WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 7.523
Volume 6, Issue 10, 1781-1792. Research Article ISSN 2277–7105

ULTRASONIC STUDIES ON MOLECULAR INTERACTION IN TERNARY LIQUID MIXTURE OF N-N DIMETHYLFORMAMIDE AT DIFFERENT FREQUENCIES

Dr. A. Suryanarayana Reddy[1] and Satyanarayana[2]*

[1]Department of Physics, S.V Degree College, Kadapha, Andhra Pradesh-516004.

[2]*Department of Physics, Osmania University, Hyderabad, Telangana.

Article Received on
23 July 2017,
Revised on 13 August 2017,
Accepted on 01 Sep. 2017
DOI: 10.20959/wjpr201710-9475

***Corresponding Author**
Dr. Satyanarayana
Department of Physics,
Osmania University,
Hyderabad, Telangana.

ABSTRACT

The density (ρ) and ultrasonic velocity (U) for ternary mixture of N-N dimethylformamide, benzoic acid and Ethyl Glycol at different frequencies (2MHZ, 4MHz, 6MHZ, and 8MHZ) have been measured at 308K. Ultrasonic technique is used for studying the acoustic properties for a number of systems including liquids, low melting solids, dilute solutions of organic liquids and their mixtures. Ultrasonic studies in organic liquids and their binary mixtures have been of considerable research interest during the last few decades. These data have been used to compute adiabatic compressibility (Ks), intermolecular free length (Lf), acoustic Impedance (Z), molar volume (Vm), molar sound velocity(R), molar compressibility (B), available volume (Va), Lennard Jones potential repulsive term exponent(n), relative association(RA).

KEYWORDS: Molar volume, dimethyl sulphoxide, interaction parameter, ternary mixture.

INTRODUCTION

Ultrasonic studies in organic liquids and their binary mixtures have been of considerable research interest during the last few decades. A liquid mixture is said to show ideal behavior if the variations in density and sound velocity etc., with mole fraction of the solute are linear. Ultrasonic velocity and adiabatic compressibility, which can be measured accurately, reflect the degree of deviation from ideal behavior. These deviations from the ideal behavior have been widely used for the study of structural variations and molecular interactions in liquid mixtures.

The present investigation is related on thermodynamic properties of ternary liquid mixture of N-N dimethylformamide which a dipolar aprotic solvent with high is boiling point and good thermal and chemical stability. The study of N-N dimethylformamide is important because of its utilization in industry and medicine. N-N dimethylformamide is an excellent proton donor as well as proton acceptor and hence it is strongly associated through intermolecular hydrogen bond. It is highly soluble in a variety of polar and non-polar solvents and readily suitable to explore solvent-solvent interactions. It is used as a solvent in the production of acrylic and elasthane fibres, pharmaceuticals, antibiotics and polyimide resins. Benzoic acid is a polar solvent used in rare metal extraction, antibiotics and other pharmaceuticals, cellulose and resin based coatings and adhesives. Ethylene Glycol is a non-polar liquid used as a solvent in the production of cellulose plastics. In view of the importance mentioned above an attempt has been made to elucidate the molecular interaction in ternary liquid mixture of N-N dimethylformamide, benzoic acid and Ethylene Glycol at different frequencies at constant temperature 308K.

Departure from linearity in the velocity versus concentration in liquid mixture is taken as an indication of the existence of molecular interactions between different species. The physicl-chemical properties of liquid mixture can be studied by the nonlinear variation of ultrasonic velocity and other related parameters with the variation of concentration in the liquid mixture.[5-11]

Theory

The acoustical parameters such as adiabatic compressibility (Ks), intermolecular free length (Lf), acoustic Impedance (Z), molar volume (Vm) and available volume (Va) have been calculated using the measured data (U and ρ) from the following relations.

$$K_s = (U^2\rho)^{-1} \quad (1)$$

$$L_f = k\,(K_S)^{1/2} \quad (2)$$

$$Z = \rho U \quad (3)$$

$$V_m = M/\rho \quad (4)$$

$$V_a = (M/\rho)\,[1-(U/U_\infty)] \quad (5)$$

Where k is a temperature dependent constant, M is the molecular mass of the liquid mixture and U_∞=1600 m/s.

