Indian Journal of Engineering & Materials Sciences
Vol. 30, October 2023, pp. 713-718
DOI: 10.56042/ijems.v30i5.6875

Study of Molecular Interaction of 2-amino-5-bromopyridine and 2-amino-3-bromopyridine with Alcohols

K S Anjali[a,b,c], C Ningappa[b,c*], M S Manjunath[d]

[a]Department of Physics, Coorg Institute of Technology, Ponnampet, Karnataka 571 216, India
[b]Department of Physics, VidyaVikas Institute of Engineering and Technology, Karnataka 570 028, India
[c]Visvesvaraya Technological University, Belagavi 590 018, India
[d]Department of Physics, Government First Grade College, Karnataka 570 008, India

Received: 9 August 2023; Accepted: 26 September 2023

Molecular interaction is useful to understand Physico-chemical characteristic of liquids. Studying ultrasonic properties of liquid mixtures and their dependence on composition and temperature are of importance in many fields of applied research and find applications in many important industrial fields like chemical, textile, leather, industrial and biological process. Interaction studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes. The compositional dependence of thermodynamic properties has proved to be very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interaction between components. Therefore using ultrasonic technique, molecular interactions were studied for the liquid mixture containing 2-amino-5-bromopyridine with aromatic alcohols (ethanol, propanol and butanol) and 2-amino-3-bromopyridine with aromatic alcohols were measured at the temperature 299 K for different molar concentration at 2 MHz frequency. Calculated the experimental results like density (ρ), viscosity (η) and ultrasonic velocity (U) and it has been utilized to determine various excess thermodynamic properties like adiabatic compressibility (β), impedance (Z), intermolecular free length (L_f) and intermolecular free volume (V_f). In this binary system, the strength and nature of molecular interactions are interpreted.

Keywords: Acoustic, Dipole, Hydrogen bond, Spectroscopy, Ultrasonic velocity

1 Introduction

The thermodynamic properties such as density and viscosity measurements in pure liquid and liquid mixtures have been successfully employed for understanding the behavior of intermolecular interactions between the molecules[1-3]. Ultrasonic velocity propagation in a medium is used to predict & estimate the different physico-chemical characteristic of the liquid mixture[4-6]. Measurement of ultrasonic velocity helps to study the molecular interaction in liquids and it provides information of changes in the internal structural like interaction of component is weakly or strongly, internal pressure, complex formation, and molecular association[7-10].

The forces that bind atoms or molecules together are fundamentally related to the ultrasonic velocity of a liquid[11-15]. The study of ultrasonic velocities in electrolyte solutions has provided to understanding of the ion-association and complex-formation processes[16] along with solute-solvent interaction.

The acoustic properties such as impedance, intermolecular free length, adiabatic compressibility and intermolecular free volume are calculated and data provide valuable information about molecular environment that exist in the liquid mixture and used as quantitative and qualitative guides to predict the extent of complex formation in liquid mixture. Additionally, it provides details on ion-dipole interaction, primarily the size of the ions and the solvent's polarity in the liquid mixture. Study of ultrasonic properties of liquid mixtures with its dependence on temperature and compositions are used in various applications in the field of pharmaceuticals, preparation of dyes, corrosion inhibitors, metal ion separation, textile, fuel, leather, industrial, biological process and many chemical processes[17-20]. It is known that alcohol is scientifically strongly self-associated and highly non-polar liquid having 3-dimensional network of hydrogen bond and amine are important class of organic compound having some degree of polar attractions [21-24].

