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Thermo-Acoustical Molecular Interaction Studies in Birnary Liquid Mixtures by Ultrasonic Velocity Measurement (Diethylamine + n-Butanol)At 303.15K

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Abstract -Densities, viscosities and ultrasonic velocities has been measured for the binary mixture involving Diethyl amine (1) + n-Butanol (2) at 303.15K over the entire range of mole fraction. Parameters like adiabatic compressibility(β_a),inter molecular free length(L_f), relaxation time(τ), acoustical impedance(Z), bulk modulus(K), free volume(V_f),internal pressure (π_i), Gibb's free energy(ΔG), classical absorption coefficient(α/f^2), molar sound velocity (R) were calculated. The deviations of the liquid mixture from ideality have been explained based on the molecular interaction between unlike molecules. The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of the liquids.

Key Words: Diethylamine ,Ultrasonic velocity, Free length, adiabatic compressibility, relaxation time, molar sound velocity, internal pressure.

1. INTRODUCTION

The ultrasonic study of intermolecular interactions plays an important role in the development of molecular sciences. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements for liquid mixtures binary and ternary mixtures. Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behavior of liquid mixtures. Ultrasonic measurements of acoustic parameters with change in mole fraction give an insight in to the molecular process. This type of study has increased in recent years due to industrial applications. In the present paper, we report density, viscosity, ultrasonic velocity for the binary system consisting of Diethylamine + n-Butanolat 303.15K and atmospheric pressure over the entire composition range. The experimental results are used to calculate adiabatic compressibility,inter molecular free length, relaxation time, acoustical impedance, bulk modulus, free volume, internal pressure, Gibb's free energy, classical absorption coefficient, molar sound velocity. These parameters are used to discuss the nature of intermolecular interaction of mixtures. So, in the present work emphasis has been placed on the determination of the parameters of the organic liquid mixtures, namely, density, and speed of sound, which are industrially important.

2. EXPERIMENTAL

The binary mixtures were prepared by mass, by mixing the calculated volumes of liquid components in airtight glass bottles. In all the measurements, INSREF thermostat with a constant digital temperature display accurate to ±0.01K was used. For all the mixtures and pure solvent triplicate measurements were performed and the average of all values were considered in the calculation. The mass measurements (±0.0001g) were made using an electronic balance. The accuracy of density measurements was 0.0001g.cm^{-3}. A set of 11 compositions were prepared for binary mixtures respectively and also their physical properties were measured. Viscosity is measured by calibrated Ostwald's Viscometer. The speed of sound was determined using a constant frequency (2MHz) ultrasonic interferometer with an accuracy of ± 2 m.s^{-1}.

3. THEORY

The excess molar volume V^E was calculated from the density data by the relationship

$$V^E = V_M - \Sigma x_i V_i, \qquad (1)$$

where V_i represents the molar volume, x_i the mole fraction of the ith component and V_M is the molar volume of the mixture, given as

$$V_M = (x_1M_1+x_2M_2)/\rho_m, \qquad (2)$$

where ρ_m is the density of the liquid mixture.

The adiabatic compressibility β_a was obtained from sound velocity and density measurements as

$$\beta_a = 1/(u^2\rho) \quad (3)$$

The excess adiabatic compressibility was calculated as

$$\beta_a^E = \beta_a^m - \Sigma_i \varphi_i \beta_{ai}, \quad (4)$$

where the φ_i is the volume fraction of the ith liquid,

$$\varphi_i = x_i V_i / \Sigma_i x_i V_i, \quad (5)$$

The excess viscosity is obtained as

$$\eta^E = \eta_m - \Sigma_i x_i \eta_i , \quad (6)$$

Where η_m and η_i refer to the viscosity of the mixture and pure components respectively .

The Wada's constant was calculated using the formula

$$W = (M_{eff}\beta_a^{-1/7})/\rho \quad (7)$$

The inter molecular free length was calculated using the formula given by Jacobson et al.

$$L_f = K_J \sqrt{\beta_a} , \quad (8)$$

where $K_J$is Jacobson's constant.K_J is the temperature dependent parameter which varies directly with the square root of the absolute temperature i.e .,

$$K_J \alpha \sqrt{T} \quad (9)$$

The excess free length is given as

$$L_f^E = L_{f\,mix} - (\Sigma x_i L_{fi}) \quad (10)$$

Where xi andL_{fi}, are the mole fractions and inter-molecular free lengths of the respective components. L_{fmix} is the free length of the binary mixture.