The excess values of the above acoustical parameters have been calculated from the following relations.

$AE = A_{exp} – (X_1A_1 + X_2A_2 + X_3A_3)$ (6)

Where X1, X1 and X3 are mole fractions of N-N dimethylformamide, benzoic acid and Ethylene Glycol respectively and A is any acoustic parameter.

Molar sound velocity(R), molar compressibility (B), Lennard Jones potential repulsive term exponent (n), relative association (RA) and interaction parameter (χ) have been calculated from the following relations.

$R= (M/\rho) U^{1/3}$ (7)

$B= (M/ \rho) (Ks)^{-1/7}$ (8)

$n= (6 V_m / Va) - 13$ (9)

$R_A= (\rho / \rho 0) (U0/ U)^{1/3}$ (10)

$\chi = (U/_{Uideal})^2 -1$ (11)

Where ρ0 and U0 are density and ultrasonic velocity of N-N dimethylformamide respectively.

The ideal mixing velocity U_{ideal} is given by

$U_{ideal} = X_1U_1+X_2U_2+ X_3U_3$ (12)

EXPERIMENTAL METHODS

Materials

The chemicals used were of analytical reagent (AR) and spectroscopic reagent (SR) grade which were obtained from E Merck Ltd (India) and were used as such without further purification. The ternary liquid mixtures of various concentrations were prepared out of which the mole fraction of benzoic acid was kept fixed at 0.4. The mole fractions of N-N dimethylformamide and Ethylene glycol were varied from 0 to 0.6 to have the mixture of different compositions.

Density Measurement

The density of liquid mixture was determined by a specific gravity bottle of 10ml capacity. The specific gravity bottle with the liquid mixture was immersed in a temperature controlled water bath. The density was determined using the relation.

$\rho_2 = (w_2/w_1) \rho 1$ (13)

Where w_1, w_2, ρ_1 and ρ_2 are mass of distilled water, mass of liquid mixture, density of distilled water and density of liquid mixture respectively.

Velocity Measurement

The velocity of ultrasonic waves in the liquid mixture was measured by using multi frequency interferometer (Model M-82S) with a high degree of accuracy operating at different frequencies. The measuring cell of the interferometer is a specially designed double walled vessel with provision to circulate water at constant temperature i.e.308K. The high frequency generator excites a quartz crystal fixed at the bottom of the vessel, at its resonant frequency. A fine micrometer screw at the top of the cell is used to raise or lower the reflector plate in the liquid through a known distance. The measuring cell is connected to the output terminals of the high frequency generator through a cable. Ultrasonic waves normal to quartz crystal are reflected from the reflector plate. Stationary waves are formed in the region between reflector plate and the quartz crystal. The micrometer is slowly moved till a number of maximum readings (N) of the anode current is passed. The total distance (d) moved by the micrometer is noted. The ultrasonic velocity was determined using the relation

$$U = \lambda f \qquad (14)$$

Where wavelength of the ultrasonic waves in the binary liquid mixture $\lambda = 2d/N$ and f is the frequency of the generator.

RESULTS AND DISCUSSION

The experimental values of density and ultrasonic velocity at 308K for frequencies 2MHz, 4MHz, 6MHz and 8MHz for pure liquids and ternary liquid mixture were used to calculate the acoustical parameters and the relevant data are presented in Tables 1 to 5 and displayed graphically in Figures 1 to 9. Experimentally measured density (ρ) and ultrasonic velocity (U) of pure liquids at 308K and at different frequencies are shown in Table 1.

Table 2 and Figure 1 show that density ρ increases with the increase in mole fraction of DMAC. The increase in density indicates the presence of solvent-solvent interactions in the ternary mixture which may bring a bonding between them.[11] Table 2 and Figure 2 show that ultrasonic velocity U in the ternary mixture increases with the increase in mole fraction of DMS. The structural changes occurring in the ternary mixture with the increase in concentration may cause the increase in ultrasonic velocity at a particular frequency which may result in the increase in intermolecular forces.

Table 1: Values of density (ρ) and ultrasonic velocity (U) of pure liquids.

