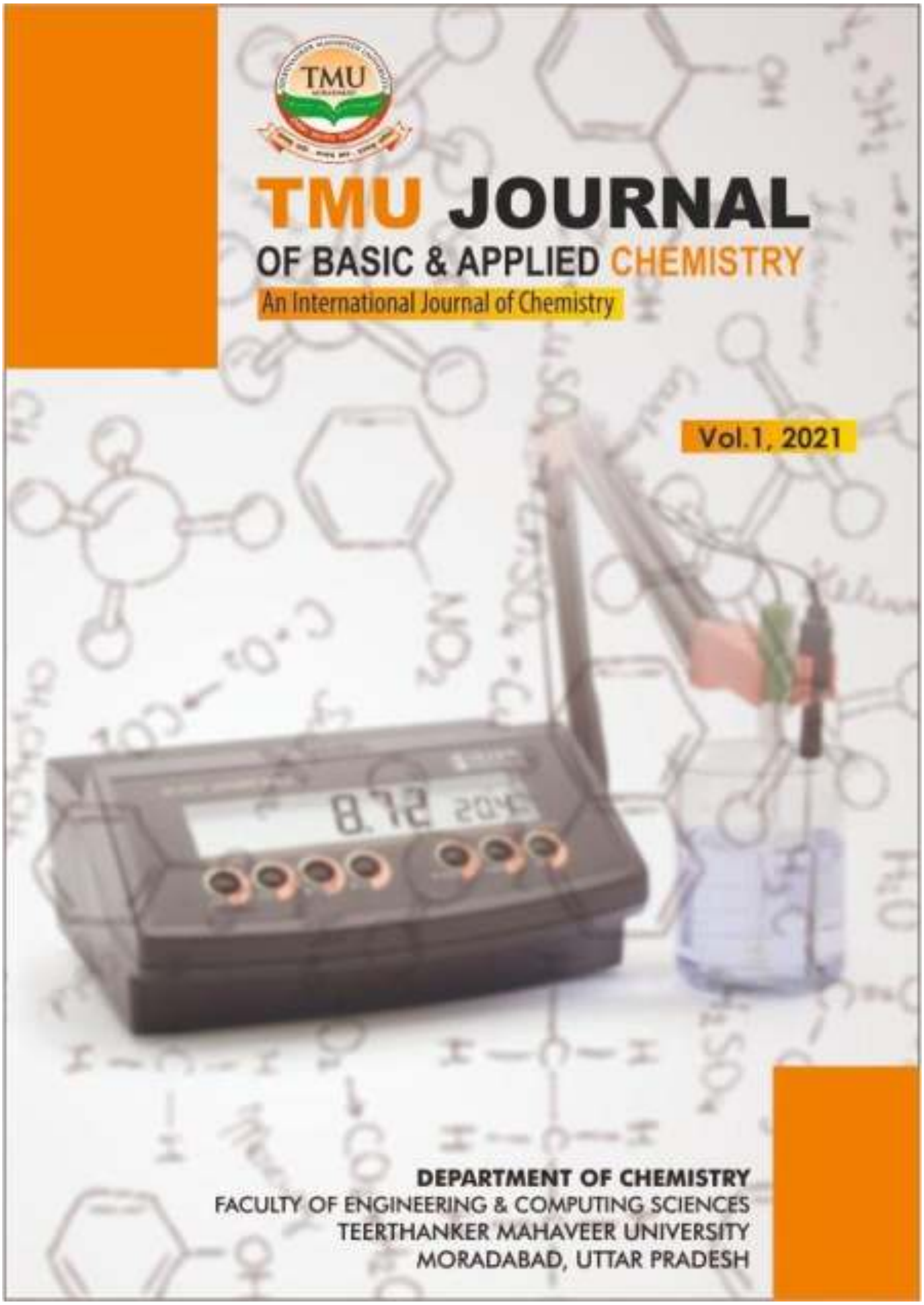

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FACULTY OF ENGINEERING & COMPUTING SCIENCES
TEERTHANKER MAHAVEER UNIVERSITY
MORADABAD, UTTAR PRADESH

About the Journal

TMU Journal of Basic & Applied Chemistry (TJBAC) is committed to worldwide promotion of systematic awareness across all fields of chemistry. This is an international scientific peer reviewed, open access journal dedicated to publishing original research from pure chemistry to applied chemistry and its wide range of applications.Coverage of the journal includes: 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. It publishes original research papers and short communications. “TMU Journal of Basic & Applied Chemistry” is issued yearly. It has high profile editorial standards, with leading editors involved in the field making swift, knowledgeable peer review 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 has been established by an ‘Act’ (No. 30) of 2008 of the Government of Uttar Pradesh and is 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 any manuscript. The papers contained in the journal carry the opinion and view of the contributors and not necessarily of the editorial Board. The editorial Board as such shall not be responsible for the authenticity and legality concerns regarding the submission made in this journal. The entire responsibility shall lie with the author of the papers or case studies.

CHIEF PATRON

Shri Suresh Jain
Chancellor,
TMU, Moradabad

I am extremely glad and feeling inner happiness for the vol-1 and issue-1 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 February, 2021. I say 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. No doubt that research in any discipline is not one day job but it needs consistence 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 was completed in the year2008 and since that day the teaching /research standard is getting advancement, and am ambitious to enhance research interest among the faculty members to grow vertically and horizontally for bright and successful endeavor in all Departments. 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 Prof (Dr) R. K. Dwivedi, Director and Principal of FOECS, Editor- in- Chief, Associate Editors , advisory committee to launch this Journal successfully up to 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 volume-1 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.

PATRON

Prof. Raghuvir Singh
Vice Chancellor,
TMU, Moradabad

I am very happy to announce the publication of a Journal of TMU, which is long overdue. The Journal is aptly titled **" TMU Journal of Basic & Applied Chemistry" ,** broadening the scope and coverage so that researchers across the University can contribute to the publication.

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.

Starting a Journal publication is expected to benefit 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-1 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.

Shri Akshat Jain

Esteemed Member of TMU Society

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 launching "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.

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Original Article

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Excess molar enthalpies of dichloromethane +acetonitrile or + furan or +2-methylfuran or + acetophenone at the temperature 303.15 K

Abstract

Excess enthalpies, H^E, at the temperature 303.15 K have been determined for dichloromethane (CH_2Cl_2) (DCM)+ acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$). The values of H^E for the systems for CH_2Cl_2 +acetonitrile or + C_4H_4O are of positive sign while negative sign obtained for the systems CH_2Cl_2 +2-methylfuran or + $C_6H_5C(O)CH_3$.The values of H^E of the different systems have been fitted with the help of smoothing equation using the least squares method. The obtained H^E data represent the presence of specific interactions.

Keywords: CH_2Cl_2 , Acetonitrile, Microcalorimeter, Hydrogen bonding, liquid state

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Introduction

Cyclic ethers e.g. furan or 2-methylfuran is of interest because the compound is of industrial significance, and its interactions are more outstanding, thus creating them better solvents. CH_2Cl_2 is an organic compound, which is colorless, hot-tempered liquid and also used as a solvent, although immiscible with water but miscible with lots of organic solvents.

Mixtures of CH_2Cl_2 with acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$) are of meticulous significance from the opinion of the occurrence of an electron transfer interaction which results in the formation of adducts between the components . The interaction of CH_3CN,C_4H_4O,$C_5H_6O$and $C_6H_5C(O)CH_3$, due to the occurrence of two nonbonding electrons on the O or N atom of these compounds, it can act as an n-donors toward CH2Cl2, which can be engaged in the creation of

H-bonds with and perform as a σ- acceptor with all aforementioned compounds. We have already reported data on excess volumes, ultrasonic velocities, dielectric constants and excess enthalpies of Chloroalkanes with n-donor compounds in our earlier communications [Nath et. al., 1983, 1984; Chadha et.al, 1995; Tripathi, 1995, 2010).

A literature investigation disclosed that wide-ranging studies on such type of systems have not been made. The values of H^E data are used to detect the strength of intermolecular forces such as hydrogen bonding and charge-transfer complex formation between the components in the liquid state. Hence, in the current programme, H^E measurements have been carried out for mixtures of of CH_2Cl_2 with acetonitrile (CH_3CN) or + furan (C_4H_4O) or + 2-methylfuran (C_5H_6O) or + acetophenone ($C_6H_5C(O)CH_3$) at the temperature *T=303.15K*. The experimental data obtained have been reported and discussed in the present programme.

Experimental

Dichloromethane (BDH, AR) was shaken with of conc. H_2SO_4 to obtain acid layer colourless, then rinsed with H_2O, after that washed with aq. 5% sodium carbonate and then with H_2O again. The compound is predried with Calcium Chloride, and distilled over P_2O_5. Purified dichloromethane was stored away from light in a ambered bottle having $4A^0$ molecular sieves.

All chemicals were subjected to fractional distillation for purification and a fixed central portion was utilized for the experiment. The specified minimum purity of chemicals were 99.5 mol%. Before using the chemicals, activated molecular sieves $4A^0$ were used for drying purpose.

The purities of chemicals used, as obtained by Gas Liquid Chromatography, are about 99%. Density measurements were made by means of a vibrating tube densimeter (Patil et.al,1990) and found to be in excellent concord with the available literature data(Riddick and Bunger,1970).

Method

A Micro calorimeter (Model no.C-80 received from Setaram, France) was used for determination of H^E data, the temperature was maintained in the range of ±0.001K. Weight of compounds were taken for Solutions preparation . Mole fractions prepared was accurate to ±0.0001. The trustworthiness of the instrument was compared with the help of H^E data for hexane and cyclohexane at 25^0C as reported earlier(Tripathi

AD,2018). The deviation in the HE measurement was 0.5% at mole fraction, x1 =0.5 while it is about 1% deviations of the H^E at other mole fractions.

Results and discussion:

The H^E data obtained in the present study , for all systems are reported in Table 1 and the data were put into to the following smoothing equation:

$$\frac{H^E}{J.mol^{-1}} = x_1 x_2 \sum_{i=0}^{m} A_i \,(x_1 - x_2)^i \qquad (1)$$

In this case x_1 refers to the mole fraction of CH_2Cl_2. The parameters Ao,A_1,A_2 and A_3, and the values of σ, are given in Table 2 . The values of deviation of the fitting , σ , are calculated by means of equation as given below(eq.2)

$$\sigma = \left[\frac{\Sigma\left(H^E - H^E_{calc}\right)^2}{(m^*-n^*)}\right]^{1/2} \qquad (2)$$

In the above equation, H^E represents measured values and H^E_{calc} for calculated excess enthalpy by using eq. (1), m* for no. of data obtained & n* refers no. of constants for a particular system. A plot of obtained experimental values of H^E data against mole fractions (x1) are given in Fig. 1.

Interactions between like molecules and the commencement of new interactions between unlike molecules, are the explanation for the values of H^E obtained . The values of H^E are endothermic for CH_2Cl_2 + CH_3CN or + C_4H_4O while exothermic for the system CH_2Cl_2 + C_5H_6O, and + $C_6H_5C(O)CH_3$.

The H^E values of DCM + CH_3CN is +ve and small, (H^E=152.2J mol^{-1} at x1=0.5) Which indicates little interaction of two components. It clearly suggests that CH_2Cl_2 + CH_3CN interaction reimburses to a great extent the -ve behavior of excess enthalpy due to structural involvement, which results on the whole positive values of H^E.

The excess enthalpy of DCM + C_4H_4O is also +ve and small (value of excess enthalpy = 223.8 J.Mol^{-1} at x1=0.5) which indicates only slight interaction between these each component. The "O" of furan is a weak hydrogen acceptor and may intermingle for forming a hydrogen bond with hydrogen atom of DCM. on the other hand , due to the occurrence of two double bonds present in the C_4H_4O ring , the O acquires less basicity, thus the chance of H- bonding is reduced to a great extent , which results in the positive values of excess enthalpy for this system.

The –ve values of H^E for CH_2Cl_2 + $C_6H_5C(O)CH_3$(H^E= -176 J mol^{-1} at x1=0.5) clearly indicates that there is only partial or weak interaction between these compounds but it is higher as compared to CH_3CN or C_4H_4O .This may also be attributed to be due to the creation of partial or weak hydrogen bond from the H atom of DCM and the π-electrons of the furan ring or via Oxygen—Hydrogen interactions. There is, however, also chance that DCM may also create a charge transfer complex with $C_6H_5C(O)CH_3$, throgh Cl atom π-electron interface. It is seen from Fig.1, that the values of H^E for the system CH_2Cl_2+2-methylfuran is more negative (H^E=-217J mol^{-1} at the minimum) than CH_2Cl_2 +acetophenone system.

The specific interactions between CH_2Cl_2 and C_5H_6O are expected to be stronger than those between CH_2Cl_2 and CH_3CN or C_4H_4O which add to the stronger complex formation and greater negative value of excess enthalpy of this system. The higher negative values for the system CH_2Cl_2 and C_5H_6O than those CH_2Cl_2 and C_4H_4O can be explained due to an increase in the basic character of the ethereal O atom owing to the occurrence of CH3 group, situated at the α-carbon atom, which is an electron -donor .

Due to presence of heteromolecules, highly negative value of H^E of these systems is obtained and this is clear indication of specific interactions. In these systems, two types of interactions are expected. First, there is creation of hydrogen bonding between the Hydrogen of CH_2Cl_2 and the oxygen of furan or methylfuran.

$CHCl_3$ with $(CH_2)_4O$ and dioxane forms a hydrogen bonded complex as given in the literature(Wilhelm A E.et.al,1982).

In the case of binarysystems the number of H-bonds created, the enthalpy of H-bond creation and other type of interactions are the main donor to the value of H^E. This point outs that the interactions other than H-bonding contribute to the value of H^E of different systems. Thus in the present case not only the Oxygen. Hydrogen and Oxygen—Chlorine interactions (Beath LA. Williamson AG.1969) are involved, but other type of interactions add to the value of H^E . However, in the case of a ethereal groups present in a cycle , the interactions of H and Cl atoms are so governing that the occurrence of a functional group or the position of O atom is not important for making any noteworthy difference to the value of H^E .

Table1. H^E values of dichloromethane (CH_2Cl_2) (1) + CH_3CN (2), or + C_4H_4O (2), or + C_5H_6O (2), or + acetophenone (2) at 303.15 K

X_1	H^E (J.mol^{-1})

CH_2Cl_2 (1) + acetonitrile (2)

0.1028	78
02166	132
0.3067	164
0.4007	168
0.5547	140
0 6564	101
0.7022	85
0.8786	31
0.9444	16

CH_2Cl_2 (1) + furan (2)

0.0876	82
0.1499	141
0.2828	221
0.3405	232
0.4247	236
0.5098	224
0.5786	199
0.6268	181
0.7204	137
0.8358	95
0.9381	43

CH_2Cl_2 (1) +2-methylfuran (2)

0.1022	-67
0.1789	-114
0.2567	-154
0.3021	-184
0.3789	-198
0.459	-212
0.5034	-221
0.5643	-216
0.6189	-211
0.7023	-201
0.8222	-169
0.8876	-138
0.9233	-109
0.9678	-56

CH_2Cl_2 (1) + acetophenone (2)

0.1763	-110
0.3362	-165
0.4052	-176
0.4229	-175
0.5115	-175
0.6248	-161
0.7449	-142
0.8520	-95
0.9467	-43

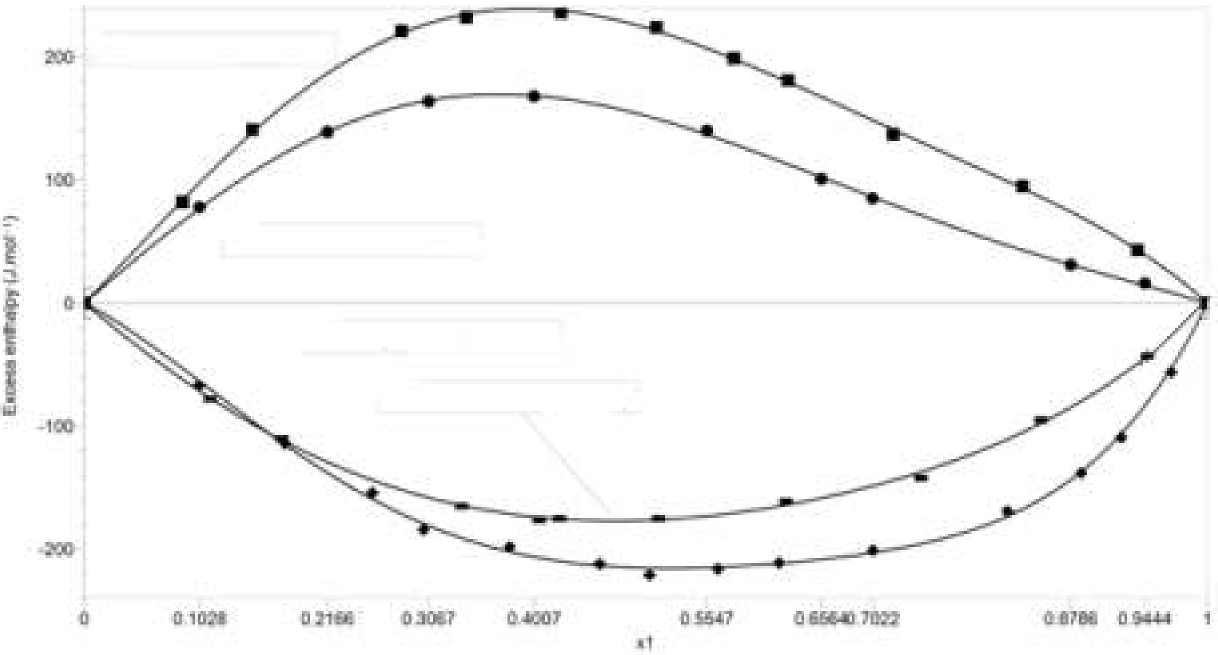

Fig. 1: H^E values of binary mixtures of x1 of Dichloromethane (CH_2Cl_2

(1) + CH_3CN (▪) (2), + furan (■)(2) ,+2-methylfuran(✦) , (2)and + acetophenone (•) (2) at the temperature 303.15 K.

Table 2. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations , σ,of CH_2Cl_2(1) + CH_3CN (2), or + C_4H_4O (2), or + C_5H_6O (2), or + $C_6H_5C(O)CH_3$ (2) at 303.15 K

System		A_0	A_1	A_2	A_3	σ/ (J mol^{-1})
CH_2Cl_2	(1) + + acetonitrile (2)	608.8	-494.2	-76.92	235.5	1.9
CH_2Cl_2	(1) + furan (2)	895.3	-528.1	-18.81	481.4	2.4
CH_2Cl_2	(1) + 2-methylfuran (2)	-868.1	-44.37	-295.1	-643.7	3.7
CH_2Cl_2	(1) + acetophenone (2)	-705.7	65.44	-134.9	-135.4	2.6

References:

1. Nath J, Tripathi AD.1983. Binary systems of 1, 1, 2,2-tetrachloroethane with benzene, toluene , *p* -xylene , acetone , and cyclohexane. Excess Volumes, Ultrasonic Velocities, and Adiabatic Compressibilities at 298.15 and 308.15 K, J.Chem.Eng.Data. 28: 263-266.

2. Tripathi AD. 2010. Excess Enthalpies of Dibromomethane with acetone, 1, 4-dioxane, pyridine, diethyl ether, ethyl methyl ketone and tetrahydrofuran , J. Chem. Eng. Data. 55: 1113–1116 .

3. Chadha R., Tripathi, AD.1995. The Excess Molar Enthalpies of Mixing of 1, 1, 2, 2-Tetrachloroethane with Methyl furan, Tetrahydrofuran, 1, 4-Dioxane, and Cyclopentanone at 308.15 and 318.15K. J .Chem. Eng.Data. 40:645-646.

4. Tripathi AD.1995. Excess Molar Enthalpies of 1, 1, 2, 2-Tetrachloroethane with Acetone, Dibutyl Ether, Acetonitrile, and Dimethyl-Sulfoxide at 298.15 K. J.Chem.Eng Data , 40: 1262-1263.

5. Nath J, Tripathi AD.1984.Binary systems of 1, 1, 2, 2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane. Part 2- Dielectric properties at 308.15 K., J.Chem.Soc.Farad.Trans.1, 80:1517-1524.

6. Riddick J.A., Bunger W.B. 1970. Organic Solvents: Physical properties and methods of purifications; 3rd ed., Wiley-Interscience, NY.

7. Wilhelm A E, lnglese, Grolier JPE , Kehiaian HV. 1982. J Chem. Thermodyn. Thermodynamics of binary mixtures containing cyclic ethers 4. Excess enthalpies of oxolane + and oxane+alkanoic acid (HCO2H to C7H15CO2H), 14: 33-36.

8. Wilhelm E, lnglese A, Grolier JPE. Kehiaian HV. 1982. Thermodynamics of binary

mixtures containing cyclic ethers 5. Excess enthalpies of 1, 3-dioxolane +, and 1, 4-dioxane + alkanoic acid (HCO2H to C7H15CO2H), J. Chem. Thermodyn., 14: 517-522.

9. Beath LA, Williamson AG,1969. Thermodynamics of ether solutions I. Enthalpies of mixing of ethers with carbon tetrachloride and with chloroform J. Chem. Thermodyn., 1: pp 51-57.

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Geometry optimization, Electronic Properties, UV spectra and NLO analysis of 5-nitro- picolinamide by using First principle

Abstract

In the present calculations of molecular geometries 5-nitro- picolinamide in the ground state have been carried with the help of combination of DFT/B3LYP method and 6-311G (d,p) basis set. Theoretical UV-Vis spectrum of 5-nitro- picolinamide is also calculated by using TDDFT calculations with same level of theory. A few electronic parameters are also calculated in the same level theory. The calculated HOMO-LUMO has been used to describe that how title molecule interacts with other species. The NLO analysis is used to study non-linear optical behaviors of the molecule.

Keywords: DFT, TDDFT, HOMO-LUMO, MESP, NLO

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Introduction:

Amides have received huge consideration in current years because of its prospective effect of derivatives of picolonamide as fungicide against R. solani (Kundu A, Saha S. 2014). It is also known that the structural organization is governed basically by means of biological metal ions and activation of definite enzymes due to their wide applications in extensive ranging fields from physical sciences to biological sciences (Rizzotto, M.2012). Picolinamide acts as an inhibitor of poly (ADP-ribose) synthetase (PARP) of nuclei from rat pancreatic cells. Its derivative may use a key role to reduce the C.difficile and act as an antibiotic for C.difficile infection(Speri E.,et.al.,2020) . A complete quantum chemical study may lead to asses every energetic as well as significant mechanistic insight within its formulation periphery.

Density functional theory provides valuable information about structure electronic and biological thermal and properties of compound (Dwivedi A.,et al,2012;2011, Pandey A. K.,et al,2013, Dwivedi A., Kumar A.,2019; Das S., 2018; Aljuboori S., & Mahmood A.2019; Sert Y., 2019). In the current study, an exploration of the properties (e.g. electronic, structural, and vibrational) of 5-nitro- picolinamide have been undertaken. We have determined the composition and harmonic wave numbers and analyzed at the density functional theory (DFT) level by using the basis set 6-311 G(d, p). The optimized geometry of 5-nitro- picolinamide and its molecular properties e.g. as frontier orbital energy gap, molecular electrostatic potential (MESP) energy map, dipole moment, equilibrium energy, polarisability and first static hyperpolarisability were obtained by calculation and explained. Calculations which are based on Density Functional Theory, make available both qualitative and the quantitative perceptive of energy distribution of each vibrational mode based on distribution of potential energy and show the way to an extra analysis of the data obtained from vibrational spectroscopy as given by various groups . NBO Analysis carried out gives conclusive information about charge transfer.

Computational details

The title molecule is modeled by using Gauss View 3.0 (Frisch A.,2000) and optimized without any symmetry constrain by using G03 program package (M.J. Frisch, et. al. 2003). The optimizations of title molecule were done by using combination of DFT/B3LYP method and 6-311G (d, p) basis set. The HOMO, LUMO, MESP of title molecule is plotted by means of gauss View 3.0. The Electronic parameters and UV spectra of 5-nitro-picolinamide are calculated by TDDFT method on optimized structure by using same level theory. The NBO is analyzed by NBO 3.0 program package (Glendening E.D., et al. 1998).

Geometry Optimization

The optimized geometry having no symmetry with ground state energy -412.170 a,u. The optimized structure of title molecule is presented in Fig.1.The optimized geometry 5-nitro- picolinamide having a nitrobenzene ring with one hydrogen at ortho position is replaced by $-CONH_2$-group.The values of C=C bond length(calculated) of nitrobenzene ring lies in between $1.37A^0$-$1.38A^0$ however bond length of C=N is 1.33 A^0. The calculated bond length in between C=O is $1.22A^0$ however bond length in between N-H is $0.996A^0$-0.995 A^0.

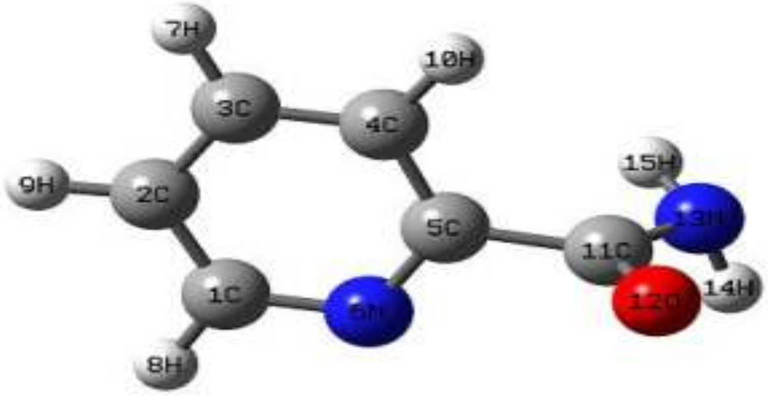


Fig-1 Optimized geometry

Electronic Properties and UV spectra

The HOMO are said to be highest occupied molecular orbitals and LUMO the least unoccupied molecular orbitals are border line molecular orbital. The frontier orbital gap gives valuable information about chemical property and molecular stability. The higher energy gap means molecule is more polarized and consequently molecule shows more reactivity (Gutowski M. et.al.1993, Bose SC.2011) . The calculated gap for title molecule is 4.14eV. The MESP, HOMO, and LUMO plot of molecule are presented in **Fig.2**. Both HOMO and LUMO distributed over whole molecule.