*Corresponding author (E-mail: ningappacvviet@gmail.com)

As a result, molecular interaction study of amines such as 2-amino-5-bromopyridine and 2-amino-3-bromopyridine with different primary alcohols such as ethanol, propanol and butanol has been carried out. The main objective of the present work to study the experimental results of density (ρ), viscosity (η), adiabatic compressibility (β), Ultrasonic velocity (U), intermolecular free length (L_f), impedance (Z), and intermolecular free volume (V_f) for the liquid mixture containing 2-amino-5-bromopyridine with alcohols and 2-amino-3-bromopyridine with alcohols (ethanol, propanol and butanol) with frequency 2 MHz at 299 K. One of the most effective methods for identifying interactions caused by hydrogen bonds present in various mixes is infrared spectroscopy. Therefore, FTIR analyses of the pure solvents and their mixtures at equi-molar concentration were carried out. Supporting data has been provided in the form of the recorded spectra and the resulting shifts in stretching frequencies. The presence of dipole-dipole interactions between dissimilar molecules and intermolecular hydrogen bonding in the systems is analysis of the FTIR data [25, 26].

The investigation of the present work is to provide a set of data of the specified liquid mixture, to find out the structural reorganization representing the structure of closely packed molecules and the dipole-dipole interactions of the permanent dipoles in constituent molecules of binary mixture of alcohol and amine, the non-linear variation showing the growing of molecular interaction between the liquid mixtures and the formation of products from reaction and the confirmation of formation of bonding between the hydrogen in the liquid mixture.

2 Materials and Methods

The interaction studies of 6 samples of binary liquid mixture have been carried out in the year 2021-22 using alcohols such as C_2H_5OH, C_3H_8O and $C_4H_{10}O$ supplied from Merck Co. which are 99.9% pure. These alcohols were used without any purification and mixed with amine 2-amino-5-bromopyridine and 2-amino- 3-bromopyridine [27].

2.1 Sample preparation

Prepared the sample solution at different volume percentage in 1- alcohols in step of 50% volume within a 0.01% error limit. The liquid systems of different desired concentration for the study have been prepared by weight fraction at laboratory temperature. Suitable concentration in step of 0.02 mole$L^{-1}$is used for all the systems. The complex in dilute solution also has been prepared by weight fraction to set same concentration. The fresh composition of liquid mixture has been performed and the mixtures were prepared freshly and stored in air tight bottles[28].

2.2 Specific gravity bottle

By applying the relative density technique, measured the density of pure liquid and their mixtures. The relative density bottle of 50 ml capacity[29] was washed with double distilled water and then acetone well and finally dried. The density of the experimental sample 2-amino-5-bromopyridine and 2-amino-3-bromopyridine with different primary alcohols are calculated using the equation,

$$\rho_s = \frac{m_s}{m_w}\rho_w \quad \ldots (1)$$

Whereρ_s, ρ_w and m_s, m_w are the densities and masses of sample liquids and water respectively.

2.3 Ostwald's viscometer

An Ostwald's viscometer is used to measure the liquid mixtures viscosities[30] kept in a constant temperature water-bath at 299K with accuracy ±0.001 Ns m^{-2}, using the value of viscosity of water at 299K from literature. The equation used for the computation of viscosity is,

$$\eta_s = \left(\frac{\rho_s\, t_s}{\rho_w\, t_w}\right)\eta_w \quad \ldots (2)$$

Where, ρ_s and ρ_w are the densities of the solution and water, $t_{w,}$ andt_s are the corresponding flow times of water and sample solution. η_s and η_w are the viscosities of water and sample respectively at temperature 299K.

2.4 Ultrasonic interferometer

This instrument was supplied by M/S. Mittal Enterprises, New Delhi, and it is a variable multi-frequency path type, and its overall accuracy is ± 2 m /s. In the present investigation, this instrument is used to measure the ultrasonic velocity of the liquid mixture using the formula[31, 32]

$U = \lambda f$ (3) Different acoustical parameter such as adiabatic compressibility (β), impedance (Z), intermolecular free length (L_f) and intermolecular free volume (V_f) for the liquid mixture are calculated using standard equation. From Laplace's equation, the adiabatic compressibility (β) has been determined[33].

$$\beta = \frac{1}{\rho U^2} \quad \ldots (4)$$

Jacobson's formula has been used to calculate intermolecular free length from adiabatic compressibility (β)[34].