The acoustic impedance is given as

$$Z = \rho u, \quad (11)$$

Where u is the ultrasonic velocity and ρ the density.

The excess acoustic impedance is given as

$$Z^E = Z_{mix} - \Sigma x_i z_i \quad (12)$$

The free volume of a liquid and liquid mixture can be calculated using the formula

$$V_f = [Mu/K_a\eta]^{3/2} , \quad (13)$$

Where M is the molar mass of the liquids, u is the ultrasonic velocity,K_a is the constant having value of $4.28x10^9$, independent of the temperature and nature of the liquids and η is the viscosity.

On the basis of the dimensional analysis using the free volume concept, Suryanarayana suggested the expression for the internal pressure as

$$P_i = bR_gT\,[K_a\eta/u]^{1/2}\rho^{2/3}/M_{eff}^{7/6}, \quad (14)$$

where b is the space packing factor (equal to 2 in the present case) ,R_g ,is the gas constant and T is the temperature in degree Kelvin.Equations (13) and (14) are used for mixtures for which parameters such as M, u, ρ and η corresponds to those mixture.

The excess free volume of the mixture is given as

$$V_f^E = V_{fmix} - \Sigma_{i=1}^{3} x_i V_{fi} \quad (15)$$

The excess internal pressure of the mixture is obtained using the relation

$$P_i^E = (P_i)_{mix} - \Sigma_{i=1}^{3} x_i P_i \quad (16)$$

The dispersion of the ultrasonic velocity in this system should contain information about the characteristic time τ of the relaxation process that causes the dispersion. The relaxation time τ is estimated from the following relation

$$\tau = 4\eta/3\rho u^2 \quad (17)$$

From the Eyring's rate process theory, the Gibb's free energy of activation for the relaxation process ΔG was obtained as

$$1/\tau = (KT/h)\exp(-\Delta G/kT) \quad (18)$$

Where k is the Boltzmann's constant and h is the Planck's constant.

The excess enthalpy of a ternary mixture is obtained from the fundamental relation

$$H^E = \Sigma_{i=1}^{3} (x_i P_{ij} V_j - (P_i)_{mix} V_m. \quad (19)$$

The classical absorption or relaxation amplitude is given by

$$(\alpha/f^2)_{cl} = (8\prod^2\eta/3\rho u^2) \quad (20)$$

The bulk modulus is given by

$$K = \beta_a^{-1} = (u^2\rho) \quad (21)$$

RESULTS AND DISCUSSION

Table -1 :Diethylamine + n- Butanol at 303.15 k

S. No	X(i) D.E.A	Y(i) n-B	ρ x10^{-3} kgm^{-3}	η Nsm^{-2}	U ms^{-1}	β_a x10^{-10} m^{2}n^{-1}	L_F x10^{-10} m	Z Kgm^{-2} s^{-1}
1	1.0000	0.0000	0.6938	0.3404	1213.05	9.7958	6.2452	8.4157
2	0.9000	0.1000	0.7136	0.4224	1236.22	9.1729	6.043	8.8200
3	0.8000	0.2000	0.7238	0.4500	1258.60	8.7301	5.8957	9.1054
4	0.7000	0.3000	0.7472	0.4833	1268.80	8.3238	5.7569	9.4744
5	0.6000	0.4000	0.7513	0.5914	1281.13	8.1112	5.6829	9.6241
6	0.5000	0.5000	0.7675	0.6290	1300.24	7.7096	5.5404	9.9775
7	0.4000	0.6000	0.7780	0.7884	1342.17	7.1369	5.3307	10.4407
8	0.3000	0.7000	0.7800	0.8593	1355.74	6.9827	5.2728	10.5690
9	0.2000	0.8000	0.7861	1.0446	1398.30	6.5089	5.0907	10.9896
10	0.1000	0.9000	0.7871	1.1608	1400.42	6.4820	5.0802	11.0194
11	0.0000	1.0000	0.8146	1.3111	1426.80	6.0369	4.9027	11.6161