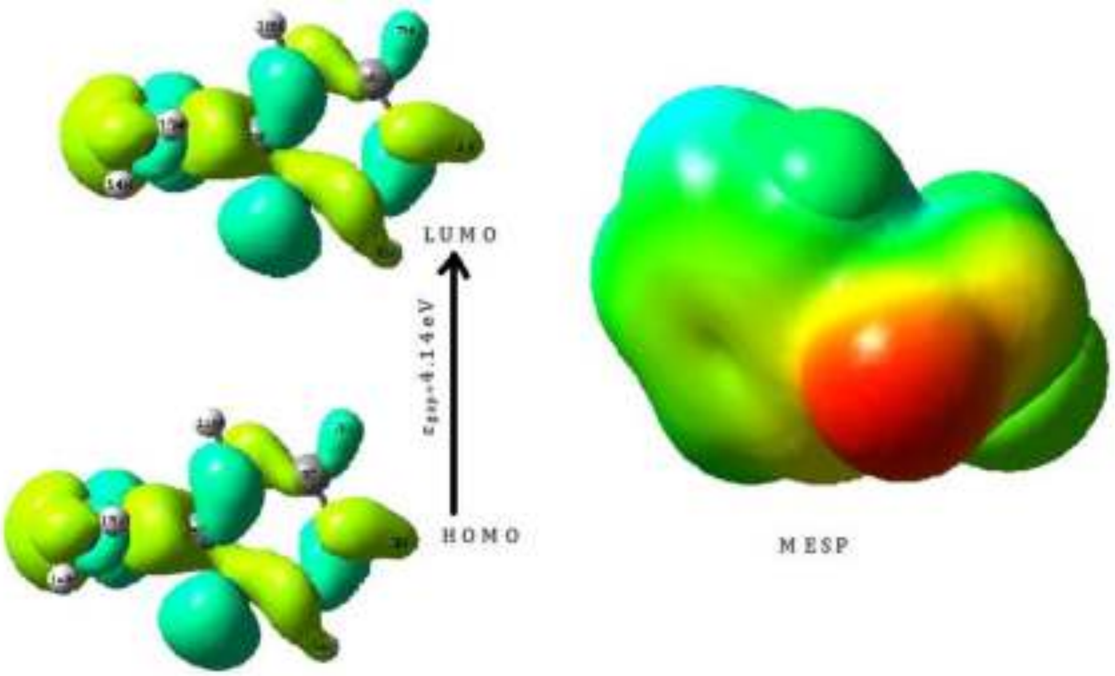


Figure-2 HOMO LUMO and MESP plot of Title molecule

The significance of MESP lies in the reality that it simultaneously exhibits the size of molecule, and the shape as well as +ve, -ve, and neutral electrostatic potential regions in terms of color grading and it is very helpful in studying the molecular structure using its chemical-physical property relationship (Murray JS et.al.1996) . The red color distributed over oxygen however violet color distributed over nitrogen of nitrile group, hence oxygen acts nucleophilic charge center and nitrogen acts as electrophilic charge center.

Several Global reactivity descriptors are calculated and reported Table-1 which are given as

$$\text{Energy band gap} = \varepsilon LUMO - \varepsilon HOMO)$$

$$\text{Electronegativity } (\chi) = -\tfrac{1}{2}\, \varepsilon LUMO + \varepsilon HOMO) \text{ ----(1)}$$

$$\text{Chemical potential } \mu = -\chi,$$

$$\text{Global hardness } \eta = \tfrac{1}{2}\, \varepsilon LUMO - \varepsilon HOMO) \text{ ---- (2)}$$

$$\text{Global softness } S = \frac{1}{2\eta} \quad \text{----------} \quad (3)$$

$$\text{Global electrophilicity index } \omega = \frac{\mu 2}{2\eta} \text{ --------} \quad (4)$$

(Parr R.G. et al.1989, 1983, Pearson R.G., 1989 , Geerlings P.,et.al.2003)

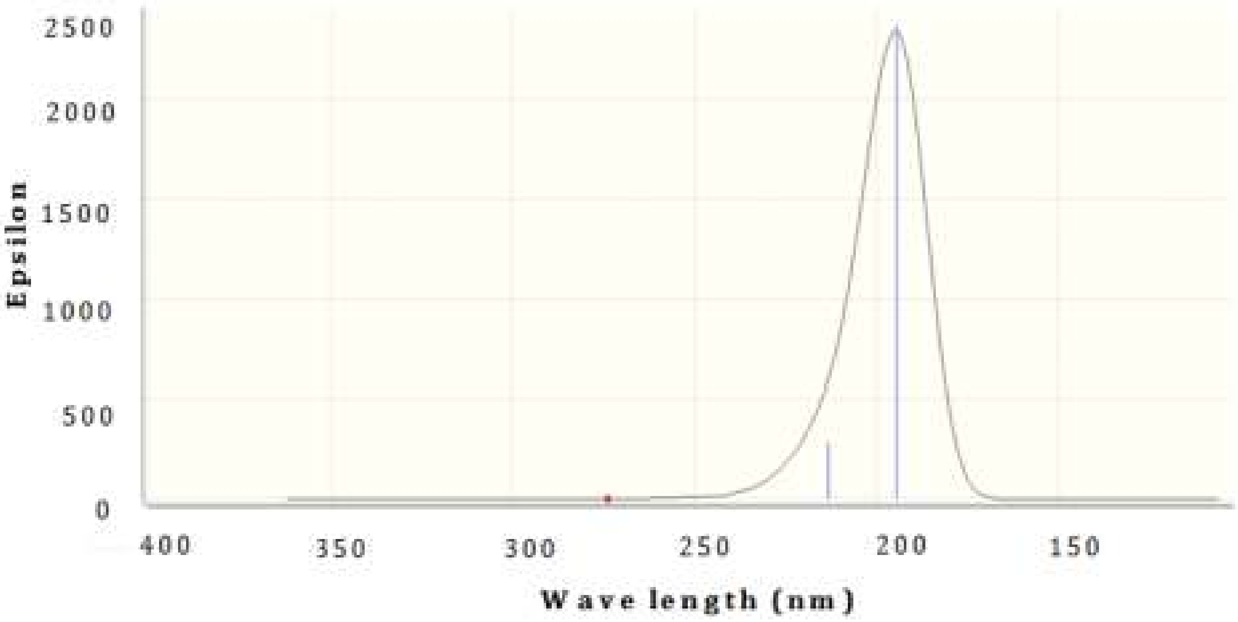
Table 1: Calculated Electronic parameter of title compound

ε_{HOMO}	ε_{LUMO}	ΔE	χ	μ	η	S	ώ
-6.98	-2.84	4.14	4.91	-4.91	2.09	0.240	5.79

The UV spectrum of title molecule is done by using TDDFT method with same level theory. The TDDFT calculation has done on optimized structure of title molecule. The calculated UV spectra and transition orbitals of title molecule is shown in Fig.3(a),and 3(b).The calculated electronic transitions E (eV), oscillatory strength (f), λ_{max} (nm) are calculated and collected in Table-2. The calculated UV spectra shows two prominent absorption peak corresponds at 213nm and 194nm wavelengths. These transitions are due to HOMO-4→LUMO(31%), HOMO-3→LUMO(21%), HOMO-4→LUMO+7(21%) and HOMO-2→LUMO+1(17%), HOMO→LUMO(80%), HOMO-3→LUMO+1(3%) respectively.

Table 2: The values of electronic transitions(calculated): E (eV), oscillatory strength (f), λ_{max} (nm) of title molecule

S.N.	Transitions	E (eV)	Oscillatory Strength(f)	λ_{max} calculated	% Contribution	Assignment
1	$HOMO-4 \rightarrow LUMO$ $HOMO-3 \rightarrow LUMO$ $HOMO-4 \rightarrow LUMO+7$	1.24	00.0068	213	31% 21% 21%	$n_p \rightarrow n_p^*$
2	$HOMO-2 \rightarrow LUMO+1$ $HOMO \rightarrow LUMO$ $HOMO-3 \rightarrow LUMO+1$	2.71	0.0568	194	17% 80%	$n_p \rightarrow n_p$



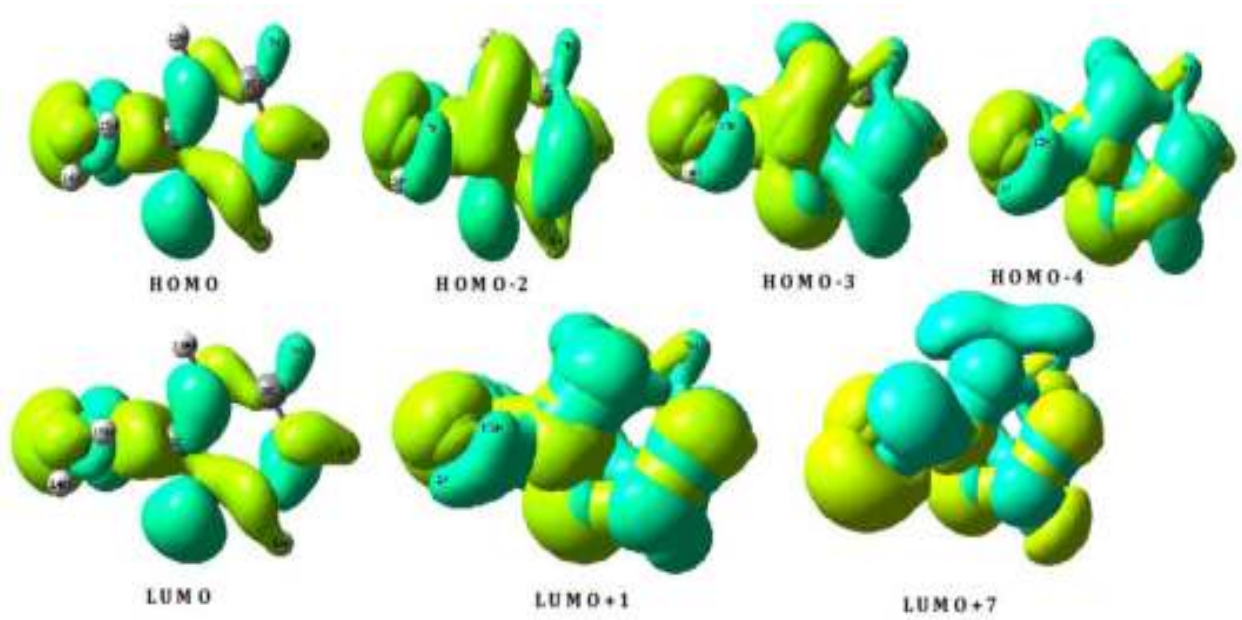


Fig-3(a) Calculated UV spectra (b) Transitions orbitals

NLO analysis

The calculations of Hyperpolarizability and Polarizability have been made by means of a grouping of the DFT / B3LYP method and a 6-311G base group (d, p). Buckingham defined the total μ(dipole moment), mean value of polarizability in a two dimensional cartesian coordinate frame and hyperpolarizability in three dimensional Cartesian coordinate frame by

$$\mu = (\mu x^2 + \mu y^2 + \mu z^2)^{1/2} \qquad (5)$$

$$< \alpha > = \frac{1}{3}[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \qquad (6)$$

$$\beta_{\text{Total}} = (\beta^2 x + \beta^2 y + \beta^2 z)^{1/2}$$

$$= [(\beta xxx + \beta xyy + \beta xzz)^2 + (\beta yyy + \beta yxx + \beta yzz)^2 + (\beta zzz + \beta zxx + \beta zyy)^2]^{1/2} — (7)$$

The calculated (Table 3) Polarizability of title molecule shows that molecule more polarize along x and y axis. The value of β_{XXY} and β_{XXZ} contains major part of hyperpolarizability. The calculated value of hyperpolarizability of 5-nitro- picolinamide is almost 3/2 greater than that of urea. Analysis of NBO indicates that the electron cloud moment of π–electron from the donor to the receiving atom is responsible for the polarization in the molecule.

Table 3 : Calculated Polarizability and Hyper Polarizability of 5-nitro- picolinamide

S. N	**Parameter**	**Polarizibility**	**S. N**	**Parameter**	**Hyper Polarizibility**
1	α_{xx}	84.908	1	β_{xxx}	-0.1470
2	α_{yy}	73.862	2	β_{yyy}	-6.934
3	α_{xzz}	19.155	3	β_{zzz}	1.0441
4	α_{xy}	1.826	4	β_{xyy}	-0.0088
5	α_{xz}	-0.004	5	β_{xxy}	-34.864
6	α_{yz}	0.001	6	β_{xxz}	-61.3815
	<α>	**-59.31 a.u.**	7	β_{XZZ}	0.0068
-	-	-	8	β_{YZZ}	2.521
-	-	-	9	β_{YYZ}	7.543
-	-	-	10	β_{XYZ}	-0.0056
-	-	-		. β_{Total}	**73.69 a.u.**
1 a.u. = 8.3693X10^{-33}e.s.u.					

Thermodynamic Property

According to vibrational analysis Enthalpy (H^0_m), Entropy (S^0_m), Heat Capacity ($C^0_{p.m}$) are major thermodynamic functions. In this communication we have calculated these major parameters by using grouping of DFT/B3LYP method and base 6-311G (d, p) in between 100K-500K temperature range. The calculated graph in between temperature and these parameters are plotted . These are temperature and Enthalpy (H^0_m), Entropy (S^0_m), and Heat Capacity ($C^0_{p.m}$). We have find a good correlation in between these parameters with temperature. The calculated correlation of these parameters with variation of temperature after quadratic fitting of order two are given below

$$H^0_m=104.77- 0 .00081T- 0.000177T^2 \, (R^2=0.99961)\text{—}(8)$$

$$C^0_{p.m}=-3.38+0.3211T-0.00066 \, (R^2=0.99941) \quad \text{—}(9)$$

$$S^0_m=74.124+0.267T-0.000041 \, T^2 \, (R^2=0.99975) \quad \text{—}(10)$$

The above correlation equations are helpful in thermochemistry for computation in thermo energy and also valuable for additional work for 5-nitro- picolinamide

Conclusion

The electronic properties such as molecular orbital energies and their distributions (HOMO-LUMO clouds, molecular electrostatic potential energy map) were calculated by using combination of DFT/B3LYP method and 6-311G base group (d,p). The ultravoilet spectrum of concerned molecule shows two prominent absorption peaks. The molecular electrostatic potential (MESP) energy map plot shows that Oxygen behaves most nucleophilic and Nitrogen is most electrophilic charge centre. The calculated HOMO-LUMO gap of title molecule shows that title molecule is less chemically reactive. The calculated optical parameters point out that title molecule is good NLO agent in future.

References:

Aljuboori S, Mahmood A.2019. Synthesis, antimicrobial evaluation, density functional theory and docking studies of some new 2 mercapto pyrimidine Schiff bases, *Asian J. Pharm. Clin. Res.* 12(2): 496-502.

Bose SC, Saleem H, Erdogdu Y, Rajarajan G, Thanikachalam V.2011. *Spectrochim.Acta part A***82 :** 260–269.

Dwivedi A, Pandey AK, Misra N, 2012. Comparative Study of Vibrational spectra of two well known natural products Lupeol and Lupenone Using Density Functional Theory, *Spectroscopy: An International Journal*, 27(3): 155–166.

Dwivedi A, Pandey AK, Misra N, 2011. Electronic Structure, Optical Properties and Vibrational Analysis of 2-Decenoic acid and its derivative by Density Functional Theory, *Spectroscopy: An International Journal* 26:367–385.

Dwivedi A, Kumar A,2019. Molecular Docking and Comparative Vibrational Spectroscopic Analysis, HOMO-LUMO, Polarizabilities, and Hyperpolarizabilities of N-(4-Bromophenyl)-4-Nitrobenzamide by Different DFT (B3LYP, B3PW91, and MPW1PW91) Methods, Polycyclic Aromatic Compounds. . https://doi.org/10.1080/10406638.2019.1591466.

Das S., Bharanidharan S., and Dhandapani A.2018. Molecular Spectroscopy and Molecular Docking Studies on (E)-1-(4-Bromobenzylidene) Thiourea, *Journal of New Developments in Chemistry* 1(3): 62-81 .

Frisch A, Nelson AB, Holder AJ, *GAUSSVIEW Inc.,* Pittsburgh PA, 2000.

Frisch M.J. et. al.,Gaussian 03 Revision C.02, Gaussian Inc.,Pittsburgh, PA, 2003.

Geerlings P, De-Proft F, Langenaeker W.2003. Conceptual Density Functional Theory, *Chem. Rev*. 103:1793–1874.

Glendening E.D, Reed AE, Carpenter JE, Weinhold F, 1998. NBO 3.0 Program Manual, NBO Version 3.0, TCI, University of Wisconsin, Madison .

Gutowski M, Chalasinski G.1993. Critical evaluation of some computational approaches to the problem of basis set superposition error *J. Chem. Phys.***98**, 4540–4554.

Kundu A, Saha S. 2014. In vitro Antifungal Activity of Novel Picolinamides against Soil Borne Fungi and Structure Activity Relationship. *Plant Pathology Journal*, 13: 152-159.

Murray JS, Sen K.1996. Molecular electrostatic potentials, Concepts and Applications Elsevier Amsterdam.

Pandey AK, Dwivedi A, Misra N, 2013.Quantum Mechanical Study on the Structure and Vibrational Spectra of Cyclobutanone and 1,2-Cyclobutanedione, Spectroscopy, Volume 2013: Article ID 937915, 11 pages .

Parr RG, Yang W. 1989.Density functional Theory of Atoms and Molecules, Oxford University Press: Oxford, New York.

Parr RG, Szentpály L, Liu S.1999. Electrophilicity Index. *J. Am. Chem. Soc*. 121:1922–1924.

Parr RG, Pearson RG. 1983. Absolute hardness: companion parameter to absolute electronegativity, *J. Am. Chem. Soc.,* 105:7512–7516 .

Pearson RG. 1989.Absolute electronegativity and hardness: applications to organic chemistry, *J. Org. Chem.* 54: 1430–1432 .

Rizzotto M. 2012. Metal complexes as antimicrobial agents in A search for antibacterial agents, Bobbarala, V. (Ed.), Chapter 5, InTech, Rijeka: Croatia: p 75.

Speri E, Janardhanan J, Masitas C, Schroeder VA, Lastochkin E, Wolter W R, Fisher J. F, Mobashery S, Chang M., ACS Infect. Dis. 2020.

Sert Y, Al-Wahaibi LH, Gokce H, Hassan HM, Alsfouk A, El-Emam AA.2019. Molecular docking, Hirshfeld surface analysis and spectroscopic investigations of 1-(adamantan-1-yl)-3-(4-fluorophenyl) thiourea - A potential bioactive agent, Chemical Physics Letters Volume 735: 136762.

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Theoretical calculation of electronic parameters, UV spectra and Thermodynamic properties of Benzotriazoles

Abstract

In present communication we have calculated geometry optimization, electronic properties and UV spectra biological and thermodynamical properties of Benzotriazoles by using combination of DFT/B3LYP and 6-311G base (d, p). The Highest occupied molecular orbital (HOMO), Lowest unoccupied molecular orbital (LUMO), Molecular electronic surface plot (MESP) are used to obtain electronic property of Benzotriazole molecule. Several thermodynamical properties are also obtained by means of same level theory. The time dependent density functional theory (TDDFT) of concerned molecule is also obtained by using same theory. Many biological activities are calculated by the program PASS. Swiss Dock is online server which is used for docking of Benzotiazole with 6LU7 protein The calculated value full fitness score and ΔG shows that Benzotriazoles dock well with 6LU7 protein.

Key word: HOMO, LUMO, TDDFT, DFT, 6LU7 protein

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1. Introduction:

Benzotriazoles (BT) such as 1H-benzotriazole (1H-BT), commonly utilized as corrosion inhibitors in aircraft de-icing/anti-icing fluids , dish washer detergents, brake fluids, metal-cutting fluids, automotive antifreeze materials, liquids for industrial cooling systems, and in solid cooling fluids (Kiss A, Fries E. 2009). BTA can highly enhance the tribiological actions of ionic liquids carrying hexafluoro phosphate anions for Steel/Cu–Sn alloy sliding pair primarily for the corrosion relief (Liu X, et.al. 2006). Benzotriazole and its derivatives have vital application in the field of pharmaceutical industry. It may also be used as agonists in reference of some of very crucial proteins. Its esters derivative may act as in activators for severe acute respiratory syndrome (SARS). It may act as an acid or base, can have capability to attach outer species by using its lone pair electron properties. The BTA can be used as antifreezer in vapor phase inhibitors etc. as well (Sease C. 1978). A complete quantum chemical study may lead to asses every energetic as well as significant mechanistic insight within its formulation periphery.

In the current programme, the investigation of the structural, electronic biological properties of benzotriazoles (BT) have been undertaken. The structure and numbers of harmonic waves were determined and analyzed at the level of density functional theory (DFT) using the set of bases 6-311 G (d, p). A number of studied have been carried out on chemical compounds which proves reliability of our method(Pandey A K, Siddiqui SA,.Misra N. 2012,2013, Dwivedi A, Kumar A.2019, Das S, Bharanidharan S, and Dhandapani A. 2018, Aljuboori S, Mahmood A. 2019. Our study on title molecule helps for researchers to understand new reactive sites for chemical reaction e.g. oxidation/reduction on polyfunctional bioactive compounds. We have docked our molecule with 6LU7 protease which is related to novel COVID 19.The optimized geometry of title molecule and its molecular properties (equilibrium energy, frontier orbital energy gap, molecular electrostatic potential (MESP) energy map) were calculated and discussed. PASS analysis may significantly support its bio-utility.

2.Experimental:

We have modeled initial structure of title molecule by using GassVew3.0 (Frisch MJ et.al.2003). The geometry of concerned molecule is optimized with grouping of DFT/B3LYP method and 6-311G (d, p) basis set without any symmetry constrains. Entire calculations are done on G03 program (Frisch A et.al. 2000), on our personal laptop. The electronic parameters are calculated by means of same level theory. The Ultravoilet of concerned molecule is calculated by means of TDDFT .The HOMO, LUMO, MESP of molecule is plotted by means of of Gauss View3.0.

3. Results and Discussion

3.1. Molecular Structure

The optimized geometry of Benzotriazole molecule is shown is **Fig.1**.The optimized geometry of title shows C_1 symmetry with ground state energy 395.96 a.u. The title molecule has benzene fused with pentene ring. In pentene ring three carbon atoms are replaced by nitrogen. The C-C bond length of benzene ring is $1.42A^0$-$1.38A^0$ however C-N and N-N bond length in pentene ring are1.34 A^0 and 1.32 A^0 correspondingly.

3.2. MESP and $HOMO - LUMO$ Plots

The chemical reactivity of title molecule are described by $\boldsymbol{HOMO}$ is known as highest occupied molecular orbitals and $\boldsymbol{LUMO}$ is known as lowest unoccupied molecular are frontier molecular orbital. The frontier orbital gap gives important result about chemical reactivity and stability of molecule. The energy gap is inversely related with polarization and reactivity of molecule (Fleming I.1976, Murray JS and Sen K.1996). The calculated gap for title molecule is 4.89eV is comparable with carbon so title molecule shows less reactivity. The calculated, $LUMO$ and MESP Plot of molecule are given in Fig. 2. The $\boldsymbol{HOMO}$ of title molecule distributed over whole molecule except N8 however $LUMO$ share out throghout whole molecule. The transition $\boldsymbol{HOMO} \rightarrow LUMO$ shows that charge transfer to N8 atom to benzene ring. The MESP plays important role to develop relationship in between molecular structure with its physiochemical property (Sponer J. and Hobza P. 1996, Kohn W**,** Sham LJ.**1965**).

3.3. Electronic and Thermodynamic properties

Pearson established relation in between hardness and HOMO-LUMO gap. The negative Eigen value HOMO and LUMO is known as ionization potential and electronegativity.

$$IP=-\varepsilon_{HOMO}\ EA=-\ \varepsilon_{LUMO}$$

Several electronic parameters are calculated and collected (Parr RG, Pearson RG.1983, Geerlings P et.al.2003**,** Parr RG, Szentpály L, Liu S.1999, P.W. Ayers and R.G. Parr.2000, Erdogdu Y, Unsalan O, Gulluoglu MT..2010) in Table-2 by given formula:

$$\text{Energy band gap} = \varepsilon LUMO - \varepsilon HOMO)$$

$$\text{Electronegativity } (\chi) = -\tfrac{1}{2}\ \varepsilon LUMO + \varepsilon HOMO) \text{ ----(1)}$$

$$\text{Chemical potential } \mu = -\ \chi,$$

$$\text{Global hardness } \eta = \tfrac{1}{2}\ \varepsilon LUMO - \varepsilon HOMO) \text{ ---- } (2)$$

$$\text{Global softness } S = \frac{1}{2\eta} \qquad \text{----------} \qquad (3)$$

$$\text{Global electrophilicity index } \omega = \frac{\mu 2}{2\eta} \text{--------} \qquad (4)$$

Several thermodynamically parameter are obtained by grouping of DFT/B3LYP method and 6-311G base (d, p) and collected in **Table-1**. The vibrational energy plays important role in entropy specific heat capacity contributes.

3.4. UV spectral analysis

The UV spectrum (Fig-3) of Benzotriazole is obtained by TDDFT calculation by using unchanged level theory. The optimized structure of title molecule is used for TDDFT calculation. The Calculated electronic transitions: E (eV), oscillatory strength (f), λ_{max} (nm) are listed in table-3.The Ultravoilet spectra of title molecule shows two prominent peak corresponds to 271nm and 217 nm. These peaks are originated by $HOMO \rightarrow LUMO$ (97%) and $HOMO - 1 \rightarrow LUMO$ $(80\%), HOMO \rightarrow LUMO + 1(20\%)$ respectively.

Biological Activity

Some biological activities of title molecule for Pa>70% are listed in table-4. These biological activities are intended by using PASS software which determined 900 pharmacological activities (Tetko IV et.al.2001) . The title molecule shows good activities against TGF beta receptor type-I kinaseinhibitor(0.991), Renal disease treatment(0.975), Aspulvinone dimethylallyltransferase inhibitor(0.842), Chymosin inhibitor(0.830).