Organic Liquids	ρ Kgm^{-3}	U ms^{-1}			
		2MHz	4MHz	6MHz	8MHz
Dimethyl acetamide	925	1488	1472	1464	1440
Isobutyl methyl ketone	765	1160	1152	1140	1120
Diethyl ether	693	928	912	904	880

Table 2: Values of density (ρ) and ultrasonic velocity (U) for DMS + benzoic acid + Ethylene glycol.

Mole Fraction		ρ Kgm^{-3}	U ms^{-1}			
X_1	X_3		2MHz	4MHz	6MHz	8MHz
0	0.6	722	1034	1016	1008	1000
0.1	0.5	745	1078	1066	1056	1036
0.2	0.4	769	1138	1128	1116	1108
0.3	0.3	792	1172	1156	1140	1128
0.4	0.2	815	1214	1200	1194	1180
0.5	0.1	838	1264	1252	1248	1244
0.6	0	860	1328	1320	1308	1296

The experimental results are in good according to which the ultrasonic velocity increases with the decrease in intermolecular free length in the liquid mixture and vice versa. Therefore, intermolecular free length is one of the predominating factors for deciding the nature of variation in ultrasonic parameters in the liquid mixture. In the present study the decrease in intermolecular free length causes increase in ultrasonic velocity, decrease in adiabatic compressibility, and increase in density and acoustic impedance as the concentration of DMS increases.

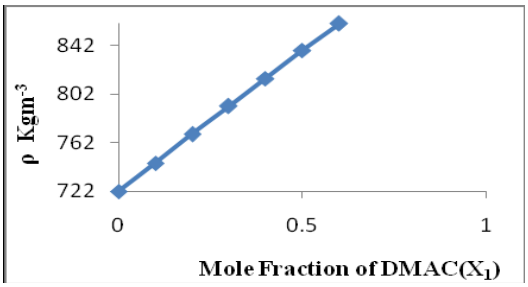

Figure 1: Variation of ρ versus X_1.

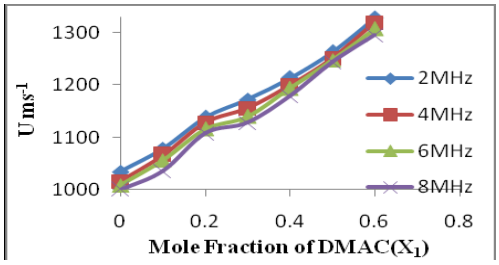

Figure 2: Variation of U Versus X_1

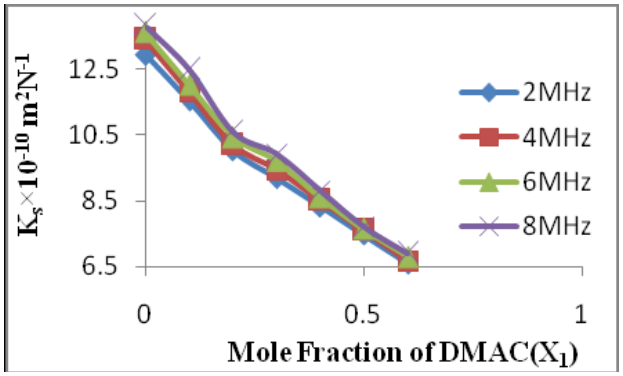

Figure 3: Variation of Ks Versus X_1.

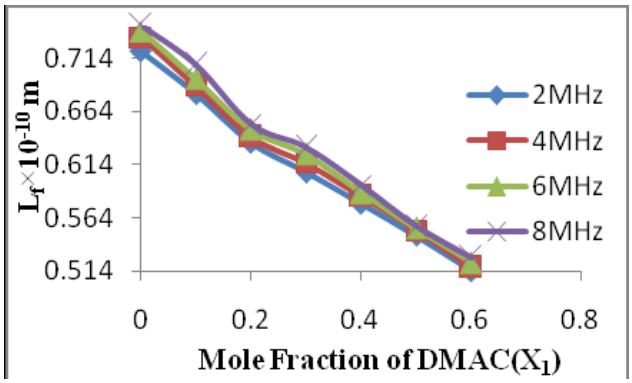

Figure 4: Variation of Lf Versus X1.

