$_3$, cm$^{-1}$):** νmax 3430, 2400, 1746, 1667, 1600, 1581, 1450, 1394

**1H NMR (200 MHz, CDCl$_3$):** δ 2.44(s, 3H), 3.79(s, 6H), 3.81(s, 3H), 6.08(s, 2H)

**Mass:** 211(M++1), 196, 181, 168, 166, 122, 107, 92, 77

**Analysis cacld for $C_{11}H_{14}O_4$ (210.227):** Found C, 58.29; H, 6.12{Required C, 58.40; H, 6.24}

**Phenyl-(2,4,6-trimethoxy-phenyl)-methanone (2f)**

**Yield:** 95%

**Colorless Solid**

**M.P.:** 110-112$^0$C

**IR (CHCl$_3$, cm$^{-1}$):** νmax 3449, 3080, 2942, 2840, 1738, 1666, 1595, 1459, 1405

**1H NMR (200 MHz, CDCl$_3$):** δ 3.68 (s, 6H), 3.86 (s, 3H), 6.16 (s, 2H), 7.35-7.60 (m, 3H), 7.83 (d, 2H, *J* = 8 Hz)

**Mass**: 272, 255, 241, 227, 196, 195, 181, 180, 171, 152, 137, 122, 105, 91, 77, 69, 57.

**Analysis cacld for $C_{16}H_{16}O_4$ (272.30):** Found C, 70.68; H, 5.79{Required C, 70.58; H, 5.92}

**(2,5-Dimethoxy-phenyl)-phenyl-methanone (2g)**

**Yield:** 94%

**Brown oil**

**IR (CHCl$_3$, cm$^{-1}$):** νmax 3414, 3154, 3101, 3055, 2948, 2836, 2668.51, 2150, 1690, 1663, 1605, 1495

**1H NMR (200 MHz, $CDCl_3$):** δ 3.68 (s, 3H), 3.80 (s, 3H), 6.93 (d, 1H, *J* = 4 Hz), 7.01 (d, 1H, *J* = 4 Hz), 7.40-7.65 (m, 3H), 7.82 (d, 2H), 8.14 (d, 1H, *J* = 2 Hz)

**Mass:** 242 (M+), 225, 211, 197, 181, 165, 151, 122, 105, 92, 77.

**Analysis cacld for $C_{15}H_{14}O_3$ (242.273):** Found C, 74.41; H, 5.69{Required C, 74.36; H, 82}

**(2,5-Dimethyl-3-hydroxy-phenyl)-phenyl-methanone(2h)**

**Yield:** 87%

**Colorless solid.**

**M.P.:** 98-99°C

**IR ($CHCl_3$, $cm^{-1}$):** νmax 3296, 1691, 1627, 1573, 1377, 1319, 1276, 1264

**$^1$H NMR (200 MHz, $CDCl_3$):** δ 2.20 (s, 6H), 2.32 (s, 1H), 6.69 (s, 1H), 7.18 (s, 1H), 7.45-7.70 (m, 3H), 7.78 (d, 2H, *J* = 8 Hz)

**Mass:** 226, 210, 121, 105, 77

**Analysis cacld for $C_{15}H_{14}O_2$ (226.271)**: Found C, 79.51; H, 6.09; {Required C, 79.62; H, 6.23}

***N*-(4-Acetyl-phenyl)-acetamide(2i)**

**Yield:** 80%

**Brown Oil**

**IR(Neat, $cm^{-1}$):** νmax 3410, 3950, 3294, 3197, 3136, 3020, 2400, 2100, 1950, 1711, 1664, 1601, 1545

**1H NMR (200 MHz, $CDCl_3$):** δ 2.34 (s, 6H), 7.22 (s, 1H), 7.34 (brs, 1H), 7.50 (m, 3H).

**Mass:** 177 (M+), 136, 135, 120, 118, 105, 94, 93, 91, 77, 65

**Analysis cacld for $C_{10}H_{11}O_2$ (171.192):** Found C, 67.85; H, 6.07; N, 7.91{Required C, 67.79; H, 6.25; N, 8.12}

**1-Thiophen-3yl-ethanone (2j)**

**Yield:** 79%

**Brown Oil.**

**IR ($CHCl_3$, $cm^{-1}$):** νmax 3474, 3095, 2920, 1725, 1661, 1550

**1H NMR (200 MHz, $CDCl_3$):** δ 2.71 (s, 3H), 7.27 (s, 1H), 7.79 (d, 2H, *J* = 8 Hz)

**Mass:** 126, 110, 83

**Analysis cacld for $C_6H_6OS$ (126.112):** Found C, 57.05; H, 4.63{Required C, 57.14; H, 4.79}

***N*-(2-Acetyl-4-methoxy-6-nitro-phenyl)-acetamide(2k)**

**Yield:** 83%

**Dark yellow solid**

**M.P.:** 115-116$^0$C

**IR ($CHCl_3$, $cm^{-1}$):** νmax 3421, 2955, 1725, 1690, 1545, 1243

**1H NMR (200 MHz, $CDCl_3$):** δ 2.31 (s, 6H), 3.93 (s, 3H), 7.21 (s, 1H), 7.63 (s, 1H)

**Mass:** 252 (M+), 210, 194, 168,164, 153, 134, 122, 95, 77, 63

**Analysis calcd for $C_{11}H_{12}N_2O_5$ (252.225):** Found C, 52.19; H, 4.65{Required C, 52.38; H, 4.80}

**1-Cyclo-oct-1-enyl-ethanone (2l)**

**Yield:** 49%

**Pale Yellow Oil.**

**IR ($CHCl_3$, $cm^{-1}$):** νmax 3365, 2965, 1715, 1670, 1601, 1559

**1H NMR (200 MHz, $CDCl_3$):** δ 1.25-2.65 (m, 15H), 5.52-5.77 (m, 1H)

**Mass:** 152, 136, 109

**Analysis cacld for $C_{10}H_{16}O$ (152.2):** Found C, 78.79; H, 10.39{Required C, 78.95; H, 10.52}

**Cyclooct-1enyl-phenyl-methanone (2m)**

**Yield:** 52%

**Yellow Oil.**

**IR (Neat,$cm^{-1}$):** νmax 3412, 2933, 1723, 1667, 1606, 1515, 1201.

**1H NMR (200 MHz, $CDCl_3$):** δ 1.27-2.70 (m, 12H), 5.65-5.85 (m, 1H), 7.40-7.95 (m, 5H)

**Mass**: 214, 198, 137, 109, 105, 77

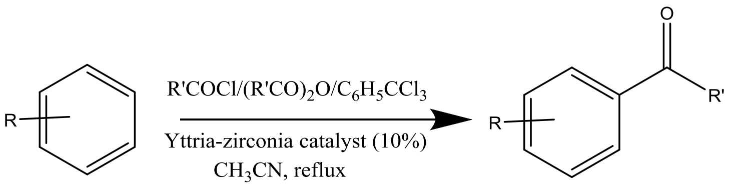
**Analysis cacld for $C_{15}H_{18}O$ (214.23):** Found C, 84.25; H, 8.79{Required C, 84.11; H, 8.88}

**Results and discussion:**

A variety of activated aromatic compounds on reaction with acid chloride or anhydride (or) benzotrichloride using 10 mol% amount of Yttria-zirconia based catalyst gave aromatic ketones in moderate to good yield. It is pertinent to note that the acylation of acetanilide with benzoyl chloride gave the aryl ketones without trans-acylation. The acylation or benzoylation of acetanilide went on regiospecifically in para position. Acylation of thiophene was successfully achieved with good yield. Mention must be made regarding regiospecific acylation of activated aromatic compound (**Table 1**) with electron donating groups such methoxy, hydroxyl & methyl groups. In all the above cases, the acylation was carried out regiospecifically at position para to methoxy, hydroxy, methyl groups. It is also worth mentioning that when benzoylation of 1,4-dimethylphenol was carried out with benzoyl chloride using 10 mol % of catalyst, benzoylation was observed on aryl position instead of O-benzoylation. When we treated anisole with neat acetyl chloride in presence of 10 mol% of Yttria-zirconia Lewis acid catalyst, it gave exclusively 4-methoxyacetophenone **2a** in 93% yield. In IR spectrum of **2a,** peak at 1673 $cm^{-1}$ indicated the presence of aromatic carbonyl group. The $^1$H NMR spectrum of **2a** showed a singlet at δ 2.51 for acyl protons, and singlet at δ 3.82 for methoxy protons. The aromatic protons appeared as two doublets at δ 6.85-6.90 and at δ 7.86-7.90 indicating the regiospecific acylation at *para*-position. The molecular ion peak at 150 in the mass spectrum of **2a** also confirmed the formation of acylated product. The exclusive acylation at aryl position of acetanilide was confirmed by its spectral data. The IR spectrum of compound **2i**showed peaks at 1711$cm^{-1}$& 1664$cm^{-1}$ corresponding to the carbonyl of amide and ketones. The$^1$H NMR spectrum of **2i** showed a peak at δ 2.34 for 6 protons of the acyl group. The aromatic protons appeared as doublet at δ 7.18-7.22 & at δ 7.50-7.54. The presence of fragmentation peaks at 120 & at 105 (for $PhCOCH_3$&PhCO) in the mass spectrum confirmed the acylation at the aryl positions.

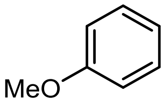
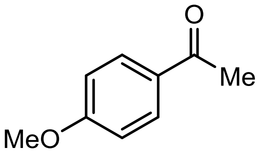
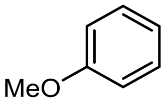
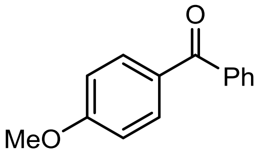
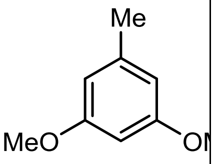
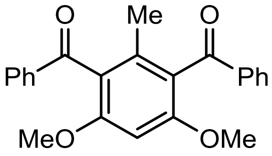
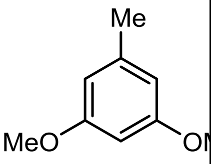
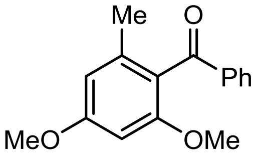
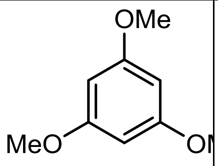
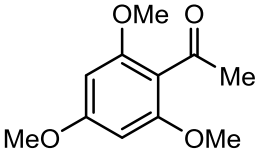
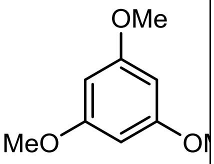
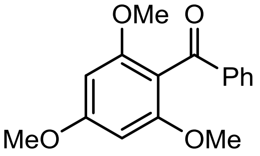
## Scheme:

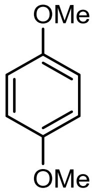
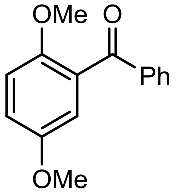
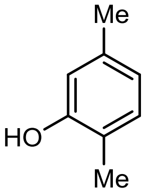
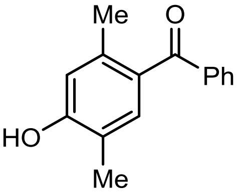
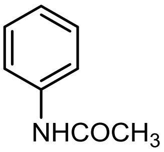
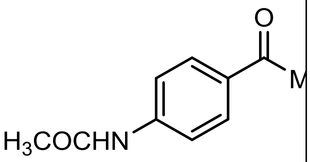
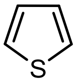
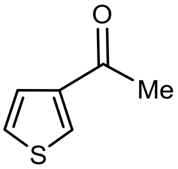
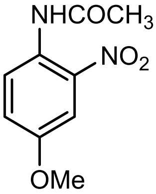
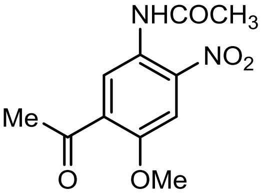
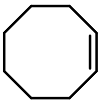
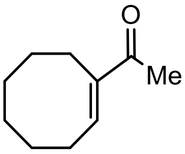
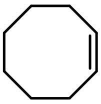
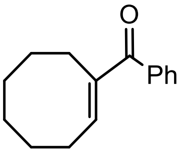
### Yttria-zirconia Lewis acid catalysed acylation of activated aromatic compounds



1 → 2

**Table: 1**

| Entry | Aromatic Used | Acylating Agent Used | Product | Reaction Time (h) | Yield* | Product code |
|---|---|---|---|---|---|---|
| **1** |  | MeCOCl |  | 4 | 93 | 2a |
| **2** |  | PhCOCl |  | 3 | 91 | 2b |
| **3** |  | PhCOCl |  | 8 | 85 | 2c |
| **4** |  | PhCOCl |  | 6 | 87 | 2d |
| **5** |  | MeCOCl |  | 3.5 | 89 | 2e |
| **6** |  | PhCOCl |  | 7 | 95 | 2f |

| | | | | | | |
|---|---|---|---|---|---|---|
| **7** |  | PhCOCl |  | 9 | 94 | 2g |
| **8** |  | PhCOCl |  | 11 | 87 | 2h |
| **9** |  | MeCOCl |  | 1 | 80 | 2i |
| **10** |  | MeCOCl |  | 2 | 79 | 2j |
| **11** |  | MeCOCl |  | 8 | 83 | 2k |
| **12** |  | MeCOCl |  | 1 | 49 | 2l |
| **13** |  | PhCOCl |  | 1 | 52 | 2m |

*Isolated Yield after column purification.

## Conclusion

The Yttria-zirconia Lewis acid serves a very good heterogeneous catalyst for acylation of activated aromatic compound in regioselective manner. Heteroaromatics like thiophene was acylated with moderate yields. Phenols were acylated at the aryl position, & no O-acylated product was obtained. In acylation of acetanilide, no transacylated product was obtained. The main advantage of this catalyst is its recovery and repeated reuse for several reactions.

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# A quantum chemical study of 2-(Imidazol-1-yl)-4-Methylphenol

**Abstract**

The derivatives of imidazole like methotrexate, and omeprazole are important medicine available in pharmaceutical industries as anti-cancer, anti-microbial, and anti-inflammatory agents. In present communication geometry optimization of imidazole derivatives 2-(Imidazol-1 yl)-4 Methylphenolars has been done by using combination of DFT/B3LYP method and 6-311G( d,p) basis set. The optimized parameters of title molecules are compared with corresponding experimental data. The vibrational analysis, electronics properties of title molecule are calculated by using same level theory. The electronic properties of 2-(Imidazol-1-yl)-4-methylphenol are explained with the help of HOMO, LUMO and MESP. The calculated band gap of title molecule shows that title molecule is chemically inactive. We hope our study on title molecule provides new path way to researchers for further work on title molecule.