Swiss dock(Grosdidier A et.al.2011) is online server which predicts and performs docking with suitable protein. Swiss dock predicts 6LU7 protein suitable for docking. The 6LU7 protein is responsible for new epidemic COVID19. The calculations of molecular docking have been undertaken as blind not covered any specific area to avoid sampling. In docking process we upload coordinate file of optimized parameter and PDB file of 6LU7 protein (Liu X et.al.2020). The full fitness score (FF) and binding affinity are used to determine strength of docking of title molecule with 6LU7 protein. The more negative of FF means protein bind well with drugs. In this docking process calculated value of FF score (-1186.93kcal/mol) and binding affinity (-5.80 kcal/mol) shows that of title molecule bind well with 6LU7 protein. The docking picture of concerned molecule with 6LU7 protein is presented in fig-7. The N8 atom of title molecule bind with hydrophobic surface amphipathic amino acid Methionine (MET17) residue at 2.39A^0.

4. Conclusions

In this paper DFT calculations B3LYP/6-311 G (d, p) on Benzotriazoles. The calculated HOMO-LUMO gap (4.41eV) shows that Benzotriazoles is chemically stable. The calculated MESP plot shows that N8 atom is suitable for nucleophilic attack. The UV spectra of Benzotriazoles have two prominent peaks. The Full fitness score and ΔG shows that N8 atom of Benzotriazoles bind with hydrophobic surface amphipathic amino acid Methionine (MET17) residue at 2.39A^0. The Benzotriazoles shows good potential against in the search of potential inhibitors for novel corona virus, COVID-19 protease. This study only based on theoretical assumption of docking so we have not considered other side effects.

Table 1: Calculated thermodynamic properties of Benzotriazole by B3LYP/ 6-311 G(d,p) level.

	E (kcal/mol) Benzotriazole	C_v (cal/K-mol) Benzotriazole	S (cal/K-mol) Benzotriazole
Total	70.633	23.452	77.233
Translational	0.878	2.893	40.238
Rotational	0.891	2.979	28.076
Vibrational	68.855	17.491	8.920

Table 2: Calculated Electronic properties of Benzotriazole by B3LYP/ 6-311 G(d,p) level .

Electronic Parameters	I.P (eV)	EA (eV)	η (eV)	χ (eV)	S (eV)	ω (eV)	E_g (eV)
Pyrozine	8.57	0.39	4.09	4.48	0.12	4.91	4.89

Table3: Calculated electronic transitions: E (eV), oscillatory strength (f), λ_{max} (nm) using TDDFT/B3LYP/6–311G (d, p) method.

S. N.	Electronic Transitions	E (eV)	Oscillatory strength (f)	Calculated (λmax)	% Contribution
1	$HOMO \rightarrow LUMO$	4.56	0.114	271.07	97%
2	$HOMO1 \rightarrow LUMO$	5.02	0.119	247.09	80%
	$HOMO \rightarrow LUMO+1$				20%

Table-4 Several Biological Activity (Pa>70%) calculated by PASS

S.N.	Biological Activity	Pa	Pi
1	TGF beta receptor type I kinase inhibitor	0,991	0,001
2	Signal transduction pathways inhibitor	0,977	0,004
3	Renal disease treatment	0,975	0,002
4	NADPH peroxidase inhibitor	0,840	0,007
5	MAP kinase inhibitor	0,826	0,003
6	5-O-(4-coumaroyl)-D-quinate 3'-monooxygenase inhibitor	0,827	0,005
7	Glycosylphosphatidylinositol phospholipase D inhibitor	0,829	0,009
8	Aspulvinone dimethylallyltransferase inhibitor	0,842	0,022
9	Saccharopepsin inhibitor	0,830	0,014
10	Chymosin inhibitor	0,830	0,014
11	Acrocylindropepsin inhibitor	0,830	0,014
12	Phobic disorders treatment	0,829	0,023
13	Nicotinic alpha2beta2 receptor antagonist	0,811	0,009
14	Arylacetonitrilase inhibitor	0,804	0,010
15	Complement factor D (inhibitor)	0,794	0,007
16	Taurine dehydrogenase inhibitor	0,799	0,013
17	Testosterone 17beta-dehydrogenase (NADP+)(inhibitor)	0,806	0,024
18	Glutamyl endopeptidase II(inhibitor)	0,790	0,011

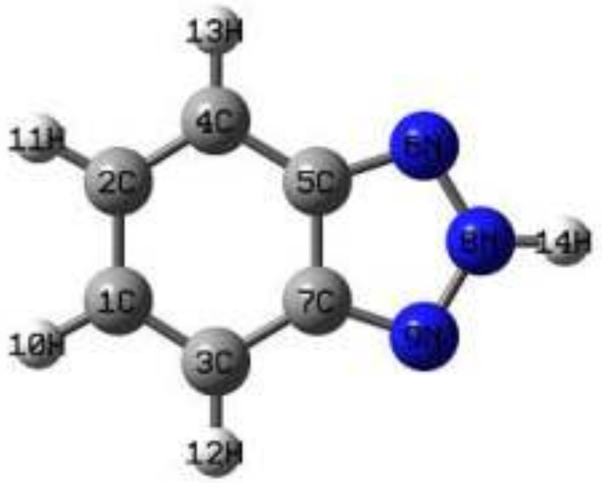

Figure 1. Molecular structure of Benzotriazole by B3LYP/ 6-311 G(d,p) level.

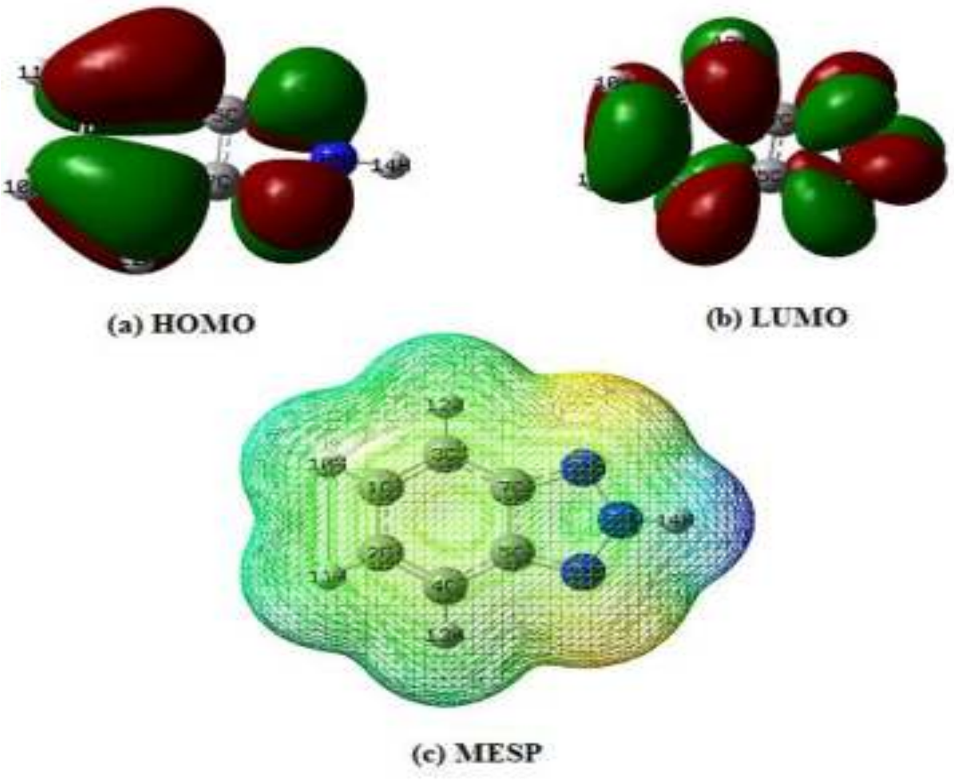

Figure2: HOMO, LUMO and MESP surfaces of Benzotriazole.

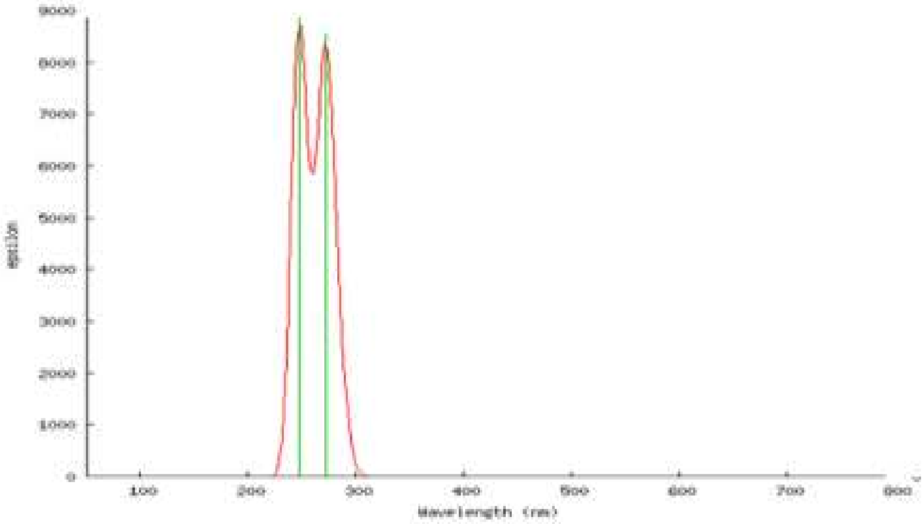

Figure 3. The Benzotriazole observed UV-vis spectrum calculated by TDDFT method at B3LYP/6-311G (d,p) level.

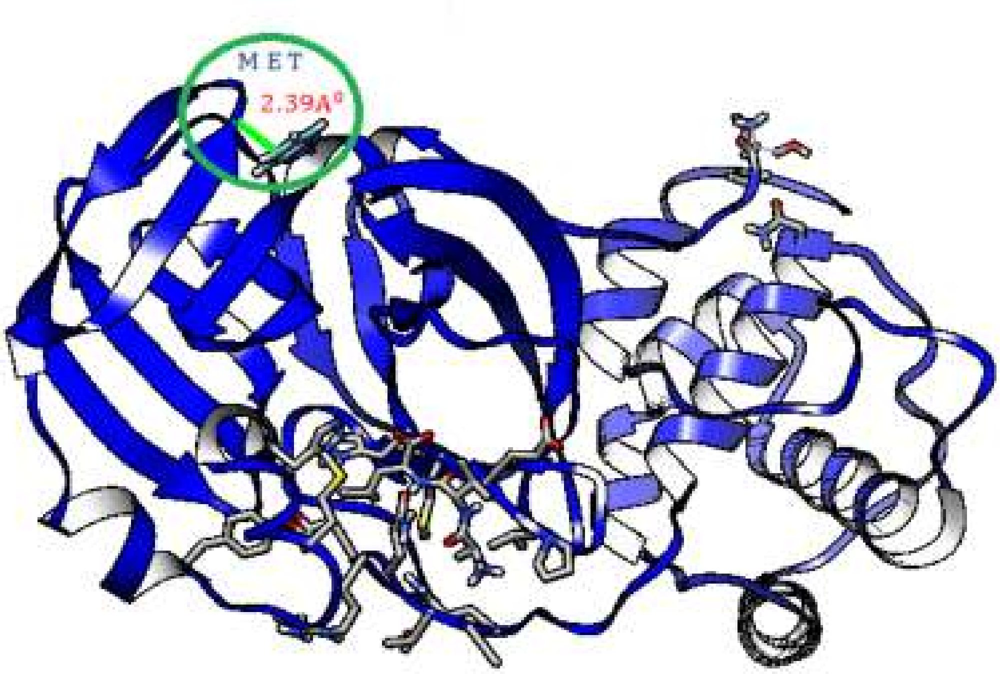

Fig-4 Molecular docking figure of title molecule with 6LU7 protein

4. References:

Ayers PW, Parr RG.2000. Variational Principles for Describing Chemical Reactions: The Fukui Function and Chemical Hardness Revisited.*Journal of the American Chemical Society*, 122(9), 2010–2018**.**

Aljuboori S, Mahmood A. 2019. Synthesis, antimicrobial evaluation, density functional theory and docking studies of some new 2 mercapto pyrimidine Schiff bases. Asian J Pharm Clin. Res. 12(2): 496-502.

Frisch MJ, Trucks GW, Schlegel HB, et al. 2003. *Gaussian 03 Revision C.02*, Gaussian Inc., Pittsburgh, PA. 2003.

Frisch A, Nelson AB and Holder A.J. 2000.*GAUSSVIEW Inc.*user manual. Pittsburgh PA.

Fleming I.1976. frontier Orbitals and Organic Chemical Reactions, John Wiley & Sons, New York, NY, USA..

Das S, Bharanidharan S, and Dhandapani A. 2018. Molecular Spectroscopy and Molecular Docking Studies on (E)-1-(4-Bromobenzylidene) Thiourea. Journal of New Developments in Chemistry 1(3): 62-81 .

Dwivedi A, Kumar A.2019. Molecular Docking and Comparative Vibrational Spectroscopic Analysis, HOMO-LUMO, Polarizabilities, and Hyperpolarizabilities of N-(4-Bromophenyl)-4-Nitrobenzamide by Different DFT (B3LYP, B3PW91, and MPW1PW91) Methods, Polycyclic Aromatic Compounds. https://doi.org/10.1080/10406638.2019.1591466.

Dwivedi A., Pandey A. K., Misra N. (2012)., Comparative Study of Vibrational Spectra of Two Bioactive Natural Products Lupeol and Lupenone Using MM/QM Method, *Spectroscopy: An International Journal,*27(3), 155–166.

Erdogdu Y, Unsalan O, Gulluoglu MT..2010. FT- Raman, FT- IR spectral and DFT studies on 6, 8- dichloroflavone and 6, 8- dibromoflavone.

*J. Raman Spectrosc.***41,** 820-828(2010).

Geerlings P, Proft FD. 18.Geerlings P, Proft FD. Langenaeker W.2003. Conceptual density functional theory . *Chem. Rev.*103, 1793–1873.

Grosdidier A, Zoete V., Michielin O. 2011. SwissDock, a protein-small molecule docking web service based on EADock DSS.Nucleic Acids Res. 39 W270 –W277.

Grosdidier A, Zoete V, Michielin O. 2011. Fast docking using the CHARMM force field with EADock DSS, J. Comput. Chem. 32: 2149 –2159.

Liu X, Zhang B, Jin Z, Yang H, Rao, Z.2020. The crystal structure of COVID-19 main protease in complex with an inhibitor N3. http://www.rcsb.org/structure/6LU7.

Kiss A, Fries E. 2009. Occurrence of benzotriazoles in the rivers Main, Hengstbach, and Hegbach (Germany) .Environmental Science and Pollution Research international. 16:702–710.

Liu X, Zhou F, Liang Y & Liu W. 2006. Benzotriazole as the additive for ionic liquid lubricant: one pathway towards actual application of ionic liquids.Tribology Letters. 23(3):191–196.

Murray JS and Sen K.1996. Molecular Electrostatic Potential, Concepts and Applications, Elsevier, Amsterdam, The Netherlands.

Pandey A K, Siddiqui SA,.Misra N. 2013. Vibrational Spectra of Two Narcotics-A DFT Study.*Chinese Journal of Physics* 51(3):473-499.

Pandey A.K, Dwivedi A, Misra N.2013. Quantum Mechanical Study on the Structure and Vibrational Spectra of Cyclobutanone and 1,2-Cyclobutanedione,Spectroscopy, 2013 Article ID 937915, 11 pages.

Pandey A. K., Dwivedi A., Misra N.2013. Quantum Mechanical Study on the Structure and Vibrational Spectra of Cyclobutanone and 1,2-Cyclobutanedione, Spectroscopy, Volume 2013, Article ID 937915, 11 pages(open access).

Kohn W, Sham LJ.1965. Self-Consistent Equations Including Exchange and Correlation Effects,Phys. Rev. A 140: 1133.

Parr RG, Pearson RG.1983. Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* 105, 7512–7516.

Parr RG, Szentpály L, Liu S.1999. Electrophilicity Index.*J. Am. Chem. Soc.*121, 1922–1924.

Sease C. 1978. Benzotriazole: a review for conservators.Studies in Conservation, 23, No. 2 : 76-85.

Sponer J. and Hobza P. 1996. DNA base amino groups and their role in molecular interactions: Ab initio and preliminary density functional theory calculations. International Journal of Quantum Chemistry. 57(5): 959-970.

Tetko IV, Tanchuk VY,Kasheva TN, Villa AEP.2001. Internet software for the calculation of the lipophilicity and aqueous solubility of chemical compounds . *J. Chem. Inf. Comput. Sci.*, *41*(2):*246*-52 .

Original Article

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Kinetic Studies of Acid Hydrolysis of Amyl Methanoate Formate in Binary Solvent Mixture and Effect of Solvent on Activation Parameters.

Abstract

The specific rate constants for acid catalyzed hydrolysis of Amyl Mathaonate formate in water-ethylene glycol system have been determined at 20-40^{0}C, the solvent composition covered the range from 30-80% by weight of the organic solvent. The variation in reaction rate as well as in activation parameters have been interpreted on the basis of solvation and dielectric properties of the solvent. The thermodynamic parameters such as activation energy(E_c) free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) have been evaluated from rate conbstants using Wynne-Jones and Evring equation .All the reactions have almost negative entropy of activation which strongly support specific salvation in reaction media with change of solvent composition. Iso kinetic relationship has been determined and found to be less than 300 (253.84K/Mole^2) which show weak interaction in reaction media.

Keywords: Kinetics, water-ethylene glycol, activation parameter, ionic strength, Amyl Mathaonate Formate.

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Introduction

The acid hydrolysis of amyl mathaonate formate in binary aqueous solvent mixture revealed that the polarity of solvent surrounding the reactant greatly influence the reaction rate in activation processes. Such polarity are affected by the addition of co-solvent . However, it can be treated as mere diluents of water modifying its dielectric properties only. In this study it has been studied that solvent effect on kinetics of amyl methanoate formate catalyzed by acid. (which is used as flavoring agent in food) in varying composition of water-ethylene glycol(EG) mixture at different temperatures. In acid catalyzed reaction the aquous-solvent affect on kinetic behavior and also play a major role in controlling the reaction rate which is usually affected by interaction of solvent with transition state and also with reactant. The dielectric constant of ethylene glycol is less than water and make miscible with water in all proportions The varying composition of water- solvent mixture showing different dielectric constants values lower than water (Akerlof. G.1932, Franks F. Water: 1973, Akerlof G. and Oliver.1936) . The properties of single solvent, do not necessarily predict the reactions as reported by many workers (Singh AK. 2019,2020, Sharma Sangita et al. 2013, Magda F Fathalla. 2011), in attempt to correlate the rate change with the nature and properties of the medium and bring confusing results. Thus Parker (Parker AJ. 1962) and Robert (Roberts DD. 1966) found that rate constants values decreases in the system with increase in dielectric constant of the solvent, as predicted by Hughes and Ingold (Hughes ED, Ingold CK. 1935) and Laidler and Landskroener (Laidler KJ, Landskroener PA.1956) . The rate of such reactions has been expected to show high values with increase of dielectric constant.

Experimental

The specific rate of hydrolysis observed volumetrically at five equidistance temperature over temperature range of 20 to 40^0 C having extraordinary attention of solvent in response mixture of water-EG media. Pure amyl methanoate (Merck) used for kinetic studies. Double distilled water is used throughout the experiment. The kinetics of acid catalyzed of ester was studied as usual by adding 0.60 ml of ester in 50 ml of 0.5M HCI solution. The values of specific rate constant were evaluated using first order rate equation and collected in Table-1. The values of rate constant for different $[H^+]$ ion concentration of the reaction media has been inserted in Table-2.The various activation parameter had been calculated using Wynne-Jones and Eyring equation (Wynne-Jones WF K, Eyring H. 1935) and given in Table-3.

Result and Discussion

Reaction rate and solvent effect:

First order kinetic equation was used to calculate the rate constant of hydrolysis of amyl methanoate in water-ethylene glycol solvent system and its value is tabulated in Table-1 It is evident from this Table that specific rate constant decreases with increasing temperature from 20 to 40^0 C. The depletion of rate to different extent with mole% in water- EG media may attributed partly due to solvation change and partly due to change in dielectric constant. The factor liable for increasing rate with temperature is because of dielectric impact and partially due to solvation in the response media. This outcome is supported through our earlier publication of Bano A. & Singh AK(Singh A K. Arjuman Bano. 2019).

Table 1 : Specific Rate Constant Values With Respect To Solvent Composition [K $X10^3$(Dm)3/Mole/Mint] In Acid Catalized Hydrolysis Of Amyl Methanoate Formate

Temp in ^{O}C	% of Ethylene glycol					
	30%	40%	50%	60%	70%	80%
$20^{O}C$	44.66	35.07	31.62	27.86	24.54	21.37
$25^{O}C$	83.17	64.56	56.88	49.54	42.65	35.39
$30^{O}C$	149.62	114.81	100.00	86.09	72.44	56.88
$35^{O}C$	263.02	204.17	169.82	146.21	121.61	91.20
$40^{0}C$	467.73	354.81	294.44	248.31	206.53	144.54

Iso-composition Activation Energy (E_c) and solvent effect

The Iso-composition Activation Energy of the reaction mixture decreases from 106.62 to 72.07 kJ/mole with increasing composition of solvent indicate that initial state is solvated and transition state is desolvated which support the recent communication of Singh AK(Singh AK. Arjuman Bano. 2019).

Iso- Dielectric Activation Energy (E_D) and solvent effect

With assist of Arrhenius plots the Iso- Dielectric Activation Energy (E_D) turned into evaluated which indicates lowering trend 84.19 to100.21 kJ/mole with increasing mole%. This is also supported by using past view of Wolford (Wolford R K, 1964) and these days view of Singh AK. et.al. (Singh AK. Arjuman Bano. 2019).

The effect of change in the concentration of $[H^+]$ ion(acid) in the reaction media,on the kinetic of acid catalyzed solvolysis of amyl formate was studied by changing the concentration of HCI solution, keeping the ionic strength of the media constant at (μ=0.9).The value of rate constant of the reaction were found increasing with increasing$[H^+]$ ion in the reaction media are given in Table-2. To establish the mechanism of reaction, the log k values were plotted against $[H^+]$ and the slope of straight line was found to be 1.005 which may be treated as unity , this concluded that hydrolysis of amyl formate follow A_{AC}^2 mechanism in water-EG media as given by Zucker and Hammett(Zucker L and Hemmet LP.1939).

Table 2: Effect Of $[H^+]$ On The Specific Rate Constant Values Of Amyl Formate In Water-EG Media At Constant Ionic Strength

$[H^+]$	[KCI]	μ	$k\times10^3$in min^{-1}	2+log$[H^+]$	3+logk	Values of slope

0.12	0.80	0.90	27.93	1.0000	1.4461	
0.15	0.75	0.90	41.70	1.1761	1.6201	
0.20	0.70	0.90	56.90	1.3010	1.7551	
0.25	0.65	0.90	70.34	1.3979	1.8472	1.005
0.30	0.60	0.90	84.57	1.4771	1.9272	
0.40	0.50	0.90	114.13	1.6021	2.0574	
0.50	0.40	0.90	142.20	1.6990	2.1529	
0.60	0.30	0.90	168.27	1.7782	2.2260	
0.70	0.20	0.90	198.52	1.8451	2.2978	
0.80	0.10	0.90	226.52	1.9031	2.3551	

Thermodynamic activation Parameters and solvent effect of reaction:

Activation parameter, like activation energy also plays an important role in ester hydrolysis. The enthalpy of activation (ΔH^*) free energy of activation (ΔG^*) and entropy of activation (ΔS^*) is determined using Wynne-jones and Eyring equation(Wynne-Jones WFK, Eyring H.), and the results are collected in Table-2 with increasing mole% of solvent. Although, the variation of (ΔG^*) with mole % is negligible as compared to the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) with increasing composition of reaction mixture but it cannot be ignored.

The enthalpy of activation (ΔH^*) decreases with increasing mole fraction of reaction mixture (ΔS^*), become more negative which indicated that there is polar transition state is preferentially solvated by water molecule. The plots of (ΔG^*) against mole % of EG shown in fig-1 at 25^0c is found to be increasing non-linearly with increasing concentration of EG. This gradual and non linear increase in mole fraction of organic co solvent in reaction media is indication of salvation or desolvation of reactant as reported earlier by Elsemongy et.al.(Elsemogy MM, Abu EMS, Mussa MNH 1975) and recently supported by Singh AK (Singh A K. 2017). Since among three thermodynamic enthalpy of activation (ΔH^*), (ΔS^*) and (ΔG^*) the value of (ΔG^*) increases with simultaneous decrease in (ΔH^*), (ΔS^*) with increasing mole% of organic component of reaction media. On the basis of thermodynamic co relation

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

The increase in (ΔG^{*}) value with decrease in ΔH^{*} and ΔS* is possible when the extent of depletion ΔS* is greater than ΔH^{*}. The greater extent of depletion in ΔS* in compare to ΔH^{*} in water-EG media indicate that the reaction enthalpy promoting and entropy deactivating.

Table-3: Calculated Values Activation Parameters of the Reaction in Water-n-propanol Media [$\Delta H^{*}$and ΔG^{*} in KJ/Mole, ΔS^{*}in J/K/Mole.]

