International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2015 Vol. 5 (1) January-March, pp. 25-31/Tumberphale et al.
Research Article

ULTRASONIC BEHAVIOUR OF BINARY MIXTURE OF ETHANOL IN ETHYLENE DIAMINE AT 3 MHZ FREQUENCY

***Tumberphale U.B.[1], Kawale R.S.[2], Pawar N.P.[1] and Kalamse V.G.[1]**
[1]Department of Physics, N.E.S. Science College, NANDED-431605, Maharashtra, India
[2]Department of Electronics, D.S.M. College, Jintur, Dist: Parbhani-431509, Maharashtra, India
**Author for Correspondence*

ABSTRACT
The measurement of Ultrasonic velocity (U) has been employed to understand the molecular interactions in the liquid mixtures. Ultrasonic velocity (U) and density (ρ) for the binary liquid mixtures of n-propyl alcohol (nPA) with Ethylene diamine (EDA), have been measured for 3MHz ultrasonic frequency at room temperature. The experimental data have been used to calculate acoustic parameters such as Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A), relaxation time (τ). These parameters are used to explain the formation of complex and the results are interpreted in terms of molecular interaction between the components of the mixture

Keywords: *Ultrasonic Velocity, Adiabatic Compressibility, Intermolecular Free Length, Ethylene Diamine*

INTRODUCTION
Mixed solvents, rather than pure solvents find practical applications in most chemical processes, their properties are less known. Derived parameters from Ultrasonic velocity measurements and the corresponding excess functions provide qualitative information regarding the nature and strength of molecular interactions in liquid mixtures (Ali *et al.,* 2002).
In recent years, ultrasonic technique has become powerful and reliable tools for the study of molecular interactions in pure liquids as well as liquid mixtures (Ubagaramary *et al.,* 2012; Shaik *et al.,* 2011). Study of molecular interactions between solute and solvent media has got great importance in many field of science including medicinal chemistry, industrial processes, biochemistry etc.
Speed of sound itself is highly sensitive to the structure and interactions present in the liquid mixtures as it is fundamentally related to the binding process between the constituents of the medium. For the qualitative estimation of the molecular interactions in solutions, the ultrasonic velocity approach was first studied by lageman (Sreekanth *et al.,* 2001). Alcohols have found various applications and commercial use in medical and other fields, for example, the largest single use of ethanol is as a motor fuel and fuel additive. Ethanol is used in medical wipes. Ethanol kills organisms by denaturing their proteins and dissolving their lipids and is effective against most bacteria and fungi, and many viruses.
Ethylene diamine (EDA) is used primarily as an intermediate in the production of bleach activators, fungicides, chelating agents, plastic lubricants, textile resins, polyamides and fuel additives. Therefore it seemed important to examine the ultrasonic behaviour of n-propyl alcohol (nPA) with ethylene diamine (EDA).

MATERIALS AND METHODS
Ethanol and ethylene diamine (EDA) used were of AR grade with minimum assay of 99.9% procured form S.D. fine chemicals and Spectrochem Pvt. Ltd. Mumbai. These chemicals are used without further purification. Samples of solution with different mole fraction EDA were prepared. The density (ρ) and viscosity (η) of pure liquids and liquid mixtures were determined by using Pycknometer and Ostwald's viscometer respectively. The Ultrasonic velocity (U) in the liquid and liquids mixtures have been measured using an Ultrasonic Fixed-frequency interferometer (Mittal type Model F-05.)

Theory
The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), free length (L_f), Acoustical impedance

(Z), Relative association (R_A), relaxation time (τ), Effective molecular weight (M_{eff}), molar volume (V_m) by the following relations (Shaik *et al.*, 2011; Gajendra *et al.*, 2012; Kawale *et al.*, 2013).

$$\beta_{ad} = \frac{1}{\rho U^2} \quad \ldots (1)$$

$$L_f = K\,(\beta_{ad})^{1/2} \quad \ldots (2)$$

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

$$R_A = \frac{\rho_s}{\rho_0}\left(\frac{U_0}{U_s}\right)^{1/3} \quad \ldots (4)$$

And $$\tau = 4/3\ \eta\ \beta_{ad} \quad \ldots (5)$$

Where, K – Temperature dependent constant, ρ_o- the density of the solvent, U_o- ultrasonic velocity of the solvent, ρ_s – the density of the solutions, U_s- the ultrasonic velocity of the solutions, V_m- Molar volume.