**Keywords:** Vibrational analysis, electronic properties, DFT, HOMO, LUMO.

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## Introduction

The Quantum chemical calculations are very useful to know geometry vibrational spectra, electronic properties, UV spectra and polarizability of any unknown molecule [*WalbaH.et.al.1961,*]. Imidazol is an organic compound with the formula $C_3N_2H_4$. It is the colourless or white solid and soluble in water. It is an aromatic heterocycle. It is classified as a diazole and has non adjacent nitrogen atoms in meta substitution [Karitzky A.R.et.al.1984]. It has density 1.23 g/cm$^3$, and acidity falls upto 6.95.Imidazol having melting point 89 to 91$^0$c and boiling point 256$^0$c [*Grimmett et.al.1997*].It is most important biological compound, planer 5 membered ring like pyrrole ring that replace two equivalent tautomeric form because it can be bound to one or another nitrogen atom [*Brown, E. G.et.al.1998*]. Imidazole was first reported in 1858 by the German chemist Heinrich Debus. It was shown that glyoxal, formaldehyde and ammonia [*Pozharskii, A. F.et al. 1997*].This pyrrole ring consists of three carbon, two nitrogen and three hydrogen atoms and two double bond . It is also known as 2-Imidazole [Gilchrist, TL et.al.1995].It beard two nitrogen atom in which one nitrogen sheared hydrogen atom and other is called pyrrole type nitrogen [Rosemeyer, H.et.al. 2004]. The nitrogen-based heterocycles ring imidazole was discovered in 1840. After discovery of imidazole attracts many researchers due to their promising anti-cancer, anti-microbial, and anti-inflammatory activities[Sherer C.et.al.2014]. The geometry of imidazole provides advantage to interact with ligand by nonbonding interactions. The natural derivatives of imidazole such as histamine, histidine, biotin, alkaloids, and nucleic acid are approved as drug by FDA. The specific charter of imidazole in therapeutics the fused imidazole derivatives played important role in pharmaceutical industries.

The derivatives of imidazole like methotrexate, and omeprazole are important medicine available in pharmaceutical industries as anti-cancer, anti-microbial, and anti-inflammatory agents. These drug of derivatives of imidazole shows some side effect [Gaba M.et.al.2016]. The researchers are trying to search potential candidate for better treatment under these desease by using Imidazole-based compounds. In this continuation [Pandey A.K.et al,2012,2015,2013,2017,2019,2020] we have selected fused imidazole derivative2-(Imidazol-1-yl)-4-Methylphenol for quantum chemical study. The Geometry optimization vibrational analysis electronic properties of 2-(Imidazol-1-yl)-4-Methylphenol is calculated by using combination of DFT/B3LYP method and 6-311G(d,p) method. We hope our study provides to calculate new biological active sites which is very useful to researchers for searching new drug with minimum side effect. In best of our knowledge no such quantum chemical study reported till now.

## Computational methods

The entire calculation on title molecule have been done on personal laptop by using Gaussian 16 program package. The geometry optimization of title moleculehas been done without any symmetry constrain. Initial geometry of title moleculeis modelled by using Gauss View 6.0 program package.[Frisch A.,20016] The entire calculations on title molecule carried out by using combination DFT/B3LYP method and 6-311G (d,p) basis set. The whole calculations are carried by Gaussian 16 program package [M.J. Frisch, et. al. 2016].The vibrational analysis on title molecule is carried on Gauss View 6.0 program.The HOMO LUMO MESP are plotted by using Gauss veiw6.0

### RESULTS AND DISCUSSION

### Optimization

The molecule having energy -2341.23a.u. with no symmetry so $C_1$ symmetry. The optimized geometry of title molecule along with bond length and bond angles are presented in fig-1.The synthesis crystal structure of title molecule is reported by Yoshinori Narutaetal. The crystal geometry of title molecule is monoclinic with $P2_1/n$ space group symmetry. The crystal having $a=6.352A^0$, $b= 10.44A^0$, $c =13.52A^0$ with $\beta=97.199^0$. [NarutaY, et.al,2001].The animated gauss view shows that the molecule having phenolic and imidazolylrings connected C1-N15 with bond length $1.427A^0$ is well matched with calculated bond length $1.439A^0$.In title molecule both ring phenolic and imidazolyl rings are slightly displaced from planarity. The calculated dihedral between both rings are $44.10^0$are well matched with observed dihedral $42.21^0$. The calculated -OH bond length placed on ortho position of phenolic ring is $1.385A^0$ is well matched with observed -OH bond length $1.352A^0$.

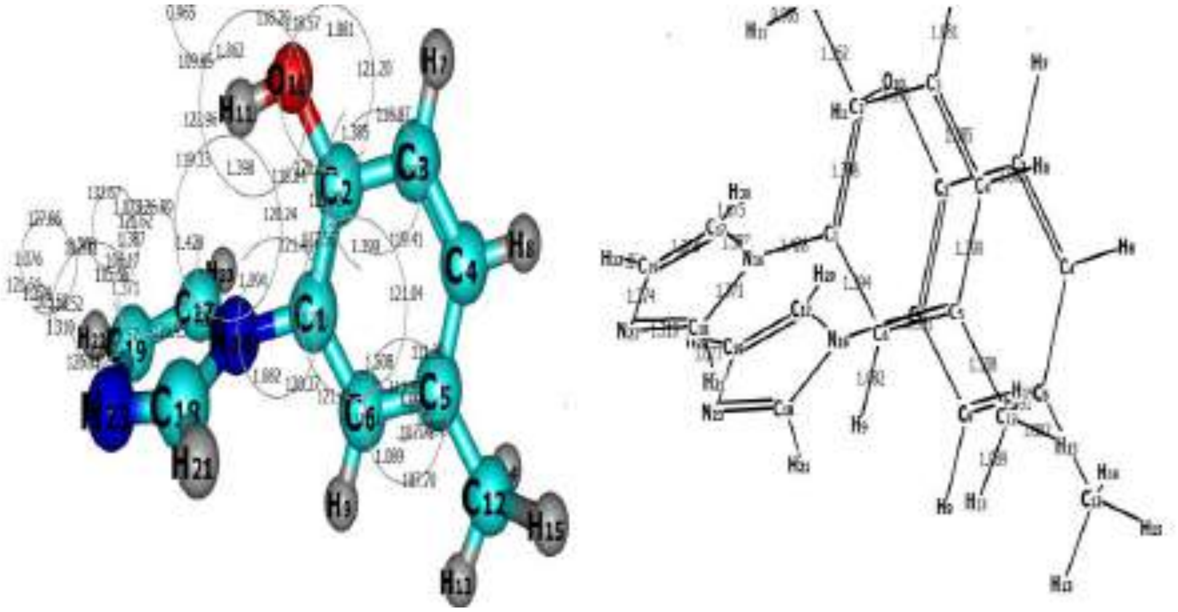

**Fig .1Modal molecular structure of 2-(Imidazole-1-yl)-4-methylphenol**

The chemical reactivity of any molecule is determined by nature of HOMO and LUMO molecular orbitals. The energy gap in between HOMO and LUMO are known as band gap and is important parameter to determine chemical reactivity of any system. The energy band gap is directly related to chemical reactivity of system. Any system having higher energy gap means less polarize high kinetic stability.[Gutowski M. et.al.1993, Bose SC.2011] The HOMO LUMO plot of title molecule is shown in fig-2. The HOMO is distributed over whole molecule however LUMO is distributed over carbmide ring. The transfer of electron HOMO → LUMO means shift means electron transfer from imidazolyl rings phenolic The MESP plot is very important to determine nature of electron density in term of color coding [Murray JS et.al.1996)]. The red color indicate more electronegative surface means better electronegative charge centre blue color represent more electropositive surface means better nucleophilic charge centre and yellow color means electrical neutral centre. The MESP plot of title molecule shown in fig-2. The $O_{10}$ atom of title molecule is encircled with red color however $N_{16}$ atom encircled with blue color which indicate that $O_{10}$ is most electrophilic charge centre however $N_{16}$ represent most nucleophilic charge centre.

Several electronic parameters are calculated by using HOMO and LUMO and listed in table-1. The chemical hardness is two times energy band gap. The negative eigenvalue of HOMO and LUMO are known as ionization potential and electronegativity.

$$IA=-\varepsilon_{HOMO} EA=-\ \varepsilon_{LUMO}\text{------}(1)$$

The value global hardness $\eta = \frac{1}{2}(\varepsilon_{LUMO} - \varepsilon_{HOMO}) = (\frac{IA-EA}{2})$------- (2)

The electronegativity (χ) [Parr R.G. et al.1989, 1983, Pearson R.G.1989,Geerlings P.,et.al.2003]is given by

$$\chi = -\frac{1}{2}(\varepsilon_{LUMO}+\varepsilon_{HOMO}) = (\frac{IA+EA}{2})\text{------}(3)$$

The negative Eigenvalue of electronegativity is known as chemical potential

$$(\mu = -\chi) \text{ --------(4)}$$

The softness parameter is given by

$$S = \frac{\mathbf{1}}{\mathbf{2\eta}} = \frac{\mathbf{1}}{\mathbf{\varepsilon LUMO - \varepsilon HOMO}} \text{-------(5)}$$

The global electrophilicity index

$$(\omega = \mu^2/2\eta) \text{ -----------(6)} \quad [22]$$

**Table-1 Several electronic properties of title molecule**

| S.N. | H(eV) | L(eV) | ΔEgap(eV) | χ(eV) | μ(eV) | η(eV) | S(eV)$^{-1}$ | ω(eV) | ΔN max |
|---|---|---|---|---|---|---|---|---|---|
| **Imidazole** | -6.505 | -1.019 | 5.486 | 3.762 | --3..762 | 2.743 | 0.1822 | 2.579 | 1.371 |

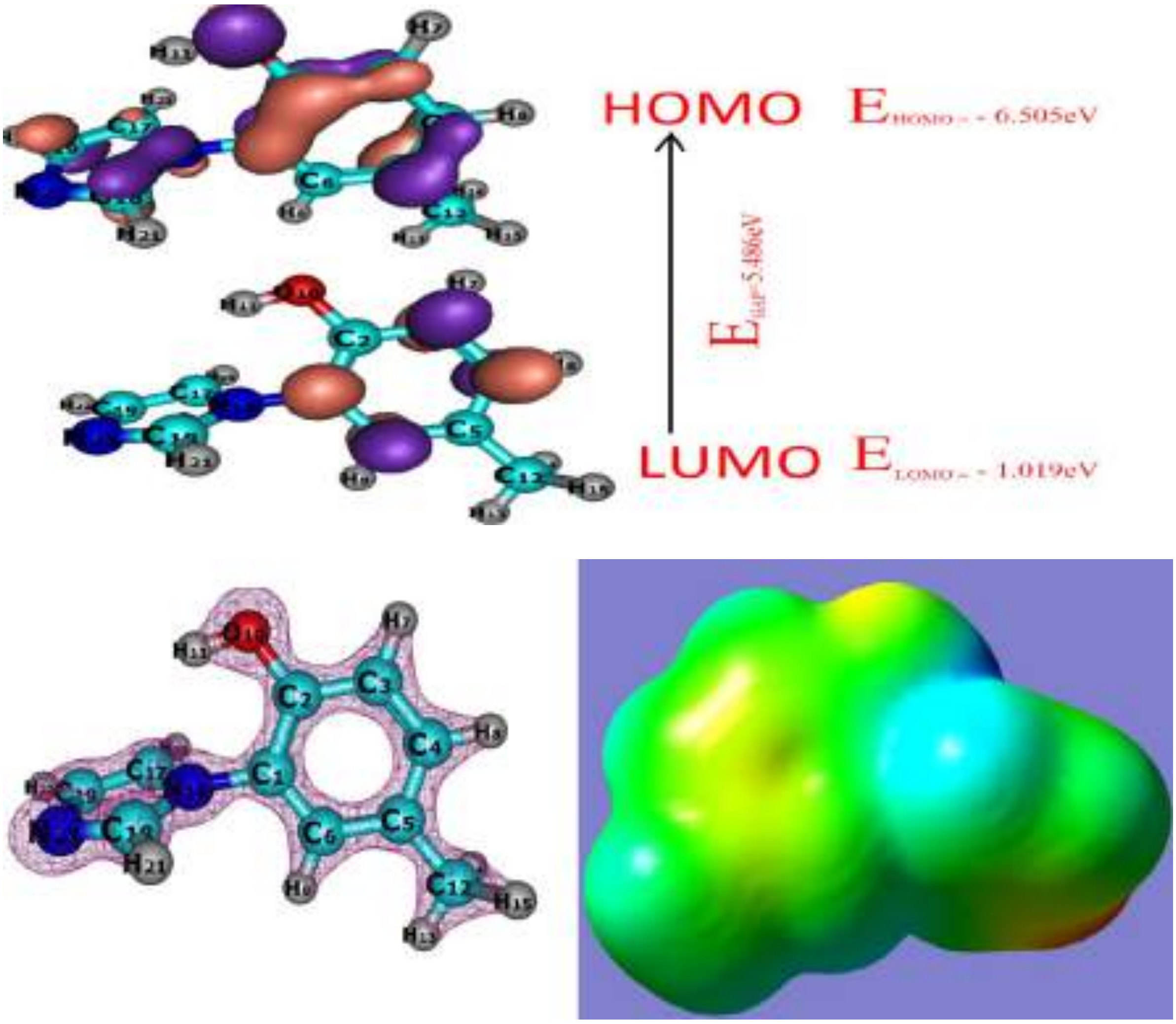

**Fig-2 HOMO LUMO MESP plot of title molecule**

## Vibrational Analysis

The title molecule having 23 atom so having 3N-5 modes of vibration so 110 modes of vibration. Out of 115 modes of vibration 114 are stretching and rest are bending modes. The whole spectra are divided in two part above 1000 are called functional group region however below 1000 modes are called finger print region. The calculated vibrational frequencies are lies some higher frequency region than observed IR spectra. The calculated IR spectra does not include molecular interaction anhormonicity electron electron correlation. To compensate these effect calculated IR frequencies are scaled by 0.96[**SunderganesanN.et.al.,2005**] The calculate IR frequencies scaled frequencies IR intensity and corresponding modes of vibrations are listed in table-2. Some important modes of vibrations are discussed below.

### VIBRATIONAL MODES DISCRIPTION

The shift of O-H modes of vibrations generally related with power of hydrogen bond it normally seen at high frequency ranges from 3600 to 3400 $cm^{-1}$[Krishnakumar V. et.al., 2003]. In this study strong peak obtained at 3403 $cm^{-1}$ which is due the stretching vibration. It observed different experimental at which low stretching for hydrogen atom and intermolecular interaction are occurring in stretching mode.In present study -CH group present and C-H vibration in the range 2800-3100 $cm^{-1}$[Krishnakumar V. et.al., 2005]. The molecules are identification C-H stretching vibration. Stretching vibrations are molecule obtained at 3108 to 3033 $cm^{-1}$Which are support by literature [Krishnakumar V. et.al., 2005]. At 1554,667 two mixed medium intense modes of vibration appears due to banding vibration in C-H molecule**.** On the lower side of spectra, two intense peaks due toscissoring modes of vibration, occur at 1612 $cm^{-1}$and 1460 $cm^{-1}$. The C-C rings are aromatic stretch known as semicircle stretching vibrations are calculated at 1644, 1281,1269,1114,1111 $cm^{-1}$ etc. It supports literature [Krishnakumar V. et.al., 2005]. The C-C modes are torsional mode have been recorded spectral value from literature.The stretching vibration of C≡N are present having frequency 1551$cm^{-1}$ to 1568$cm^{-1}$ which agrees with the literature.