% of propanol	**Mole %**	**ΔH^{*} in Kj/Mole**	**20^{0}C**		**25^{0}C**		**30^{0}C**		**35^{0}C**		**40^{0}C**	
			ΔG^{*}	**-ΔS^{*}**	**ΔG^{*}**	**-ΔS^{*}**	**ΔG^{*}**	**-ΔS^{*}**	**ΔG^{*}**	**-ΔS^{*}**	**ΔG^{*}**	**-ΔS^{*}**
30%	12.16	87.89	89.53	5.59	89.57	5.05	89.65	5.80	89.68	5.81	89.69	5.75
40%	17.73	83.76	86.58	22.59	90.20	21.61	90.32	21.65	90.33	21.33	90.41	21.24
50%	24.42	82.84	90.38	25.73	90.52	25.30	90.67	25.84	90.80	25.84	90.78	25.36
60%	32.42	82.09	90.96	30.27	90.86	27.75	91.04	29.53	91.19	31.88	91.44	29.87
70%	42.94	78.84	91.00	41.50	91.23	41.57	91.48	41.71	91.66	41.62	91.70	41.08
80%	56.34	77.41	91.33	47.50	91.70	47.95	92.09	48.44	92.40	48.66	92.64	48.65

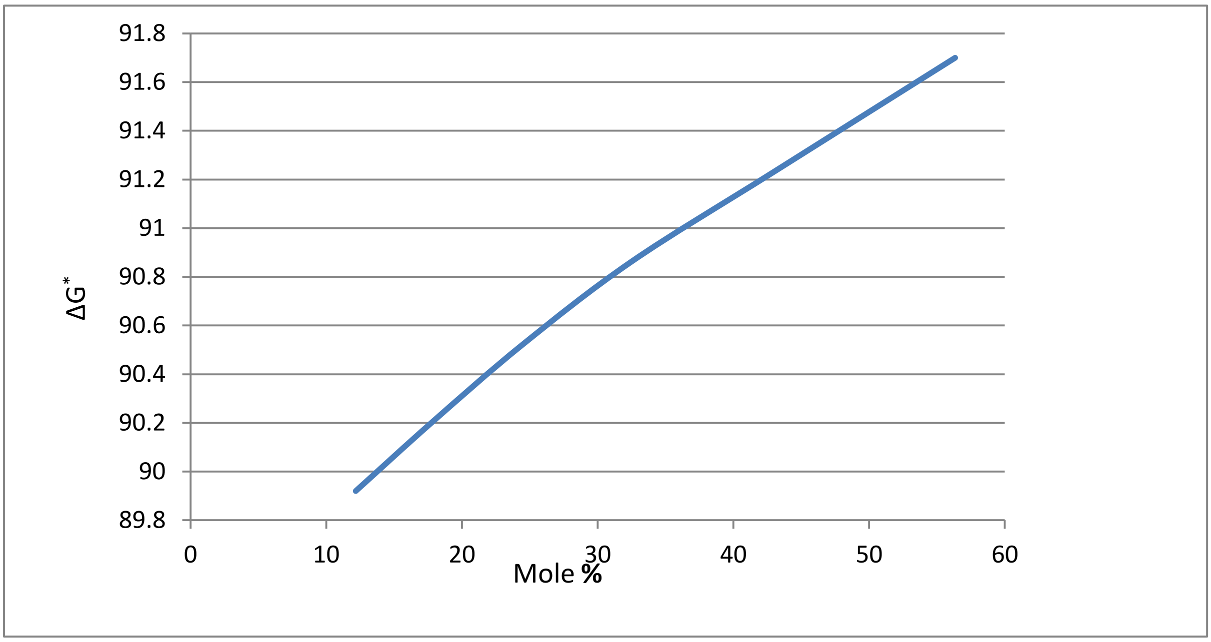

Fig (1)- Variation of ΔG^* with mole % at 25^0c (water-ethylene glycol)

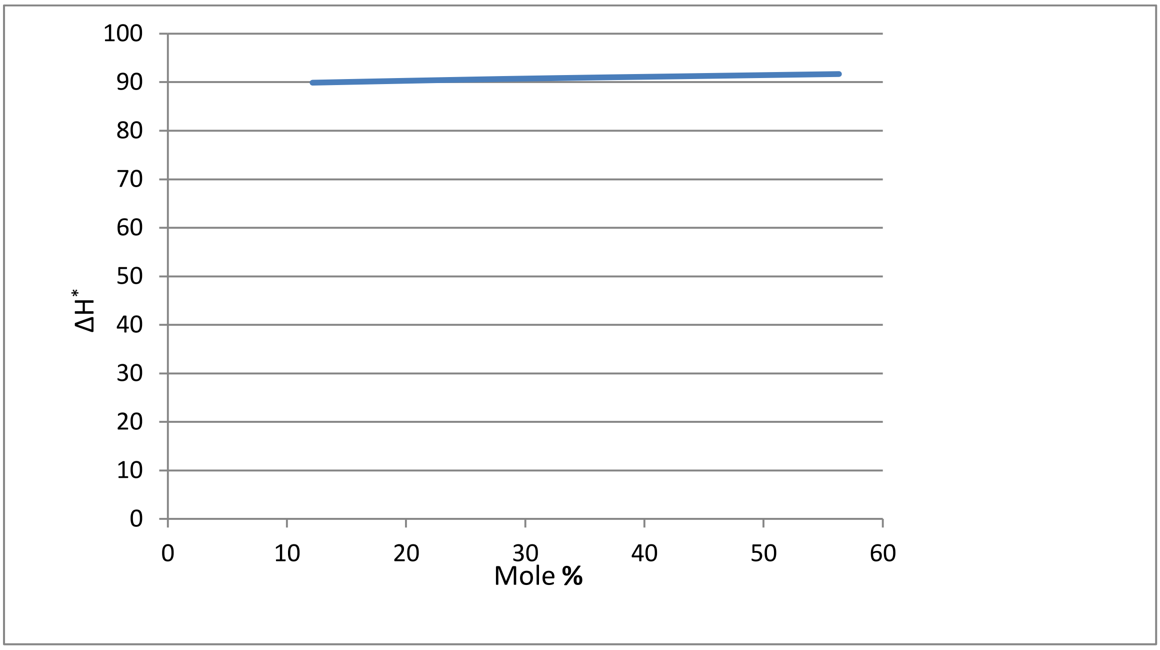

Fig (2)- Variation of ΔH^* with mole % at 25^0c (water- water-ethylene glycol)

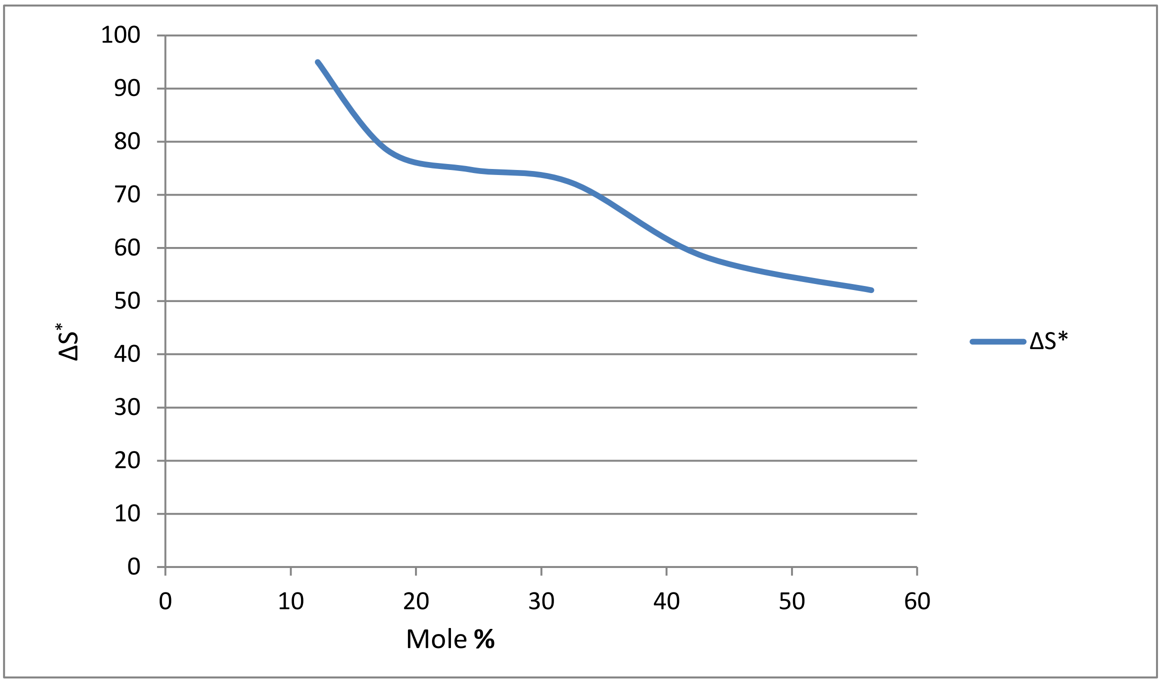

Fig (3)- Variation of ΔS^*+100 with mole % at 25^0c (water-ethylene glycol)

Iso-kinetic Temperature and solvent effect: The values of iso-kinetic temperature of the reaction was evaluated using Barclele-Butler (Barclay and Butlar JAV. 1938) relationship which is expressed as

$$\Delta\delta\,(\Delta H^*) = \beta\,(\Delta S^*).$$

It is relation between enthalpy and entropy of activation, β is known as iso-kinetic temperature or Laffler-Grunwald solvent stabilizer operator (Laffler J E. ,Grundwald E. 1963). The value of iso-kinetic temperature was evaluated from the slopes of straight line plotting between ΔH^* versus ΔS^* at 25^0c which is shown in fig-4.

From the slope of straight line of the plots, the value of iso-kinetic temperature was evaluated to be 253.84K/Mole$^{2.}$(less than300). Thus, in the light of Lefler(Lefler JE. 1955) guiding communication, it can be concluded that there may be no appreciable exchange in structure of reactant or in the solvent or in each the reactant or in solvent or both the reactant and solvent due to weak interaction between solvent and solute present in reaction media in similar ways as reported by Singh AK (Singh AK. **2020**).

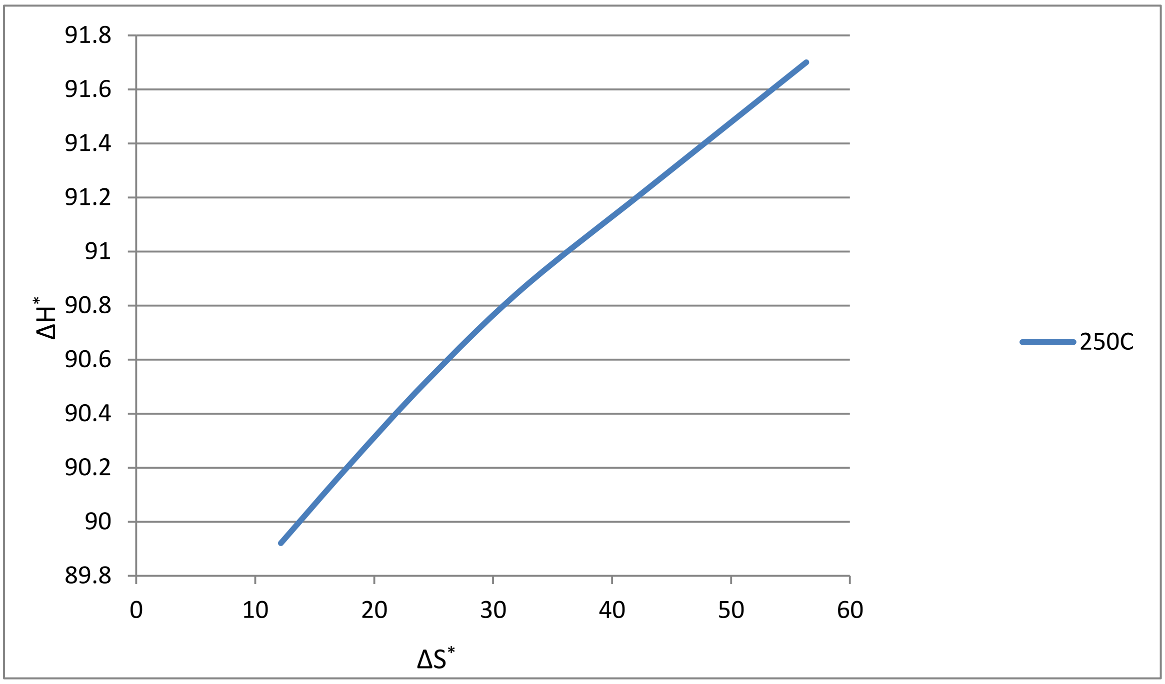

Fig. 4: Variation of ΔH* with ΔS*+100 (wate- water-ethylene glycol) system

Conclusion

The results of above project hydrolysis of Amyl Formate in water-EG media, following conclusion are found as: the solvent effect was discussed considering the dielectric constant of the medium and water water concentration effect on the reaction rate. Activation parameters calculated with help of Wynne-jones and Eyring equation and there is considerably change was found which shows that there is specific change taking place during the hydrolysis of amyl methanoate. The lower values of ionic strength shows weak interaction between solvent ant solute in the reaction media.The value of ionic strength the mechanism followed by hydrolysis is A_{AC}^{2} type.

References:

Akerlof G.1932. Dielectric constant of some organic solvent-water mixture at various temperature.*J am. Chem Soc*.54(11):4125-4139.

Akerlof G, Oliver.1936. A Shorter The dielectric constant of dioxane-water mixture between 0 and 80^{0}c.*J Am. Chem Soc.* 58(7):1241-1243.

Barclay and Butlar JAV. 1938. The entropy of solution. *Trans. Faraday. Soc.* 34:1445-1454.

Elsemogy MM, Abu EMS, Mussa MNH 1975. Kinetics and mechanism of acid hydrolysis of acetomide in dioxane-water mixture., *Z. Physik chem* (Neuetold) 94(69): 215-226.

Franks F. Water: 1973, A comprensive Treatrise Plenum Press New York vol-2 p422.

Hughes ED, Ingold CK. 1935. Mechanism of substitution at saturated carbon atom part IV, A discussion of constitution and solvent effect on mechanism, kinetics, velocity, and orientation of substitution. *j chem. Soc.* 244- 255.

Laffler JE. Grundwald E. 1963. Rate and equilibiria in organic reaction. Jons Wiely&sons, inc,New York.

Laidler KJ, Landskroener PA.1956. The influence of the solvent on reaction rates . Trans Faraday Soc. 52, 200.

Lefler JE. 1955. Entropy relationship and implication for organic Chemistry.*J. org. chem.*, 20: 1201.

Magda F Fathalla. 2011. Kinetics of reaction of 2-chloro-quinosalin with Hydroxide ion in CAN- H_2O *and DMSO-* H_2O *binary solvent mixture. Journal of solution chemistry. 40: 1258-70.*

Parker AJ. 1962. The effect of salvation on the properties of anion in dipolar Q Rev Issue-2, p163.

Roberts DD. 1966. Solvent effect III. The influence of aqueous. aprotic solvents dimethyl solfoxide on alkyl benzoate ester saponification reaction. *J Org. Chem.*31(12):4037-4041.

Sharma Sangita et al. 2013. Kinetic study of specific base catalysed hydrolysis of Ethyl Acrylate in water-Ethanol binary system. Russian Journal of physical chemistry A. 87(5):730-736.

Singh AK.2017. Studies of Solvent Effect of Aquo-Methanol Solvent System on Kinetics and Activation Parameters of *Base Catalyzed Hydrolysis of Ethyl Cinnamate. J Phys Chem &Biophys.* Volume 7 (3): 1000251 August 14(open access journal).

Singh AK. 2020. Study of Solvent effect of Protic solvent on Solvolysis of Hexanoate ester and Activation parameters. Asian journal of Research in Chemistry. ISSN 0974-4150,12(2)Nov: pp 216-218.

Singh AK. 2019. Kinetics and solvent effect on activation parameter of aquo-propanol solvent system for acid catalyzed solvolysis of propyl formate. *International Journal of Chemical Science,*3(4):85-88.

Singh A K. Bano A . 2019 .Kinetics and Solvent effect on Aquo-dipolar protic organic-solvent system of Hexanoate ester. *Asian journal of Research in Chemistry,* 12(6)Nov : 341-344.

Singh AK, Bano A. 2019. Solvent effect and kinetics on ethyl benzoate in aqueous solvent system. International Journal of Chemical Science, 3(5) 5: . 26-28.

Singh A K. 2020. Study of Solvent effect of Protic solvent on Solvolysis of Hexanoate ester and Activation parameters. Asian journal of Research in Chemistry.12(2) Nov: 216-218.

Singh A K, *2019*. Solvent effect and kinetics on solvolysis of propyl formate in water-propanol solvent mixture. *International Journal of Chemical Science,* 3(4):*82-84.*

Singh A K. 2019. Kinetics and solvent effect on activation parameter of aquo-propanol solvent system for acid catalyzed solvolysis of propyl formate. International Journal of Chemical Science,vol-3, issue-4, July, pp85-88

Singh AK, Bano A.2019 Solvent effect and kinetics on ethyl benzoate in aqueous solvent system. *International Journal of Chemical Science.* , 3(5): September; Page No. 26-28.

Singh AK. Bano A. 2019, Solvent effect and kinetics on ethyl benzoate in aqueous solvent system. *International Journal of Chemical Science*. 3(5): 26-28.

Wynne-Jones WF K, Eyring H. 1935. The Absolute Rate of Reaction in condensed Phase. *J. chem. phys.* 3: 492-502.

Wolford R K, 1964. Kinetics of acid catalised hydrolysis of Acetal in dimethylsulfoxide-water solvent system at 15,25 and 35^0c. *Phys Chem*. 68: 3392.

Wynne-Jones WFK, Eyring H. The Absolute Rate of Reaction in condensed Phase. 1935. *J. chem. phys*. 3: 492-502.

Zucker L, Hemmet LP. 1939.Kinetikc of the iodination of acetophenon in sulphuric and perchloric acid solution. *J Am. Chem. Soc.*61(10):2791-2798.

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Excess Molar Enthalpies of acetylene tetrachloride with cyclohexanone, pyrrolidin-2one , methyl ethyl ketone, and acetophenone at the temperature 303.15K

Abstract

The excess molar enthalpies, H^E, of mixtures of acetylene tetrachloride with cyclohexanone $(CH_2)_5CO)$, pyrrolidin-2one (C_4H_7NO), methyl ethyl ketone $(CH_3C(O)CH_2CH_3)$, and acetophenone $(C_6H_5C(O)CH_3)$at the temperature 303.15K, have been measured throughout the whole composition range by means of a microcalorimeter at the temperature T= 303.15 K. The excess molar enthalpies , H_m^E , are -ve for all the mixtures . The values of H^E for n-donor compounds raise in the order : acetophenone > methyl ethyl ketone > pyrrolidin-2one > cyclohexanone. The values of H^E are used to calculate the excess partial molar enthalpies of the particular component at the same temperature..

Key Words: Microcalorimeter, $C_6H_5C(O)CH_3$, acetylene tetrachloride, tetrahydrofuran, C_4H_7NO and excess partial enthalpy

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Introduction

Binary systems of acetylene tetrachloride (ATC) $(CHCl_2\ CHCl_2)$ with n-donor compounds are of great interest from the perspective of the presence of an electron releasing and accepting groups interaction which leads to the creation of intermolecular complexes between the components. The specific interaction can be thought of as being due to the existence of two Hydrogen atoms with four Chlorine atoms in $CHCl_2\ CHCl_2$, which would thus be able to act as σ-acceptors toward and be engaged with the creation of hydrogen bonds with cyclohexanone $(C_6H_{10}O)$, pyrrolidin-2one(C_4H_7NO) ,methyl ethyl ketone$(CH_3COC_2H_5)$, and acetophenone $(C_6H_5COCH_3)$ **.** Then again**,** the existence of non-bonding electrons on the O atoms of latter compounds, can prove itself as n-donors toward $CHCl_2\ CHCl_2$. A writing review uncovered that far and wide examinations on such frameworks have not been completed to date. Recently we have reported data on excess molar enthalpies H^E of mixtures of $CHCl_2\ CHCl_2$ with C_4H_4O or C_5H_6O or $(CH_2)_4O$ or $C4H_8O_2$ over the entire composition range at the temperature T= 308.15 K (Tripathi AD.2018) and the results obtained have been discussed from the perspective of molecular interaction between the components. In the current program experimental data on the H^E values of acetylene tetrachloride, with cyclohexanone, pyrrolidin-2one ,methyl ethyl ketone, and acetophenone have been taken with the help of microcalorimeter at the temperature 303.15 K. The values obtained for H^E are used to get the excess partial molar enthalpies . The outcomes, accordingly got have been reported and deciphered in this paper.

Experimental Section

Acetylene tetrachloride(AR), and and methyl ethyl ketone were collected from Sisco Research Laboratories, Pvt. Ltd., Bombay,India . Both compounds were agitated with K_2CO_3 solution, isolated, and afterward it was kept for drying above anhydrous K_2CO_3, and it was distilled fractionally. Cyclohexanone is of AR quality and lowest specific purity of 99.5%, HPLC High quality chemicals were also sourced from Sisco Research Laboratories, Ltd., Mumbai, India. Cyclohexanone was applied over anhydrous sodium sulfate to eliminate traces of water and the purest form of the mixture collected in the fractional column and was used for the experiments. The arrangements were placed in a dry box that completely prohibited contact between materials and air humidity. All estimates were made on fresh samples to avoid any dissociation upon standing.

Pyrrolidin-2one (Fluka) (E. Merck) and acetophenone were taken as such. All compounds were dried over recently activated molecular sieves. Purities of chemicals utilized are > 99.6 % as decided by Gas Liquid Chromatography.

With the help of Gas Liquid Chromatography, chemicals purities have been obtained, and are collected in Table 1. These purities have also been obtained by determining thr density values with the help of a vibrating tube densimeter (Tripathi et.al.2018) using under static mode. A thermostat (Haake F3) and a digital thermometer (Anton-Paar DT) were also used for regulating 0.01K the temperature. Prior to each determination the apparatus was calibrated at normal pressure with deionised water and $C_5H_{10}O$ (Fluka,purity99%).The density value of $C_5H_{10}O$ at 298.15K was in good concord with the literature value (Riddick JA, Bunger WB.1970).

The resuls obtained experimentally were compared with the theoretical results of densities are given (Riddick JA, Bunger WB.1970, Timmermans,1950) in Table 1.

Table 1. **Values of different Densities for Pure Components at T= 30^{0}C**

Compound	Mol%Purity	Density(g.cm^{-3})	
		Experimental	Literature
Acetylene tetrachloride	99.6%	1.578 57	1.578 60[a]
Cyclohexanone	99.7%	0.93754	0.93761[a]
pyrrolidin-2one	99.8%	1.1009	1.1020[a]
Methyl ethyl ketone	99.9%	0.794 49	0.794 53[a]
Acetophenone	99.7%	1.02766	1.028[b]

[a]values taken from ref. (Timmermans,1950), [b]values taken from ref. (Riddick JA, Bunger WB.1970).

Experimental

A Micro calorimeter (C-80 model manufactured from Setaram, France) was utilized for determination of excess molar enthalpies, H^E, the temperature was adjusted within ±0.001K.. solutions preparation was done by mass. Accuracy of mole fractions is ±0.0001. The trustworthiness of the instrument was earlier checked by measuring H^E for binary systems of $C6H12$ + $C6H14$ at 25^0C as given elsewhere(Tripathi AD,2018). At mole fraction, x_1=0.5, the deviation is 0.5% whereas it is approximately about 1% in case of the deviations(mean) of the H^E is estimated.

Result and Discussion

The values of H^E, for different systems are collected in Ttable 2and data were put into to the following equation:

$$\frac{H^E}{J.mol^{-1}} = x1x2\sum_{i=0}^{m} \mathrm{Ai}(x1-x2)^{\mathrm{i}} \qquad (1)$$

In this case $x1$ represents to the mole fraction of ATC. The different parameters, and the standard deviations, σ, are collected in Table 3 . The values of, σ , have been obtained using equation

$$\sigma = [\sum(H^E - H^E_{cal})^2/(m-n)^{1/2} \qquad (2)$$

where H^E is experimental values of excess enthalpy and H^E_{calc} refers to calculated excess enthalpy with the help of equation (1), m represents number of data measured experimentally & n is number of constants which are distinctive of a binary system. A plot of measured values of H^E data Vs mole fractions(x1) are plotted in **Fig. 1**.

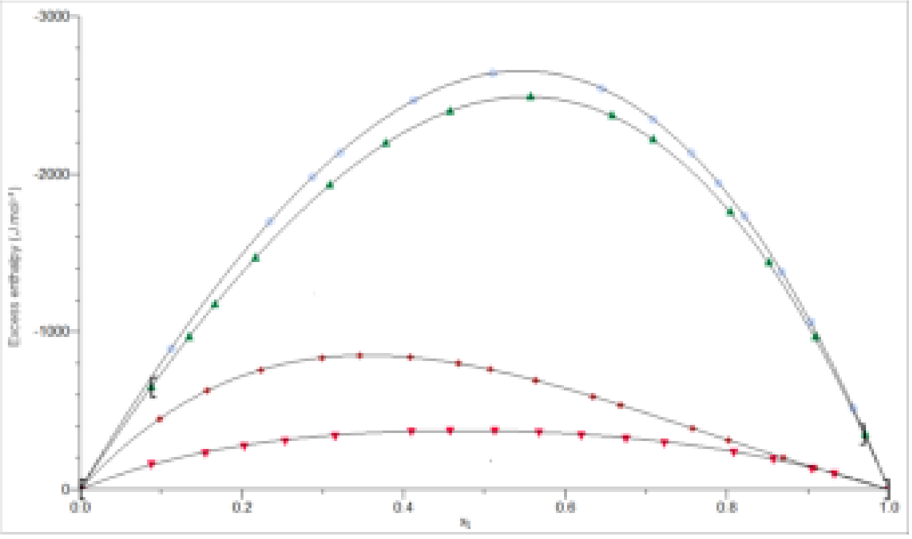

Fig.1 Excess molar enthalpies of binary liquid mixtures of X_1 of Acetylene tetrachloride($CHCl2.CHCl2$(1) with Cyclohexanone .

.($C_6CH_{10}O$(2) (○) , + 2-pyrralidinone (▲)(2) ,+methyl ethyl ketone(◆) , (2) and + acetophenone (▼) (2) at 303.15 K. The smoothed curves are based on the parameters A0,A1, A2and A3 given in Table 2.

Interference of interactions between resembling molecules and the beginning of fresh interactions between dissimilar molecules, are the main reason for the values of H^E obtained . The values of partial excess enthalpies $H^E_{m,}1$, and $H^E_{m,}2$ have been obtained with the help of experimental H^E data by using equations 3 and 4 and are represented graphically in Figures 2 and 3.

$$H^E_{m,1} = \frac{H^E}{x1} + x_1x_2\left[\frac{\delta\left(\frac{H^E}{x_1}\right)}{\delta x_1}\right]p,T \qquad (3)$$

$$H^E_{m,1} = \frac{H^E}{x_2} + x_1x_2\left[\frac{\delta\left(\frac{H^E}{x_2}\right)}{\delta x_2}\right]p,T \qquad (4)$$

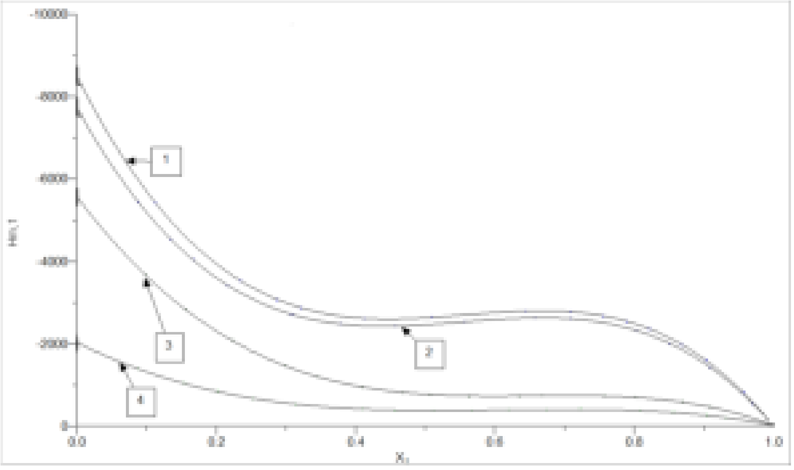

Fig 2. Partial molar excess enthalpies Hm,1 of binary liquid mixtures of x1 acetylene tetrachloride+x2 cyclohexanone [1], x1 acetylene tetrachloride +x2pyrralidin-2-one [2], x1 acetylene tetrachloride +x2 methyl ethyl ketone [3] and x1 acetylene tetrachloride + x2 acetophenone at 303.15 K.