In order to know the nature of interactions between the component molecules of the ternary liquid mixture, it is of interest to discuss the same in terms of the excess values of acoustical parameters rather than the actual values. It is learnt that dispersive forces are responsible for weak interaction between unlike molecules. This leads to positive excess values of adiabatic compressibility, intermolecular free length, molar volume and available volume and negative excess values of velocity and acoustic impedance. The attractive forces are responsible for strong interaction between unlike molecules which leads to negative excess values of adiabatic compressibility, intermolecular free length, molar volume and available volume and positive excess values of velocity and acoustic impedance. Non-ideal liquid mixtures show considerable deviation from linearity from their physical properties with respect to mole fraction and these have been interpreted as the presence of both strong and weak interactions

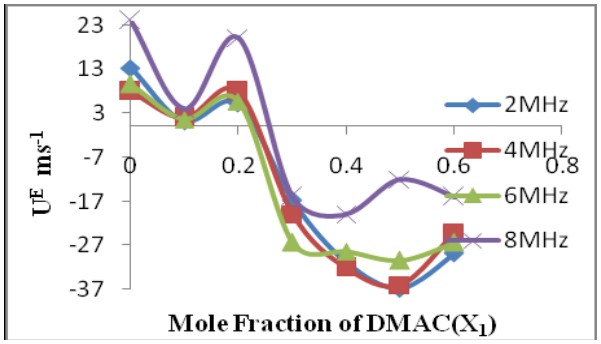

Figure 7: Variation of UE Versus X_1.

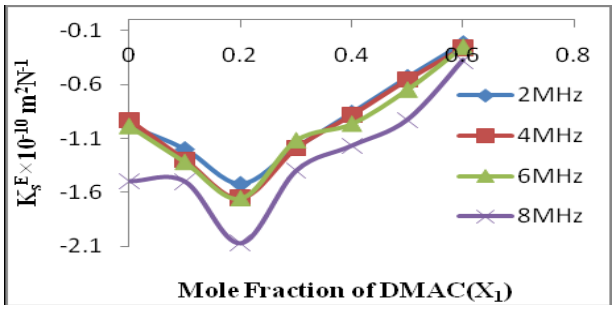

Figure 8: Variation of K_s^E Versus X_1.

Table 5 and Figure 7 show that the values of excess velocity UE are positive for the mole fraction of DMS between 0 to 0.2 and negative for the mole fraction of DMS between 0.3 to 0.6 for all frequencies. The positive values of UE indicate the presence strong molecular interactions at lower concentration of DMS. The negative values of UE indicate the presence dispersive forces between unlike molecules in the ternary mixture.

The values of K_s^E are negative as shown in Table-6 and Figure 8 for the entire range of mole fraction of DMS for frequencies 2MHz, 4MHz, 6MHz and 8MHz. The negative value of K_s^E is associated with a structure forming tendency but the positive value is associated with a structure breaking tendency due to hetero-molecular interaction between the component molecules of liquid mixture.[15] In the present investigation the negative values of K_s^E predict the existence of strong molecular interactions in the ternary liquid mixture.

Table 6 and Figure 9 show that the values of L_f^E are negative for the entire range of mole fraction of DMS for all frequencies. The positive excess values of free length are attributed to the dispersive forces and the negative excess values of L_f^E are due to due to charge transfer, formation of hydrogen bond, dipole-induced dipole and dipole-dipole interactions. In the present study the negative excess values of L_f^E predict the existence of strong molecular

interactions in the ternary mixture due to charge transfer, formation of hydrogen bond, dipole-induced dipole and dipole-dipole interactions.

Table 5: Values of excess velocity (UE) the ternary mixture for DMS + benzoic acid+ Ethylene glycol.