$$M_{eff} = \Sigma\, m_i x_i \quad \ldots (6)$$

$$V_m = M_{eff} / \rho \quad \ldots (7)$$

On assuming the additives of molar sound velocity (R) and no volume change on mixing. Nomoto established the relation for ultrasonic velocity in binary liquid mixtures.

$$U = \left[\frac{(X_1R_1 + X_2R_2)}{(X_1V_1 + X_2V_2)}\right]^3 \quad \ldots (8)$$

Where, X_1, X_2 are the mole fractions of the species and R is related to the molecular weight (M) and density (ρ) as:

$$R = \frac{M}{\rho}\,U^{1/3} = VU^{1/3}$$

Where, U is the ultrasonic velocity and the molar volume is given by

$$V = \frac{(M_1X_1 + M_2X_2)}{\rho}$$

On the basis of ideal mixing of adiabatic compressibility Van Dael obtained ideal mixing relation for ultrasonic velocity

$$\frac{1}{U^2} = (M_1X_1 + M_2X_2)\left(\frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2}\right) \quad \ldots (9)$$

Where, U = Ideal mixing Ultrasonic Velocity in liquid mixture.U_1 & U_2 are ultrasonic velocities in species and X_1 and X_2 are mole fractions of the species.

The impendance relation is

$$U_{IR} = \frac{\sum X_iZ_i}{\sum X_i\rho_i} \quad \ldots (10)$$

Where, Z_i is Acoustic Impedance.

Rao's specific sound velocity relation is

$$U_{Rao} = (\sum X_i\, r_i\rho_i)^3 \quad \ldots (11)$$

Where, $r_i = \frac{(U_i)^{1/3}}{\rho_i}$

According to the simple mixing Relation,

$$U_{SMR} = U_1X_1 + U_2X_2 \quad \ldots (12)$$

Jungie's equation is

$$U_j = \frac{\left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right)}{\left[(M_1X_1 + M_2X_2)^{1/2}\left(\frac{M_1X_1}{\rho_1U_1^2} + \frac{M_2X_2}{\rho_2U_2^2}\right)^{1/2}\right]} \quad \ldots (13)$$

Where, M1, M2 are molecular weights of constituent components. P1 and P1 are the densities of constituent components.

The strength of interaction between the component molecules is well reflected in the deviations, in excess viscosity (Δη) Excess Adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f), Excess Acoustic impedance (ΔZ) etc. These parameters were calculated using the relation.

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2) \quad \ldots (13)$$

Where, ΔY is any excess parameter, and y refers to above mentioned parameter. The subscripts m, 1 and 2 used in the above equation are respectively for the mixture, component (1) and component (2). X_1 and X_2 are the mole fractions of two components in the liquid mixture.

RESULTS AND DISCUSSION

The values of density (ρ), ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z), and relative association (R_A), Relaxation time (τ) of the binary liquid mixture of EDA + ETHANOL obtained at 303 K are listed in table (1) and the values of excess viscosity ($\Delta\eta$), excess ultrasonic velocity (ΔU), Excess adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f) are reported in table (2).

Values of Ultrasonic velocity (U) along with the values calculated by using the Nomoto relation, Van Dael ideal mixing relation, Impedance relation, Rao's specific velocity relation Simple mixing relation, and Junjie's equation are listed in table (3). The validity of different theoretical formulae is checked by percentage deviation.

From figure (1), it is observed that ultrasonic velocity (U) increases with mole fraction of EDA non-linearly which indicates that there is intermolecular interaction exists with mixture (R.S. Kawale et al, 2013) . The maximum deviation from the linearity at a point of mole fraction, where change in the slope is maximum indicating the complex formation (Tumberphale, 2013). In present system the formation of the complex is at 0.5 mole fraction of EDA.

On the basis of the model for the sound propagation proposed by Eyring and Kincaid ultrasonic velocity (U), increases on decrease of intermolecular free length (L_f) and vice-versa (Kawale *et al.*, 2013) as shown in figure (2). Also the maximum deviation from linearity in the intermolecular free length curve occurs at 0.5 mole fraction of EDA which supports to our earlier conclusion.

Adiabatic compressibility (β_{ad}) decreases with increases in concentration of EDA as shown in Figure (3). indicates that the free dipoles of Ethanol molecules would induced moments in the neighbouring molecules of the EDA resulting in dipolar - induced dipolar interaction leading to contraction in the volume. This leads to subsequent decrease in the adiabatic compressibility (β_{ad}) as well as intermolecular free length (L_f) (Kawale *et al.*, 2013) as shown in figure (3) & (2) respectively. Also the maximum deviation occurs at 0.5 mole fraction of EDA supports to our earlier conclusion drawn in ultrasonic velocity curve.