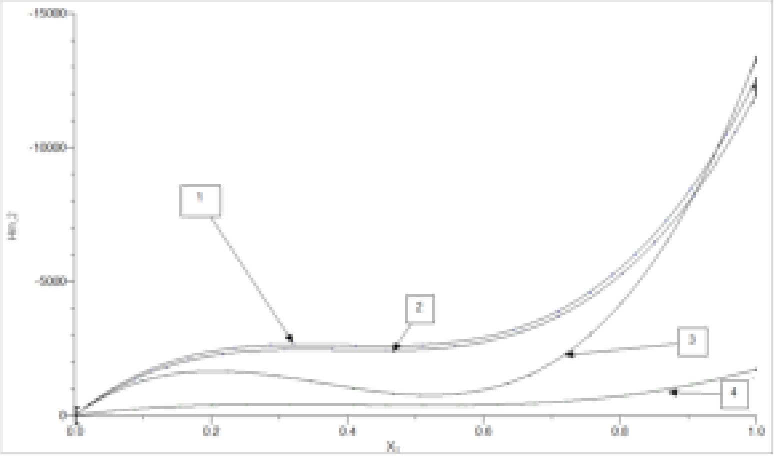

Fig 3. Partial molar excess enthalpies Hm,2 of binary liquid mixtures of x1 acetylene tetrachloride+x2 cyclohexanone [1], x1 acetylene tetrachloride +x2pyrralidin-2-one [2], x1 acetylene tetrachloride +x2 methyl ethyl ketone [3] and x1 acetylene tetrachloride + x2 acetophenone at 303.15 K.

The values of $H^E_{m,}1$, and $H^E_{m,}2$ depends greatly upon the selection of the quantity of fitting constants in the Redlich–Kister equation (Mehta SK, Chauhan RK, Tripathi AD .1997). The values of $H^E_{m,}1$, and $H^E_{m,}2$ are pinpointing of the type of consequences dominating on the whole performance of H^E in the concerned liquid mixtures. The –ve values of H^E for binary solutions suggest that the interactions between disimilar molecules are more effective than like-like interactions in the pure liquids. The net result of +ve and -ve involvement caused the extent of H^E for the current mixtures because of the breaking of bonds or interactions between like-like molecules, and from the creation of new bonds like hydrogen bonds between unlike molecules (Mehta SK, Chauhan RK, Tripathi AD .1997).

The values of excess molar enthalpies H^E for all above-mentioned binary mixtures are exothermic in nature. The values of H^E for the system ATC+ $(CH_2)_5CO$ are highly -ve thrroghout the whole range with a minimum value of ≈-2630 $J.mol^{-1}$. The extremely exothermic mixing of this system indicates strong specific interactions, the hydrogen bonding between the H of ATC and the O of $(CH_2)_5CO$. In the present mixtures which are of hydrogen bond forming systems, the the chief providers to the H^E values are the number of Hydrogen bonds formed, the enthalpy of Hydrogen-bond formation and other specific interactions. The H^E values for the system ATC+ (C_4H_7NO) are also highly -ve all over the whole range with a lowest value of ≈-2462 $J.mol^{-1}$ but less than the system ATC+$(CH_2)_5CO$. Pyrrolidin-2-one consists of pyrrolidine in which the hydrogens at position 2 are replaced by an oxo group. It is an organic compound which consists of a five-membered lactam, thus it is the simplest γ-lactam. There is a resonance between electrons of oxygen and 5 membered ring, causing less exothermicity for the system ATC+ C_4H_7NO .

The H^E values for the system ATC+methyl ethyl ketone are more negative (-767 $J.mol^{-1}$at mole fraction 0.5) than the values for the system ATC+ acetophenone(-373 $J.mol^{-1}$at mole fraction 0.5) , because in acetophenone, ethyl group of methyl ethyl ketone is replaced by phenyl group which causes resonance thus decreasing the exothermicity during the hydrogen bond formation.

Taking into consideration the reality that the little difference in electronegative character (0.5) between Oxygen and Chlorine leads to specific interactions, there is a chance of hydrogen bond-type interaction between the Chlorine of $CHCl_2.CHCl_2$ and hydrogen of all other mentioned compounds. When ATC combines with cyclohexanone or pyrrolidin-2-one, not only the O... H and O--Cl interactions (Pathak G ,1992) but interactions between CH_2 groups and chlorine atoms add to the H^E values . several i.r. spectroscopic studies (Walmsley JA, 1976,1978) of dilute solutions of pyrrolidin-2-one in non-ionic solvents have revealed that the self-association of pyrrolidin-2-one is somewhat strong. The molecule has a relatively high dipole moment 11.84 X 10^{-30} C m at T=25^0C. Besides its high dipole moment, C_4H_7NO has the carbonyl group(basic) and acidic -NH groups of the naturally occurring –CO- NH- peptide bond.

Table 2. Excess Molar Enthalpies of Acetylene tetrachloride (CHCl2CHCl2) (1) with Cyclohexanone (2), Pyrrolidin-2-one (2), Methyl ethyl ketone (2), and Acetophenone (2) at 303.15 K

$CHCl_2CHCl_2$+ cyclohexanone		$CHCl_2CHCl_2$+ pyrrolidin-2one	
x1	H^E	x1	H^E
	(J.mol^{-1})		(J.mol^{-1})
0.1123	-893	0.0879	-650
0.2345	-1697	0.1345	-966
0.2875	-1980	0.1665	-1171
0.3211	-2136	0.2165	-1467
0.4122	-2464	0.3087	-1929
0.5098	-2639	0.3777	-2193
0.6445	-2544	0.4567	-2398
0.7086	-2346	0.5567	-2490
0.7558	-2132	0.6578	-2367
0.7889	-1946	0.7089	-2215
0.8221	-1729	0.8034	-1758
0.8678	-1377	0.8511	-1437
0.9034	-1060	0.9087	-961
0.9567	-512	0.9699	-346

$CHCl_2CHCl_2$+ METHYL ETHYL KETONE		$CHCl_2CHCl_2$+ ACETOPHENONE		
x1	H^E	x1	H^E	
	(J.mol^{-1})		(J.mol^{-1})	
0.1567	-625	0.0876	-149	
0.2234	-758	0.1543	-233	
0.2987	-832	0.2021	-273	
0.3456	-849	0.2532	-309	
0.4088	-839	0.3145	-342	
0.4678	-800	0.4098	-371	
0.5071	-762	0.4567	-374	
0.5633	-692	0.5123	-374	
0.6345	-586	0.5678	-364	
0.6678	-531	0.6198	-348	
0.7568	-381	0.6744	-324	
0.8022	-306	0.7223	-298	
0.8694	-197	0.8085	-238	
0.9089	-135	0.8567	-192	
		0.9045	-143	
		0.9324	-104	

Table 3. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies , and the standard deviations,σ,of Acetylene tetrachloride (CHCl2.CHCl2)(1) +Cyclohexanone ($C_6H_{10}O$)(2)or + pyrrolidin-2one (2),or + Methyl ethyl ketone (2),or +Acetophenone (2) at 303.15 K

System	A0	A1	A2	A3	σ/ (J mol^{-1})
$CHCl_2$ $CHCl_2$(1)+ $C_6H_{10}O$ (2)	-10520	-2013	-0.2732	-2.676	0.2635
$CHCl_2$ $CHCl_2$(1) +2-Pyrralidinone (2)	-9848	-2115	-2.891	-5.549	0.3209
$CHCl_2$ $CHCl_2$(1) + MEK (2)	-3067	2113	-424	46.77	2.53
$CHCl_2$ $CHCl_2$(1) +Acetophenone(2)	-1491	148.4	-359.8	-16.14	2.059

The interaction between cyclic ketones(>C= O) and Br- or Cl- compounds are managed by the complete saturation of their rings. C_4H_7NO or $(CH_2)_5CO$ has saturated ring, which maks the interaction stronger.Thus showing higer -ve values of enthalpy of mixing.

The values of $H^E_{m,1}$, and $H^E_{m,2}$ Vs mole fraction of each binary liquid mixtures have been plotted in Figures 2 and 3 which clearly supports the above-mentioned explanations.

Information about the difference between the enthalpy of complex formation in solution and the enthalpy in the pure form is given by the values of $H^E_{m,1}$, and $H^E_{m,2}$. The -ve values of $H^E_{m,1}$, and $H^E_{m,2}$ are due to the presence of strong hydrogen bonds formed between Hydrogen atom of $CHCl_2.CHCl_2$ and non bonding pair of electrons present on the oxygen atom of $(CH_2)_5CO$ or C_4H_7NO or $CH_3C(O)CH_2CH_3$ or C6H5C(O)CH3 as reported elsewhere between $CHCl_2.CHCl_2$ and $(CH_3)_2CO$ (Nath J, Tripathi AD**.**1984).

References:

Mehta SK, Chauhan RK, Tripathi AD .1997. Excess molar enthalpies of mixtures of pyrrolidin-2-one with methanol, or ethanol, or propan-1-ol, or butan-1-ol, or pentan-1-ol at the temperature 303.15 K, *J. Chem. Thermodyn*. 29, 151: 353–358.

Nath J , Tripathi AD.1984. Binary systems of 1,1,2,2-tetrachloroethane with benzene, toluene, ***p***-xylene, acetone and cyclohexane. Part 2.—Dielectric properties at 308.15 K ,*J. Chem. Soc., Faraday Trans. I*, ,80: 1517-1524.

Pathak G, Tripathi AD, Pradhan S. 1992.The excess molar enthalpies of mixing of 1,1,2,2-tetrachloroethanewith acetone, n-dibutyl ether, acetonitrile and dimethylsulphoxide. *Thermochim Acta.* 197: 329-33.

Riddick JA, Bunger WB,1970. *Organic Solvents: Physical Properties and Methods of Purifications*, 3rd ed., Wiley-Interscience, New York.

Timmermans,1950. *J. Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam.

Tripathi AD , Khan M, Choudhary N, Pal S. 2018. Excess Molar Enthalpies of Acetylene Tetrachloride with Furan, Methylfuran, Tetrahydrofuran and 1,4-dioxane at the Temperature 308.15K ,*BPAS*,37C, No.2:52-58.

Walmsley JA, Jacob EJ, Thompson, H B,1976. An investigation of the self-association of 2-pyrrolidinone in cyclohexane and carbon tetrachloride by means of spectroscopic and dielectric polarization measurements ,*J. Phys. Chem.* , 80: 2745-2753.

Walmsley, J A,1978. Self-association of 2-pyrrolidinone. 2. Spectral and dielectric polarization studies of benzene solutions, *J. Phys. Chem*. 1978, 82, 2031-2035.

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Cold Emission Properties of Solvo-thermally Synthesized Carbon Spheres

Abstract

Amorphous carbon spheres with varying diameters have been prepared by a low temperature solvothermal route. The structure of the as prepared sample has been investigated by several sophisticate electron microscopic techniques like TEM and FESEM. X-ray diffraction studies show the amorphousness of the sample. The atomic force microscopy gives detail about the topology of the sample. It has been shown that the carbon materials have the potential to be used as cold cathode emitter with a turn on field 4.99 V/ m. The cold cathode characteristics of the sample with different cathode to anode distance have been studied in detail.

Keywords: Carbon, Electron microscopy, Electron emission, Work function.

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Introduction

It is an established fact that the different carbon structures find its extensive applications in various fields of science and technology. With the discovery of CNTs by Iijima (Iijima S.1991) and even before that the extensive uses of carbon fibers and diamond like carbon films in various fields like field emission devices, bio-medical applications, coating industry, magnetic storage device etc. (Salgueiredo E.et.al.2008; May PW et.al.1999) have accelerated researchers to explore more and more carbon structures and their applications, especially with the advent of nanotechnology. Different carbon nanostructures like carbon flakes, onion, carbon tree as well as carbon spheres and their different applications have been reported by many workers (Kinoshita H.et.al2008, Mehraban Z.et.al.2009). Although numbers of reports are available in field of synthesis of spherical carbon, its different properties still now have not been studied rigorously. Being propelled with this fact we have reported here a very simple low temperature solvothermal route for synthesizing the carbon spheres. The sample thus prepared was characterized by XRD, SEM, transmission electron microscopy TEM and AFM. Carbon spheres showed good field emission properties. Cold emission properties of the sample with cathode to anode distance have been investigated.

Experimental

The synthesis involves taking ferrocene and sulfur in 1 : 2 ratio and mixing it in a mortar. The mixture was then shifted to 1 Teflon coated stainless steel autoclave of 100 ml in volume that was already 90 % filled with benzene. The whole system was then isolated for 72 hours in an air oven kept at 573 K temperature. A blackish powder was obtained after letting the mixture be cooled normally and was collected through filtration process. The residue was washed several times with alcohol and distilled water and dried over night at 330 K overnight. The sample, thus prepared with characterized by XRD (Bruker D8 Advance), SEM (JEOL-JSM-6360), HRTEM (JEOL-JEM 2100) and AFM (NT-MDT, Solver Pro). The cold cathode characteristics of the as prepared material were examined in high vacuum cold emission set up system.

Results and Discussions

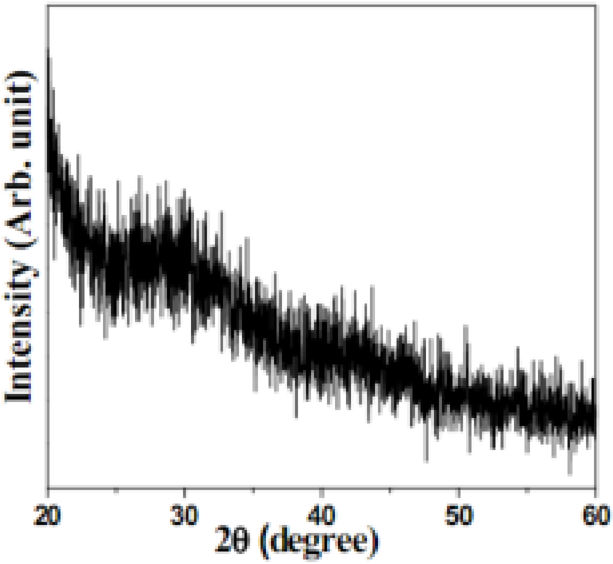

Fig.1: XRD patterns of the amorphous carbon spheres prepared at 200 ^{0}C.

X-Ray Diffraction Analysis:The crystalline behavior of our samples has been investigated with the help of an x-ray diffractometer by Cu Kα radiation. The XRD pattern is shown in **Fig.1**. From the XRD pattern it

of the sample has also been confirmed from the SAED pattern, obtained from the microscopic study (discussed later.)

Microscopic Study

It can be seen that no distinct peak appeared indicated the amorphousness of our sample. The amorphousness

Fig. 2 shows the SEM images of the samples taken with different magnification. It can be seen that there are mainly two kind of distinct features. One is spherical in shape and other is sponge like. The diameters of the spheres are not uniform and vary from 2-3 µm to 600-700 nm. The structure of the sponge like region was not clearly resolved in the SEM image. Hence TEM study was performed as discussed in the next section. The reason of appearance of such region may be due to the incompleteness of the reaction due to either of the insufficient time or reaction temperature. The growth mechanism of such a structure may be a topic of further research.

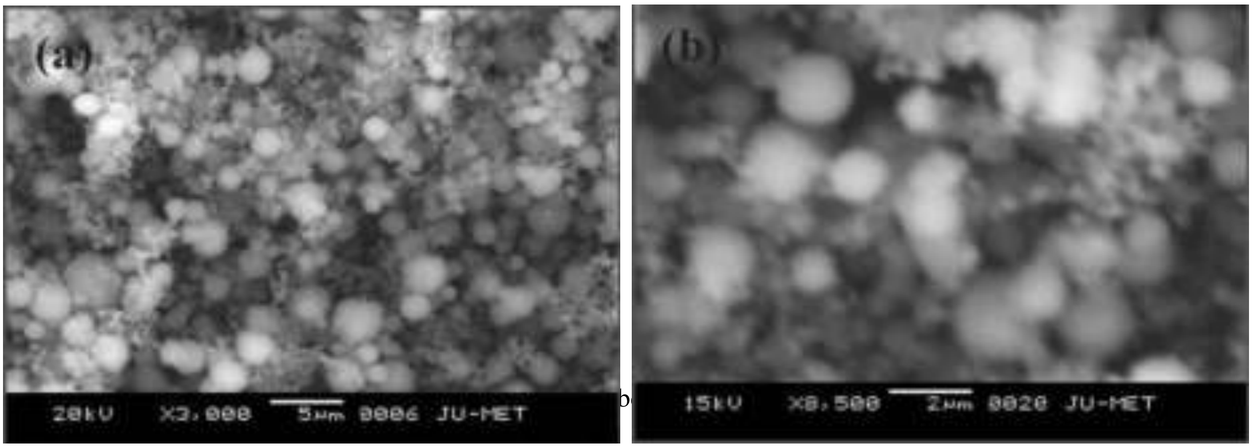

Fig. 2: SEM micrograph of the prepared sample with different magnification.

spherical in shapes having diameter from 5 to 25 nm. The observed particle size does not match with that obtained from SEM image. These lead us to conclusion that the TEM results indicate the spongy region of the SEM picture. Although the exact growth mechanism is not clear but it can be speculated that probably these small spheres with the completion of the reaction grows up to form the bigger spherical particles. The AFM histogram (discussed later) data also supports the presence of small particles. The SAED pattern shown inset of fig.3b shows that the samples are completely amorphous supporting the XRD result.

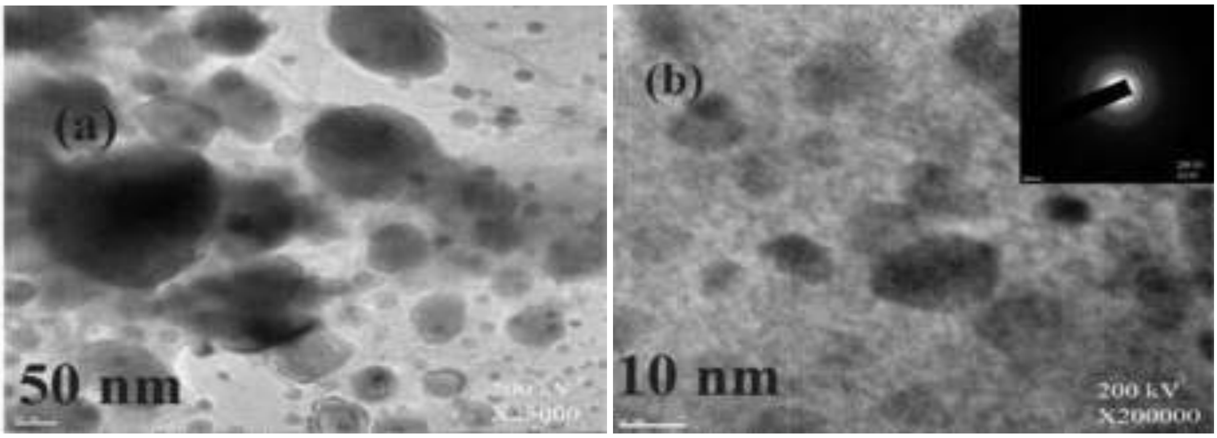

Fig.3: TEM micrograph of the prepared sample with different magnification (3a-3b) and inset 3b the SAED patterns of carbon sphere

For AFM study the sample was dispersed in ethanol and a thin film has been prepared on glass substrate by dip coating technique. When the alcohol gets evaporated the film became ready for AFM study. The corresponding 3D picture with histogram is shown in **Fig. 4**. It can be seen in **fig. 4a** that the surface is a rough one with rms roughness 50 nm.

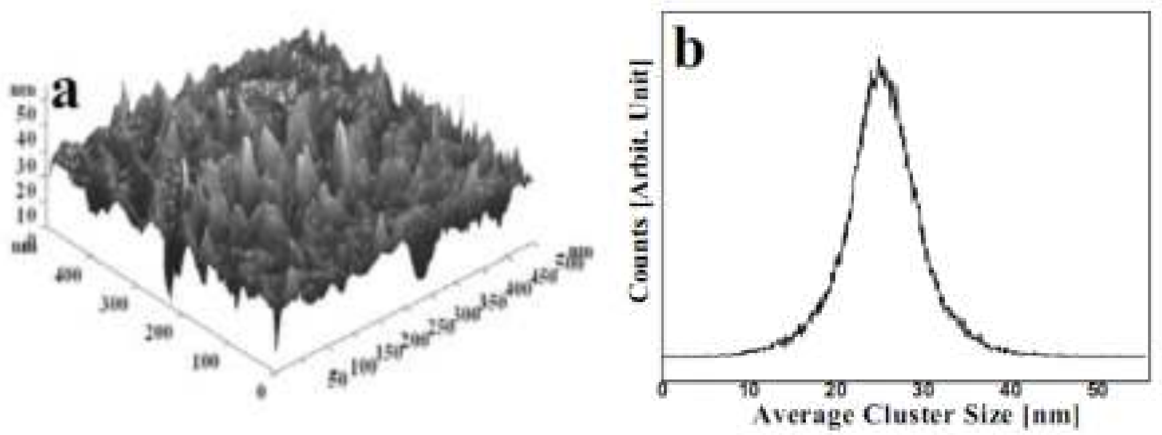

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Fig. 4: (a) 3D AFM image of dispersed carbon film (b) corresponding histogram.

Field Emission Study

Cold emission experiment has been done at room temperature. The emission ccurrent with applied electric field has been related to each other by well-known Fowler Nordheim equation (Fowler RH, Nordheim L. 1928) given below:

$$I = Aat_F^{-2}\phi^{-1}(\beta E)^2 \exp\{-bv_F\phi^{3/2} / \beta E\} \qquad (1)$$

Here the meaning of different constants may be found in the previous report [7].

The values of F-N constants are respectively

$a=1.541434\times10^{-6}$ AeV V^{-2} and $b= 6.830890\times10^{9}$ $eV^{-3/2}$ Vm^{-1}.

Equation (1) when simplifies takes the form

$I= AC\beta^2E^2/\varphi)\exp[-B\varphi^{3/2}(\beta E^{-1})$ (2)

Where A, B, C are the constants.

The experimental voltage current plots of our sample taken for various cathodes to anode distances are summarized in **Fig.5**. The turn on field (E_{TO}) defined as the field required obtaining an emission current of 0.6 μA, decreases from 12 to 5 V/μm as cathodes to anode distances was increased from 120 to 300 μm. The variation of E_{TO} with inter-electrode distance has been summarized in **Table 1**. F-N plots, which is a plot of ln (I/E^2) with 1/E have been shown in **Fig.6** and can be seen that it has three different linear region for high, medium and low field domain. Separate calculation of enhancement factors β and effective work function (Banerjee D, Jha A, Chattopadhyay KK. 2009 has been done for each region. The result is summarized in **Table-2.**

It is evident that β varied from one region to other. This is indeed a different result as compared to the other results reported previously [8]. This can arise from the tip geometry of our field emission set up. The above mentioned findings clearly prove that if we can synthesis the structure by a controlled manner it would be a material of potential for using in cold emission display.

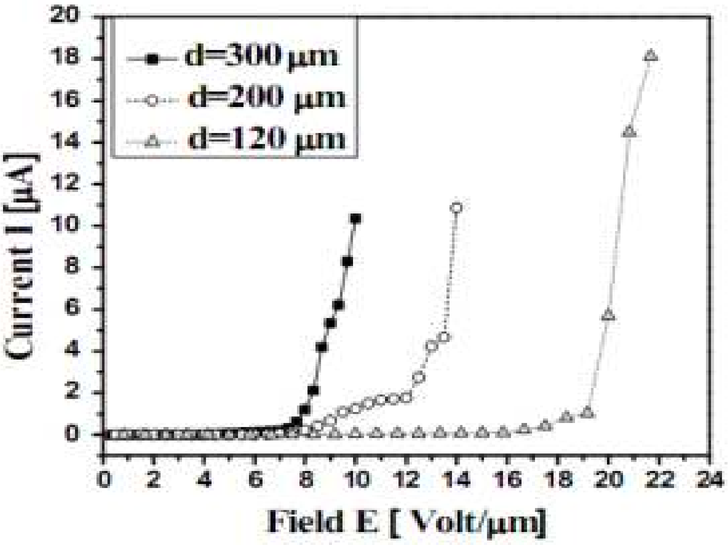

Fig. 5: cold cathode characteristics of carbon nano/micro structures with different inter electrode distances.