**Table-2 Calculated IR frequencies along with respective intensity and assignment of title molecule**

| S.N. | Cal.Fre | Scaled Fre | Infra. Inte | Assignment |
|---|---|---|---|---|
| 1 | 411.66 | 370.49 | 70.70 | $\alpha$ ($O_{10}H_{11}$) |
| 2 | 677.65 | 609.89 | 20.73 | $\mu$ (C18H23N16) + $\mu$ ($C_{19}H_{22}$) |
| 3 | 741.87 | 667.68 | 26.79 | $\alpha$ ($C_{17}H_{20}$) + $\alpha$ ($C_{19}H_{22}$) |
| 4 | 783.66 | 705.29 | 26.014 | $\beta$ ($C_5C_6C_{12}$) + $\mu$ ($C_6H_9$) +$\beta$ ($C_2C_1O_{10}$) |
| 5 | 831.40 | 748.26 | 22.09 | $\alpha$ ($C_{18}H_{21}$) +$\alpha$ ($C_{19}H_{22}$) |
| 6 | 841.78 | 757.53 | 31.34 | $\alpha$ ($C_4H_8$)+ $\alpha$ ($C_3H_7$) +$\gamma$ ($C_{12}H_{14}H_{15}$) |
| 7 | 916.97 | 825.27 | 10.78 | $\beta$ ($N_{23}C_{19}C_{18}$) +$\mu$ ($C_{19}H_{22}$) +$\psi$ ($C_{18}N_{16}$) |
| 8 | 996.81 | 897.13 | 12.54 | $\alpha$ ($C_{12}H_{13}H_{14}H_{15}$)+$\psi$ ($C_4C_5$)+$\gamma$ ($C_3C_4H_7$)+$\mu$ ($C_{19}H_{22}$) |
| 9 | 1068.15 | 961.34 | 19.01 | $\alpha$ ($C_{12}H_{13}H_{14}H_{15}$)+$\mu$ ($C_{17}H_{20}$)+$\mu$ ($C_{18}H_{21}$) |

| | | | | |
|---|---|---|---|---|
| 10 | 1068.89 | 962.00 | 34.21 | α ($C_{12}H_{13}H_{14}H_{15}$) + μ ($C_6H_9$)+ μ ($O_{10}H_{11}$)+ψ ($N_{16}C_{18}$)+ μ ($C_{17}H_{20}$)+ μ ($C_{18}H_{21}$) |
| 11 | 1133.45 | 1020.11 | 13.94 | ψ ($N_{23}C_{19}$)+ μ ($C_{19}H_{22}$)+ μ ($C_{18}H_{21}$)+ψ ($C_4H_8$) |
| 12 | 1204.54 | 1084.09 | 101.87 | μ ($O_{10}H_{11}$)+ψ ($C_3C_2$)+ψ($C_4C_5$)+ μ ($C_3H_7$)+ μ ($C_4H_8$)+ μ ($C_6H_9$) |
| 13 | 1217.56 | 1095.80 | 24.12 | μ($C_{18}H_{21}$)$R_1$ +ψ ($N_{23}C_{19}$)$R_1$ + μ ($O_{10}H_{11}$)+ μ ($C_3H_7$)+ μ ($C_6H_9$)+ψ ($C_{12}$ $C_5$) |
| 14 | 1261.73 | 1135.56 | 58.64 | ψ ($C_1C_6$)+ μ ($C_6H_9$)+ μ ($C_4H_8$)+ μ ($C_3H_7$)+ψ ($N_{16}C_{18}$) |
| 15 | 1266.88 | 1140.19 | 13.34 | μ ($C_{18}H_{21}$)+ψ ($C_{18}N_{16}$)+ μ ($C_{19}H_{22}$)+ μ ($C_{17}H_{20}$) |
| 16 | 1300.30 | 1170.27 | 22.30 | ψ ($N_{16}C_{18}$)+ μ ($C_{18}H_{21}$)+β ($N_{23}C_{18}C_{19}$)+ψ ($N_{16}C_{17}$)+ μ ($C_{19}H_{22}$)+ μ ($C_6H_9$) |
| 17 | 1335.41 | 1201.87 | 57.59 | ψ ($N_{23}C_{19}$)+ψ ($N_{16}C_{18}$)+ μ ($C_{19}H_{22}$)+ μ ($C_{17}H_{20}$)+ψ ($C_5C_6$)+ψ ($C_1C_2$) |
| 18 | 1366.71 | 1230.04 | 12.54 | μ ($C_6H_9$)+ μ ($C_4H_8$)+ μ ($O_{10}H_{11}$) |
| 19 | 1393.49 | 1254.14 | 18.48 | μ ($O_{10}H_{11}$)+ψ ($N_{16}C_1$)+ψ ($N_{23}C_{18}$)+ μ ($C_{19}H_{22}$) |
| 20 | 1502.34 | 1352.11 | 23.79 | $\Psi_S$($C_{12}H_{15}H_{14}$)+ $\Psi_S$ ($C_{12}H_{14}H_{13}$)+ μ ($C_{18}H_{21}$)+ μ ($C_{17}H_{20}$)+ψ ($N_{16}C_{18}$) |
| 21 | 1512.71 | 1361.44 | 35.61 | $\Psi_S$ ($C_{12}H_{14}H_{15}$)+$\psi_{AS}$ ($C_{12}H_{13}H_{14}$)+μ ($C_{17}H_{20}$)+ $\psi_{AS}$ ($N_{16}C_1C_{17}$) |
| 22 | 1531.08 | 1377.97 | 70.89 | ψ ($N_{23}C_{18}$)+ Ψ ($C_{17}C_{19}$)+ Ψ($C_{19}H_{22}N_{23}$)+μ ($C_{18}H_{21}$)+μ ($C_{17}H_{20}$) |
| 23 | 1543.45 | 1389.11 | 140.94 | γ ($C_3H_7$)+ γ ($C_4H_8$)+ γ ($C_6H_9$)+ψ ($O_{10}C_2$)+$\psi_S$($C_1C_2C_3$)+ ψ ($C_{17}C_{19}$) |
| 24 | 1628.65 | 1465.79 | 17.91 | β ($O_{10}C_2H_{11}$)+ψ ($C_1C_2$)+ ψ ($C_5C_4$)+β ($C_1C_6C_5$)+α ($C_2C_3C_4$)+β ($C_{12}C_5H_{13}$) |
| 25 | 3033.96 | 2730.56 | 33.15 | $\Psi_S$ ($C_{12}H_{13}H_{14}$)+ $\Psi_S$ ($C_{12}H_{14}H_{15}$) |
| 26 | 3078.64 | 2770.78 | 14.12 | $\Psi_{AS}$($C_{12}H_{14}H_{15}$) |
| 27 | 3108.78 | 2797.90 | 13.76 | Ψ($C_{12}H_{13}$)+ $\Psi_S$ ($C_{12}H_{14}H_{15}$) |
| 28 | 3780.99 | 3402.89 | 114.76 | Ψ ($O_{10}H_{11}$) |

**Where ,ψ--stretching ,β –scissoring ,α—wagging ,γ—rocking, μ -twisting**

## Conclusion

We have reported study of Imidazole through geometric parameters, vibrational frequency, electronic title molecules using DFT/B3LYP method and 6-311 G (d.p.) basis set. The calculated optimized parameters are well matched with corresponding observed value which shows that our calculation method well defined geometry of title molecule. The vibrational analysis of title molecule well represents its geometry. The calculated band gap shows that title molecule is chemically nonreactive molecule. We hope that our study provides new path for researcher for further work on title molecule.

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# Determination of hardness in ground water samples of Moradabad by titrimetric method

**Abstract**

The water which contain high concentration of calcium, magnesium chlorides, sulfates and bicarbonates is hard water. Water is the essence of life . But water with high degree of hardness is of no use for domestic and industrial applications. Twenty samples of ground water have been collected from district Moradabad and two different villages. The hardness of water is determined by EDTA titrimetric method. Out of all the samples tested 39 (32.5%) samples were moderately hard, 76 (63.33%) samples were hard water and 5(4.16%) samples were of very hard water . Very hard water is dangerous to health. The present Study did not revealed any soft water. There is a false notion that hard water is harmful to health , it's not hard water , it is very hard water $(> 180ppm)$. It has been noticed that minerals may be beneficial for good health to some extent .So public should be educated about degrees of hardness and its effects.

**Keywords:** Titrimetric method, Ground water, Hardness, samples, calcium

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## Introduction

Hardness of water is a physic- chemical property of water . The concentration of calcium and magnesium ions is determined in water samples. Some time presence of Aluminium, Zinc , Iron , Strontium , also contribute to hardness of water. However they are generally present in very low concentrations(NRC, 1974). These ions reach the water supply by leaching from minerals of rocks and soil. The calcium is obtained from lime stone (calcium carbonate ) and chalk ( calcium sulfate). The magnesium is obtained from dolomite which also gives calcium ions (Gumashta et al., 2012). Water hardness is the soap consuming capacity of hard water. When hard water is rubbed with hard water. It produce sticky substance as calcium /magnesium stearate or palmitate. Initially the presence of polyvalent cations like Ca, Mg, Sr, Ba, Fe, Al, Mn etc. were considered, as hardness producing cations but later on hardness was defined as the sum of the calcium and magnesium concentrations, determined by EDTA titrimetric method, and expressed in ppm or mg/l( Standard Methods , 1998).The presence of anions classify the types of hardness e.g. temporary hardness and permanent hardness. The temporary hardness can be removed by simply boiling the water while permanent hardness can not be removed by boiling the water. The temporary hardness is also known as carbonate hardness while non carbonate hardness is known as permanent hardness. The total hardness means both temporary hardness and permanent hardness.

Based on the types of calcium and magnesium salts in water, it is categorized as soft or hard and very hard water (Sengupta, 2013). From the technical point of view, multiple different scales of water hardness have been suggested ( eg. Very soft- soft-medium hard –very hard). It is expected that both extreme degrees i.e very soft and very hard are considered as undesirable concordantly from the technical and health points of view ,but the optimum Ca and Mg water levels are not easy to determine, since the health requirements may not coincide with the technical ones (Kosisek, 2003).

The awareness about the hardness of water evidenced in late 1950's. The relationship between water hardness and the incidence of vascular disease was first described by a Japanese chemist Kobayashi(Kobayashi, 1957), who showed , based on epidemiological analysis , higher mortality rate from cerebrovascular diseases (Stroke) in the areas of Japanese rivers with more alkaline (i.e harder) water used for drinking purposes .

The WHO says that "there does not appear to be any convincing evidence that water hardness causes adverse health effects in humans "(WHO, 2003).In fact, the United State National Research Council has found that hard water can actually serve as a dietary supplement for calcium and Magnesium (NRC,1974).It has been found that generally hard water is not harmful to one's health. But can pose serious problems in industrial applications. The hard water produce scales, sludges, corrosion, priming, foaming and caustic embrittlement including cooling towers and other equipments that handles hard water. In domestic settings, hard water is often indicated by a lack of suds formation when soap is agitated in water, and by the formation of lime scale in kettles and water heaters. The hard water is soften by various methods for the proper use in domestic and industrial usage. Keeping in view of all adverse effect of hard water the present study was carried out to estimate the amount of hardness in the ground water of Moradabad and nearby villages of Sambhal and Amroha.

## Experimental Section

### Material and Method

One hundred and twenty (120) ground water samples were collected from district Moradabad Uttar Pradesh and two adjacent villages . All the water samples were collected aseptically in a sterilized screw capped glass bottles and brought to the laboratory. The hardness of all water samples was tested by using EDTA titrimetric method by taking 50 ml of water sample into a conical flask along with 100ml of ammonia buffer solution and 100-200mg of Eriochrome Black –T indicator followed by titration with EDTA solution present in burette .End point is noted down by changing of the water solution colour from wine to blue and expressed as $CaCO_3$equivalent in mg/l ( Standard Methods, 1998).amount of hardness in water was calculated by using the formula:

Hardness as mg/l $CaCO_3$ =ml of EDTA solution x1000/ volume of water sample taken.

## Hard and soft water, as per the table below

| Classification | Hardness in mg/l | Hardness in ppm |
|---|---|---|
| Soft (S) | 0-60 | less than 60 |
| Moderately hard (MH) | 61-120 | 60-120 |
| Hard (H) | 121-180 | 120-180 |
| Very hard (VH) | ≥181 | ≥180 |

## Table showing the results for hardness of different ground water samples

| S. No | Place of sample | No of samples | Showing degree of hardness | % of sample |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | Moradabad | 40 | S-0 | S-0 |
| | | | MH-17 | MH-42.5 |
| | | | H-21 | H-52.5 |
| | | | VH-02 | VH-5 |
| 2 | Village sambhal | 40 | S-0 | S-0 |
| | | | MH-12 | MH—30 |
| | | | H-27 | H-67.5 |
| | | | VH-01 | 2.5 |
| 3 | Village Amroha | 40 | S-0 | S-0 |
| | | | MH-10 | 2.5 |
| | | | H-28 | 70 |
| | | | VH-02 | 0.5 |

**S=Soft water, MH=Moderately hard water, H=Hard water, VH= Very hard water**

## RESULTS AND DISCUSSION

The present studies have revealed that out of three places, the two villages have shown high level of hardness as compared to the town. In Moradabad town, out of 40 water samples collected, almost all the samples were moderately hard (42.5%)and hard water samples (52.5%) . Only few samples were very hard water (5%).

The results of villages were different from the results of town. Forty each number of samples were collected from two villages.

In Sambhal village, more number of samples have shown hardness between 150-300mg/l of $CaCO_3$ (67.5%) i.e hard water. Some of the samples have shown moderate hardness (30%) and very few of them have shown extreme hardness (2.5%) . Similar type of results was found in the study of samples of Amroha village also. The results are Hard water (70%), Moderately hard water (2.5%) , and very hard water (5%). Finally

No soft water sample was found in all the 120 samples(Table).Altogether out of 120 samples , most of the samples are found hard water (63.33%).There are only 5 samples (4.16%) which are found to be very hard water. According To Kozisek (2003) both the extreme degrees of hardness are dangerous to human health i.e very hard and very soft water. The present study did not find any soft water. But it has been reported that there are few samples (4.16%) which are very hard and can be ignored. Water intake of cattle and milk production have been found unaffected by water containing up to 290 ppm of hardness (NRC,1974). Hence The water is safe for cattle in the town and villages. Hard drinking water is generally not harmful to human health(WHO, 2003) but can pose serious problems in industrial settings. Most of the people especially House wives dislike hard water because it is useless for washing the clothes. Calcium is the element which reduces the corrosion and less likely to leach toxic trace minerals, such as cadmium and lead, out of metal pipes (Seelig, 1977).According to the US National Academy of Sciences , 1977 , there had been more than 50 studies , in nine countries that it has inverse relationship between water Hardness and mortality from cardiovascular disease (Harold and Foster, 1994).

Most of the scientists have indicated a negative statistical association of various types of cancer morbidity /mortality with the hardness of water and calcium (Yang, 1998). Some studies showed increased eczema in children (Miyake et al, 2004) and Arnedo –Pena, 2007).

## CONCLUSION

The present study has proved that extreme degree of hardness is only 4.16% of the samples which may not be harmful to the people. Although majority of people dislike the use of hard water. It has been found that concentration of Ca and Mg ions show some protective effect on cardiovascular mortality. The use of hard water does not give any evidence to prove casualty among those people who are using hard water. The required concentration of Ca and Mg are good for sound health but excess of Ca is not good for bones as it causes extra growth of bones specially in the back bone and become a big problem. Some people think that hard water is harmful to health. It has been found that extremely hard water creates exosmosis of blood cells . This is important to bring awareness among the people about soft, moderately hard , hard and very hard water.