Specific acoustic impedance (Z) of the medium is governed by the inertial & elastic properties of the medium (Thirumaran *et al.*, 2009). In the present system the acoustic impedance (Z) increases with increase in concentration of EDA. Increasing trend of acoustic impedance supports the possibility of the molecular interaction between solute and solvent molecules as shown in fig 4. Also, relaxation time (τ) in table (1) have completely reverse trend with that of ultrasonic velocity. This indicates significant molecular interactions (Bedare *et al.*, 2012).

Figure (5) represents the variations of Excess free length (ΔL_f) with mole fraction of EDA. As observed ΔL_f values are negative over entire range indicates presence of intermolecular interactions in the system (Bhatnagar *et al.*, 2010). The maximum negative value of Excess free length (ΔL_f) at the 0.5 mole fraction of EDA indicates the formation of complex.

Figure (6) shows the variation of excess adiabatic compressibility ($\Delta\beta_{ad}$) with mole fraction of EDA. The values of ($\Delta\beta_{ad}$) are negative over entire concentration range, this suggests the strong molecular interaction between the unlike molecules of the component liquids (Thirumaran *et al.*, 2011). The maximum negative value of ($\Delta\beta_{ad}$) exists at 0.5 mole fraction of EDA indicates the formation of complex this supports to our earlier conclusion.

The excess viscosity ($\Delta\eta$) values are positive over entire range indicating the strong interaction between unlike molecules of the system.

From the figure 7, it can be seen that the values of ultrasonic velocity computed by various theories shows deviations from experimental values. The bracketed values are represents the percentage deviations in theoretical values with respect to the experimental values of ultrasonic velocity shown in table (3). The limitations and approximations incorporated in these theories are responsible for it. It is assumed that all the

molecules are spherical in shape, which is not true every time (Rama *et al.,* 2005). In Nomoto theory, it is supposed that the volume does not change on mixing. Thus, no interaction between the components of liquid mixtures has been taken into account. Similarly, the assumptions for the formation of ideal mixing relation are that, the ratios of specific heats of ideal mixtures and volumes are also equal. Again no molecular interaction is taken into account. But on mixing two liquids, the interactions between the molecules of the two liquids takes place because of the presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and diploe-induced dipole interactions. Thus, the observed deviation of theoretical values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixtures.Fig.7 shows that in the system of EDA and Ethanol, there is a good agreement between the experimental and theoretical values calculated by Impedance relation and Rao's relation. Here, smaller deviations are observed for Nomoto's relation, where as higher deviations are observed in Van Dael ideal mixing relation and Junjee's relation

The higher deviations in some intermediate concentration range suggest the existence of strong tendency for the association between the component molecules, where hydrogen bonding may be formed (Rama *et al.,* 2005).

Table 1: The values of density (ρ), ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z) and relative association (R_A) of the binary liquid mixture of EDA+ Ethanol with mole fraction of EDA

Mole fraction of EDA (X)	P (Kg m^{-3})	Viscosity	Sq. of R.I.	U (ms^{-1})	ß$_{ad}$ ($10^{-10}m^2N^{-1}$)	L_f (10^{-11}m)	Z ($10^6kgm^{-2}s^{-1}$)	R_A	τ x10^{-13}
0.0000	789.00	1.1000	1.8541	1176.00	9.16449	6.23622	0.927864	1.0000	13.4412
0.1405	815.39	1.4326	1.9080	1237.80	8.00449	5.82819	1.009290	1.01595	15.2896
0.2761	835.39	1.5692	1.9386	1313.10	6.94490	5.42875	1.096570	1.02023	14.5305
0.4111	851.23	1.6895	1.9780	1403.10	5.96727	5.03217	1.194361	1.01720	13.4421
0.4643	854.59	1.7804	2.0063	1458.00	5.50462	4.83316	1.245992	1.00824	13.0671
0.6560	854.68	1.8322	2.0264	1516.26	5.08920	4.64720	1.295917	0.99526	12.4326
0.7744	854.78	1.7852	2.0522	1568.52	4.75516	4.49211	1.340740	0.98419	11.3185
0.8891	854.68	1.7424	2.0750	1613.10	4.49649	4.36822	1.378684	0.97493	10.6785
1.0000	899.00	1.7000	2.1228	1658.84	4.0423	4.1417	1.491297	---	9.16254