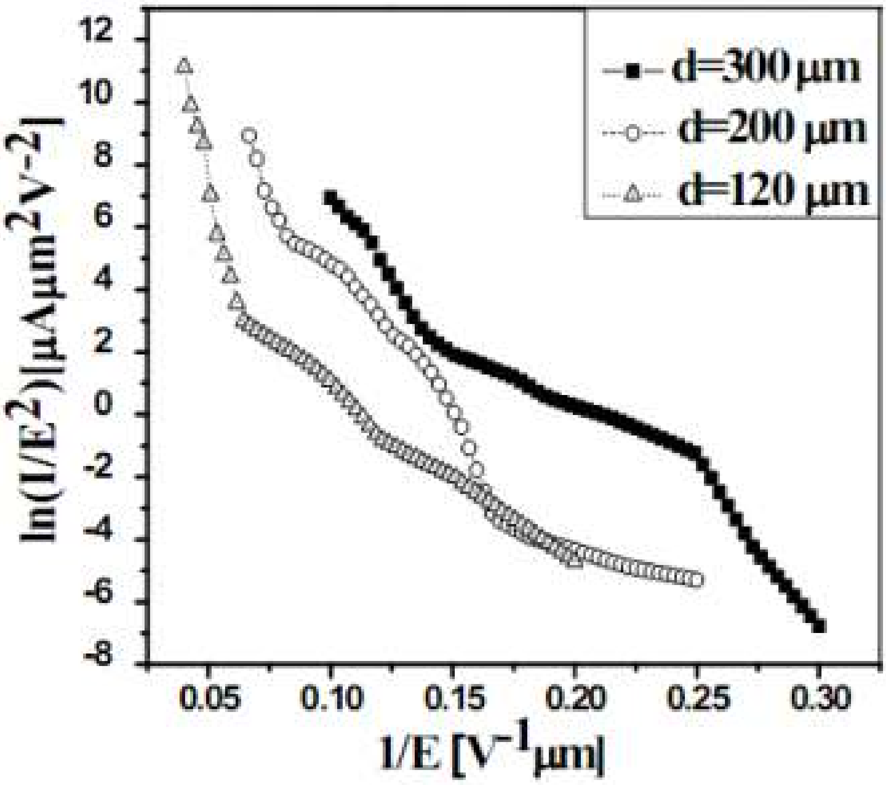

Fig. 6: F-N plot of voltage current response of **Fig.5**

Table 1: Change of E_{TO} with inter-electrode distance

Electrode Distance (µm)	Turn on Field (V/µm)
120	12
200	6.9
300	5

Table 2: Values of effective work functions and enhancement factors of carbon spheres for different inter-electrode distance

	Distance (mm)	**Enhancement Factor (β)**	**Effective work function**
High Field region	120	644	0.066
	200	410	0.09
	300	237	0.13
Medium Field region	120	2386	0.028
	200	821	0.057
	300	1174	0.045
Low Field region	120	701	0.063
	200	3636	0.021
	300	1488	0.038

Conclusion

Amorphous carbon micro/nano spheres were synthesized by an easy solvothermal process. The as prepared sample has been studied with XRD, SEM, TEM and AFM.

The microscopic study revealed the fact that there are spheres with different diameter from micro to nano range. XRD as well as SAED pattern obtained from TEM proves the amorphousness of the sample. The sample thus developed shows promises towards being used as cold emitter with turn on field 4.99 V/mm for an inter-electrode distance as high as 300 μm

Acknowledgement

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References

Banerjee D, Jha A, Chattopadhyay KK. 2009. Low-temperature synthesis of amorphous carbon nanoneedle and study on its field emission property Emission. *Physica E* 41: . 1174-1178.

Fowler RH, Nordheim L. 1928.Electron Emission in intense Electric Fields. *Proc. R. Soc. Lond*. A, 119: 173-181.

Iijima S.1991. Helical microtubules of graphitic carbon. *Nature.* 354: 56-58

Kinoshita H, Vacher B, Belin M, Montagna G, Martin JM, Ohmae N.2008. Diamond-derived carbon onions as lubricant additives. *Tribology.* 41: 69-78.

May PW, Kuo MT, Ashfold MNR.1999.Field emission conduction mechanisms in chemical-vapour-deposited diamond and diamond-like carbon films. *Diamond and related Materials.* 8: 1490-1495.

Mehraban Z, Farzaneh F, Dadmehr V. 2009.Catalytic chemical vapour deposition synthesis of carbon spheres. *Materials Letters*. 63: 1653-1655.

Murphy EL, Good Jr. LH. 1956. Thermionic Emission, field Emission, and the Transition Region. *Phys.Rev.* 102: 1464-1473.

. Salgueiredo E, Vila M, Silva MA, Lopes MA, Santos LD, Costa FM, Silva RF, Gomes PS, Fernandes MH.2008. Biocompatibility evaluation of DLC-coated Si_3N_4 substrates for biomedical applications. *Diamond and related Materials.* 17: 878-881.

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Scalable Production of Carbonaceous Nanomaterials in Supercritical Fluids

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Abstract
When fluids are operated above critical point, Supercritical fluids(SCFs) are obtained which are the short-lived states of matter. It may be applied as substitute media in chromatography, energy production, drug development and food processing . It is now well acknowledged in materials processing . The mainly used SCFs are the supercritical CO_2 (SCC) and supercritical H_2O (SCW). SCC guides a series of exceptional way of manufacture of carbonaceous nanomaterials. Demonstration of the science of supercritical fluids, and its probable application in industries in progress and amendment of carbonaceous nanomaterials has been undertaken in the current programme.

Keywords: Carbonaceous nanomaterials, Critical point, Density, Fluid Phase Equilibrium, nanocomposites

Introduction

SCF are inexpensive, non toxic, non flammable media with pressure tunable density, viscosity, diffusivity and surface tension. Solvent properties of SCFs were first reported over by Hannay and Hogarth around 1879.Density, viscosity and diffusivity are the common physical characteristics of SCFs that they share with liquids. High penetrating power of SCFs is due to their 100 to 1000 times greater densities over liquids, 10 to 100 times reduced viscosities over gases and high rate of diffusion @ 10^{-3} to 10^{-4} cm^2/s times over liquids. Such unique combinations of physical behavior SCFs are effused across solids leading to swelling or solubilzation (Skerget M., et al. 2011). Judicious variations in temperature and pressure equalizes the densities of liquid and gas phases, restricting phase transitions in SCFs regardless to applied pressure (Vansant J., et al. 2019; Noyori. R. et al. 1999; Abdullah I., et al 2019). Among SCF, the most investigated are the SCC and SCW (Kenz Z., et al 2014; Qian Z., et al 2019; Styring P., et al, 2014). The preference to these SCF is due to the prominent abundance of their precursors, viz; carbon dioxide and water in nature. These naturally existing precursors are easily transformed into their respective supercritical states either under ambient temperature or ambient pressure (Vansant J., et al. 2019; Noyori. R. et al. 1999; Abdullah I., et al 2019; Caputo,G, et al 2013; Aymonier C., et al. 2013; Johnston KP., et al 2004; Zhao J. et al.2019; Bhamidipati M. et al, 2013; Grignard B, et al. 2019; Tomasko D, et al 2003; Manjare SD, et al. 2019; Goutam SP, et al 2019; Elmaaty TA, et al 2017; Fifield LS, et al 2004).

Fig.2. demonstrates the low pressure phase diagrams of carbon dioxide (left) and water (right). The diagrams are consist of well defined areas that represent the physical parameters under which carbon dioxide or water represents their solid states (A,D), liquid (B) and gaseous (C,E,F) states.

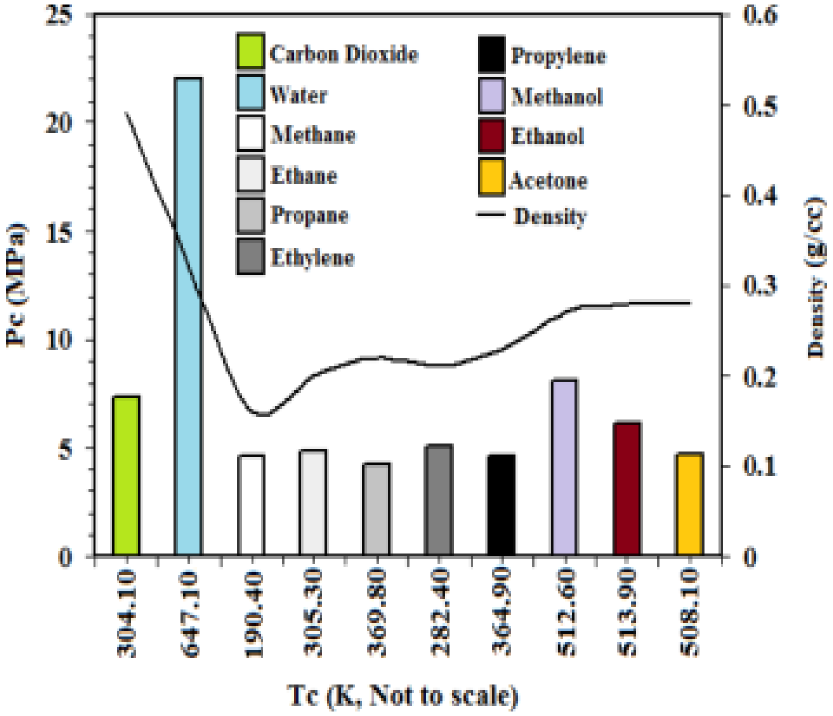


Fig.1. Critical Point and Density Variation in SCF

Solid lines represent the phases transitions between two phase. The heavy dashed lines represent effect of temperature and pressure on phase states of the matter. The point representing co - existence of all the three phases is defined triple point of phase diagram. For carbon dioxide the triple point falls, around -56.6 ^{o}C and 5.1atm whereas for water it falls around of 0 .0099 ^{o} C at pressure of about 1/166 times the pressure of Earth's environment at sea level.At A, carbon dioxide condenses directly into dry ice. Increase in pressure from 'E at constant temperatures renders solid-gas transitions in carbon dioxide to reached into dry ice. Whereas, increase in pressure imparts solid-liquid transition that leads to solidification of carbon dioxide at point H. However, at G, increase in pressure does not impart additional changes in the phase state of carbon dioxide (Fig.2a).

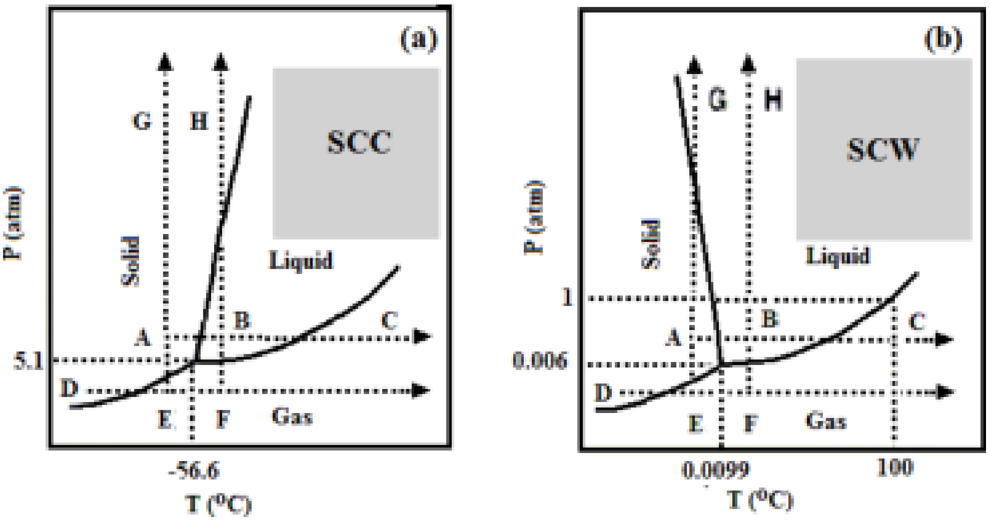


Fig.2. Fluid Phase Equilibrium of SCC (a) and SCW (b)

From point A, at constant pressure, increase in temperature imparts solid liquid transitions at melting point of ice. Further increase in temperature imparts liquid gas transitions in water at B, that induce evaporation at C. At D, increase in temperature imparts solid-gas transitions to water system where in ice evaporate directly into the gas phase through sublimation. The temperature of gases from additional heating warms the resulting gases ('E' and 'F'). At G, increase in pressure allows solid-liquid transition where ice melts (Fig.2b).

Industrial Importance of SCF

SCF finds their prominent industrial status as environmentally benign media for processing of wide range of materials with diverse properties and applications (Kenz Z, et al 2014, Qian Z, et al 2019). Since, SCF are operated above their critical points, they are referred as dense gases (Styring P, et al, 2014). Academic and industrial significance of SCFs was well established since 1980's. Presently, more than two dozen SCF are well investigated for various industrial applications. SCFs finds their place as an alternative solvent in industrial and laboratory operations involving extraction of bioactive molecules from living resources, carrier medium for chromatography, food processing and solvent for disposal of organic waste (Noyori. R. et al. 1999; Abdullah I. et al. 2019; Caputo G. et al. 2013).

The ease of abundance, non flammable, non toxic nature of CO_2 makes this more viable for production of SCF for variety of industrial processes (Skerget M., et al. 2011, Kenz Z., et al 2014; Qian Z., et al 2019; Caputo,G, et al 2013). Because of gas similar to diffusion and liquid resembling density of SCC facilitates the swelling or partial dissolution of inorganic (Aymonier C., et al. 2013), carbonaceous (Johnston KP., et al 2004) and soft materials like polymers (Zhao J. et al.2019; Bhamidipati M. et al, 2013; Grignard B, et al. 2019; Tomasko D, et al 2003). Such potential of SCC has opened the avenues of transforming inorganic (Aymonier C., et al. 2013) and carbonaceous materials from macro size into their highly dispersed nano sized analogues (Johnston KP., et al 2004). Polymerizations in SCC imparts improved control over molecular mass of polymers (Zhao J. et al.2019).

Exposure of SCC to soft materials like polymers imparts reduction in their Tg, making them processable into foam, scaffolds (Bhamidipati M. et al, 2013), composites, blends (Grignard B, et al. 2019; Tomasko D, et al 2003) and functional nanostructures ((Johnston KP., et al 2004; Grignard B, et al. 2019; Tomasko D, et al 2003), purification and separation of materials, high quality leather (Goutam SP, et al 2019) and fabrics in attractive shades with improved color and light fastness under ambient temperatures (Elmaaty TA, et al 2017). SCC has been exclusively used as medium for noncovalent functionalization of CNT (Fifield LS, et al 2004), nanofluids (Wang XB, et al. 2005), patterning on one-dimensionals carbon nanomaterials (Xiao LZ, et al 2010), synthesis (Ye S, et al 2009), growth (Li Z, et al. 2007),purification of CNT (Wang JS, et al. 2007; Bertoncini M, et al. 2011), coating polymers over CNT (Wang J, et al. 2005), polymer functionalized CNT and related polymer nanocomposites (Yue B, et al. 2007; Hao J, et al. 2011; Liu Z, et al. 2009; Nguyen VH, et al. 2004), polymer nanocomposites involving graphene (Li L, et al. 2013; Li M, et al. 2015), graphene derived NHs (Wei J, et al. 2019), C60 functionalized with polyvinyl pyridine (Bhullar N, et al. 2007; Zaidi MGH, et al. 2011) vinyl monomers (Agarwal V, et al. 2009; Agrawal V et al. 2010).

Fig.3 demonstrates the dispersion of MWCNT into epoxy resin under pressure of SCC ranging 1200-1800 psi.

Owing to gas similar to diffusion and liquid resembling density, SCC introduce into the *van der Waals* stacking zones of nanotube that on depressurization exfoliate them into fully dispersed structures. Curing of such nanotube epoxy formulations results highly durable polymer nanocomposites with improved dispersion of nanotube into epoxy matrix (Table 1)

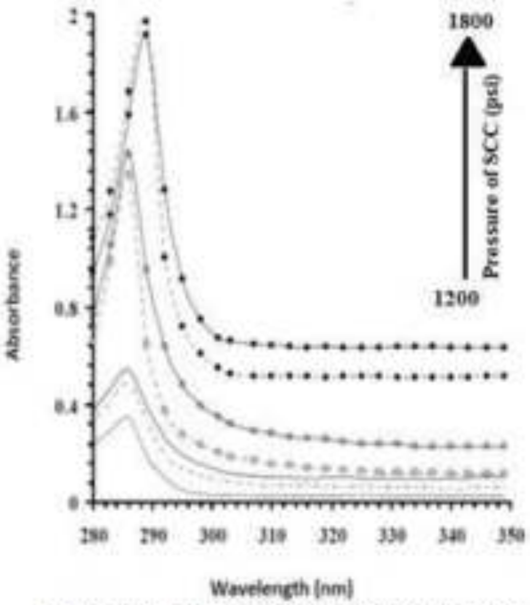
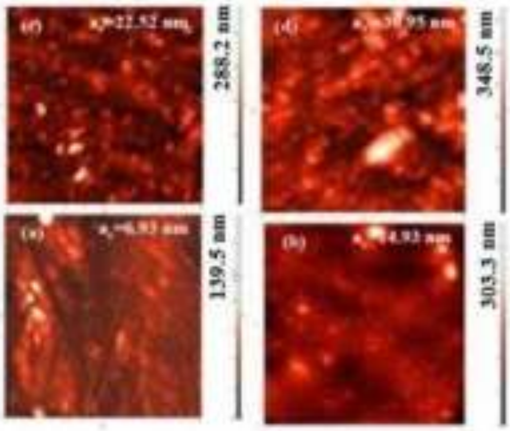
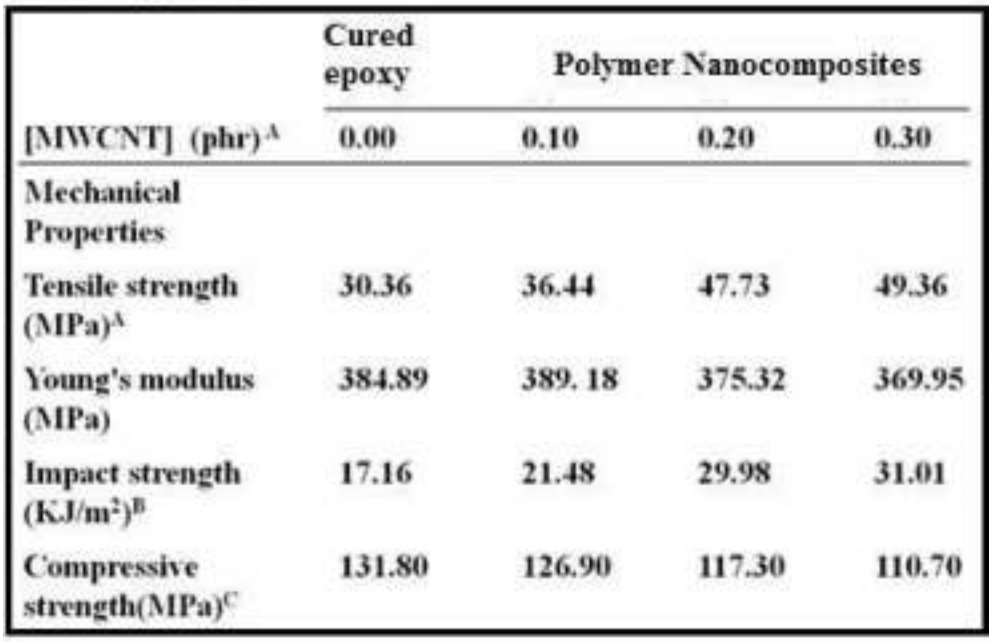


Fig.3a;Dispersion of MWCNT into epoxy resin with pressure of SCC



3b:Atomic force micrographs (XY=10 um) of cured epoxy (a) , polymer nanocomposite with 0.1 (b), (0.2) and (0.3) wt % of MWCNT

Table 1:Mechanical properties of supercritically synthesized nanocomposites



	Cured epoxy	Polymer Nanocomposites		
[MWCNT] (phr)^{A}	0.00	0.10	0.20	0.30
Mechanical Properties				
Tensile strength (MPa)^{A}	30.36	36.44	47.73	49.36
Young's modulus (MPa)	384.89	389. 18	375.32	369.95
Impact strength (KJ/m^{2})^{B}	17.16	21.48	29.98	31.01
Compressive strength(MPa)^{C}	131.80	126.90	117.30	110.70

ASTM D 638 (a), 256 (b) & 695 (c)

Conclusions:

Supercritical fluids, particularly SCC offers wide scope of applications in modification and scalable production of a variety of carbonaceous nanomaterials. Production methods involving SCC are highly scalable, clean and environmentally benign. Process involving SCC leads in the absence or at a low concentration of toxic and flammable solvents with ease of separation of products through venting off carbon dioxide without expense of power or energy..Liberated carbon dioxide may further be recycled and used , that make the overall process to be industrially continuous in nature.

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References

Abdullah I, Asiri MI, Isloor A.2019.Supercritical carbon dioxide as green solvent in green sustainable process for chemical and environmental engineering and science, 1st Edition.

Agarwal V, Zaidi MGH, Alam S, Rai AK. 2009. Fullerene 60 mediated polymerization of polyacrylic acid in supercritical carbon dioxide, *International Journal of Polymer Analysis and Characterization* 14 (1): 52-67.

Agrawal V, Vishnoi S, Zaidi MGH, Alam S, Rai AK. 2010. Synthesis and characterization of C60-polymethyl methacrylate conjugates in supercritical carbon dioxide. *International Journal of Polymer Analysis and Characterization* 15(5): 267-276.

Aymonier C, Serani AL, Reverón H, Garrabos Y, Cansell F.2006. Review of supercritical fluids in inorganic materials science. *Journal of Supercritical Fluids*.38(2): 242-251.

Bertoncini M, Luiz AFC, Indhira O. Pezzin SH. Purification of single wall carbon nanotubes by heat treatment and supercritical extraction. 2011. *Material Research* 14(3): 380-383.

Bhamidipati M, Scurto AM, Detamore M S.2013 The future of carbon dioxide for polymer processing in tissue engineering,Tissue Engineering Part B: Reviews, 19(3): 221-232.

Bhullar N, Zaidi MGH, Alam S, Singh R. 2007. Synthesis of C60 caged polyvinyl pyridine in supercritical carbon dioxide. *Int. J. Nanosci. Nanotech* 1(3): 64-68.

Cansell F, Aymonier C,.Serani AL.2003. Review on materials science and supercritical fluids, *Current Opinion in Solid State and Materials Science* 7(4-5):331-340.

Caputo,G, Fernández IG, Saldaña MDA., Galia A.2013. Advances and perspectives of supercritical fluid technology ,*Journal of Chemistry*, Article ID 243653, 3pp

Elmaaty TA, Abd Al Aziz E. 2017. Supercritical carbon dioxide as a green media in textile dyeing:

A review. *Textile Research Journal* 88(10): 1184-1212.

Fifield LS, Dalton LR, Addleman RS, Galhotra RA, Engelhard MH, Fryxell GE,

Aardahl CL. Noncovalent functionalization of carbon nanotubes with molecular anchors using supercritical fluids. 2004. *Journal of Physical Chemistry B* 108(25): 8737–8741.

Goutam SP, Kumar A, Kumar D, Shastri R, Yadav AK. 2019. Application of supercritical CO_2 in the leather industry. *Materials Research Foundations* 50: 147-164.

Grignard B, Gennen S, Jérôme C, Kleij C, Detrembleur C.2019. Advances in the use of CO_2 as a renewable feedstock for the synthesis of polymers .*Chemical Society Reviews*, 48 : 4466- 4514.

Hao J, Lian Y, Guan, D. Yue, X. Guo, S. Zhao, Y. Zhao, K. Ibrahim, J. Wang, H. Qian,

J. Dong, H. Yuan, G. Xing, B. Sun. 2011. Supercritical synthesis and characterization of SWNT - based one dimensional nanomaterials. *Nanoscale* 3: 3103–3108.

Johnston KP, Shah PS. 2004.Making nanoscale materials with supercritical fluids, *Science,*303 (5657) :482-483.

Kenz Z, Markocic E, ,.Lietgeb M, Primozic M, Kenz M, Serkjet HM. 2014. Industrial applications of supercritical fluids: *A review Energy.* 77: 235-243.

Li Z, Andzane J, Erts D, Tobin JM, Wang K, Morris MA, Attard G, Holmes JD. 2007. A Supercritical-fluid method for growing carbon nanotubes. *Advanced Materials* 19(19): 3043–3046.

Liu Z, Han B. 2009. Synthesis of carbon nanotube composites using supercritical fluids and their potential applications. *Advanced Materials* 21(7): 825–829.

Li L, Zheng X, Wang J, Sun Q, Xu Q. 2013. Solvent exfoliated and functionalized graphene with assistance of supercritical carbon dioxide. *ACS Sustainable Chemical Engineering* 1(1): 144-148.

Li M, Cheng P, Zhang R, Luo G, Shen Q, Zhang L. 2015. Preparation of PMMA/graphene oxide microcellular foams using supercritical carbon dioxide. *IOP Conf. Series: Materials Science and Engineering* 87: 012042.

Manjare SD, Dhingra K. 2019. Supercritical fluids in separation and purification: A review. *Materials Science for Energy Technologies* 2(3): 463-484.

Nguyen VH, Shim J. 2013. Supercritical fluid-assisted synthesis of a carbon nanotubes-grafted biocompatible polymer composite. *Composite Interfaces*. 20(2): 155-162.

Science, 303 (2004) (5657) 482-483

Noyori. R.1999. Supercritical Fluids: *Introduction Chemical Reviews,* 99(2) 353-354

Qian Z. Developments on CO_2-utilization technologies 2014. *Clean Energy*. 3(3) (2019)85–100 pp 506.

Skerget M, Kenz Z, Hrncic K. 2011.Solubility of solids in sub and supercritical fluids..*Journal of Chemical Engineering Data.* 56(4): 694-719.

P. Styring, E. Quadrelli, K. Armstrong, CO_2 Utilisation: Closing the Carbon Cycle: First Edition. (2014) pp311 ISBN: 9780128173886

Tomasko D, Li H, Liu D, Han X, Wingert M, Lee L, Koelling K.2003. A Review of CO_2 applications in the processing of polymers. *Industrial & Engineering Chemistry Research.* 42 : 6431-6456.

Vansant J,Koziel PW. 2019, Technical and industrial applications of CO_2, 73-104,ISBN 978-3-030-15867-5

Wang XB, Liu ZM, Hu PA, Liu Y, Han Q, Zhu DB. 2005. Nanofluids in carbon nanotubes using supercritical CO_2: a first step towards a nanochemical reaction. *Applied Physics A* 80(3): 637-639.

Wang JS, Wai CM, Shimizu K, Cheng F, Boeckl JJ, Maruyama B, Brown G. 2007. Purification of single walled carbon nanotubes using a supercritical fluid extraction method. *Journal of Physical Chemistry C*, Nanomaterial Interfaces, 111(35): 13007 -13012.

Wang J, Khlobystov AN, Wang W, Howdle SM, Poliakoff M. Coating carbon nanotubes with polymer in supercritical carbon dioxide. 2006. *Chemical Communications* 1670 – 1673.

Wei J, Peng S, Xue B, Yang Z, Qin S, Yu J, Xu G. 2019. Effect of silane functionalized graphene prepared by a supercritical carbon dioxide process on the barrier properties of polyethylene terephthalate composite films. *RSC Advances* 9: 21903-21910.