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# Kinetics and Binary-Solvent Effect on Acid Catalysed Hydrolysis of Butyl Formate

**Abstract**

The rate of the acid catalysed hydrolysis of butyl formate has been investigated in presence of dimethyl sulfoxide (DMSO) in the temperature range of 20 to $40^0$ c. The reaction rate was decreased with progressive addition of dimethyl sulfoxide.The iso-composition activation energies, iso dielectric activation energies and activation parameters like enthalpy of activation, entropy of activation and Gibbs free energy of activation, were also calculated and discussed in term of solvent effect. A mechanism was also proposed to account for the solvent effect on reaction rate.

**Keywords:** Butyl Formate, specific rate, hydrolysis, kinetic solvent effect,. Water-DMSO

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## Introduction

The rate of chemical reaction is changed with the change of solvent composition of reaction mixture which has great importance in laboratory as well as in chemical industry. Sometimes , it is found that the rate is increased by a factor$10^9$ with change of solvent(Cram D. J,et.al.,1961). The solvent affects the reaction- rate in two ways. One through static or equilibrium solvent effect and another through dynamic or fractional solvent effect(Reichardt C,2003, Rose S et.al, 1995, Singh AK.,2015, Herodes K., et.al. 1999). The static solvent effect on reaction- rate can be understood in terms of Transition State Theory. The second method influences the rate of fast reaction. The solvent effect is also closely related to nature and extent of solvent-solute interaction. Solvent-solute interaction are very much complex in mixture of the solvent than pure solvent due to the possibility of specific solvation of any solvent present in the mixture. In this investigation, studies of solvent effect in hydrolysis of butyl formate has been reported, which has greater use as polar aprotic solvent, a flavouring agent and fragrance.

## Experimental Section: *Material and method*

Butyl formate is a formate-ester which is formed by condensation of formic acid with hydroxyl group of butanol-1. It is found in apple strawberries, sherry and parmesan cheese. It has a fruity plum-like odour and taste. Its molecular formula is $C_5 H_{10} O_2$. The reaction kinetics of the formate ester has been studied under first order condition and the entire chemical used are from Pub Chem. NIH. Calculated amount of organic solvent (DMSO) water and stock acid (HCl) has been mixed in 250 ml conical flask in such a way that total volume of the solution was 50 mL and its strength became 0.5M. The conical flask containing the solution and small stoppard bottle containing pure Butyl formate has been thermostated for 30 minutes. Then 0.60 ml of ester has been withdrawn and added quickly to the acidic solution of water-solvent mixture. Now the strength of solution in terms of ester becomes 0.1M.Immediatly 2 mL of aliquot of the reaction mixture was withdrawn and allowed to run into a conical flask containing 25mL of ice cold water so that the reaction may be arrested quickly. The acid of the solution was titrated as soon as possible by means of standard baryatha solution using phenolphthalein as indicator. The moment, at which half of the aliquot was added into the ice cold water, the stop clock was started. This time has been considered as the starting time or zero time. Taking into account of zero time, kinetics of reaction was studied by estimating the amount of remaining ester at definite desired interval of time. This reading was recorded as $T_{t..}$

## RESULTS AND DISCUSSION

### Solvent Effect Dependence and Rate Constant

The rate of hydrolysis of Butyl formate has been measured in water-DMSO medium by the slope of log k against time(Table-2 and Fig-1). The plot of log k againt reciprocal of time has been found to be linear.The retardation of rate with increase solvent composition may be explained on the basis of the fact that the formation of polarised transition state is favoured with increased proportion of DMSO.This fact is also supported by Hugh and Ingold(Hughes E.D, Ingold C.K.. 1935 ) qualitative theory. The rate determines the step of hydrolysis of ester is an addition of hydroxyl ion to the carbon of carbnoyl group and after which rapid reaction with water is followed. Hence, if the activity of hydroxyl ion decreases, the reaction-rate must be decreased as suggested by Tommila et al. 1935 . The lower the rate in water-ethanol mixture suggested that interaction between water and DMSO increases with increased concentration of free water available for salvation of hydroxyl ion. The curve of log k against mole fraction represents smooth decrease (fig-1), which implies that solvation of hydroxyl ion is stronger and hence the values of rate constant decreases(M.S.Metwally, 1992 , Singh, AK, 2021).

**Table 1.Bimolecular rate constant *k* x$10^4$(dm)$^3$/mole/min**

| Temp in $^{O}$C | % of DMSO | | | | |
|---|---|---|---|---|---|
| | 30% | 40% | 50% | 60% | 70% |
| 20$^{O}$C | 74.98 | 64.56 | 53.70 | 41.68 | 32.35 |
| 25$^{O}$C | 162.18 | 137.72 | 116.14 | 94.40 | 77.62 |
| 30$^{O}$C | 330.36 | 316.22 | 242.66 | 206.53 | 175.79 |
| 35$^{O}$C | 653.13 | 568.85 | 489.77 | 436.51 | 380.18 |
| 40$^{O}$C | 1318.25 | 114.15 | 1000.00 | 931.10 | 860.99 |

**Table 2.log k values with different mole %**

| Percentage of DMSO | | 4+ log k | | | | |
|---|---|---|---|---|---|---|
| | Mole% | $20^oC$ | $25^oC$ | $30^oC$ | $35^oC$ | $40^oC$ |
| **30** | 9.77% | 1.875 | 2.210 | 2.519 | 2.815 | 3.12. |
| **40** | 14.40% | 1.810 | 2.139 | 2.500 | 2.755 | 3.060 |
| **50** | 20.17% | 1.730 | 2.065 | 2.385 | 2.690 | 3.000 |
| **60** | 27.49% | 1.620 | 1.975 | 2.315 | 2.640 | 2.969 |
| **70** | 37.09% | 1.510 | 1.890 | 2.245 | 2.580 | 2.935 |

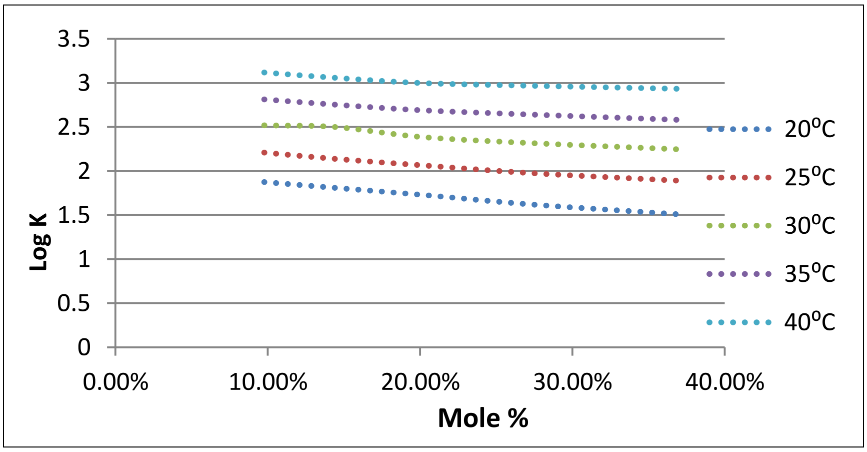

**Fig. 1.Plots of log k with mole %**

**Activation Energy (Ec) and Rate of Reaction**

Arrhenius plots (Log k against 1/T) has been used to calculate value of activation energy ($E_c$). Table-4, collects the obtained values of activation energies under different solvent composition. The increase in ($E_c$) values with increase in solvent composition has been noticeable because it will only happen when there is solvation change taking place either in initial level or transition level or both.

The increasing value of ($E_c$) as a function of solvent composition indicates that solvation occurs at initial level whereas desolvation takes place at transition level(Singh A.K..et.al, 1984) .

**Table3.Different log *k* values as a function of temperature**

| Temp in $^{O}C$ | | 4 + Log*k* | | | | |
|---|---|---|---|---|---|---|
| | $10^3/T$ | 30% | 40% | 50% | 60% | 70% |
| $20^{O}C$ | 3.412 | 1.875 | 1.810 | 1.730 | 1.620 | 1.510 |
| $25^{O}C$ | 3.355 | 2.210 | 2.139 | 2.065 | 1.975 | 1.890 |
| $30^{O}C$ | 3.300 | 2.519 | 2.500 | 2.385 | 2.315 | 2.245 |
| $35^{O}C$ | 3.247 | 2.815 | 2.755 | 2.690 | 2.640 | 2.580 |
| $40^{0}C$ | 3.195 | 3.120 | 3.060 | 3.000 | 2.969 | 2.935 |

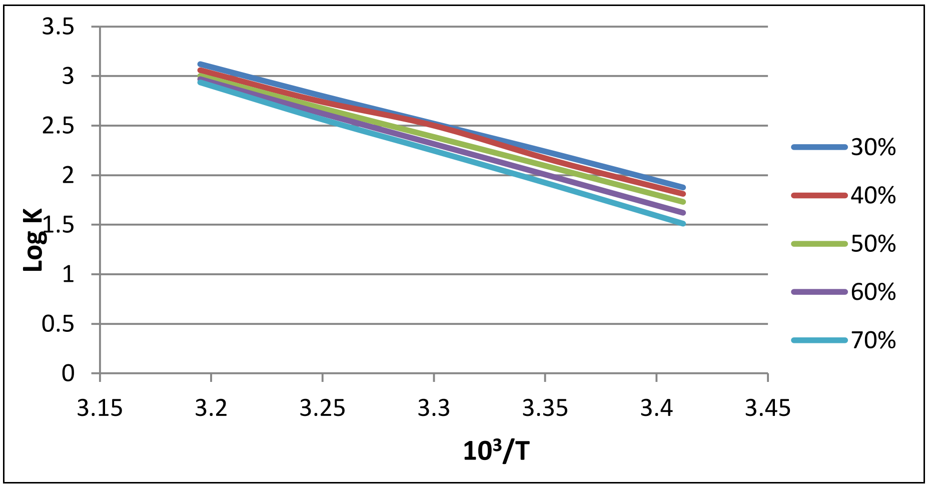

Fig- 2. Plots of log k with $10^3/T$

**Table 4.Iso- Composition activation energy at different solvent fraction**

| % of $E_c$ | 30% | 40% | 50% | 60% | 70% |
|---|---|---|---|---|---|
| $E_{exp}$ in KJ/mole | 109.60 | 110.65 | 113.02 | 119.79 | 124.92 |

**Table 5.The values log $k_D$at different D**

| Temp in $^{O}C$ | $10^3/T$ | D=68 | D=70 | D=72 | D=74 | D=76 |
|---|---|---|---|---|---|---|
| $20^{O}C$ | 3.413 | 1.380 | 1.460 | 1.560 | 1.650 | 1.740 |
| $25^{O}C$ | 3.356 | 1.820 | 1.905 | 1.990 | 2.075 | 2.160 |
| $30^{O}C$ | 3.300 | 2.240 | 2.315 | 2.390 | 2.465 | 2.530 |
| $35^{O}C$ | 3.247 | 2.620 | 2.680 | 2.740 | 1.790 | 2.859 |
| $40^{0}C$ | 3.195 | 2.990 | 3.055 | 3.120 | 3.175 | 3.230 |

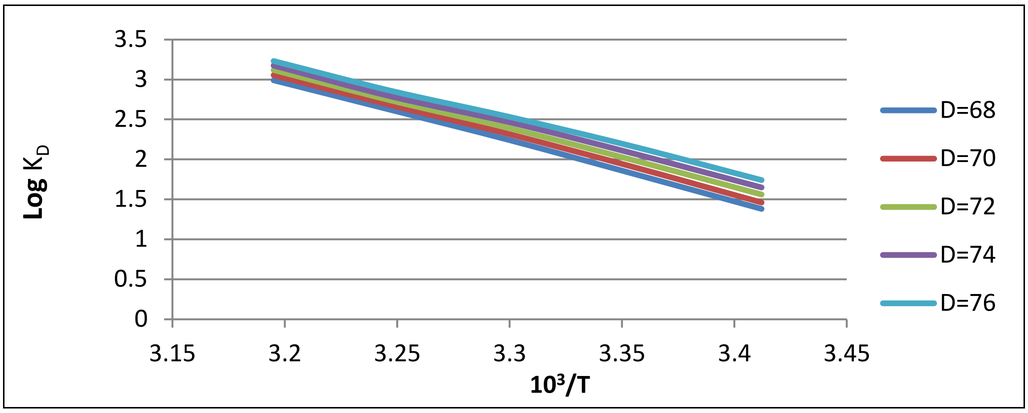

**Fig. 3. Variation of log $k_d$ with $10^3$/T**

### Dielectric Effect on reaction rate

The another aspect of effect solvent may also be considered by observing the effect of dielctric constant D on reaction rate. If there is an increase in rate,it is found to increase in D whereas the rate decreses with decrease in D. The dielectric constant values are obtained by interpolation of Akerlof data(Akerlof G., 1932 ). Linear relationships are obtained between log k and D-1/2D+1 for dipole-dipole interaction as given byLanndskroner(Laidler K.J. and Landskroener P. A,. 1956). However, for ion-dipole linear relations are obtained by plotting log k and log D or log k against 1/D. With the help of slopes of plots of Log $k_D$ against reciprocal of absolute temperature, the iso-dielectric values has been calculated [ Table-5,Fig-3] with the help of slope of different linear line. The depletion in ($E_D$) with decreasing D[Table-6], showed that depletion in($E_D$) values followed similar trend as (Ec) values with increasing proportion of solvent composition(RK. Wolfod. 1964, Bano Arjuman, Singh AK.. 2017, Singh A K. Bano Arjuman. 2019).

**Table 6.Calculated values of ($E_D$) at constsnt D**

| **Dielectric constant(D)** | D=68 | D=70 | D=72 | D=74 | D=76 |
|---|---|---|---|---|---|
| **$E_D$ in kJ/mole** | 137.28 | 136.53 | 1.33.20 | 130.33 | 125.22 |

## CONCLUSION

The gradual decrease of rate is constantly found with increased proportion of solvent composition due to increased concentration of free water available for solvation of hydroxyl ion. The increase of activation energy with increasing composition of solvent indicates desolvation in transition state and solvation in initial state. Dielectric value follows similar trend as iso-composition activation energy.

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# Reciprocating Wear Characteristics of Surface Modified Ti64 Alloy under Variable Load

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## Abstract

The surface of the Ti64 alloy was modified by ultrasonic shot peening technique to nano-structure. This was done to enhance the tribological properties of the alloy. The new surface formed was investigated for reciprocating wear performance against the AISI52100 tribo-pair. An increase in surface hardness was found in the case of the shot-peened sample in comparison with a non-ultrasonic shot-peened sample. The microhardness was measured using the Vickers hardness test. The tribological test was carried out for both samples with different loading conditions. SEM, EDX of the worn surface, was carried out to know the mechanism of wear. It was found that the wear resistance was improved due to shot peening.