Table 2: The values of Excess viscosity (Δη), Excess ultrasonic velocity (ΔU), Excess adiabatic compressibility (Δ β_{ad}), Excess intermolecular free length (Δ L_f) of the binary liquid mixture of EDA+ Ethanol with mole fraction of EDA

Mole fraction of EDA (X)	Excess Viscosity (Δη)	Excess Ultrasonic Velocity (ΔU) ms^{-1}	Excess Adiabatic compressibility Δ ß$_{ad}$ ($10^{-10}m^2N^{-1}$)	Excess intermolecular free length Δ L_f (10^{-11}m)	Excess Acaustic Impendence ΔZ ($10^6kgm^{-2}s^{-1}$)
0.0000	0.0000	0.0000	0.0000	0.0000	0.00000
0.1405	0.2483	-6.0390	-0.4403	-0.1137	0.0022
0.2761	0.3035	3.7878	-0.8053	-0.2292	0.0131
0.4111	0.3428	28.6044	-1.0915	-0.3430	0.0348
0.4643	0.4018	57.8173	-1.2816	-0.4305	0.0564
0.6560	0.3386	23.5169	-0.7151	-0.2150	-0.0015
0.7744	0.2205	18.6087	-0.4427	-0.1221	-0.0234
0.8891	0.1089	7.8069	-0.1138	-0.0057	-0.0502
1.0000	0.0000	0.0000	0.0000	0.0000	0.00000

Table 3: The values of density (ρ), Molar volume (V), ultrasonic velocity (U) expt, ultrasonic velocity (U) by various theoretical formulas such as Simple Mixing rule, Rao's relation, Impendance Relation, Nomato Relation, Vandeel Relation, Jungies Relation of the binary liquid mixture of EDA+ Ethanol with mole fraction of EDA

Mole fraction of EDA (X)	Molar Volume (V)	ρ (Kg m^{-3})	U (ms^{-1})	S.M. Rule	U_{Rao}	U_{iR}	Nomato Relation	Van Dael Relation	Jungies Relation
0.0000	0.05839	789.00	1176.00	1176.00	1175.99	1176.00	1175.84	1175.98	1324.04
				(0.00)	**(0.00)**	**(0.00)**	**(-0.013)**	**(-0.002)**	**(11.18)**
0.1405	0.05902	815.39	1237.80	1248.43	1237.81	1237.80	1244.19	1204.10	1364.54
				(0.851)	**(0.00)**	**(0.00)**	**(0.513)**	**(-2.798)**	(9.288)
0.2761	0.05998	835.39	1313.10	1309.31	1313.03	1312.64	1312.09	1238.26	1408.37
				(-0.289)	**(-0.005)**	**(-0.035)**	**(-0.076)**	**(-6.044)**	**(6.764)**
0.4111	0.06118	851.23	1403.10	1374.49	1403.18	1403.10	1378.00	1280.89	1456.72
				(-2.081)	**(0.005)**	**(0.00)**	**(-1.821)**	**(-9.540)**	**(3.680)**
0.4643	0.06184	854.59	1458.00	1400.18	1458.10	1457.99	1387.86	1300.44	1477.44
				(-4.129)	**(0.006)**	**(0.00)**	**(-5.053)**	**(-12.11)**	**(1.315)**
0.6560	0.06513	854.68	1516.26	1492.74	1516.35	1516.26	1497.72	1387.80	1559.56
				(-1.575)	**(0.005)**	**(0.00)**	**(-1.237)**	**(-9.256)**	**(2.776)**
0.7744	0.06715	854.78	1568.52	1549.90	1568.58	1568.52	1552.46	1459.56	1617.88
				(-1.201)	**(0.003)**	**(0.00)**	**(-1.034)**	**(-7.465)**	**(3.051)**
0.8891	0.06912	854.68	1613.10	1605.28	1612.40	1613.10	1607.10	1548.01	1681.16
				(-0.487)	**(-0.043)**	**(0.00)**	**(-0.373)**	**(-4.204)**	**(4.048)**
1.0000	0.06752	899.00	1658.84	1658.84	1659.72	1658.89	1658.69	1658.69	1749.66
				(0.00)	**(0.053)**	**(0.00)**	**(-0.009)**	**(-0.009)**	**(5.131)**