$$L_f = \sqrt{\beta} K_T \quad \ldots (5)$$

Acoustic impedance Z is evaluated by using the equation[35]

$Z = U\rho$ (6)Free volume is evaluated by using the equation.

$$V_f = \left[\frac{MU}{K\eta}\right]^{\frac{3}{2}} \quad \ldots (7)$$

Where ρ, η and M are the density, viscosity and molecular weight of the mixtures. $K_T$stands for Jacobson's constant, a temperature-dependent constant with value K_T = 206 and K= 4.28 × 10^9 is the independent constant respectively[36].

2.5 Fourier-transform infrared (FTIR)

This instrument is used to measure the spectra of the binary mixtures at room temperature using JASCO FTIR 4100 type spectrometer. It has a resolution of 1 cm^{-1} at 299 K for absorption spectra [37-39].

3 Results and Discussion

The resultant data was achieved from the experiments related to density, viscosity and ultrasonic velocity at temperature of 299 K for frequency 2 MHz are for giving liquid mixture and calculated the results of impedance, adiabatic compressibility, intermolecular free length and intermolecular free volume which have been tabulated in Table 1.

The experimental results of density (ρ), viscosity (η) and sound velocity (u) of the liquid mixture at 299 K are presented in Table 1 for respective liquid

Table 1 — Acoustic parameters of liquid mixtures containing amines with alcohols for different molar concentration at 299 K

Sl. No.	Mole Fraction M (g)	Density of Sample ρ (Kg m^{-3})	Viscosity of sample η (m P)	Ultrasonic Velocity of sample U (ms^{-1})	Impedance z × 10^{-4} ($Kgm^{-2}s^{-1}$)	Adiabatic compressibility β× 10^{-9} ($ms^{-2}Kg^{-1}$)	Intermolecular free length L_f × 10^{-7}(m)	Intermolecular free volume V_f × 10^{-10} (m^3mol^{-1})
				2-amino-5-bromopyridine and Ethanol				
1	0.108	791.5	7.893	1232	97.512	0.8323	1.8793	0.17726
2	0.216	794.79	7.987	1089	86.552	1.0609	2.1218	0.40940
3	0.432	798.81	8.213	1078	86.111	1.0772	2.1380	1.09354
4	0.864	802.07	8.681	980	78.602	1.2981	2.3470	2.46708
				2-amino-5-bromopyridine and Propanol				
5	0.108	797.31	16.141	1162	92.647	1.0766	2.1374	0.05552
6	0.216	805.16	17.545	1044	84.058	1.1339	2.1935	0.11801
7	0.432	806.50	18.197	946	76.294	1.3855	2.4247	0.27257
8	0.864	812.62	18.523	910	73.948	1.4860	2.5111	0.70829
				2-amino-5-bromopyridine and Butanol				
9	0.108	810.05	20.914	1188	96..233	0.8746	1.9265	0.03891
10	0.216	811.19	20.944	1168	94.746	0.9036	1.9581	0.10070
11	0.432	811.96	21.466	1062	86.230	1.0919	2.1525	0.25305
12	0.864	817.88	22.065	1058	86.531	1.0922	2.1528	0.68292
				2-amino-3-bromopyridine and Ethanol				
13	0.108	787.37	25.200	981	77.240	1.3197	2.3664	0.02207
14	0.216	789.28	32.401	978	77.191	1.3246	2.3708	0.04263
15	0.432	792.54	39.336	955	75.687	1.3834	2.4229	0.08698
16	0.864	797.12	46.58	940	74.929	1.4197	2.4545	0.18645
				2-amino-3-bromopyridine and Propanol				
17	0.108	806.15	14.265	1082	87.225	1.0595	2.1203	0.0602
18	0.216	807.30	15.096	1074	86.704	1.0738	2.1346	0.1548
19	0.432	808.65	16.683	1054	85.231	1.1131	2.1733	0.3667
20	0.864	810.77	17.291	982	79.617	1.2790	2.329	0.8833
				2-amino-3-bromopyridine and Butanol				
21	0.108	809.66	26.162	1193	96.592	0.8677	1.9188	0.02799
22	0.216	811.19	26.336	1017	82.498	1.191	2.2418	0.06169
23	0.432	813.87	27.178	982	79.922	1.274	2.3251	0.15794
24	0.864	816.93	28.417	948	77.444	1.362	2.4041	0.39631