Xiao LZ, Qun X, Zong PL. Supercritical CO_2 driven, periodic patterning on one- dimensionals carbon nanomaterials. 2010. *Science China Chemistry*, 53(7): 1525-1529.

Ye S, Wu F, Ye XR, Lin Y. 2009. Supercritical fluid assisted synthesis and processing of carbon nanotubes. *Journal of nanoscience and Nanotechnology* 9(5): 2781-2785.

Yue B, Wang Y, Huang CY, Pfeffer R, Iqbal Z. 2007. Polymeric nanocomposites of functionalized carbon nanotubes synthesized in supercritical CO_2. *Journal of Nanoscience and Nanotechnology* 7(3): 994-1000.

Zaidi MGH, Agarwal T, Alam S, Rai AK. 2011. Synthesis of fullerene (60) polyvinyl pyridine composites in supercritical carbon dioxide.Fullerene, *Nanotube and Carbon Nanostures* 19(4): 329-333.

Zhao J, Park. M.2019. Recent trends of foaming in polymer processing.: A Review, *Polymers.11:* 953.

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Excess Molar Volumes of Binary Mixtures of Acetylene Tetrachloride ($CHCl_2CHCl_2$)+Benzene(C_6H_6),+Toluene($C_6H_5CH_3$)+Acetone(CH_3COCH_3) and + Pyridine (C_5H_5N) at 303.15 K

Abstract
Excess molar volumes, V^E, at T = 303.15 K, have been measured for binary liquid mixtures of Acetylene tetrachloride ($CHCl_2$ $CHCl_2$) + Benzene (C_6H_6),+Toluene($C_6H_5CH_3$),+ Acetone (CH_3COCH_3), and + Pyridine (C_5H_5N) at 303.15 K. The values of V^E have been fitted in appropriate equations using a least-squares method. V^E has been found to be negative throughout the entire range of composition for all mixtures. The results obtained have been discussed from the viewpoint of existence of specific interactions between the components in the liquid state.

Keywords: Acetylene tetrachloride, acetone, toluene, specific interaction, excess volume.

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Introduction

Mixtures of Acetylene tetrachloride ($CHCl_2$ $CHCl_2$)+ Benzene(C_6H_6),+Toluene($C_6H_5CH_3$),+Acetone(CH_3COCH_3) ,and + Pyridine(C_5H_5N) are of meticulous attention from the perspective of electron transfer interaction which results to the creation of new complexes between the different species taken in the liquid state. The specific interaction of $CHCl_2$ $CHCl_2$ with the above compounds can be visualized as resulting from the presence of two H atoms and four number of Cl atoms of Acetylene tetrachloride, which can make this species perform as σ-acceptor in the direction of these compounds. In contrast, C_6H_6,$C_6H_5CH_3$, can participate in the creation of H-bond with, and perform as π-donors on the way to $CHCl_2CHCl_2$, whereas CH_3COCH_3 and C_6H_5N , together will operate as n-donors . Although Many workers (Nath J.et.al.1983,1984, Pathak G. et.al.1995, Tripathi AD 2010) have measured excess volumes, V^E , speeds of sound, u, dielectric constants, excess enthalpy and refractive indices, for acetone or cyclopentanone, furan or methylfuran with tetrachloroethane and dibromomethane, wide-ranging studies regarding interactions between the components of different mixtures of chloroalkanes and donor components of additional complexity are not accessible in the literature. Consequently, in this work, we have measured excess volumes,V^E, of $CHCl_2$ $CHCl_2$+C_6H_6,+$C_6H_5CH_3$,+ CH_3COCH_3 ,and + C_5H_5N at the temperature 303.15K, and the achieved data are collected and interpreted in this paper.

EXPERIMENTAL SECTION

Materials

C_6H_6,and $C_6H_5CH_3$, both were of AR quality, were subjected for purification in the same way as given by by elsewhere (Nath et.al. 1983). Acetone (AR grade) was kept over anh. $CaCl_2$ for 8 hrs and then fractionally distilled from P_2O_5. $CHCl_2$ $CHCl_2$ (Reidel) was shudderd with K_2CO_3 solution and was further dried over anhydrous K_2CO_3, and then finally distilled . Pyridine is purified in the manner as given in our earlier communication (Tripathi AD 2010). An Anton- Paar vibrating – tube densimeter (Model DMA 60/ 602) was taken for the measurement of densities. A thermometer with a precision of 0.01 K was used. For the densimeter calibration, N_2 and distilled H_2O were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

The purity of chemicals was checked by determining their densities and the results obtained were compared with the literature values(Riddick JA. 1970).For dosimeter calibration, nitrogen and distilled H_2O were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

Method

Excess volumes, V^E, were obtained (in the order of reproducibility of ±0.002 cm^3,mol^{-1}), with the help of a two-branched, glass made dilatometer that was a similar which is was utilized in our prior publication (Nath J.et.al.1983). Weighed quantities of the two liquids were locked up individually over Hg in the inadequacy of air gaps in both the extremities of the dilatometer, which (situated on a wooden stand) was submerged in water of a thermostat (reproducibility ±0.01 K). Both the liquids were mixed by shaking the cell from side to side through a specific angle, and the Hg level in the capillary was noted by means of a a cathetometer (accuracy of 0.001 cm). The functioning of the dilatometer was tested by measuring V_m^E for the system of C_6H_6+ C_6H_{12} at 303.15 K as described elsewhere (Nath J et.al.1983). The measured value of excess molar volume for this system agrees well with the literature data.

Results and discussion

The data obtained for V^E of the binary mixtures of $CHCl_2$ $CHCl_2$ at the Temperature 303.15 K are reported in Table 1 and plotted against mole fraction $x1$ in Figure 1. V^E data for all binary mixtures have been fitted by using following equation

$$V^E\ /(\mathrm{J.mol}^{-1}) = x1x2\sum_{i=0}^{m} Ai(x1-x2)^i \qquad (1)$$

where $x1$ refers to the mole fraction of $CHCl_2$ $CHCl_2$. The values of all constants A_i alongwith standard deviations, σ, are collected in Table 2.

Following equation have been used to calculate standard deviations, σ

$$\sigma = \left[\frac{\Sigma(V^E - V^E_{cal})^2}{(m-n)}\right]^{1/2} \qquad (2)$$

where V^E is the experimental value of excess molar volume and V^E_{calc} refers to calculated value by means of eq.1, m represents number of experimental data and n , the number of constants . In fig.1 , a plot of experimental values of V^E vs mole fraction is given.

It is observed that if V^E values are negative, interaction factor leads whereas the positive V^E values are indicative of steric factor in the binary mixtures.

When values of V^E are negative, it is due to increased interactions between the dissimilar molecules or it would arise from specific interactions between the molecules of the two components. These -ve values of V^E shows that between unlike molecules, there is high probability of the H-bonded type interaction which occurs at the time of mixing. The packing effect may be the reason behind this. When the values of V^E are +ve , the decrease in specific interactions may take place.

The sign of V^E shows the force of association acting between the molecules of the different parts. Negative values of V^E is due to a closer move toward dissimilar molecules , cause to decrease in absolute volume and compressibility. Various types of powers acting between the contrasting components are dispersion , hydrogen bonding, dipole–dipole, charge transfer and dipole induced dipole type interactions. Attraction between the molecules is expected due to dispersion forces , and the relative magnitudes of the A–A, B–B, A–B type contacts between the molecules of components A and B of a mixture are essential for determination of excess properties. In the case, if shape and size of components of a mixture do not differ very much, the dispersion forces causes +ve contributions to V^E. However, other remaing interactions must lead to -ve contributions to V^E . All systems are operated by dispersion forces , and if there is more than one type of interaction occur in a system, the sign of V^E depends upon the total effect of the contributions made by all types of interactions.

From the Table 1, it is clear that V^E is negative all over the entire range of mole fraction for binary liquid mixtures of $CHCl_2CHCl_2$ + Benzene(C_6H_6),+Toluene($C_6H_5CH_3$),+Acetone(CH_3COCH_3) ,and + Pyridine(C_5H_5N) . At $x1 = 0.5$, the values of V^E for the different systems of $CHCl_2CHCl_2$ has the order:

Benzene(C_6H_6),>Toluene(C6H_5CH_3)>Acetone(CH_3COCH_3) > Pyridine(C_5H_5N)

The -ve values of V^E for mixtures of $CHCl_2CHCl_2$ Benzene(C_6H_6),+Toluene(C6H_5CH_3),+Acetone(CH_3COCH_3) ,and + Pyridine(C_5H_5N) can be expected due to a closer approach of the dissimilar molecules in solution, thus representing the presence of specific interaction between π electrons of benzene or toluene and H (of $CHCl_2CHCl_2$), or between O atom of acetone or N atom of pyridine , it is similar to that a complex is created by means of hydrogen bonding between CH_3COCH_3 and CH_2Br_2 in the liquid state as given elsewhere (Tripathi AD 2010). $CHCl_2CHCl_2$ in this case will perform as σ-acceptor . The specific interactions of $CHCl_2CHCl_2$ with all these compounds may also be due to a charge transfer interaction of Cl atoms of $CHCl_2CHCl_2$ with lone pair electrons on oxygen atom of acetone or N atom of pyridine. It is observed that the strength of these intermolecular forces is more for the those systems which have more Cl atoms connected to C−H pair atoms. It is thus revealed that the factor due to interaction is presiding over for the mixtures with -ve sign of V^E values while the factor due to steric hindrance succeeds for mixtures with +ve sign. For interaction between the alkanes having chloro group and cycloketones , different forms of interaction occur : formation of charge-transfer complexes, due to the interactions of Cl atoms from chloro-compounds with the non-bonding pair electrons of the oxygen atom in ketones, hydrogen bonding, due to the interaction of H atoms from chloroalkanes with the non-bonding -pair electrons of the O atom present on ketones. Also there is likelihood of dipole-dipole interactions between dissimilar molecules, which has been explained as being due to the charge-transfer interaction between Cl atoms of $CHCl_2CHCl_2$ and the nonbonding -pair electrons present on acetone or pyridine molecule.

Table 1. Experimental Values of the Excess Molar Volumes, V^E, for Acetylene tetrachloride ($CHCl_2$ $CHCl_2$)+ Benzene(C_6H_6),+Toluene($C_6H_5CH_3$),+Acetone(CH_3COCH_3) ,and + Pyridine(C_6H_5N), at 303.15 K.

$x1CHCl_2CHCl_2 + (1 - x1)C_6H_6$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.0987	-0.004
0.1434	-0.008
0.2098	-0.018
0.2567	-0.025
0.3099	-0.032
0.3675	-0.043
0.4123	-0.045
0.4644	-0.046
0.5411	-0.049
0.6088	-0.041
0.7233	-0.031
0.8177	-0.017
0.9064	-0.008
0.9544	-0.003

$x1CHCl_2CHCl_2 + (1 - x1)C_6H_5CH_3$

$x1$	V^E ($Cm^3.mol^{-1}$)
0.0678	-0.038
0.1075	-0.059
0.1789	-0.096
0.2045	-0.118
0.2611	-0.134
0.3245	-0.150
0.3597	-0.157
0.4156	-0.163
0.4698	-0.163
0.5145	-0.159
0.6789	-0.113
0.7231	-0.095
0.8677	-0.034
0.9034	-0.025

0.9586	-0.006
0.0678	-0.038

$x1\mathrm{CHCl_2CHCl_2} + (1 - x1)\mathrm{CH_3COCH_3}$

$x1$	V^E (Cm^3.mol^{-1})
0.1124	-0.303
0.1785	-0.430
0.1902	-0.458
0.2608	-0.544
0.3266	-0.621
0.3678	-0.630
0.4311	-0.653
0.5288	-0.654
0.6444	-0.601
0.7089	-0.545
0.7654	-0.480
0.8043	-0.425
0.8567	-0.337
0.9099	-0.230
0.9533	-0.127

$x1\mathrm{CHCl_2CHCl_2} + (1 - x1)\mathrm{C_5H_5N}$

$x1$	V^E (Cm^3.mol^{-1})
0.0784	-0.023
0.1133	-0.026
0.1765	-0.040
0.2234	-0.049
0.2965	-0.061
0.3244	-0.065
0.3897	-0.073
0.4522	-0.078
0.5213	-0.085
0.6155	-0.077
0.7098	-0.069
0.7567	-0.062
0.8009	-0.053
0.8666	-0.039
0.9316	-0.022

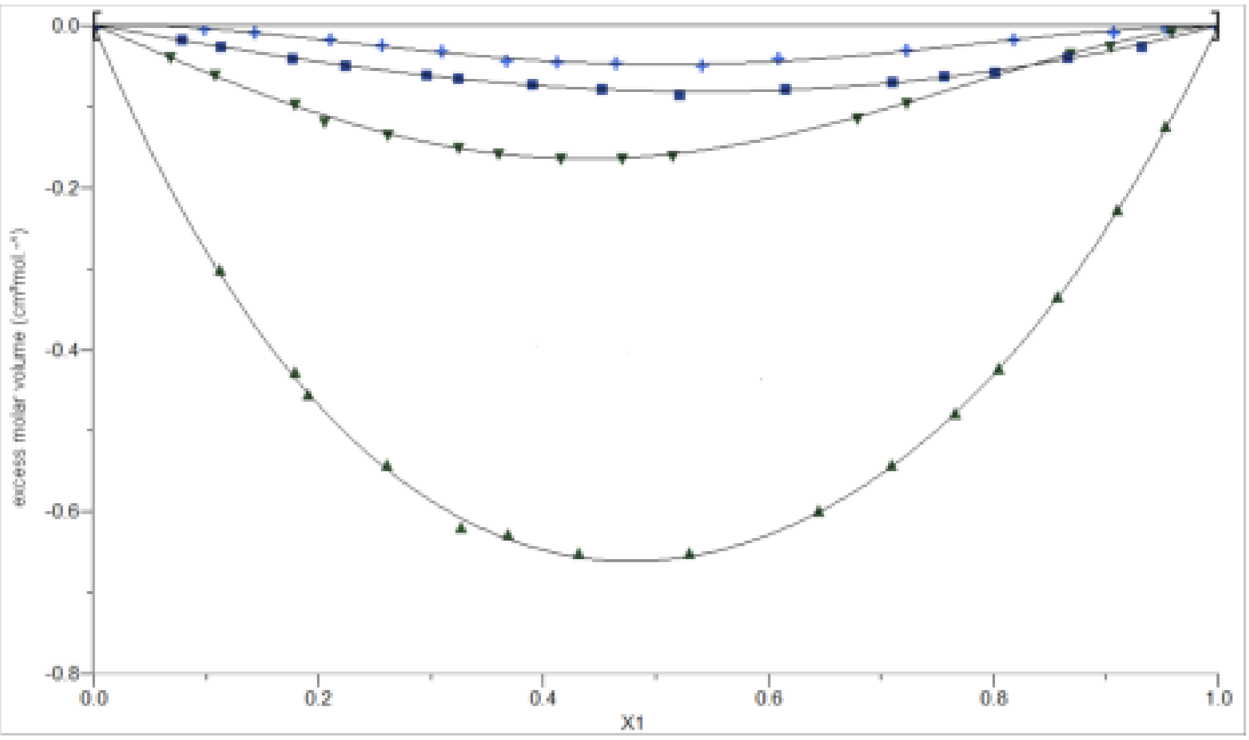

Fig.1 Excess molar volumes of binary liquid mixtures of X_1 of Acetylene tetrachloride(CHCl2.CHCl2(1) with Benzene (C_6H_6(2) (+) , + toluene (▼)(2) ,+acetone(▲) , (2) and + pyridine (■) (2) at 303.15 K. The smoothed curves are based on the parameters A0,A1, A2and A3 given in Table 2.

Table 2. Least Squares Coefficients of Eq 1 for the Excess Molar Volumes , and the standard deviations,σ,of Acetylene tetrachloride (CHCl2.CHCl2)(1) +Benzene(C_6H_6)(2)or + Toluene (2),or + Acetone (2),or +Pyridine(2) at 303.15 K

System	A0	A1	A2	A3	σ/ (J mol^{-1})
$CHCl_2$ $CHCl_2$(1)+ C_6H_6 (2)	-0.1907	-0.0148	0.2069	0.0008	0.002
$CHCl_2$ $CHCl_2$(1) + C_6H_5 CH_3 (2)	-0.6417	0.2416	0.2954	0.0007	0.003
$CHCl_2$ $CHCl_2$(1) + CH_3 $COCH_3$ (2)	-2.641	0.1962	-0.4711	-0.0008	0.004
$CHCl_2$ $CHCl_2$(1) + C_6H_5N (2)	-0.3217	- 0.04854	0.03298	0.0007	0.002

References

Nath J , Trlpathi AD.1983. Binary Systems of 1 ,I ,2,2-Tetrachloroethane with Benzene, Toluene, p-Xylene, Acetone, and Cyclohexane. 1. Excess Volumes, Ultrasonic Velocities, and Adiabatic Compressibilities at 298.15 and 308.15 K. *J.Chem.Engg.Data*, 26:263-266.

Nath J , Trlpathi AD .1984. Binary Systems of 1, I ,2,2-Tetrachloroethane with Benzene, Toluene, p-Xylene, Acetone and Cyclohexane Part 2.-Dielectric Properties at 308.15 K , *J. Chem. Soc., Faraday Trans. I,* 80: 1517-1524.

Pathak G, Tripathi AD, Phalgune UD, Pradhan SD.1995.Enthalpies of mixing of tetrachloroethane with furan, methylfuran, tetrahydrofuran, cyclopentanone and 1,4-dioxane. *Thermochimica Acta* 258: 109- 115.

Riddick, J A, BungerWB.1970. Techniques of Chemistry, Organic Solvents: Physical Properties and Methods of Purification, 3rd ed.; Wiley-Interscience: New York.

Tripathi AD 2010.Excess Enthalpies of Dibromomethane with Acetone, 1,4-Dioxane, Pyridine, Diethyl Ether, Ethyl Methyl Ketone, and Tetrahydrofuran at 303.15 K. *J. Chem. Eng. Data* 55: 1113–1116.

Original Article

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Determination of Fe, Ni, bicarbonate, Pb, Sn, and Cr in drinking water

Abstract

The physicochemical characteristics of drinking water obtained from 10 locations in Moradabad have been tested to determine the quality of drinking water. This paper is about the correlation study of drinking water in various locations of Moradabad. This aims to bring about the value of groundwater quality at the site. Following traditional sampling methods and procedures from the different locations to analysis of different physical and chemical parameters. The findings were compared to Indian WHO and BIS standards. This research revealed that the area's water is heavily contaminated and quality control is urgently needed. Titrimetric analysis have been made for measurement of Fe, Ni, bicarbonate, Pb, Sn, and Cr in drinking water.Measurements have also been carried out on conductivity and pH of these elements/compounds. Total dissolved solids are determined gravimetrically.

Keywords: Water sample, titration, indicator, groundwater, parameters, eriochrome-black T indicator , distilled water.

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Introduction

Water is a substance held capable of prolonging life indefinitely and is one of the most essential resources. It is chief for living organisms, but as the human population has increased, this valued resource is gradually more in danger, raising the demand for more high-quality water for household purposes and commercial operations. It makes up approximately seventy percent of the mass of the body of nearly all living things. About ninety seven percent of the earth's water is saline and nearly 3% is available as clean water from which about twenty percent makes ground water. Groundwater is highly efficient, priced because of certain characteristics that surface water does not have. Water quality relies on the weathering of the parent rocks and chemicals in the anthropogenic activities of the physical and chemical constituents. The studies of quality of Groundwater are more appropriate by reason of human-created operations such as household manufacturing and agricultural actions. Groundwater pollution occurs mostly in city areas because of household and manufacturing releases. Such practises as the discarding of manure water, diseased tanks and toxic waste. These studies are not necessary when alternate supplies are available. The world's substitute supplies, however are not adequate for the entire population in many areas, especially in city areas.The areas are not available , mainly in Moradabad region . 90 percent of the water supplied to the city and to India, according to the Central Pollution Control Board,Cities are infected, with just 1.6 percent of them being treated. Water quality control, therefore is important to human well-being (Gupta SC. 1991). Often, Total Dissolved Solids is examined in to create an ecosystem of water quality conducive to the growth of the organism. (CO2) Pollution Free Carbon Dioxide occurs naturally in water in different quantities. In drinking water, the majority of the groundwater contains < fifty mg/l of CO2. If we consider H2O, a large amount of CO2 causes acidic H2O conditions. The following happens when CO2 dissolves in water;

Carbonic acid (H_2CO_3)is formed by water (H_2O) plus carbon dioxide (CO_2). Hydrogen (H+) and bicarbonate alkalinity result from the dissociation of carbonic acid . When the concentration of CO2 increases in water, pH value will decrease and, conversely, when the HCO_3^- alkalinity substance raises, it will increase. CO_2 usually includes mineral acids such as H2SO4 or HCl acid in water with a pH of 3.5 or below. Carbon dioxide may occur in H_2O having pH values ranging from 03.6 to 08.4, but it will not exist in waters with pH values of equal to or more than eight point five. The value of pH is not an indicating the quantity of CO2 in the H_2O , but to a certain extent the association between CO2 and alkalinity of Bicarbonate . Different parameters have been correlated with the help of statistical regression . Such type of investigation determines the closeness of the relationship between the chosen different type of self-determining and dependent variables. It is seen to be closer to +1 or -1 when the correlation coefficient is the likelihood of a linear connection between different inconsistents x and y. The purpose of this method analysis is to evaluate the significance of the variable’s connection and thus provide a predictive or forecasting context. (Madhuri U et.al 2004, Mulla JG et al.2007, Draper NR,1966).

The correlation coefficient is a valuable method for supporting research on water pollution problems. Till now, effort has not been made yet to consistently expect the groundwater parameters of the concerned region with the help of the correlation coefficient of various types parameters which are used for studying the quality of water.

Over the last few decades, Moradabad has seen quick industrialization and population expansion. The primary business is brassware, steelware, paper mills, sugar mills, crushers, dye manufacturing and a number of associated additional industries. In multiplying the amount of water pollution, most of these factories and various kinds of man working play their part. To provide people with clean water in an efficient way, it is important to undertake a broad study of the parameters of water drank by people. This will aid in improving the water quality.

MATERIAL AND METHODS

In order to measure pH and conductance measurement, a pH meter and a conductivity meter were taken. Titrimetric calculations were made of total hardness, available Cl, CrO_4^{-2}, CO_3^{-2}, Calcium ion, Magnesium ion, dissolved CO_2, alkalinity, Chloride ion, Copper ion, and Zinc ions.

COLLECTING SAMPLE

A total of 10 groundwater samples were collected using standard sampling methods and procedures from Indian Mark II (IM2) hand pumps (Snedeco GW et.al.1967, Kumar J et.al.2005,APHA 1995, Merck E. 1974). After running the water straight from the hand pumps, water samples were collected for around 40 minutes.

ANALYSIS BY MEANS OF TITRATION

With +99 percent purity registered, the salts taken in these experiments were AR grade and without moisture. Ethylene Diammine Tetra Acetic Acid (Aldrich), Potassium iodide from Darmstadt, $Na_2S_2O_3$ (AR), Sodium hydroxide from Fluka, Silver nitrate from SAS Chemicals, Hydrochloric acid and sulfuric acid from Qualikem, all salts were dried by means of a vacuum oven at one twenty degree centigrade for many days before use. By using double-distilled water, stock solutions were prepared for the measurement. The concentrations were obtained using density measurement with the help of a densimeter (vibrating tube) from Anton Paar Co.,Ltd.. Complete hardness was measured and titrated with 0.01M EDTA solution by using (20 CC of water + 5 cc of buffer solution (ammonium chloride +ammonia)+ few drops of the indicator(Eriochrome black-T). The solution switches from deep red wine to blue at the end stage. In order to determine Cl_2 ,water sample with CH_3COOH and potassium iodide solution is taken , which is titrated against 0.01 M $Na_2S_2O_3$ solution until the color is yellow. Now the blue colour is obtained after adding starch solution, the entire substance is titrated again with the regular 0.01 M $Na_2S_2O_3$ until the disappearance of blue colour . Water sample + 3-4ml H2SO4+ 0.5gm NaHCO3+2gm potassium iodide is taken for chromate estimation in drinking water, which is titrated against

0.01 M Na2S2O3 solution. At the end point the color is yellow. Now after applying the starch solution, blue color is seen, the entire mixture is titrated against $Na_2S_2O_3$ again, blue color diminishes at end point. Water sample is collected in a beaker for CO_3^{-2} estimation, few drops of MO indicator added and Titration is done against 0.01M Hydrochloric acid, the colour varies from yellow to red at last. Gravimetric processes for calculating TDS is used which includes the liquid solvent being evaporated and the mass of remains remaining being weighed. In general, this approach is the safest, even though it takes time. In case the salts of inorganic compounds form the greater part of total Dissolved solids, gravimetrical analysis are suitable. Water sample is combined with few drops of suitable indicator and titrated against NaOH (0.02N) for the measurement of dissolved carbon dioxide. In order to measure Ca, in the presence of few drops of EBT indicator , water sample along with Buffer solution (ammonium chloride +ammonia) and titrated against O.01M ethylene diammine teraacetic acid .To determine the full alkalinity of fresh water, titration is done with 0.02N sulfuric acid standard solution with few drops of MO indicator. For chloride ion determination, water sample with few drops of fluorescein indicator is taken in a conical flask and titrated against with 0.001M Silver nitrate solution . At the end stage, the AgCl coagulates noticeably, and the precipitate immediately takes on a pinkish colour. To detect Cu, water sample is taken, added 3-6ml of ammonia to obtain pH equal to six to thirteen, then added few drops of Murexide Now titrated with 0.001 M ethylene diammine teraacetic acid solutions. At the end point colour changes to blueish violet.

For estimation of Zinc, water mixed with 2 ml buffer (pH=10) and few drops of EBT indicator .Titrated with 0.001 M ethylene diammine teraacetic acid solution. Colour changes to blue at the end stage.

During correlation, a one +Ve (increasing) linear relationship (correlation) indicates the degree of linear dependence between the variables, −1 in the case of a perfect decrease (-Ve) and between −1 and 1. The nearest the coefficient is to either -1 or 1, the greater the variables' association is.

Strength calculation

After molarity was obtained by titration method, the strength calculation of element or compound was done with the help of following relation:

Strength = M x molecular weight of element or compound

Where M=Molarity

Results and discussion

For different ions, elements or compounds, the results obtained are given in Table 1 and 2.For groundwater samples, the different physicochemical property values were judged against with the Bureau of Indian Standard and World Health Organization parameters in Table 3.