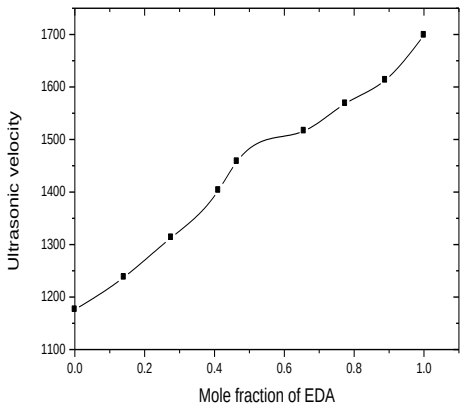


Figure 1: Variation of Ultrasonic velocity V/S Mole fraction of EDA

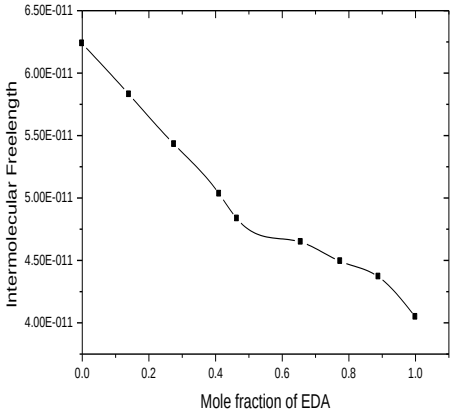


Figure 2: Variation of Intermolecular free length V/S Mole fraction of EDA

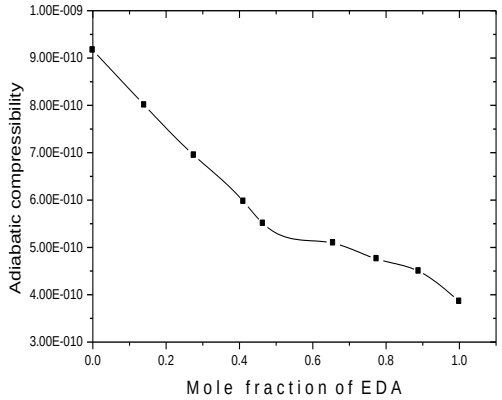


Figure 3: Variation of Adiabatic compressibility V/S Mole fraction of EDA

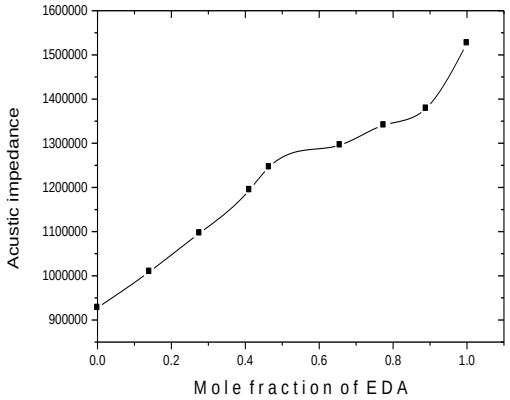


Figure 4: Variation of Acoustic impedance V/S Mole fraction of EDA

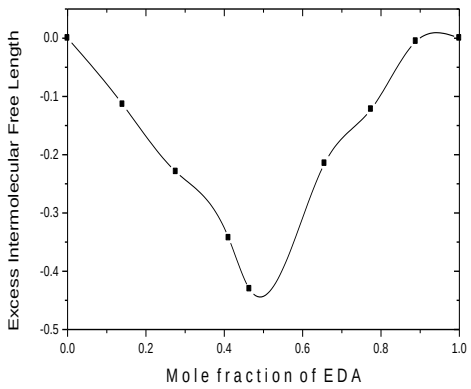


Figure 5: Variation of Excess Intermolecular free length V/S Mole fraction of EDA