mixture and exhibited good agreement with literature values. Dispersion force, charge transfer, hydrogen bonds, dipole-dipole interaction, and other forms of forces all contribute to the contact between the molecules of the two liquids[18]. It is noted that the value of density in all the combination of liquid mixtures increases with increase in mole fraction indicating the association in component molecules[40]. This result is due to the structural reorganization which indicating component molecules are closed packed structure. The viscosity in this binary liquid mixture increases due to the interaction of dipole-dipole of permanent dipoles in molecules of alcohol and amine binary liquid mixture. Ultrasonic velocity decreases with increase in the mole fraction of the liquid mixture in Figs. 1 & 3.

The non-linear variation shows the growing of molecular interaction between the liquid mixtures. Decrease the acoustic impedance with increases in the mole fraction of all the liquid mixture and results in products formation from reaction. This is confirmed from the hydrogen bonding formation in the liquid mixture. It is demonstrated that van der Waals interactions exist between amino acids and alcohols by the formation of an H-bond between the N of the amino group and the H of the hydroxyl group. As solution concentration increases, adiabatic compressibility increases as well in Figs. 2 & 4. It occurred as a result of the molecules of the solvent collection around the ions, supporting the weak ion-solvent connection. This suggests that solute-solvent interaction is significant. Intermolecular free length increases with mole fraction attributed due to the loose packing of molecules inside the shield. This leads to the presence of ion-solvent interaction molecules and assesses the attraction between the components. The increasing in the free volume indicates the strength of interaction increases slowly

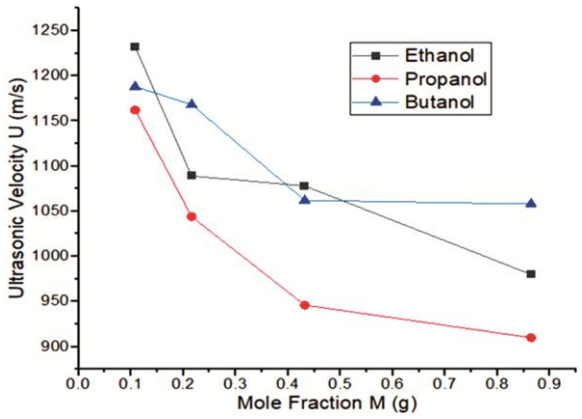

Fig. 1 — Graph of ultrasonic velocity v/s mole fraction 2-amino 5-bromopyridine with Ethanol, Propanol and Butanol.

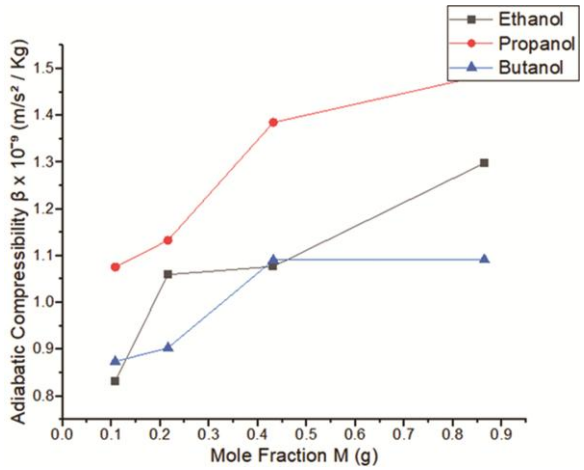

Fig. 2 — Graph of adiabatic compressibility v/s mole fraction 2-amino-5-bromopyridine with Ethanol, Propanol and Butanol.