As per the procedure mentioned above, correlation analysis for the groundwater samples was performed. For TH-Cl_2 (r=0.5368), The values of the correlation coefficient are positive, suggesting mild correlation.

The r value is positive for alkalinity-chloride ion(r=0.5555), suggesting a mild correlation, indicating that low y variable scores tend to go for high x variable scores. For Ca-Mg ions, the r=0.1693 value is logically connected with +ve, but the variable relationship is weak. We obtain The positive and too low value of r for EC-Magnisium ions (r= 0.0045), while the variable relation is theoretically small + ve correlation. In case of Alkalinity-Chromate the value of r is equal to 0.213, the vector relationship is also small.

Conclusion

We have concluded from the above results that the quality of drinking water declines due to increased industrialization, and therefore adequate water analysis and prior care are needed.This research revealed that the area's water is heavily contaminated and quality control is urgently needed. It is important to research the quality of water consumed by individuals in order to provide people with clean water in an efficient way. this will aid in improving the water quality. The stored water had physic-chemical constituents within Ghana standards/ WHO guidelines values and therefore not suitable for potable use. Easy water treatment techniques at home, such as chlorination, filters, solar disinfection, etc. Researches on water quality parameters are consistently required in the world because much disease occurs due to impure water.

TABLE 1: Properties* OF water samples taken from various places

Sample water taken from	pH	Electrical conductivity	Total dissolved solids	Total hardness	Chlorine	Chromate ion, CrO_4^{-2}
Amroha	6.92	0.69	467.8	127	4.6	0.001
Rampur	6.99	0.73	381.67	126	4.4	0.002
Mandi Chowk	7.68	0.69	466.01	120	4.7	0.002
IFTM	6.92	0.69	345.94	124	9.0	0.0011
Budh Bazar	6.99	0.54	297.86	116	8.8	0.0014
Katghar	7.68	0.39	178.85	112	6.4	0.0016
Kanth	7.98	0.41	428.63	122	9.0	0.0017
TMU	8.11	0.39	43.15	116	8.8	0.0011
Pili Kothi	8.09	0.41	189.03	112	6.4	0.0014
Civil Line	8.09	0.25	302.89	122	5.8	0.0016

*UNITS are in mg/l excluding CONDUCTIVITY microsiemen per centimeter and pH.

TABLE 2: Properties* OF water samples taken from various places

SAMPLING STATION	CO_2	Ca^{2+}	Mg^{2+}	ALKALINITY	Cl^-	Cu^{+2}	Zn^{+2}
Amroha	8.12	72.86	17.2	267	11.87	2.4	2.7
Rampur	9.84	69.24	14.2	287	22.62	2.5	1.9
Mandi Chowk	12.2	66.42	23.4	256	16.91	3.1	1.4
IFTM	8.12	64.79	21.3	287	17.81	1.7	2.7
Budh Bazar	8.856	24.45	15.7	297	16.53	1.8	1.9
Katghar	11.1	42.63	13.4	343	45.62	2.2	1.4
Kanth	7.22	54.85	10.8	323	44.97	0.8	2.7
TMU	9.54	31.51	15.5	267	34.13	0.7	1.9
Pili Kothi	11.2	49.47	16.9	287	14.12	0.6	1.4
Civil Line	10.4	53.17	19.4	299	17.30	0.9	2.2

*units in mg/l

Table 3: Comparing of results of GROUNDWATER QUALITY PARAMETERS WITH intake WATER QUALITY necessities With literature values (BIS 1991, WHO 1984)

PARAMETERS	**Samples limit**	BIS STANDARD		**WHO LIMIT(mg/l)**
		Acceptable	Maximum	
	Minimum **Maximum**			
TOTAL HARDNESS	117 122	299	599	101
TDS	165 489	499	1999	499
CHLORINE	0.3 2.1	0.21	**----**	**----**
CHROMATE AS HEXAVALENT ION	0.002 0.0018	0.101	1.0	0.045
CALCIUM	18.78 75.87	75.01	199	74
MAGNESIUM	11.2 26	31	100	150
CARBON DIOXIDE	3.12 11	**--**	**--**	**--**
ALKALINITY	266 299	199	599	**-----**
CHLORIDE	12 58	249	999	249
COPPER	0.5 04.6			
ZINC	1.6 3.45	5.001	14.999	**1.999**
PH	7.33 8.19	6.49-8.37	9.31	6.49-9.31
CONDUCTIVITY*	0.31 0.78	299	**---**	**-----**

*UNITS for CONDUCTIVITY µS.CM^{-1}

References

APHA 1995, Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington, D.C. 19th edition.

BIS 1991, Specifications for drinking water, ARE: 10500:1991, Beaurow of Indian Standard, New Delhi, India.

Kumar J, Jana AK, Bansal A. Garg R. 2005. Development of correlation Between BOD and COD for refinery waste. *Indian Journal of Environmental Protection.* 25, 5: 405-409.

Draper NR, Smith H. 1966. *Applied Regression Analysis* - Wiley, New – York.

Gupta SC. 1991. Chemical character of ground waters in Nagpur district, Rajasthan, *Indian Journal of Environmental Health* 33, 3: 341-349.

Madhuri U, Srinivas T, Sirresha K.2004. A study on ground water quality in commercial area of Visakhapatnam, *Pollution Research* 23, 3: 565-568.

Merck E. 1974. The Testing of Water, Federal Republic of Germany, Darmstadt.

Mulla JG, Farooqui M, Zaheer A.2007 A correlation and regression equations among water quality parameters, *International Journal of Chemical Sciences* 5,2 : 943-952.

Snedeco GW, Cohran WO.1967. Statistical Method, The Lowa State University Press, Ames, 6th edition.

W.H.O.1984. WHO Guidelines for Drinking Water, Geneva, Switzerland, 1.

Original Article

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Physico-Chemical studies on the water of Ramganga River, Moradabad

Abstract

The pH, Hardness, alkalinity studies of various water samples have been carried out to check the quality of various water samples collected from different places (hand pumps, wells, ponds, ditches, etc.).The pH scale is a measure of hydrogen ion concentration. The pH scale varies from 0-14. Below pH -7 is acidic & above pH-7 is considered basic. The pH-7 is considered neutral. The solubility of the metals & Non-metals depend upon the pH of the solution.

The Alkalinity is produced in water system due to the presence of alkaline salts. The alkalinity may be due to OH ions, or due to carbonate ions or bi-carbonate ions. The alkalinity causes hazardous effect on the fauna & flora of the water system.The hardness of water is caused due to the presence of calcium & magnesium Sulfates, chlorides, Bi-carbonates. The slight hard water 60mg/l is almost soft water. The 60mg/l to 100mg/l the water becomes moderately hard water. 101mg/l to 180mg/l the water becomes hard water. 180 onward the water becomes very hard.
The pH, high level of hardness and alkalinity are dangerous and causes cardio vascular problems.

Keywords: Hardness, water sample, titration, indicator, pH, parameters, indicator, distilled water.

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Introduction

The determination of Hydrogen ion concentration is a important tool to identify the acidic and basic character of water samples. The pH scale varies from 0 to 14. Below pH-7 is acidic and above pH-7 is considered basic. The pH -7 is considered neutral. The water samples collected from various sources may have variable pH (StummW.1995) .The hydrogen ion concentration is also effected by discharge The different samples showed different pH values. The change in pH means water is changing chemically. The pH of rivers and underground water shows the quality of water. If water is acidic it means carbonates, sulfite and sulfates are present. If water is basic it shows that more alkali metals are present which changes the pH by making basic hydroxides in the underground water. **T**he solubility of the metals and non metals depends upon the pH of the solution .The pH of solution plays an important role in controlling the eco system of water. The higher concentration is harmful to aquatic life and also to human health. If the pH is basic it means the earth crust is rich in alkali metals. The acidic medium is also bad and causes corrosion in the pipe lines. The solubility of metals and non metals also depend upon the pH of the water .The solubility of heavy metals also enhances the solubility of other metals. Due to the presence of heavy metals the toxicity of water increases.

The pH scale is a measure of hydrogen ion concentration. The diagram given below shows pH in various colors. The zero pH is dark reddish and this type of pH is used in battery water. The sulfuric acid has pH -1 and shows orange color. The pH of lemon juice is 2. The orange juice shows pH-3 and cold drinks shows pH -4. The yellow color indicates the pH of banana. The healthy pH starts from 6.5 to 6.8. The pure water has pH 7.0. The alkalinity start from 7.1 but sea water has alkalinity about 8.0. The Baking soda has pH 9.0. The milk of magnesia (magnesium hydroxide) has pH around 10 and used as antacid i.e used to neutralize the excess acid in the body (WHO1973, National Research Council 1977).

As mentioned in the pH scale the alkalinity is produced in water system due to the presence of alkaline salt. The soil act as buffering effect on the pH change of the water system. The alkalinity is of two types. The phenolphthalein alkalinity and total alkalinity which is measured by methyl orange. The alkalinity may be due to OH ions, or due to carbonates ions or bicarbonates ions. The alkalinity due to OH and carbonates is called phenolphthalein alkalinity. The total alkalinity due to OH, carbonates and bicarbonates causes total alkalinity. The alkalinity causes hazardous effect on fauna and flora of the water system. The animals are also affected by the high alkalinity. It causes disturbance in digestive system. It also changes pH of the blood. The high alkaline value has negative impact on health. .The acid rain also changes the alkalinity of the soil. The slightly acidic soil is good for plants. Few plants prefer slightly alkaline soil .The carbon dioxide also balances the alkalinity of soil and water reservoirs. Normal acidity and alkalinity has no adverse effect on human health.

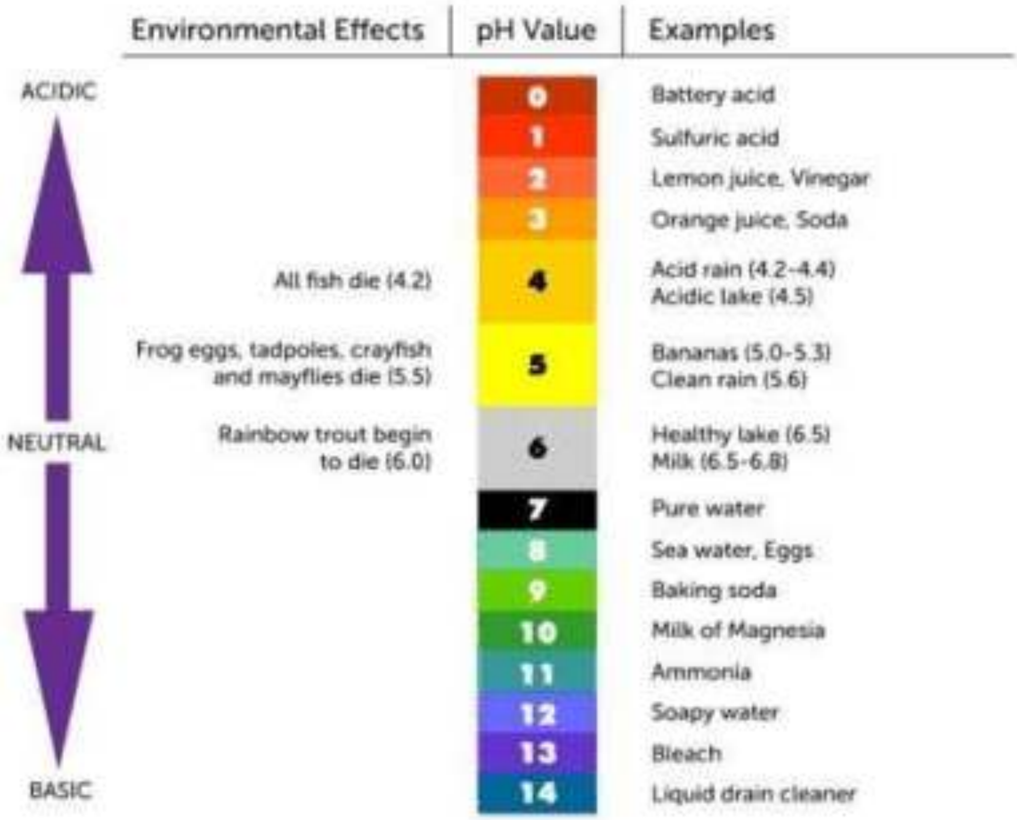

Fig 1: pH scale of various chemical substances. The pH of ammonia is 11.00 and soapy water shows high alkalinity. The bleach and liquid drain cleaner has highest alkalinity

High acidity and alkalinity causes' adverse effect on aquatic life, insects, and human health.The high alkalinity is produced due to the large amount of detergents in bodies (Neri LC.1978). The soap and detergents produce colloidal particles in water system which are precipitated by coagulating agents. The softening of water is done by external and internal methods. Alkalinity also causes caustic embrittlement in boilers (Sawyer CN et.al.1978)

The hardness of water is caused due to the presence of calcium and magnesium sulfates, chlorides and bicarbonates. The temporary hardness is caused due to the presence of bicarbonates of calcium and magnesium. The permanent hardness is caused due to the presence of sulfates and chlorides of calcium and magnesium. The temporary hardness is removed by simple boiling the water or by treating temporary hard water with lime. The lime is added into the water. The carbonates of calcium and magnesium are precipitated along with the magnesium hydroxides. The permanent hardness is removed by soda-lime process or by Zeolite. The hard water on large scale is treated with ion exchange resins. The cation exchange resin remove the all cations like calcium, magnesium, aluminium, and ferrous ions (McNally NJ. 1998). The hardness is of four types. The slight hard water (60mg/l) is almost soft water. The 60mg/l to 100mg/l the water become moderately hard water. 101mg/l to 180mg/l the water become hard water. 180 onward the water becomes very hard. It is given in Table no.1 &2.

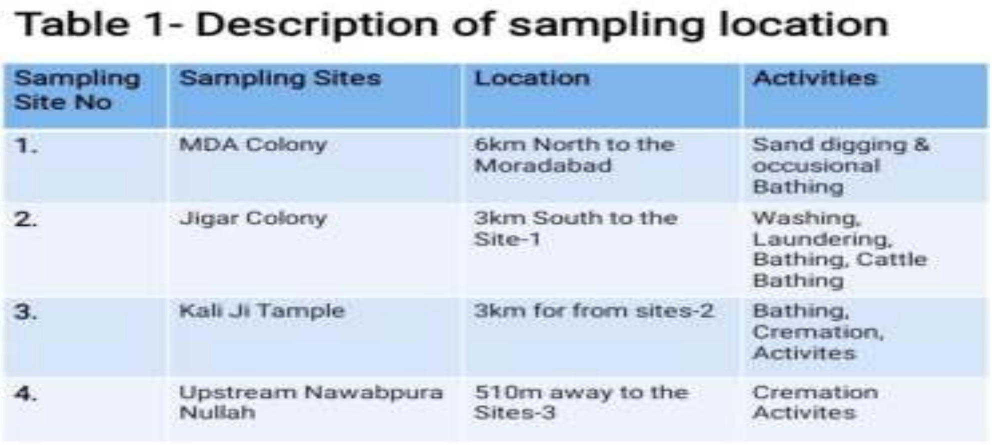

Table 1- Description of sampling location

Sampling Site No	Sampling Sites	Location	Activities
1.	MDA Colony	6km North to the Moradabad	Sand digging & occusional Bathing
2.	Jigar Colony	3km South to the Site-1	Washing, Laundering, Bathing, Cattle Bathing
3.	Kali Ji Tample	3km for from sites-2	Bathing, Cremation, Activites
4.	Upstream Nawabpura Nullah	510m away to the Sites-3	Cremation Activites

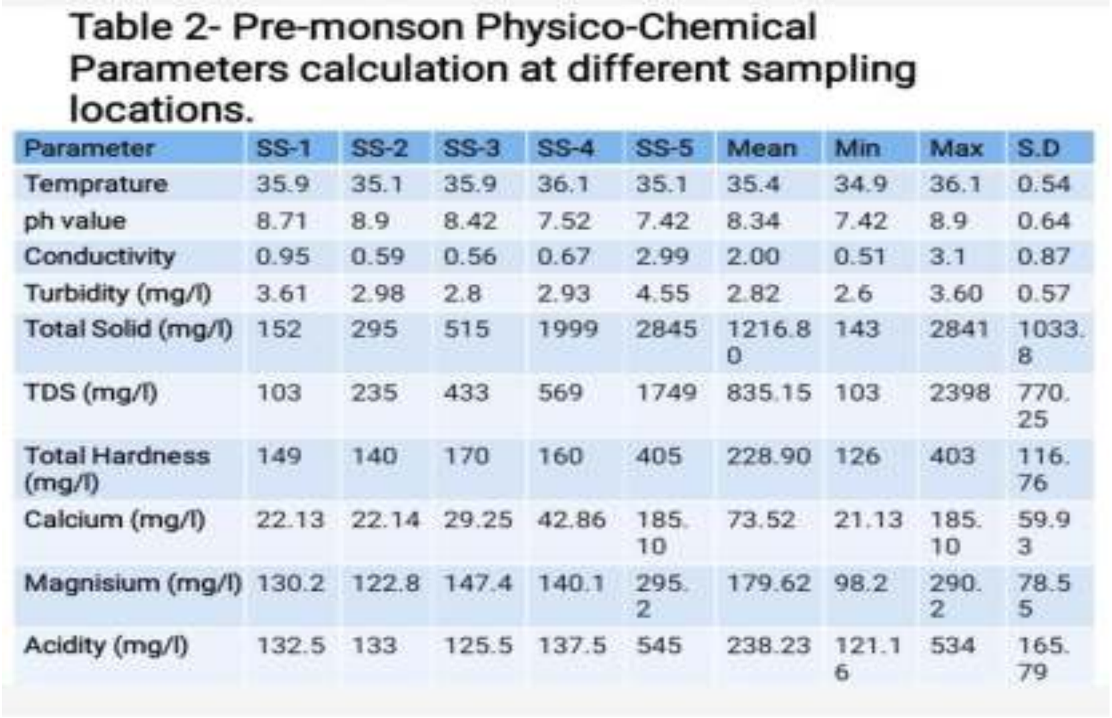

Table 2- Pre-monson Physico-Chemical Parameters calculation at different sampling locations.

Parameter	SS-1	SS-2	SS-3	SS-4	SS-5	Mean	Min	Max	S.D
Temprature	35.9	35.1	35.9	36.1	35.1	35.4	34.9	36.1	0.54
ph value	8.71	8.9	8.42	7.52	7.42	8.34	7.42	8.9	0.64
Conductivity	0.95	0.59	0.56	0.67	2.99	2.00	0.51	3.1	0.87
Turbidity (mg/l)	3.61	2.98	2.8	2.93	4.55	2.82	2.6	3.60	0.57
Total Solid (mg/l)	152	295	515	1999	2845	1216.80	143	2841	1033.8
TDS (mg/l)	103	235	433	569	1749	835.15	103	2398	770.25
Total Hardness (mg/l)	149	140	170	160	405	228.90	126	403	116.76
Calcium (mg/l)	22.13	22.14	29.25	42.86	185.10	73.52	21.13	185.10	59.93
Magnisium (mg/l)	130.2	122.8	147.4	140.1	295.2	179.62	98.2	290.2	78.55
Acidity (mg/l)	132.5	133	125.5	137.5	545	238.23	121.16	534	165.79

MATERIALS AND METHODS

Determination of pH value by pH digital meter

The pH meter is placed on a plane surface. The pH electrode is washed with distilled water and kept in water. The digital pH meter is calibrated with help of two buffer solutions 4.00 and 9.00.Now the pH values of different water samples are noted by dipping electrodes in the water samples. The calibration is repeated every after 10 samples. The pH meter is handled with safety and there should not be any fluctuation in electric current.

Determination of Alkalinity by titrimetric method

In this case the reagents N/50 standard sulfuric acid, phenolphthalein, methyl orange indicator, ethyl alcohol,and distilled water is used. The determination of alkalinity is based on the principle that there may be OH ions or Carbonates ions or bicarbonates ions. The presence of OH ions and carbonates ions is determined by Phenolphthalein indicator and the total alkalinity is determined by methyl orange alkalinity.The alkalinity is expressed in equivalent of calcium carbonates. The concentration of CO_2 also changes the alkalinity of water.

$$CO_2 + H_2O \Rightarrow H_2CO_3$$

$$H_2CO_3 \Rightarrow HCO_3^- + H^+$$

$$HCO_3- \Rightarrow CO_3^{2-} + H^+$$

In acidic medium the alkalinity becomes negative. In slightly basic medium the alkalinity exist as bicarbonates. At about pH 11.5 the alkalinity exists as carbonates. 25 ml of water sample is taken in a beaker and few drops of phenolphthalein as indicator is added in it. If OH ions are present the pink color appear and then it is titrated against the N/50 HCl or H_2SO_4 solution. The acid is filled in burette and added drop by drop in the conical flask. The disappearance of pink color shows end point. The concordant reading is noted and alkalinity is calculated. The normality of water is calculated by using the formula:

$$N_1V_1=N_2V_2$$

The strength of phenolphthalein Alkalinity(S) is calculated and expressed in equivalent of calcium carbonate by using S=NE, where N denotes for normality and E for equivalent weight. In order to determine the total alkalinity, water sample is taken in a conical flask. The Methyl Orange indicator is added in it. The color becomes yellow.Now it is titrated against the standard HCl solution. The appearance of pink color shows end point. The titration is repeated and concordant reading is obtained. $N_1V_1=N_2V_2$ and S=NE is applied to calculate total alkalinity.

Estimation of hardness by EDTA method

The hardness determination is based on the formation of complex with calcium and magnesium in presence of buffer solution.The Eriochrome Black T+ calcium and magnesium form wine color. The EDTA solution is added in the conical flask drop by drop.The color change from wine to blue.This is called end point. The concordant reading is obtained by repeating the process.

Determination of Total hardness

The 25 ml of water sample is taken in conical flask and 10 ml of buffer solution is added to maintain 9.00-10 pH. The EDTA solution is added drop by drop till color change from wine to blue. The concordant reading is obtained and permanent hardness is calculated. N1V1=N2V2 and S=NE are applied for the calculation of total hardness of water sample. The temporary hardness is also calculated. The water samples are boiled. In this way temporary hardness is removed. The bicarbonates are converted in to Carbonates, the carbonates are filtered and permanent hardness is calculated after titration again.

Temporary hardness= Total hardness - Permanent hardness

RESULTS AND DISCUSSION

Sampling method

When we go for collecting the water sample. Firstly we locate the number of water sources in a particular area. We keep plastic bottles.The bottles are filled with water sample. In this way we collect all water samples. As per standard, the samples can’t be analyzed immediately. They are stored at zero degrees centigrade to stop any change in the composition of water. Values of different parameters have been collected in Table3, whereas standard values of different parameters are given in Table 4.

Table 3: Table showing Hardness, pH and alkalinity of water samples collected from different places

S. No.	Sample	Sample Source	Hardness	pH	Alkalinity (ppm)
1.	A	Hand pump- Bank colony, Gajraula.	200	9.20	80
2.	B	Hand pumpTeacher's colony, Gajraula.	226	8.70	100
3.	C	Rain water-Kavi Nagar, Gajraula.	260	5.30	40
4.	D	Ditch-Basti, Gajraula.	670	8.20	150
5.	E	Drain water-Mda colony, Gajraula .	956	12.50	133
6.	F	Ditch-Mehal colony, Hasanpur.	867	10.60	140
7.	G	Hand pump-Lal Bagh Mohalla, Hasanpur.	320	6.90	50
8.	H	Drain waterRajput colony, Hasanpur.	450	11.3	90
9.	I	Hand pump- Kayasthan Mohalla, Hasanpur.	160	8.4	78
10.	J	Rain water-Block Wala Mohalla, Hasanpur.	110	6.50	54
11.	K	Hand PumpNaveen Nagar, Moradabad.	340	8.9	137
12.	L	DitchMadhubani, Moradabad.	760	8.0	143
13.	M	Ditch- Ashiyana1, Moradabad.	560	13.8	130
14.	N	Hand Pump-Jama Masjid, Moradabad.	210	8.6	67
15.	O	River-Ramganga Vihar. Moradabad.	650	4.7	90

Table 4 : Water standard of various parameters(in ppm):

Parameter	BIS Standards(BIS 2012)		WHO Standards (McGowan W; 2000)
	Desirable	Max. permissible	
Colour	5	30	-
Odour Taste	Unobjectionable	No problem	-
TA TDS	Agreeable	Agreed	6.4-9.0
$C1^-$	6.5-8.5	6.4-8.4	315
SO_4^{2-}	300	645	-
NO_3-	200	656	550
F^- , Ca^{2+}	300	1501	255
Mg^{2+}	250	1007	204
K^+	250	405	55
Na^+	45	46	0.6
	1.0	1.7	101
NH_4^+	75	204	151
Phenol	30	102	205
B		-	200
Fe	-	-	1.6

Conclusion

The present studies have been carried out to compare the pH, alkalinity and hardness of12 water samples from the surrounding of Moradabad and Gajrola. The water samples collected were studied for pH, alkalinity and hardness. The water samples showed a wide range of variation in pH, alkalinity and hardness of water. Out of 12 samples 5 samples are having pH below 7.00 and they varied from 6.2 – 6.8. This type of water is good for plants like rose plants but for drinking it is harmful as it enhances the acidity in the digestive system. 3 samples showed pH above 7.0 that 7.9, 8.3, and 8.5. The other three samples are having pH 7.4, 7.4, and 7.5. Such water is not bad for drinking.

Alkalinity also showed variation in the values. Five samples are having high level of alkalinity and such water is very bad for drinking as it disturb the physiology of the human body as well as bad for animals, fishes and other animals (Soyinka CN, 1980**).** The values are reported in the table -1. The water samples also showed variable values of hardness. The 4 samples were showing very high hardness. The 2 samples can be used for drinking, rest of the 6 samples are hard water as values are ranging from 120 -190 mg/l. The studies are very useful for the people, as they are informed about the quality of water. The calcium and magnesium concentration were found high. The traces of aluminum and ferrous salts were also determined by ion exchange method.

References

BIS specifications (IS 10500-2012) Indian Standard *DRINKING WATER* — SPECIFICATION.

McGowan W (2000) Water processing: residential, commercial, light-industrial, 3rd ed. Lisle, IL, Water Quality Association.

McNally NJ. 1998. Atopic eczema and domestic water hardness. *Lancet*, 352(9127):527-531.

National Research Council .1977. *Drinking water and health*. Washington, DC, National Academy of Sciences.

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