Mole Fraction		U^E ms^{-1}			
X_1	X_3	2MHz	4MHz	6MHz	8MHz
0	0.6	13.2	8	9.6	24
0.1	0.5	1.2	2	1.6	4
0.2	0.4	5.2	8	5.6	20
0.3	0.3	-16.8	-20	-26.4	-16
0.4	0.2	-30.8	-32	-28.4	-20
0.5	0.1	-36.8	-36	-30.4	-12
0.6	0	-28.8	-24	-26.4	-16

The values of excess molar volume VmE are negative for the of mole fraction of DMS between 0.1 to 0.6 for all frequencies and positive in the absence of DMS as shown in Table 7 and Figure 10. Excess molar volume is influenced by (i) the loss of dipolar association and the difference in size and shape (ii) dipole-dipole and dipole-induced dipole interactions or charge transfer complexation between the unlike molecules.

Table 6: Excess values of adiabatic compressibility (KsE) and free length (LfE) for DMS + Benzoic acid+ Ethylyne glycol.

Mole Fraction		$K_s^E \times 10^{-10}$ m^2N^{-1}				$L_f^E \times 10^{-10}$ m			
X_1	X_3	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	0.6	-0.9849	-0.9318	-0.9864	-1.4982	-0.0207	-0.0183	-0.0195	-0.032
0.1	0.5	-1.2014	-1.3012	-1.3195	-1.5003	-0.0231	-0.0249	-0.025	-0.0283
0.2	0.4	-1.5234	-1.6573	-1.654	-2.0721	-0.0315	-0.0342	-0.0334	-0.044
0.3	0.3	-1.1851	-1.193	-1.1182	-1.3992	-0.0212	-0.0202	-0.0172	-0.0242
0.4	0.2	-0.8646	-0.8848	-0.9652	-1.1684	-0.0127	-0.0126	-0.0147	-0.0199
0.5	0.1	-0.5338	-0.557	-0.6493	-0.9274	-0.0055	-0.0059	-0.0087	-0.0175
0.6	0	-0.222	-0.26	-0.2532	-0.3735	-0.0009	-0.0024	-0.0018	-0.006

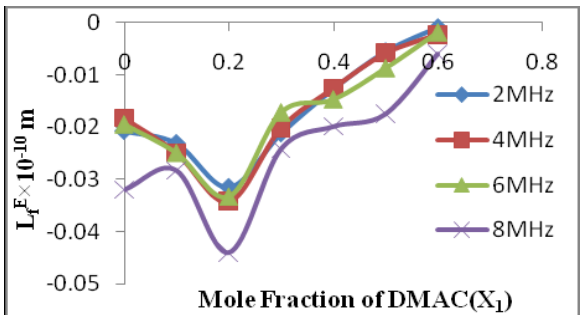

Figure 9: Variation of L_f^E Versus X_1

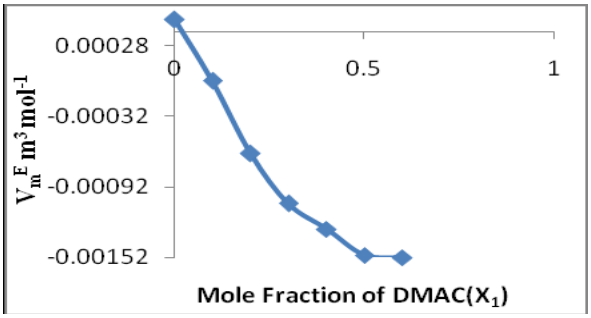

Figure 10: Variation of V_m^E Versus X_1.

Table 7: Excess Values of molar volume VmE, acoustic impedance (ZE) and available volume (VaE) for DMS + Benzoic acid + Ethylene glycol.

Mole Fraction		V_m^E m³ mol⁻¹	$Z^E \times 10^5$ Kgm²s⁻¹				V_a^E m³mol⁻¹			
X_1	X_3		2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	0.6	0.0005	0.0572	0.0183	0.0304	0.1337	0.00006	0.00052	0.00026	-0.00074
0.1	0.5	-0.00002	-0.1174	-0.105	-0.1077	-0.0902	0.00009	0.00005	0.00002	-0.00007
0.2	0.4	-0.00064	-0.1236	-0.102	-0.1206	-0.01	-0.00088	-0.0011	-0.00102	-0.002
0.3	0.3	-0.00106	-0.3259	-0.3504	-0.4016	-0.319	0.00005	0.00024	0.00064	-0.00003
0.4	0.2	-0.00128	-0.4473	-0.4555	-0.427	-0.5504	0.00058	0.00068	0.0004	-0.00016
0.5	0.1	-0.0015	-0.4824	-0.4734	-0.4276	-0.2723	0.00071	0.00062	0.00016	-0.00109
0.6	0	-0.00152	-0.3872	-0.3427	-0.3648	-0.2736	-0.00006	-0.0004	-0.0002	-0.001