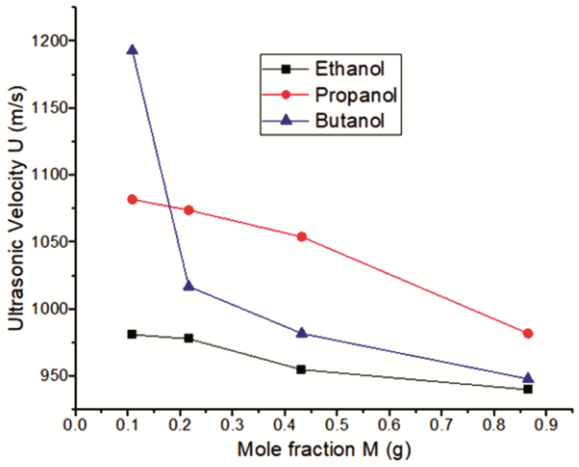

Fig. 3 — Graph of ultrasonic velocity v/s mole fraction 2-amino-3-bromopyridine with Ethanol, Propanol and Butanol.

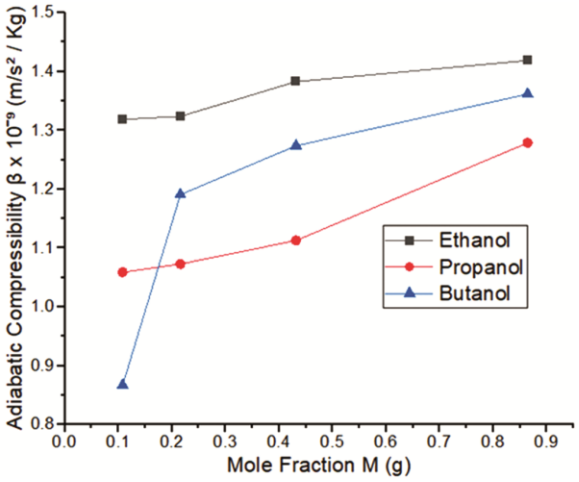

Fig. 4 — Graph of adiabatic compressibility vs mole fraction of 2-amino-3-bromopyridine with Ethanol, Propanol and Butanol

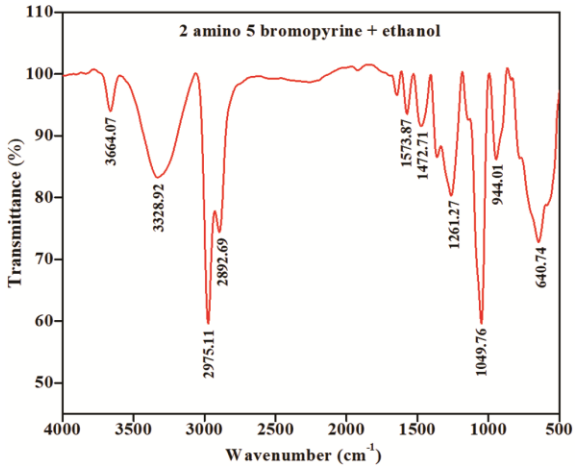

Fig. 5 — FTIR spectrum of 2-amino-5-bromopyridine with Ethanol.

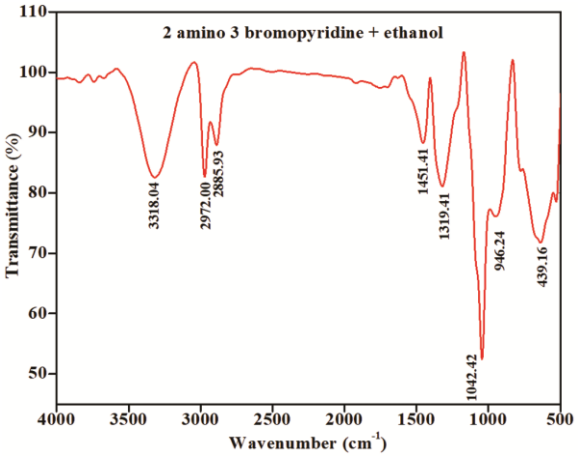

Fig. 6 — FTIR spectrum of 2-amino-3-bromopyridine with Ethanol.