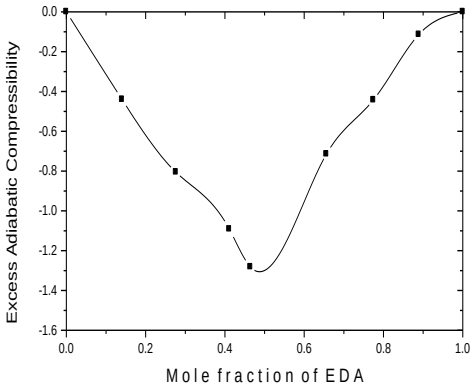


Figure 6: Variation of Excess Adiabatic compressibility V/S Mole fraction of EDA

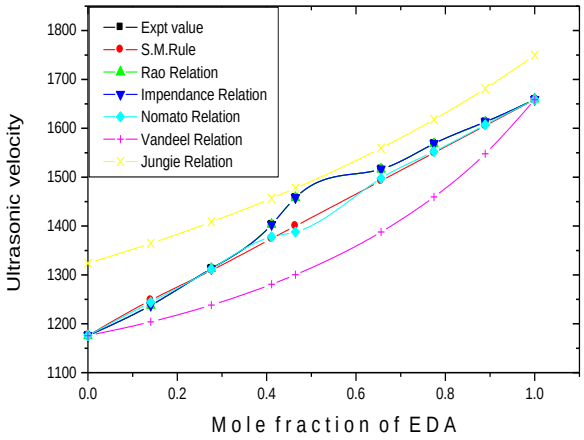
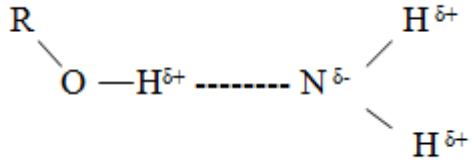


Figure 7: Variation of Theoretical Ultrasonic velocities V/S Mole fraction of EDA

In the present system the complex formation may be favoured by the linkage between $N^{\delta-}$ of EDA with $H^{\delta+}$ of Ethanol as represent below.



Conclusion

1. The acoustical parameters in the Ethanol + EDA system suggests the strong molecular interactions in the unlike molecules of the system.
2. Non linear behavior of Acoustic parameters suggests the formation of complex in the mixture.

REFERENCES

Ali A and Nain AK (2002). Ultrasonic study of molecular interaction in Binary liquid mixtures at 30^0C. *Pramana- Journal of Physics* **58**(4) 695-701.

Bedare GR, Bhandakkar VD and Suryavanshi BM (2012). Studies of Acoustic and Thermodynamic Properties of Binary liquid Mixtures at 308K. *Journal of Chemical & Pharmaceutical Research* **4**(2) 1028-1032.

Bhatnagar Deepa, Joshi Deepa, Gupta Reeta and Jain CL (2011). Studies on Thermo acoustic Parameters in binary liquid mixtures of MBIK with 1-propanol, 1-butanal & 1-pentand at 303.15 K. A new approach by Direct Measurement of Acoustic impedance. *Research Journal of Chemical Science* **1**(5) 6-13.

Gajendra Bedrare, Vivek Bhandakkar and Bhagwat Suryavanshi (2012). Study of Acoustical parameters of binary liquid mixtures. At 298 K. *International Journal of Applied Physics and Mathematics* **2**(3) 197-200.

Kawale RS, Tumberphale UB, Kalamse VG and Kalamse GM (2013). Ultrasonic Behaviour of Thiophenol in Benzene, carbon tetracholoride, Cyclohexane & n-Hexane. *Bionano Frontier* **6**(2) 204-206.

Narwade BS, Gawali PG, Rekha Pande and Kalamse GM (2005). Dielectric studies of Binary Mixtures of n-propyl alcohol and ethylene diamine. *Journal of Chemical Sciences* **117**(6) 673-676.

Rama Rao GV, Vishwanatha Sharma A, Siva Rama Krishna J and Ram Babu C (2005). Theoretical Evaluation of Ultrasonic velocities in binary liquid mixtures of o-chlorophenol at different temperatures. *Indian Journal of Pure and Applied Physics* **43** 345-354.

Shaik Babu and Radha Kirshanamurty A (2011). Ultrasonic studies on Binary mixtures of Acetyl Acetone at 301 K. *E-Journal of Chemistry* **8**(3) 1094-1101.

Sreekanth K, Sravana Kumar D, Kondaiah M and Krishna Rao D (2001). Study of molecular interactions in the mixtures of secondary alcohols with equimolar mixture of ethanol + formamide from acoustic and thermodynamic parameters. *Journal of Chemical and Pharmaceutical Research* **3**(4) 29-41.

Thirumaran S and Deepesh George (2009). Ultrasonic study of intermolecular association through hydrogen bonding in ternary liquid mixtures. *APRN Journal of Engineering & Applied Science* **4**(4).

Thirumaran S and Rajeswari M (2011). Acoustical studies on Binary liquid mixtures of some aromatic hydrocarbons with dimethyl sulphoxide (DMSO) at 303.15 K. *Archives of Physics Research* **2**(2) 149-156.

Tumberphale UB (2013). Ph.D. Thesis, S.R.T.M.U. Nanded 24-26.

Ubagaramary D and Neeraja P (2012). Ultrasonic study of molecular interaction in Binary liquid mixture at 308K. *IOSR Journal of Applied Chemistry* **2** 01-19.