**Keywords:** Friction;wear;composite; titanium alloy; lubrication

## Introduction

The growing need for materials with strength/weight ratio at high temperature and applied force for aerospace applications increases the demand of Ti-based composites. Pure Ti and its alloy are used commercially in the aerospace industry due to lightweight (low density of about 60 % to that of steel), high strength and excellent corrosion resistance. Most widely used Ti alloy is Ti64 (Ti-6Al-4V) [Chen KM et al.2015, Kumar S et.al.2017]. Ti64 can be used for air-frame, engine parts; apart from this, it can also be used for manufacturing blades, discs, rings, fasteners, vessels, cases, hubs, or in forged parts and biomedical implants [Kumar S et.al.2016]. However, there are some limitations of these materials due to their poor tribological properties and hardness [Hu ZY X et.al.2017, Dixit T, Singh I, Prasad KE.2018]. Various processes like laser shock peening [Ye C, Liao Y, Suslov S, Lin D, Cheng GJ.2014], shot peening [Child DJ, West GD, Thomson RC.2011], ultrasonic peening [Amanov A, Cho IS, Pyoun YS, Lee CS, Park IG.2012], laser-assisted ultrasonic nanocrystal surface [Liu J, Suslov S, Ren Z, Dong Y, Ye C.2019], surface mechanical attrition treatment are used for enhancing the mechanical properties through surface modification of materials at the nano level. Various researches have been done to improve the surface property of Ti64 [Maire L, Faure L, Philippon S, Novelli M, Marcos G, Czerwiec T.2015 ].

In the present investigation, the hardness, average coefficient of friction (COF) variation, wear resistance of un-shot peened as well as shot-peened Ti64 samples at different loads were studied.

## Experimental Section

The alloy Ti–6Al–4V was procured from M/s Mishra Dhatu Nigam Limited, Hyderabad, as hot rolled and annealed rod of 50 mm diameter. The chemical composition of the alloy is recorded in Table1. The batch contain two sample one without shot peening (Ti64) and one with ultra-sonic shot peen (Ti64USSP). The sample bar of Ti-6Al-4V was cut into 20mm X 15 mm cylindrical bar, and the surface was polished with various grades of emery paper followed by cloth polishing with alumina and diamond paste. Disc of 20mm (Diameter) X 15mm (thickness) were sectioned from the sample rod and subjected to ultrasonic shot peening using Stress Voyager (SONATS). This system works on the acoustic assembly, which creates mechanical vibration, and this is transfer to hard balls of 100C6 grade steel. The vibration is transferred from steel ball to specimen surface, which is kept in the horizontal position to have uniform shot peening on the surface, while the frequency is set at 20 kHz. Vickers test was carried out on both samples under a normal load of 1kgf (9.807N) with a 10 sec holding time. Nine indentations were carried taken, and diagonals were measured using a digitally calibrated objective. An increase in surface hardness was observed as 334HV for shot-peened samples, while for un-USSP, it was 301HV.

Both polished Ti6Al4V samples (Ti64USSP and Ti64) were subjected to Dry sliding reciprocating tests in ambient temperature and humidity, against AISI52100 steel ball (6 mm diameter) as counter body using a wear tester (Rtec multipurpose tribometer) for 20 minutes. The frequency of 5 Hz, the stroke length of 1mm, and loads of 10,15, 20, and 25 N were applied on the ball, where the platform was reciprocating, and the ball was kept stationary. The wear volumes of the flat test samples were measured using with a vertical scanning interferometer Rtec multifunctional tribometer and image processing software. The specific wear rate (in $mm^3/Nm$) was calculated from wear volume ($mm^3$) for all loading conditions. SEM and EDX were done to analyze the wear mechanism.

**Table 1. Chemical composition of the Ti–6Al–4V alloy (wt.%).**

| Al | V | C | O | N | H | Fe | Ti |
|---|---|---|---|---|---|---|---|
| 6.24 | 4.11 | 0.015 | 0.163 | 0.004 | 0.005 | 0.040 | Balance |

## RESULTS AND DISCUSSION

The variation of average COF and wear rate is shown in figure 1. It can be observed from fig.1(a) that there is an increase in average COF with the load for un-USSP Ti64 till 20N and a slight decrease in the value of COF is observed after that. For Ti64USSP sample, the variation is fluctuating with the load increasing for 10N and 20N while decrease for15N and 25N. The average COF was found to be lower in the case of USSPed samples for all the loads. The overall lowest COF was seen for 25N in Ti64USSP sample. From fig.1(b), it can be seen that there is an increase in wear rate from 10N to 15N for both Ti64/Ti64USSP with a decreasing trend till 25N for Ti64 but not the similar trend is observed for Ti64USSP. Wear rate is observed to lower for the USSPed samples for all the loads except at 25N. The lowest wear rate was seen at 10N for Ti64USSP sample. Grooves along with debris are visible for 10N and 25N Ti64USSP. Groves marks are clearly visible, surface cracks, and brittle fracture which can be noticed more prominently in 25N of USSPTi64.

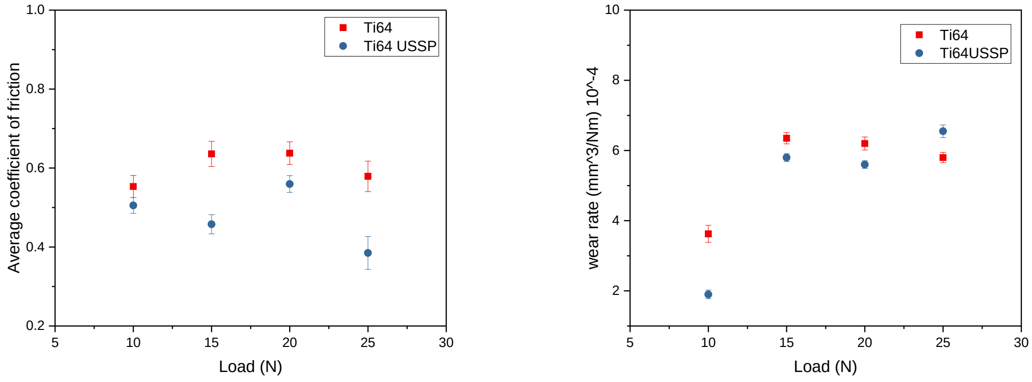
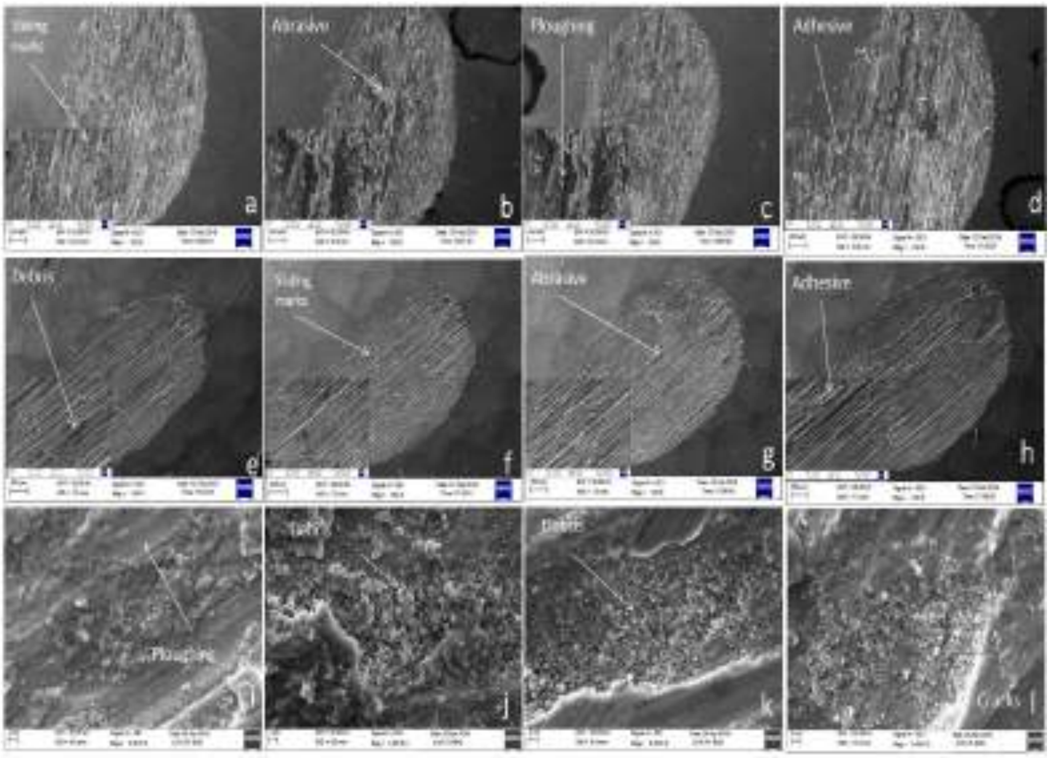


**Fig 1(a).Show the variation of average COF with the load. 1(b). show the variation of wear rate with the load.**



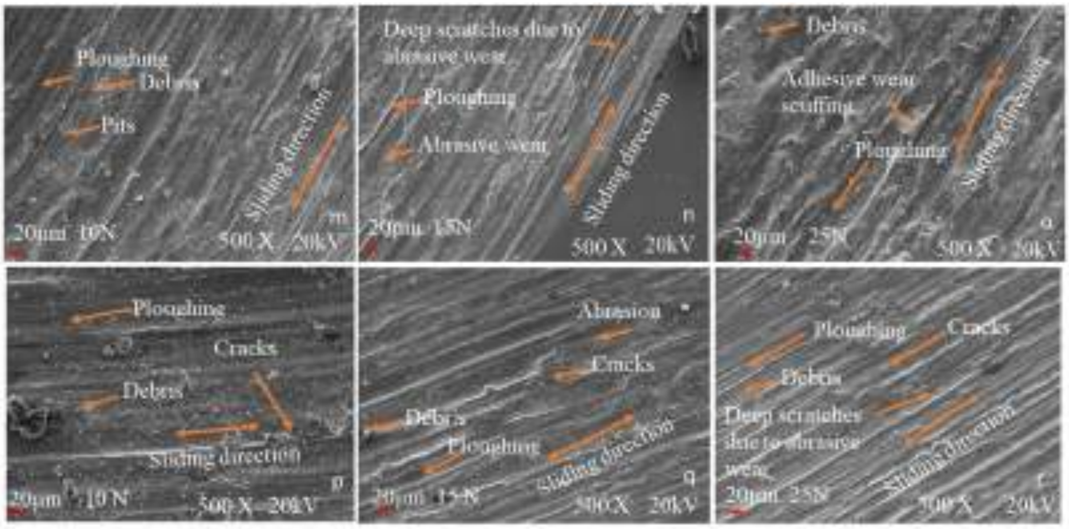


**Fig 2. SEM images of Ti64USSP (a,b,c,d,i,j,m,n,o) and Ti64(e,f,g,h,k,l,p,q,r) for 10N fig 2(a,e,m,p) 15N fig 2(b,f,n,q), 20N fig 2(c,g), 25N fig 2(d,f,o,r), fig 2 (i,j,l,k) shows the magnified view of worn surfaces at 10 and 25 N for both Ti64USSP and Ti64 samples.**

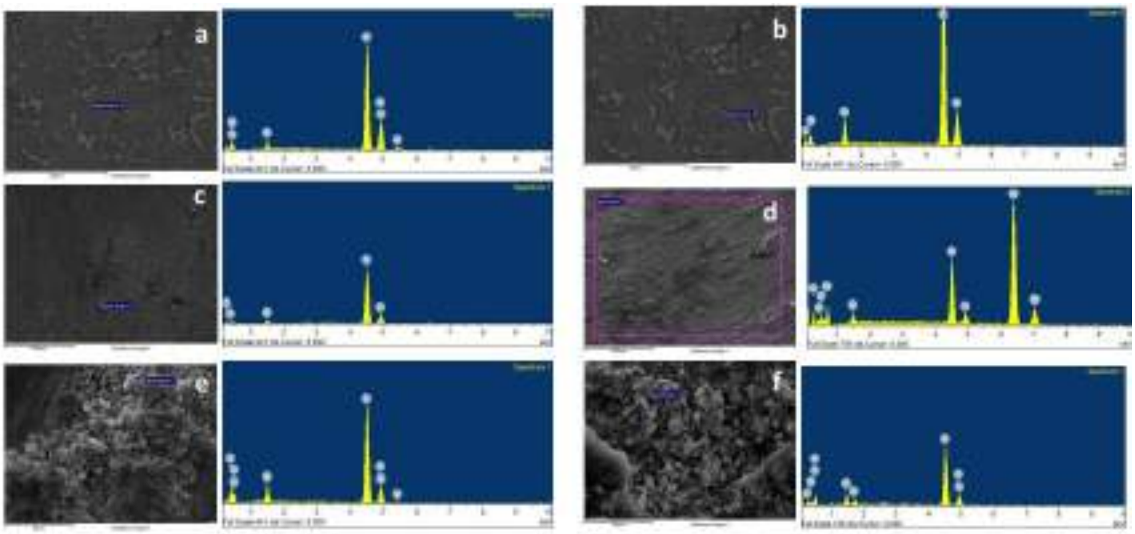


**Fig 3. EDX of counter body (a,b) base sample(c,d) and Worn Surface(e,f).**

Fig 1(a).Show the variation of average COF with the load. 1(b). show the variation of wear rate with the load.

Fig 2 shows the wear micrograph at the various loads of Ti64 and Ti64USSP samples. In fig 2.(a,e, m ,p) for 10 N the sliding marks and grooves can be seen in Ti64/Ti64USSP. In fig 2(b,f,n q) for 15N, these groves become deep, and sliding marks are more prominent. A similar trend is observed in micrographs of 20N in fig.2(c,g) ploughing, abrasive wear marks, and cracks are visible. In fig.2(d,h,o,r) the cracks are more prominent for both samples.

From fig 2. (i,j) for 10N and 25N Ti64 sample, we can see it can be seen that debris is spread everywhere on the worn surface. From fig 2. (k,l) microcracks and deep. From fig 3.(a,b) presence of the white region indicates the formation of the oxide surface, which is clearly visible in SEM micrographs. Furthur it is verified by EDX of the surface which shows the oxygen content. In Ti64 the wear is more at 10N due to abrasive wear and no surface layer compaction of debris, while material removal in Ti64USSP is less due to ploughing, surface hardening, and surface layer compaction clearly visible SEM images. From fig 3.(c,d) the counter body shows the transfer of material from the samples to ball i.e presence of specimen debris on the ball. EDX of the ball also shows the peak of C, Fe, and O along with base material. In EDX the peaks of Ti, V, Fe, O, Al, and C can be seen on the worn surfaces and a similar observation was reported elsewhere [Euh K, Lee J, Lee S.2001, Chen G, Jiao Y, Tian T, Zhang X, Li Z, Zhou W.2014, Revankar GD, Shetty R, Rao SS, Gaitonde VN.2017]. It indicates the formation of the oxides on the surface of samples creating a protective layer for further wear of surface. From fig 3.(e,f) the nature of debris as particles can be seen. The presence of both specimen and counter body in the debris is shown by EDX of the materials and few O peaks indicated that the oxidation of the particles.

The hardness of the Ti64USSP sample in comparison to Ti64 samples is high, measured on Vickers microhardness tester. USSP is used to refine the grain structure which causes the stress on the treated surface is more severe than the inside layer up to some micron and induce work hardening phenomena to increase the microhardness of Ti64USSP. There is an increase in wear resistance of the surface and the hardness of the USSP sample.