increases in the amine concentration[41]. It indicates that, presence of weak force of interaction between the amine and alcohol molecules because of positive excess attributes and also magnitude of interaction increases[42]. It is observed that for all systems, ultrasonic velocity decreases off concentrations increase. This suggests that there is substantial molecular interaction occurring in the liquid combination. Adiabatic compressibility, which is denoted by β, is one of the essential properties when studying the interactions between solutes and solvents. It increases with increase in mole fraction of the liquid mixture or increase in the percentage of organic solvent. This result in weak interaction inside the solution. FTIR spectra for 2-amino-5-bromopyridine with primary alcohol under observation are presented in Figs. 5 & 6 between 500 cm^{-1} and 4000 cm^{-1}. This method is important because it uses band shift and shape analysis to help quantify a component's ability to form H-bonds, association qualities, and interactions. It is observed that the intensity value 100 was almost constant for all type of liquid mixture at all wave numbers.

This constant increase at definite wavenumber indicates the O-H bond existence in the liquid mixture. There is decrease in intensity at certain wave numbers at 3000 cm^{-1} and 1000 cm^{-1} indicates the existence of stretching vibrations between the carbon and oxygen molecules in the liquid mixture[43].

4 Conclusion

The present work deals with the determination of thermodynamic properties of amine with alcohol. Since alcohols are naturally predominating in dispersive molecular interactions, the computed acoustical parameters and their positive values that indicate the existence of weak contacts and dispersive interactions between the molecules in the mixture under study.

Acknowledgments

Authors are thankful to the Sigma-Aldric in providing 99% pure amines for our work. Special thanks to Department of Chemistry, SJCE, Mysuru for supporting and providing the FTIR spectroscopy facility for its characterization study and Dr. Nithin K S for his guidance in conduction of experiment.

References

1 Khasanshin T, Golubeva N, Samuilov V, & Shchemelev A, *J Eng Phys Thermophys*, 87 (2014) 213.
2 Mahendraprabu A, Sangeetha T, Kannan P, Karthick N, Kumbharkhane A, & Arivazhagan G, *J Mol Liq*, 301 (2020) 112490.
3 Manjunath M & Sannappa J, *Int J Pure Appl Phys*, 4 (2008) 71.
4 Vanathi V, Mullainathan S,& Nithiyanantham S, *Russ J Phys Chem*, 86 (2012) 1204.
5 Martínez-Reina M, Amado-González E, & Goméz-Jaramillo W, *J Solution Chem*, 44 (2015) 206.
6 M Mato, S Cebreiro, P Verdes, J Legido, and M Paz Andrade, *J Therm Anal Calorim*, 80 (2005) 303.
7 T Vijaya Krishna, S Sreehari Sastry, & V Murthy, *Ind J Phy*, 85 (2011) 379.
8 Iloukhani H & Jafari M, *Monatsh Chem*, 142 (2011) 1005.
9 Savaroglu G, Tasagal D, & Aral E, *Int J Thermophys*, 28 (2007) 245.
10 Raghuram N, Suresh R, Ramesh G, Sowjanya G, & Jyostna T S, *J Therm Anal Calorim*, 119 (2015) 2107.
11 Kabane B, Chokkareddy R, & Redhi G G, *Heliyon*, 5 (2019) 01548.
12 Martins M A, Neves C M, Kurnia K A, Carvalho P J, Rocha M A, & Santos L A, , *Fluid Phase Equilib*, 407 (2016) 188.