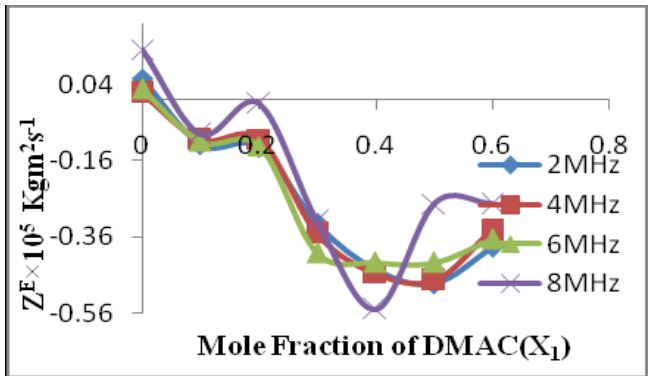

Figure 11: Variation of ZE Versus X_1.

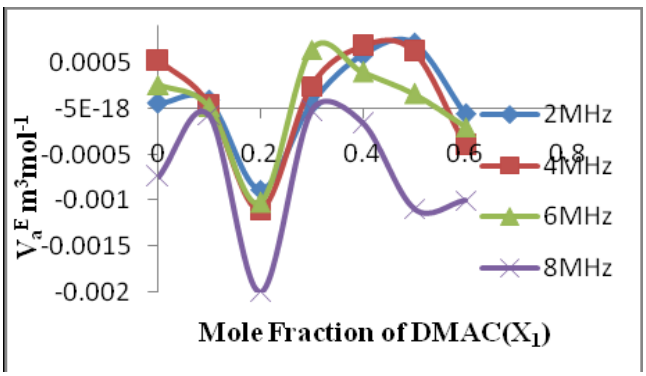

Figure 12: Variation of VaE Versus X_1.

The values of excess acoustic impedance Z^E are negative for the mole fraction of DMS between 0.1 to 0.6 as shown in Table 7 and Figure 11 for all frequencies and positive in the absence of DMS in the liquid mixture. The negative values of Z^E indicate the presence of dispersive forces between unlike molecules in the ternary mixture. Table 7 and Figure 12 show that the values of excess available volume V_a^E are both negative and positive which indicate the presence of strong interactions and dispersive forces in the liquid mixture.[16] The excess acoustic parameters are also changed with the increase in frequency in the ternary mixture.

CONCLUSION

On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and some of their excess values for the ternary liquid mixture, it is concluded that there exists molecular association and molecular interaction between components in the ternary liquid mixture of DMS, Benzoic acid and Ethylene glycol. The negative excess values of adiabatic compressibility and intermolecular free length indicate a strong molecular interaction in the ternary mixture due to charge transfer, formation of hydrogen bond, dipole-induced dipole and dipole-dipole interactions.

REFERENCES

1. A. K. Dash and R. Paikaray, “Acoustical study in binary liquid mixture containing dimethyl acetamide using ultrasonic and viscosity probes”, Der Chem. Sinica, 2014; 5(1): 81-88.
2. R. Palani, S. Saravanan and R. Kumar, “Ultrasonic studies on some ternary organic liquid mixtures at 303, 308 and 313K”, RASAYAN J. Chem., 2009; 2(3): 622-629.
3. R. Paikaray and N. Mohanty, “Evaluation of Thermodynamical Acoustic Parameters of Binary mixture of DBP with Toluene at 308K and at Different Frequencies”, Research Journal of Chemical Sciences, 2013; 3(5): 71-82.
4. A. A. Mistry, V. D. Bhandakkar and O. P. Chimankar, “Acoustical studies on ternary mixture of toluene in cyclohexane & nitrobenzene at 308k using ultrasonic technique”, J. of Chem. and Pharm. Res, 2012; 4(1): 170-174.
5. R. Uvarani and J. Sivapragasam, “Intermolecular interaction studies on ternary liquid mixtures at 303K”, J. of Chem. and Pharm. Res, 2012; 4(1): 653-655.