Surface hardening can increase the performance of the sample. The COF is low for Ti64USSP samples at all loading conditions while the wear rate is low till 20N with a slight increase with load at 25N. This increase in wear of Ti64USSP is may be due to the breaking of the oxide layer and brittleness of the surface exposing the inner layers at high load. In fig.2(r) it is visible from the SEM micrographs at 25N for Ti64USSP revealing the dominant mechanism of wear and increase in the wear rate. There is no pattern observed with an increase in load for both samples. The Ti64USSP sample has improved wear and friction properties in loading condition at 10,15, and 20N, but at 25N the wear is slightly high may be due to the strain hardening of the material makes the surface more brittle and forces are high enough to break the tribolayer causing loss of materials which does not happen for Ti64 while due where ploughing is dominant which result in plastic deformation of material rather than breaking the tribolayer. The COF is minimum for the USSP sample at 10N while increasing a little at 25 N because of the breakage of tribolayer and deep scratches due to abrasive mechanism is dominant at higher load and these abrasive scratches cause the failure.

## Conclusion

USSP is used to refine the grain structure and causes work hardening to increase the microhardness of Ti64. There is an increase in wear resistance of the surface due to an increase in the hardness of the USSP sample. The wear rate, in general, decreases for the USSP sample, however, it increases a little at 25 N because of ploughing and abrasive wear. The Ti64USSP sample has improved wear and friction properties in loading conditions at 10,15,20 and 25N. The dominant mechanism of wear is a combination of abrasive and adhesive along with ploughing.

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*Original Article*

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# Nature and Nanotechnology: Use of Contact Angle for the Calculation of Surface Energy

**Abstract**

Very often we say the human body is much more complex than even a pioneer researcher can think of that. Many of our milestone discoveries were first originated from observation of the natural phenomena. For example, if there was no apple fell in front of Sir Isaac Newton, it might take another 50 years to discover the concept of gravitation. With the discovery of more and more sophisticated tools one by one it was realised that nature has keen resembled with many sophisticated systems developed so far. In this article one of such natural effect has been studied in depth. This effect called “Lotus effect”, which has changed the concept of hydrophobicity and coating industry. In this consequence the concept of the surface energy which happens to be one of the key factors related to concept of nanoscience and technology has been discussed in detail.

Here it has been shown that how a simple contact angle data can be used to determine the surface energy of any flat surface. Not only that this project also has shown that the surface energy has two components and that can be calculated separately. This polar and dispersive part of the surface energy has its different parts in determining the surface properties and thus should be taken care of separately.

In this consequence the basic concepts of nanoscience and technology and how a nanomaterial becomes novel in comparison with the bulk form has also been revisited.The article will enable one to have mastery over the structure property relation of any material in planer form.

**Keywords:**Nanoscience; Material; Surface energy; Contact angle; Aromatic compounds.

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## Introduction

Nanotechnology is an interdisciplinary science in which material scientists, mechanical and electronic engineers, biologists, chemists & physicists work together to extend the nanoscale boundaries. Nano is a Greek word, which means micro or small. Every particle, whose size is 100 nm or smaller is considered a nanoparticle.

Nanoscience is the study of the fundamental principles of molecule and structure with at least one dimension roughly between 1 & 100nm.

In 1959, Richard Feynman, an American physicist at the California Institute of Technology said during one of his lectures "There's plenty of room at the bottom". These lines later give the foundation of nanotechnology that's why the father of nanotechnology is known as Richard Feynman.  To indicate the object is how much small then we compare it with human hair. We know that the average diameter of human hair is about fifty thousand nanometres. In comparison the smallest features that one commonly etched on a commercial microchip is less than 100nm. The smallest things the human eye can resolve are 10,000 nm across. **Fig.1** shows the size dependence of different object in universe.

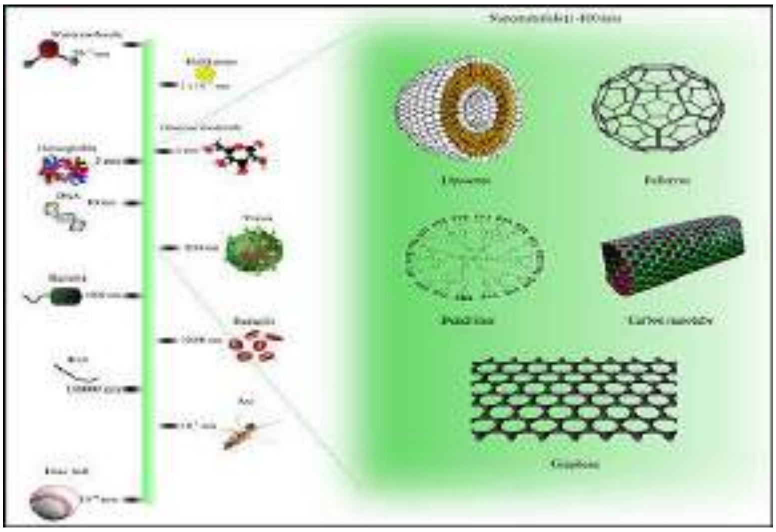


**Fig.1: S**ize dependence of different object in universe.

The topic of Nanoscience deals with small things and the use of nanotechnology in various places. The chemical and physical characteristics of nanoparticle change due to the extremely microscopic shape. For example, the cubes of sugar are less sweet than the castor sugar because the surface area of the castor sugar is larger surface area than the cubes of sugar. With the help of the nanotechnology, we have ability to see the control of atoms and molecules. The materials which we use in nanotechnology are called nanomaterial.Reason for different properties in nanomaterials than their bulk materials are as under:

**Higher ratio between surface and volume:** The very high surface to volume ratio gives rise to higher numbers of dangling bond. This higher numbers of dangling bonds in turn develops very high chemical activities within the nanomaterial making them different from its bulk form.

**Quantum effect:** From the very basic particle in a box, problem one faces in quantum mechanics, it is seen that the energy gap between the two successive energy levels or rather any two energy levels depends inversely on the square of the box dimension thus enhancing the optical gap of the material. This optical gap governs the optical properties of the nanomaterial.

**Density of states:** Density of state i.e the numbers of states per unit energy interval per unit volume is highly dimension dependent and thus shows marked difference for 0, 1, 2 and 3 dimensional structure of same material. There are two techniques to synthesize nanomaterials as given below:

**Top- Down Approach:** It is a physical process. In this approach, a large-scale object is progressively decrease in dimension. We take a bulk material which is broken into fragments and then to nanoscale particles. It consists of ultra-fine micro machining of material using lithography, epitaxy and etching. This method required too much time and also costly. There are some top-down methods to synthesize nanomaterials and these are all physical methods: Ball Milling, Physical Vapour Deposition, Lithography, Thermal Evaporation.

**Bottom-Up Approach:** It is chemical process. In this process atom come together to form the clusters and clusters material come together to form nanoscale particles. In this approach different materials and devices are synthesized from molecular components on their own which do not require any external agent to assemble them. This method is relatively cheaper than the top-down approach. There are some bottom-up approaches to synthesize nanomaterials, these are chemical methods: Sol- Gel, Chemical Vapour Deposition, Co-Precipitation, Micro Emulsions, Hydrothermal, Sonochemical, and Microwave. **Fig.2** shows both the approaches schematically.

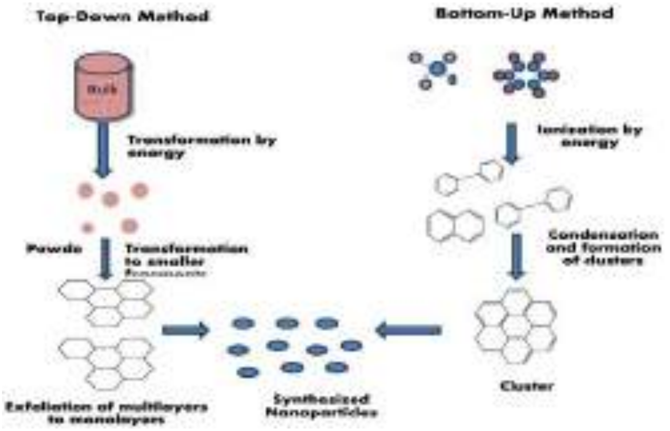


**Fig.2:** Schematics of top-down and bottom up approaches

There are many evidences by which it is observed that nanotechnology is used from ancient time.

**Table 1** summarizes some important point from the history of nanotechnology according to their timeline: In today’s world the use of nanotechnology in the field of medicine, nano fertilizer, nano weed, etc. to save our main crop in agriculture areas. With the help of nanotechnology today’s electronic item is smaller than earlier electronic items. Nanomaterials are those with particle sizes measurable in nanometres. Most common examples are activated carbon, aerogel, graphene. In nature, colours of insects are often not pigmenting at all, but very tiny structures which scatter light selectively to give an effect of colour. Titanium dioxide nanoparticles have found to have peculiar property of killing germs when walls are painted with it and thus can be very useful in hospitals. There are many examples of nanomaterials, and new ones are being discovered, which will bring about a revolution in engineering, medicines and many walks of life. For comparison, a full stop, or a period, in print could be about 1 million nanometres.

**Table 1:** Some milestones in the history of nanotechnology according to their timeline

| | |
|---|---|
| **2000 years ago** | Nano crystal of Sulphide used by Greeks and romans to dye hair. |
| **1000 years ago** | Gold nanoparticles of various sizes used to fabricate many colours in stained glass windows. |
| **1959** | Physicists Richard Feynman gives sentence “There’s plenty of room at the bottom.” |
| **1974** | The word “Nanotechnology” first time used by the professor Norio Taniguchi. |
| **1981** | IBM develops Scanning Tunnelling Microscope. |
| **1986** | The first book on nanotechnology named “Engines of creation” which was written by the K.E. Drexler. |
| **1991** | S. Ijima discovered Carbon nanotubes. |
| **1999** | R. Freitas written first book on nano medicine named “Nano Medicine”. |
| **2000** | National Nanotechnology Initiative was launched by US |

Most objects we come across in daily life have particle size bigger than these unimaginable material dimensions, and are bulk materials. We are making extensive use of nanomaterials today- cosmetics, sunscreen lotions, super-capacitors, some new batteries, robotics, and now they are invading computers, and many more things.

## Classification of Nanomaterials

Nanomaterials can be classified dimension wise into following categories shown in **Table 2**

**Table 2:** Classification of Nanomaterials

| Classification | Examples |
|---|---|
| **Zero dimension< 10nm** | Particles, quantum dots, hollow Spheres, etc. |
| **One dimension < 100nm in any two dimension** | Nanorods, nanowires, nanotubes etc. |
| **Two dimensions < 100nm in any one dimension** | Flakes, sheets etc. |

## Applications of Nanotechnology

Nanotechnology has various applications in the area of science and technology as shown in **Fig.3.**

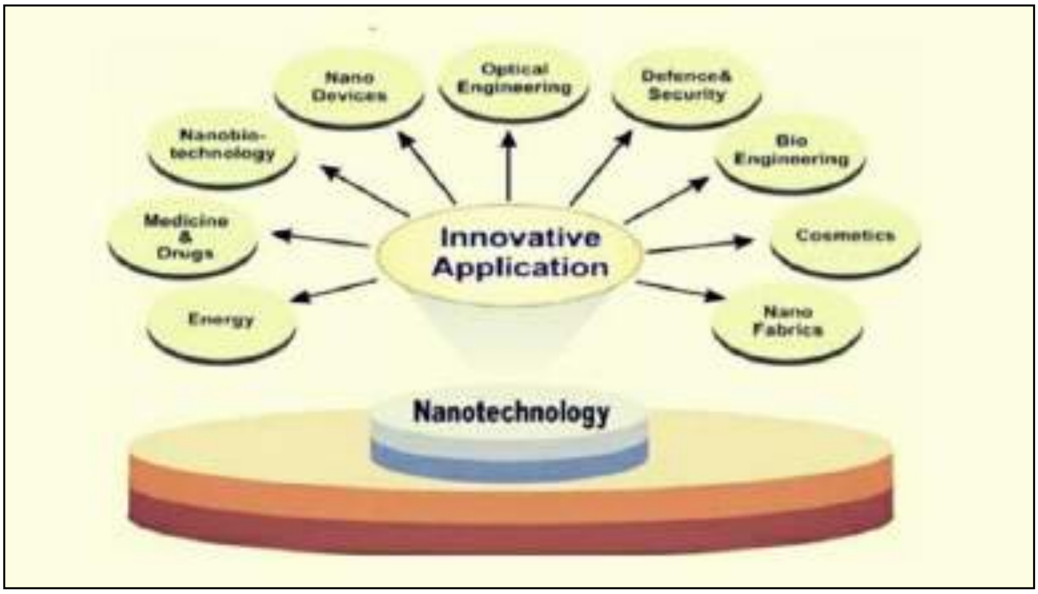


**Fig.3:** Applications of Nano technology

Few specific fields are as under:

### a) Energy:

Nanotechnology has brought a revolution in the energy sector which is one of the most serious concerns in the present day. For instance nanomaterial based illumination technology can reduced the power significantly, while using LED compared to the ordinary bulb. The later can use only 5% of the electricity fed to it. In another example if we talk about present solar driven cars the best one can covert the 40 % of the solar energy whereas for ordinary commercial car, it cannot exceeds 15 – 20 %. Use of Nanomaterials with proper band gap can help conversion of the energy in much higher extend.

### b) Defence and Security:

Application of nanotechnology has enough prospects to redesign the present defence and security system. This is possible by miniaturizing the deadly weapons or developing unmanned vehicles for combat. Also there are plenty of scopes to develop different sensors, display, satellite component and others all of which may prove their importance in different part of defence and security system.

### c) Information & Communication:

The conventional silicon based electronics is now getting bit obsoleted due to its very high cost and other related issues. The nanomaterial based development of transistor, capacitors and other components are so far the hope for the new era of electronics. Also researchers are now being able to develop molecular transistors which show the hope in this sector in the coming years.

### d) Medicine:

The effectiveness of nanomaterial in the field of medicine and drug delivery came to the mind of the researchers from the fact that the size of nanomaterials is almost similar to the most of the biological molecules. It thus readily suggests that that nanomaterial based technology can effectively be used in-vivo and in-vitro medical applications. There is a remarkable success of nanomaterial based treatment that offers targeted drug delivery to a particular position of the body, say where cancer cell evolves. The other application is development of contrast agent, or different analytical tools, tools that needed for physical therapy and many others.

## Literature Review

There are several reports of developing hydrophobic surfaces that may be based on carbon nanotubes, graphene or other. Here the literature review regarding the development on silicon nanowire (SiNWs) based on hydrophobic surfaces have been given.

Superhydrophobic surfaces were prepared by fabricating SiNWs to enhance the surface roughness and then the chemical nature of the surface was modified with a self-assembled octadecyltrichlorosilane monolayer to lower the surface energy. The dynamic contact angle data revealed that the water droplet on those surfaces of nanowires could exhibit a transition from the Wenzel state to the Cassie state by simply controlling the etching time and the contact angle hysteresis was less than 10° [Shao Mingwang et.al..2009]. The contact angles depend on the surface roughness and the structure possesses stronger mechanical strength and could reach the Cassie state because of the shorter etching time [Shao Mingwang et.al..2009, Wei-Fan Kuan and Li-Jen Chen.2009]. Fluorine carbon coatings were used to convert the surfaces from superhydrophilic to superhydrophobic to maintain the Cassie-Baxter state stability by reducing the surface free energy to a quarter compared with intrinsic silicon. The morphology of the SiNWs demonstrated that their critical height exceeds several hundred nanometers for superhydrophilicity, and surpasses a micrometer for superhydrophobicity.