13 Sikorska E, Dawgul M, Greber , Iłowska E, Pogorzelska A, & Kamysz W, Biochimica et *Biophysica Acta (BBA)-Biomembranes*, 1838 (2014) 2625.
14 Akiyama Y, Fujita S, Senboku H, Rayner C, Brough S, & Arai M, *J Supercrit Fluids*, 46 (2018) 197.
15 Deng W & Li Y, *Sep Purif Technol*, 254 (2021) 117656.
16 Mohabansi N P, *J Sci Res*, 64 (2020) 352.
17 Shakila A, Ravikumar S, Pandiyan V, & Gaba R, *J Mol Liq*, 285 (2019) 279.
18 Babavali S F, Shakira P, Srinivasu C, & Narendra K, *Karbala Int J Mod Sci*, 1 (2015) 172.
19 Chimankar O & Pawar N, *Int J Eng Res Technol*, 3 (2014) 315.
20 A Chandrasekhar & A Krishnaiah, *Phys Chem Liquids*, 17 (1988) 315.
21 Al-Dulaimy Z A, Al-Heetimi D T, Khalaf H S, & Abbas A M, *Orient J Chem*, 34 (2018) 2074.
22 Dubey G P &Rani S, *Phys Chem Liquids*, 59 (2021) 315.
23 Derkach S R, Voron'ko N G, Sokolan N I, Kolotova D S, & Kuchina Y A, *J Dispers Sci Technol*, (2019).
24 Narasimha Rao C, Venkataramana L, Prabhavathi C, Sivakumar K, & Gardas R, *J Therm Anal Calorim*, 123 (2016) 881.
25 Audiseshaiah O, Raveendra M, Kiran Babu L, Sivakumar K, & Rami Reddy Y, *Phys Chem Liquids*, 59 (2021) 232.
26 Hashemi M, Moosavi M, Omrani A, & Rostami A A, *J Mol Liq*, 256 (2018) 445.
27 Kwaterski M, Rezanova E N, & Lichtenthaler R N, *J Chem Thermodyn*, 38 (2006) 1199.
28 Azhagiri S, Jayakumar S, Padmanaban R, Gunasekaran S, & Srinivasan S, *J Solution Chem*, 38 (2009) 441.
29 Girija A M, Arasu M A, & Devi D, *J Indian Chem Soc*, 99 (2022) 100437.
30 Watane R & Raghuwanshi P, *Der Pharma Chemica*, 6 (2014) 162.
31 Ibrahim P S, Jeyakumar J E, & Vinayagam S C, *INDIAN J CHEM A*, 60 (2021) 943.
32 N. Siddharthan and S Jayakumar, *Int J Chem Sci*, 14 (2016).
33 Praharaj M K & Mishra S, *Int J of Science and Research*, 3 (2014) 642.
34 Dash A K & R. Paikaray, *Int J Adv Sci Technol*, 66 (2014) 89.
35 Dikko A, Ezike S, & Ike E, *Int J Sci Engg Appl Sci*, 1(2015) 454.
36 Bedare G, Bhandakkar V, & Suryavanshi B, *IOP Conf Ser Mater Sci Eng*, (2012) 012028.
37 Lasalle B S I, Pandian M S, Arivazhagan G, and Ramasamy P, *Optik*, 262 (2022) 169213.
38 Kannan P, Karthick N, & Arivazhagan G, *Spectrochim Acta A Mol Biomol Spectrosc*, 229 (2020) 117892.
39 Zheng Y Z, Tian X Y, & Zhang Y C, *J Mol Struct*, (2022) 133488.
40 Bedare G, Bhandakkar V, & Suryavanshi B, *Int j appl phys mathe*, 2 (2012) 197.
41 Elangovan S, *J Chem*, 2022(2022) 1.
42 Praharaj M K, *J Chem Pharm Res*, 8 (2016) 519.
43 Ghaleb J Q, Undre P B, Yaseen S A, Saif F A, Alameen A S, & Patil S S, *Integr Ferroelectr*, 202 (2019) 89.