6. C. Shanmuga Priya, S. Nithya, G. Velraj and A. N. Kanappan, "Molecular interactions studies in liquid mixture using ultrasonic technique", Int. J. of Adv. Sc. and Tech, 2010; 18: 59-73.
7. M. K. Praharaj, P. R. Mishra, S. Mishra and A. Satapathy, "Study of thermodynamic and transport properties of ternary liquid mixture at different temperatures", Adv. in Appl. Sc. Res, 2012; 3(3): 1518-1530.
8. S. K. Pradhan, S. K. Dash, L. Moharana and B. B. Swain, "Molecular interaction parameters of binary mixtures of diethyl ether and apolar solvents using ultrasonic probe" Indian J Pure and Appl. Phys, 2012; 50: 161-166.
9. R. Kubendram, F. L. Ali Khan, J. Asghar, M. Aravinthraj and J. Udayaseelan, "Ultrasonic studies of N, N-dimethylacetamide and N-methylacetamide with alkoxyethanols in carbon tetrachloride at different temperatures", Arch. in Appl. Sc. Res, 2011; 3(2): 568-576.
10. V. Kanappan and J. R. Santhi, "Ultrasonic study of induced dipole-dipole interactions in binary liquid mixtures", Indian J Pure and Appl. Phys, 2005; 43: 750-754.
11. R. Natrajan and P. Ramesh, "Ultrasonic velocity determination in binary liquid mixtures", J. Pure appl. And Ind. Phys, 2011; 1(4): 252-258.
12. D. Bhatnagar, D. Joshi, R.Gupta, Y. Kumar, A. Kumar and C. L. Jain, "Studies on Thermo acoustic Parameter in Binary Liquid Mixtures of MIBK with 1-Propanol and 1-pentanol at 303.15K-A new approach by Direct Measurement of Acoustic Impedance", Res. J. of Chem. Sc, 2011; 1(5): 6-13.
13. H. Eyring and J. F. Kincaid, "Free Volumes and Free Angle Ratios of Molecules in Liquids", J. Chem. Physics Chem. Physics, 1938; 6: 620-629.
14. M. K. Praharaj, P. R. Mishra, S. Mishra and A. Satapathy, "Ultrasonic study of ternary liquid mixture containing substituted benzene", Arch.of. Phys. Res, 2012; 3(3): 192-200.
15. S. Thirumaran and M. Rajeswari, "Acoustical studies on binary liquid mixtures of some aromatic hydrocarbons with dimethylsulphooxide (DMSO) at 303.15K", Arch.of. Phys. Res, 2011; 2(2): 149-156.
16. K. Rajagopal and S. Chenthilnath, "Excess thermodynamic studies of binary mixtures of 2-methyl 2-propanol with ketones", Indian J. Pure and Appl. Phys, 2010; 48: 326-333.
17. A. K. Gupta, K. Kumar and B. K. Karn, "Studies of binary liquid mixtures of o-cresol with ethylmethyl ketone, acetone acetophenone and ethylacetate", J. Ind. Coun. Chem, 2009; 26: 77-81.

18. A. K. Dash and R. Paikaray, "Ultrasonic Study on Ternary Mixture of Dimethyl Acetamide (DMAC) in Diethyl ether and Acetone", Res. J. of Phys. Sc, 2013; 1(3): 12-20.
19. A. K. Dash and R. Paikaray, "Study of molecular interaction in binary liquid mixture of dimethyl acetamide and acetone using ultrasonic probe", Adv. in Appl. Sc. Res, 2013; 4(3): 130-139.
20. A. K. Dash and R. Paikaray, "Acoustical study on ternary mixture of dimethyl acetamide (DMAC) in diethyl ether and isobutyl methyl ketone at different frequencies", Phys. and Chem. of Liquids, 2013; 51(6): 749-763.