As stated before the superhydrophobic and superhydrophilic surfaces are differentiated in terms of the contact angle, water droplet makes with the solid surface at equilibrium. If the angle is over 150 ° It is called super-hydrophobic, if it is less than 90° the surface is super-hydrophilic [Wei-Fan Kuan and Li-Jen Chen.2009, Kim Beom Seok , Shin Sangwoo, Shin Seung Jae, Kim Kyung Min, Cho Hyung Hee . 2011]. The super-hydrophobic surface has further advantages of having self-cleaning properties which allows to clear dirt particle during rolling of a water droplet through the surface at a very small rolling angle without wetting the surface. On the contrary sometimes we want water to wet the surface i.e. the surface to be hydrophilic. This simply can be done by giving the hydrophobic surfaces to the UV light. This surface containing nanoholes can simultaneously repel oil and water or for other surfaces it can partially allow water over oil thus can be aced as partial oil water separator [Togonal AS,He Lining,Cabarrocas PR, Rusli.2014]. These have other applications like water harvest, anti-biofouling, paint, coating, cosmetic industry and other [Togonal AS,He Lining,Cabarrocas PR, Rusli.2014].

SiNW has been found to be very easy to synthesize with very high uniformity and high yield. The modulation of its hydrophobic behaviour is also very easy and thus it is a very promising candidate for developing hydrophobic electronic device [ Wei-Fan Kuan and Li-Jen Chen.2009,Kim Beom Seok , Shin Sangwoo, Shin Seung Jae, Kim Kyung Min, Cho Hyung Hee.2011,Togonal AS,He Lining,Cabarrocas PR, Rusli.2014].

There are report of synthesizing SiNWs by chemical vapour deposition, which during growth process, attain a critical roughness value, give water contact angle nearly 0°, thus exhibiting superhydrophilicity. These super hydrophilic properties may be converted again to hydrophobicity by a vacuum treatment with the exposure to it by polymer like polydimethylsiloxane (PDMS) material. In turn, this material again be converted to hydrophilic by simple nitrogen treatment at an elevated temperature as high as 873 K [Tae-il Kim, Dongha Tahk, and Hong H. Lee. 2009]. Thus, in this way, a constant swinging between hydro-phobicity and hydro-philicity may be done by simple and cheap method.

There are reports of multi-structured pyramid/nanowire network on silicon substrate by a complex NaOH and silver catalysed etching process. A superhydrophobic property with contact angle as high as 162° and very small rolling angle (less than 28 °) has been achieved for SiNW by octadecyltrichlorosilane (ODTS) induced modification. These kinds of surfaces have found their applications in silicon based solar cell and in many other applications as mentioned before [Cheng Yung Kuo and Chie Gauz.2010].

# Discussion

## Nature and Nanotechnology

Although nanoscience is often comprehended as a science of the future, in true sense it is the basis for all systems that are present in our living and mineral world. Natural nanomaterials proffer a great starting point to bring nanoscience among masses. Images from microscopes are great resources to understand basic structure of nanomaterial. Starting from a macro object (such as a plant leaf) and showing by zooming in with subsequent factors reveal finer and finer structures, (**Fig.4.**).

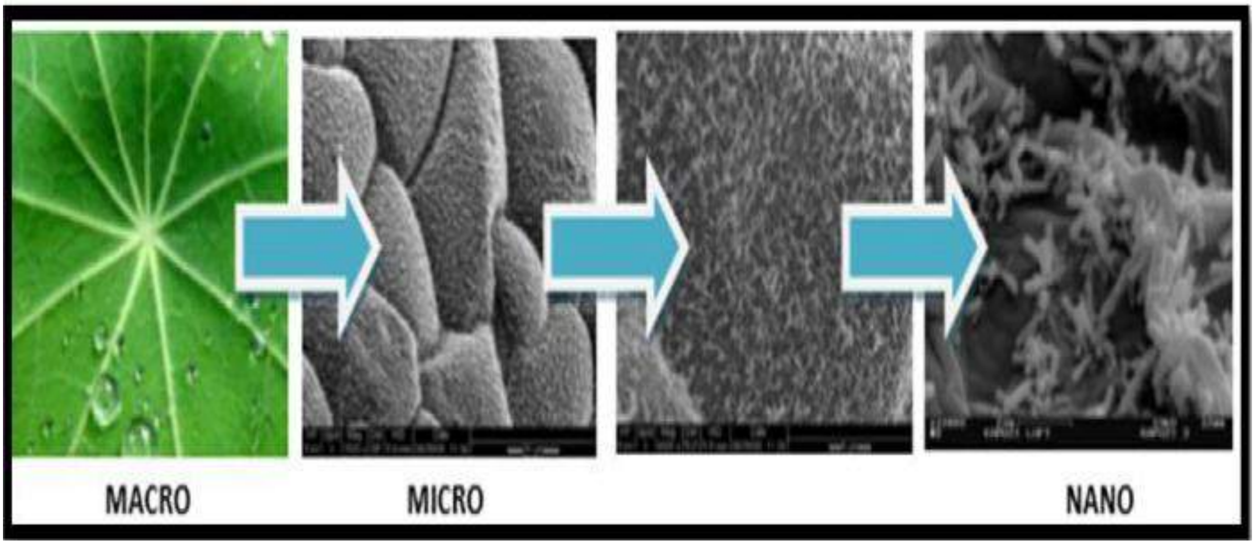


**Fig.4:** Close-up views at progressive magnification of a Nasturtium leaf revealing the presence of surface nanocrystals.

Another example of natural “Nano” effect is seen in Gecko who can walk on almost any substrate along any direction vertically upward or with a certain angle. It can hang upside down on a smooth surface like cleaned glass. Walking on a dirty or wet surface is also not a problem for them. They in principle do not have any suction like features and or do not produce any sticky substance. Here it is to be noted that Gecko has a series of structures called scansors containing a numerous projections called setae. Each setae has dimension of 5 μm in diameter and 100μm in length and consisting of numbers of tiny projections called spatulae of dimension 200 nm. This helps the surface area of the Gecko’s feet increased enormously. Also the spatulaare very flexible and thus they are capable of being mold into molecular structure into any substrate increasing the adhesion which is completely Van der Waals force. Also as the surface energy of such structures are such that the particles, dirt or mud will prefer to stay on the substrate rather than to stick on the feet. Thus the feet of the Gecko remained clean. The structure can clearly be seen in the below figure (**Fig.5**)

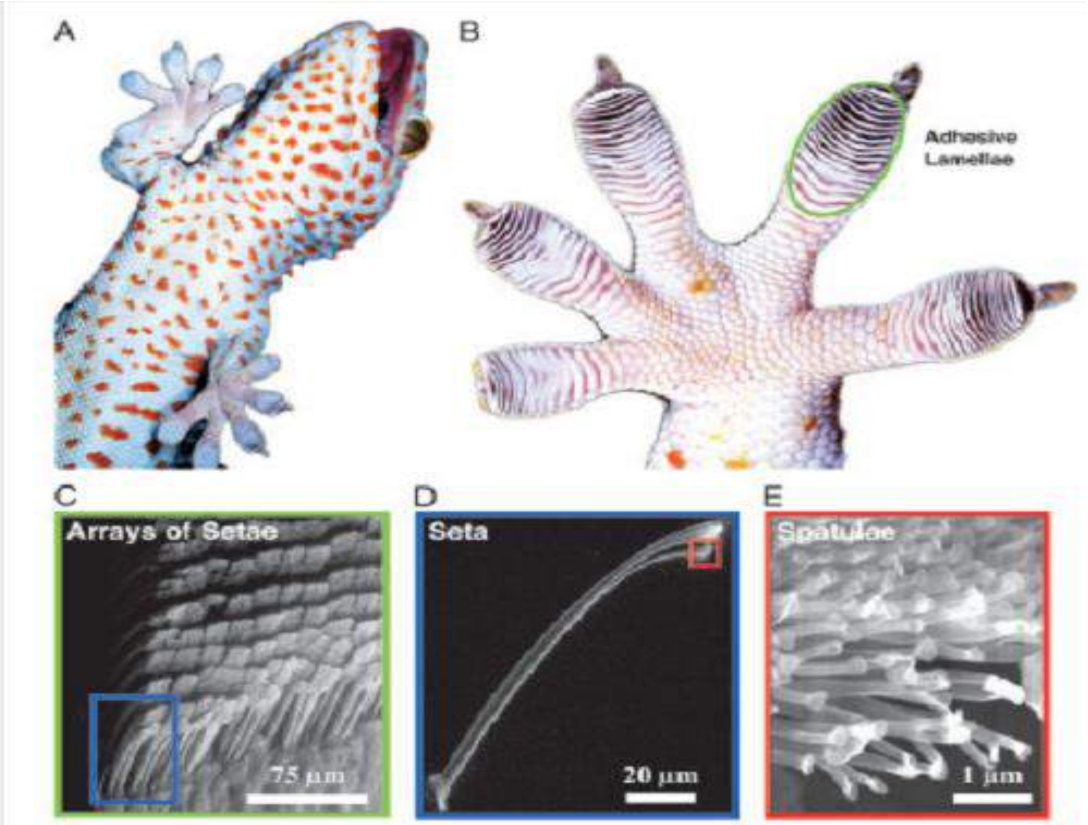


**Fig.5:** (A-E) The macroscopic and nanoscopic structures of Gecko’s feet with different magnifications

## What distinguishes nanomaterial from bulk?

It is to be noted that though the micro-form of the material shows almost the same properties as that of the bulk material, its nano-form shows significantly different properties and this is mainly because of the following reasons:

1. In nano-dimension the numbers of atoms at the surface increases significantly
2. It has a surface area much higher compared to its bulk form
3. It shows confinement effect and thus very different optical properties.
4. It has different density of state for 0, 1, 2, 3 dimensional material and thus fascinating electrical properties

The advantages of using nano-materials firstly involve the miniaturization of the system. In this present era when we all wants entire world within our arm. This supports the Moor's law speculating numbers of transistor gets increased exponentially obviously forcing the dimension of the electronic component to be reduced.

The second advantages or rather the second characteristics of nanomaterial is the enhanced surface area and thus many more numbers of dangling bonds present in the surfaces exposed to the environment. This enhanced dangling bonds are basically chemically unstable and are always in a need of interaction with other material in order to make the bond and thus to get the minimum energy configuration. This helps nanomaterial to be exceptionally chemically active and performance in any surface induced properties like catalysis, adsorption etc is exceptional. As mentioned before, result of the changes that occur in particles with reduced particle size, nanomaterials can have extremely high biological and chemical reactivity. For example, catalytically active nanomaterials enhance either chemical or biochemical reactions by tens of thousands, and even a million times. This attribute explains, even 1 g of nanomaterial can be more effective than 1 ton of a similar but macro substance.

Another aspect we must be taken account is that the free surface is a place of accumulation (sink) of crystallographic defects. At small particles sizes, the surface concentration of such defects increases considerably. It was calculated classically and showed that the largest changes of proportions between facets, edges, corners, and micro defects at the surface occur between 1 and 5 nm. As a result, strong lattice distortion and even a change of lattice type can take place on the surface layer. In fact, due to accumulation of structural defects and chemical impurities on the surface, we can observe purification of the bulk area of the nanoparticles.

An important specific characteristic of nanomaterial properties (we mean here polycrystalline materials with grain size less than 40 nm) is an increase of the role of interfaces with decrease of the size of grains or crystallites in nanomaterials. Experimental research has shown that the state of grain boundaries has a non-equilibrium character, conditioned by the presence of the high concentration of grain boundary defects. This non-equilibrium is characterized by extra energy of the grain boundaries and by the presence of long-range elastic stress. At the same time, the grains have ordered crystallographic structure, while the grain boundary defects act as a source of elastic strains. Non-equilibrium of the grain boundaries initiates the occurrence of the lattice distortion, the change of interatomic distances, and the appearance of sufficient displacement of atoms, right up to loss of an ordered state. Another important factor peculiar to nanoparticles is their tendency to aggregation. The possibility of migration (diffusion) of either atoms or groups of atoms along the surface and the boundaries, as well as the presence of attractive forces between them, often leads to processes of self-organization into various cluster structures. This effect has already been used for creation of ordered nanostructures in optics and electronics.

One more important aspect of nanomaterial properties is connected with the fact that, during transport processes (diffusion, electro- and thermal conductivity, etc.), there are certain effective lengths of free path of a carrier of this transport (Le), such as phonon and electron mean free paths, the Debye length, and the exciton diffusion length for certain polymers. While proceeding to sizes smaller than Le, transport speed starts to depend on both the size and the shape of the nanomaterial; generally, the transport speed increases sharply.

The principal characteristics of nanomaterials are conditioned not only by their small the size, but also by the appearance of new quantum mechanical effects in a dominating role at the interface (Esaki 1991; Serena and Garcia 1997). Those quantum size effects occur at a critical size, which is proportionate with the so-called correlative radius of one or another physical phenomena, for example, with the length of the free path of electrons or photons, the length of coherence in a superconductor, sizes of magnetic domains, and so on. As a rule, quantum size effects appear in materials with crystallite sizes in the nano range $D < 10$ nm. As a result, in nanomaterials with characteristic size, one can expect the appearance of effects which cannot be observed in bulk materials.

## Surface Energy

The surface energy ($\sigma$), is one of the main parameter that characterize a surface and its activity. It is mainly related to the numbers of dangling bonds or uncompensated bonds. It is easy to understand that when a material goes from bulk to nano more numbers of surfaces get exposed to the environment and thus due to the inherent tendency of any natural system to be in minimum energy state they try to interact with environment and make bonds. Thus in other word its chemical activities get very high. Surface energy is also defined as energy associated with the energy required breaking a bond.

Intermolecular bond or bond strengths in the middle of a liquid with molecules cause surface tension. If the water comes into contact with another substance, there is an attractive force between them. The coupling forces between the water and the second one is effective on the coupling of the forces acting on the fluid. Liquids with low correlation to bonds and a strong adhesion to the other materials will tend to lay out over the material. Liquid with a strong, cohesive bonds, and weak adhesive forces, get ready to create a droplet in contact with other materials. $\sigma$ Influences the surface properties and the associated interaction, such as adsorption, wetting, adhesion etc.

## Wetting

The property of a liquid to keep in touch with a solid surface arising from the interaction between molecules of both solid and liquids at their actual points of contact. Degree of wetting is measured by the energy balance between the grip and the bonding force. The bonding force between the liquid and the solid causes the liquid to drop to a higher degree.

The cohesive force within the liquid causes a rise in elevation and avoids contact with the surface.

To check the wet condition, take a drop of water on a solid specimen. When the surface strength of a specimen differs to the addition of a drop, the specimen is known as a wetting. The distribution variable can be used to measure this statistically:

$$\mathbf{S = Y_s - Y_l - Y_{s\text{-}l}} \qquad \mathbf{(1)}$$

where S is the distribution variable ,

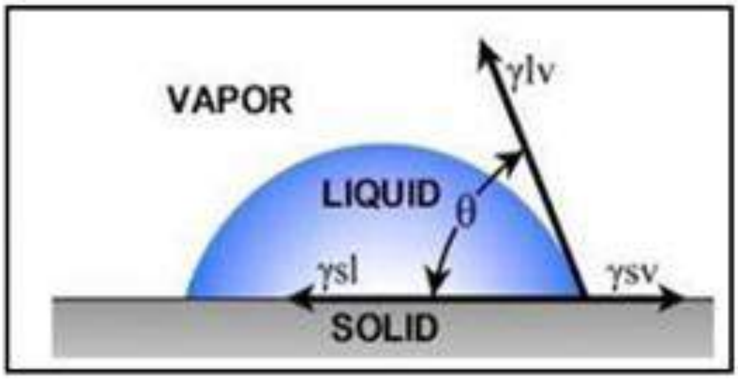
$Y_s$ is the Eof the specimen,

$Y_l$ is the E of the water, and

If, S < 0 the specimen gets partly wet by the liquid and if S > 0 specimen gets completely wet.

## Contact angle:

It can be explained as the angle formed at the joint of the liquid / solid contact and the liquid / air contact. It can also be defined as the angle b/w the face of the solid sample, and the tangent of the egg-shaped droplet and droplets edge. As shown in **Fig.6**



m

A high value of θ depicts a small energy of the solid, and a small amount of wetting. A small value of θ indicates a high energy of solids and for high-and sometimes the full extent of the wetting. Several of the factors influencing the contact angle are harshness, functional group present on the surface, contamination, porosity and surface energy. Another method of measuring the liquid surface wetting element is to measure θ of the liquid drop on the surface of the object. Water wet areas where θ is less than 90 degrees. For an input to generate, θ must be as low as possible. In fact, the θ of most liquids is very close to zero degrees. In liquid penetration tests, there are commonly three visible combinations, a solid-gas contact, a liquid-gas contact, and a solid-liquid contact. In order for the liquid to set more than a certain fraction, two conditions should be met. First, the surface strength of the solid-gas contact should be larger than the total strength of the liquid gas and the solid liquid interface. Second, the surface power of the solid- gas contact must surpass the surface power of the solid-liquid contact. The wetting factor also plays a key role in its capability to fill the gap. Penetrant materials are pulled in surface breaking defects by action of capillary. The capillary force that guides a penetrant into a crack is a function of the complexity of the liquid-gas interface, the angle of contact, and element opening size( **Table 3).**

**Table 3: Values of contact angle and associated inference**

| Contact angle | Degree of wetting | Strength of Solid/liquid interaction | Strength of Liquid/liquid interaction | Pictorial Representation |
|---|---|---|---|---|
| $\theta = 0°$ | Perfect wetting | strong | weak | |
| $0 < \theta < 90°$ | high wettability | strong | Strong | |
| | | weak | weak | |
| $90° \leq \theta < 180°$ | low wettability | weak | Strong | |
| $\theta = 180°$ | Perfectly non-wetting | weak | Strong | |

## Surfaces with high energy and low energy

Solid surfaces are categorized into high-energy solid-and low-energy types. Solid materials, such as metal, glass, are well-known as a "hard solids" as for the chemical bonds that connect them to each other, such as covalent, ionic, or metallic) are very strong. Thus, the distribution of these structures, it requires a large amount of energy, and that is the reason why they are called "high-energy". Nearly all of the molecular liquids are designed to be a complete wetting with high-energy surfaces.

Next is weak molecular crystals (e.g., ammonia, hydrocarbons, etc.) what are the molecules are connected to each other, mainly as a result of physical forces (like van der Waals, and hydrogen bonds). Because of this, the bodies are connected to one another by weak forces, very little energy is needed to split them, and so they are called the "low-energy". Depending on the nature of the fluid has been selected, low- energy surfaces can be assumed to be either completely wet or partially wet.

## Hydrophobicity, Hydrophilicity and Lotus Effect

Hydrophobicity ("it's a fear of water"), is a physical property of a substance which appears to have been derived from the weight of the water. A polar molecule or part of a molecule is a molecule that is able to communicate with, or dissolve in water and other polar substances. Hydrophobic particles have the ability to repel water, and, therefore, prefer other neutral molecules and non-polar solvents. Superhydrophobic surfaces with a θ greater than 150° c, which indicates that there has been almost no connection between the drop and the surfaces of the earth. It is also sometimes referred to as the "Lotus-effect"

Because of the amorphous carbon films have been, it is easy to film it on various substrates, that is why, when you are in control of their hydrophobic characteristics, they will be useful to create water-and stain-resistant surfaces.

On the other hand hydrophilicity stands for loving water and thus in such surface water gets attracted and show low contact angle. Hydrophilic compounds take the water from the air. The sugar and salt, are absorbent, and can be used to remove water from the foods. This is thermodynamically favourable and is soluble in water as well as in other polar solvents. Soap, which has a hydrophilic head and a hydrophobic tail, which allows it to disintegrate in both water and oil is also another example.

A hydrophilic molecule or part of a molecule is a common charge and is able to combine hydrogen, allowing it to disintegrate more easily in water rather than oil or other hydrophobic solvent. Polar molecules and weak molecules are also referred to hydrophilic and Hydrophobic molecules, respectively. Some polar substances do not disintegrate. This type of compound is called colloid. Hydrophilic membrane filters are used in some industries to filter various beverages. These hydrophilic filters are used in the medical, industrial, and chemical fields to filter out bacteria, viruses, proteins, particles, drugs, and other pollutants.

## The Lotus-effect

The lotus effect (shown in **Fig.7**) tends to properties of self-cleaning that are a consequence of very high water repellency (superhydrophobicity), as shown on lotus leaf. The dirt builds up on the drop of water due to the microscopic -and nanoscopic architecture on the surface, so the sticking of the droplets in the plane was brought down. Superhydrophobicity and self -leaning features are also discovered in other plants, such as tropeolus, (West Indian cherry), prickly pear (opuntia), and on certain insects wings. In 1997, the self-cleaning properties of superhydrophobic (microstructural) surfaces have been studied by Barthlott , that is, for the first time explained their self-cleaning and superhydrophobic properties, such as the "lotus effect" [ Barthlott, W. and Neinhuis, C., 1997].

**Fig.7:** Lotus effect

The natural hydrophobicity of the plain area be increased by adding textures with a variety of hardness scale lengths. The red roses makes use of it by considering a hierarchical structure of microstructure and nano-structures on each petal) to ensure enough rigidity for the super-hydrophobicity. In particular, every group has a group of micropapillaries on the surface, and each of these, on its part, offers a lot of nanofolds.

The phrase "petal effect" to explain the fact that the drops of water on the face of the rose and have a circular shape, but that will not fall out, even turned down. Water droplets retain its spherical shape nature due to the superhydrophobicity of the petals of a flower (the contact angle was about 152.4° c), but do not fall off, due to the fact that some of the deeper subsurface is characterized by a high adhesion force of water .

The differentiation of the "petal effect" with the "lotus effect", there are some significant differences between them. The lotus petal has an uneven, rough surface, and a low hysteresis of the θ, which means that a drop of water does not wet the micro-structure of the space between the rods. This means air can remain in space to the interior of the grains, which makes the structure of the surface is made up of air and solid. As a result, the adhesion force between the liquid and a solid plane is very low, so the water can easily fall (that is, the self- clean phenomenon).

However, the microstructure and nano-structures of the petals are, the higher in the scale than that of the lotus leaves, by which a liquid layer go all the way to the texture . The fluid can be given in larger slots, but can't get into the lower spikes. This is known as the Cassie wetting mode. Because the liquid can wet the major groove, and the adhesion force b/w the water and the solids are very strong. This is why a drop of water does not run down the hill, even as the petals of a flower, put at an angle or turned upside down. However, this effect is likely to be destroyed if the drop has a large capacity, such as the balance between the weight and the surface tension is exceeded **(Fig.8).**

**Fig.8: Petal Effect**

The hydrophobicity of a surface can be determined on basis of the θ. The greater the θ values the greater the hydrophobicity of the surfaces. Surfaces with a θ of < 90° and are called hydrophilic, while those with θ >90°, hydrophobic called. Some of the plants show θ up to 160° c, and are called superhydrophobic, which means that it is only 2 to 3% of the droplet- contact. Plants have a double structure of the surface, such as the lotus, can be extended to the θ of up to 170°. All of this tends to a self-clean effect. This effect is more important to plants, such as defense from bacteria, such as algae , fungi and animals, such as butterflies, dragonflies, and many other insects that are not in a position to have to clean all of the parts of the body.

## The application of the hydrophilic and hydrophobic surfaces/ particles

If the self-cleaning feature, it was observed that the nature of this discovery opens up the possibility of the use of this result in the man-made surfaces. Few nanotechnology scientists have made, treatments, coatings, films, paints, tiles other surface which can remain dry and clean to make their own, to duplicate a scientific approach to the self-clean features of plants such as the lotus plant. This can also be accomplished with the help of a fluoro-chemical or silicone treatments on a clean surface or in the compositions of micro-particles. Superhydrophobic coatings with Teflon micro-particles have been used in the field of medical diagnostic slides for more than 30 years of age. This result is achieved by the use of a mixture of polyethylene glycol, glucose, and sucrose, in a combination with a hydrophobic compound. Additional applications, such as self-cleaning mirrors mounted on German motor control unit sensors and sprayers have been produced to create self-cleaning films in different parts. Superhydrophobic coverage installed in microwave radiation antennas can notable reduce rainwater runoff and snow and ice formation. products that are easy to clean in advertising are usually mistaken for hydrophobic or superhydrophobic self-cleaning products. Well-designed superhydrophobic properties also deliver the promise of microfluidic lab on a chip devices can notably improve further bioanalysis. Also superhydrophobic or hydrophobic features are used for dew harvesting, or for liquid mixing in the borehole for irrigation. **Fig.9** explains the phenomena.

**Fig.9: Application of hydrophobicity and hysteresis effect**

## Relationship between energy and θ

The surface free energy is the amount of increase of free energy when the area increases, per unit of A. The surface free energy of the samples, it is usually accomplished by calculating the θ to liquid and the sample surface. The relationship between the E of the samples (Y) the θ usually, it is described by the equation of Youngs equation

$$Y_{s-g} = Y_{s-l} + Y_{l-g} \cos\theta \qquad (2)$$

Surface energy can be sub characterized due to the different connections that root them, like surface energy because of van-der-Waals forces, hydrogen bonding, polar interactions, acid/base interactions, etc. The total surface energy both for liquid and the solid is suppose conventionally to simply be the addition of the dispersive and polar components.The equation explaining the further division of surface energy into the distribution of disruptive connections and polar interactions would be

$$\sigma_S = \sigma_{Sd} + \sigma_{Sp} \qquad (3)$$

$$\sigma_L = \sigma_{Ld} + \sigma_{Lp} \qquad (4)$$

## Cassie and Wenzel State

If a surface is the same in every shape or character like shape, size, weight, height distribution, then it is called a uniform surface otherwise it is known as a non-uniform surface. The uniform wetting is when the liquid fills the barriers of local hardness grooves. On opposite side, a non-uniform wetting is when the surface is covered with 2 varieties of patches. A prime case of such a compound environment is air and solid dots patches. Such areas have a different effect on the θ of a liquid. Cassie - Baxter and Wenzel gave two key models that try to define wetting.

The Wenzel model explains the uniform wetting reign, as shown in **Fig.10 (b)**, and is explained with the below equation for the θ on a harsh area

$$\cos\theta^* = r \cos\theta \qquad (5)$$

Here θ* is the plain contact angle that is analogous to the steady balanced condition (i.e. min. free energy phase for the system), r is the harshness ratio and θ is the contact angle

The harshness ratio, r, is a result of how surface roughness affects uniform surface. The roughness ratio is explained as the ratio of real area of the solid surface to the apparent area.

The Cassie equilibrium states can be explained by the equation as:

$$\cos(\theta) = \Phi \cos(\theta_1) + (1-\Phi)\cos(\theta_2) \qquad (6)$$

where θ is the contact angle,

$\theta_1$ is the contact angle of liquid on a plane area of the specimen in examination

$\theta_2$ 180 is the contact angle of liquid on air

Φ is the solid fraction of A at the top of the asperities fp = (1- Φ) would show the surface porosity on a hydrophobic surface, liquid has a very wide angle, and it can also very simply fall , that is to say, a very, very small hysteresis. This is simply because a drop of water sits on top of an uneven surface, and the water, can't go down into the grooves as shown in **Fig.10 (a)**,.

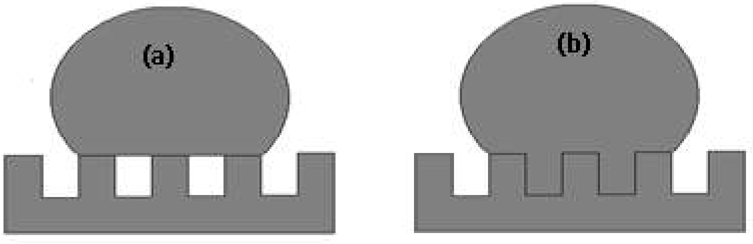


**Fig.10:** (a) Cassie state and (b) Wenzel state

## Calculation of Surface Energy:

From the young's equation we have

$$S_{lv} \cos \theta = S_{sv} - S_{sl} - \pi_e \qquad (7)$$

where, θ contact angle between solid and liquid

$S_{lv}$ and Ssv are liquid and solids free energies which act against their saturated vapour pressure.
Ssl is the interface energy between solid and liquid

πe is balanced pressure of adsorbed vapor of the liquid on the solid.
Surface energy can be solved into polar (SP) and disruptive component (Sd). The widespread part of the discrepancy between solids and liquids is given by the compound law of Good - Girifalco - Fowkes

$$S_{dsl} = S_{dsv} + S_{dlv} -2 [S_{dsv} * S_{dlv} ]^{1/2} \qquad (8)$$

Rearranging, the Young's equation takes the final form as:

$$[1 + \cos \theta] = 2/S_{lv} [\{S_{dsv} * S_{dlv} \}^{1/2} + \{S_{psv} * S_{plv} \}^{1/2}] \qquad (9)$$

If polar and dispersive component of surface vapour and liquid vapour components of two liquids of known polarity are known then the polar and dispersive part of solid-liquid interface can be known.

## Conclusion

The hydrophobicity phenomenon given by nature to different biological species, such as the lotus flower and the butterflies wings, has generated a great deal of interest in education and industry. Super-hydrophobicity has now been recognized as one of the top 50 technologies. Research over the past decade has shown that it is dealing with serious problems such as those related to rust and biological degradation, as evidenced by the effective use of hydrophobic facilities in engineering systems such as aircraft, automobiles, pipelines and marine vessels In the current article I have discussed the basic concepts of low dimensional materials mainly low dimensional materials and have shown how they exhibits novel properties. I have also shown some ready resemble of natural effect with the concept of nano and how they affect our daily life.

I have reviewed an easy concept to determine the surface energies of any flat surfaces and its components. In this consequence different equilibrium state of any liquid droplets on a surface came into the discussion.

After studying a practical data set it is seen that that it is the polar part of the surface energy that probably determine the hydrophobicity of any surface provided the chemical composition, roughness, nanostructures and other parameters remains same.

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# Instructions to Authors

## TMU JOURNAL OF BASIC & APPLIED CHEMISTRY

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### 1. Introduction

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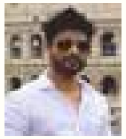
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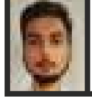
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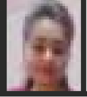
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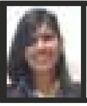
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