Table -2:Diethylamine + n- Butanol at 303.15 k

S.no	X(i) D.E.A	Y(i) n-B	R	τ× 10^{-10} (s)	K×10^9 Kg/m^2	V_fx 10^{-3} m^3	π_i x10^6 Pa	α/f^2 x10^{-12} m^{-1}s^2	(-ΔG) x10^{-21} KJ/mole
1	1.000	0.0000	1.1216	4.4408	1.0208	3.5632	0.3357	7.2268	2.8670
2	0.1000	0.9000	1.0974	5.1368	1.09016	2.5783	0.3783	8.2377	2.8578
3	0.2000	0.8000	1.0884	5.2380	1.1454	2.3499	0.3915	8.1989	2.8566
4	0.3000	0.7000	1.0571	5.3272	1.2013	2.1158	0.4137	8.3258	2.8556
5	0.4000	0.6000	1.0548	6.3808	1.2328	1.5655	0.4581	9.8427	2.8442
6	0.5000	0.5000	1.0376	6.3733	1.2970	1.4402	0.4767	9.8023	2.8442
7	0.6000	0.4000	1.0345	7.4224	1.4011	1.0211	0.5313	11.019	2.8346
8	0.7000	0.3000	1.0353	7.9137	1.4320	0.8992	0.5540	11.623	2.8306
9	0.8000	0.2000	1.0379	9.0256	1.5363	0.6722	0.6060	12.779	2.8223
10	0.9000	0.1000	1.0371	10.0250	1.5427	0.5750	0.6403	14.118	2.8157
11	0.0000	1.0000	1.0083	10.5441	1.6564	0.4801	0.6913	14.569	2.8125

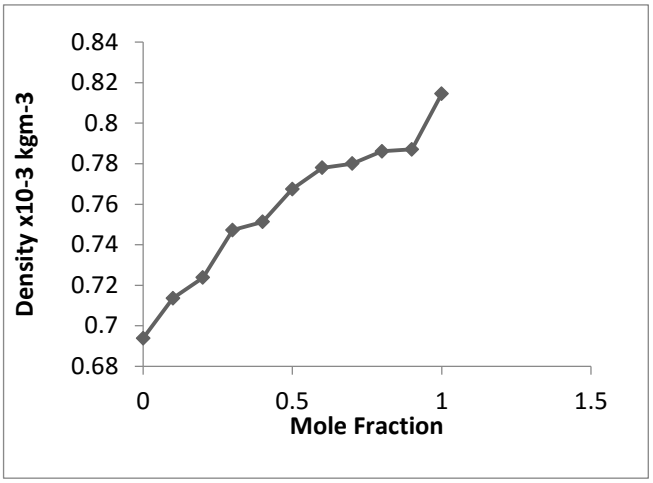

Fig 1 Variation of Density with Mole Fraction

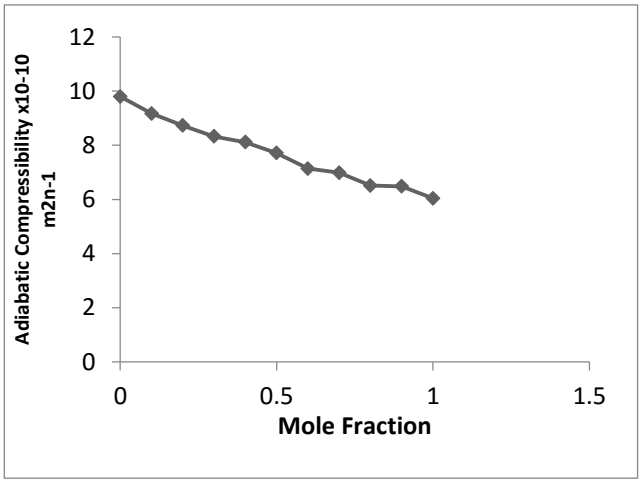

Fig 4 Variation of adiabatic Compressibility with Mole Fraction

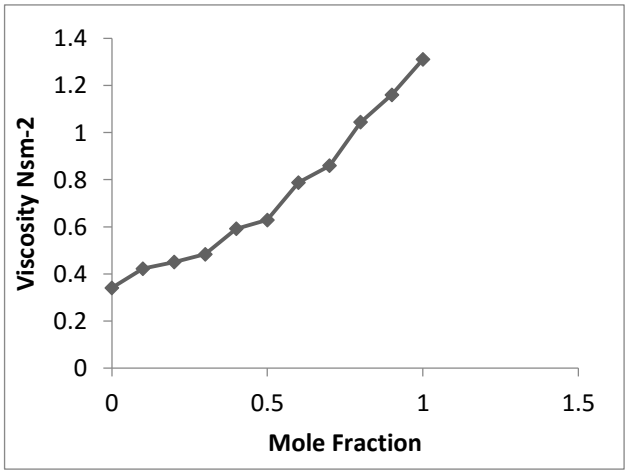

Fig 2 Variation of viscosity with Mole Fraction

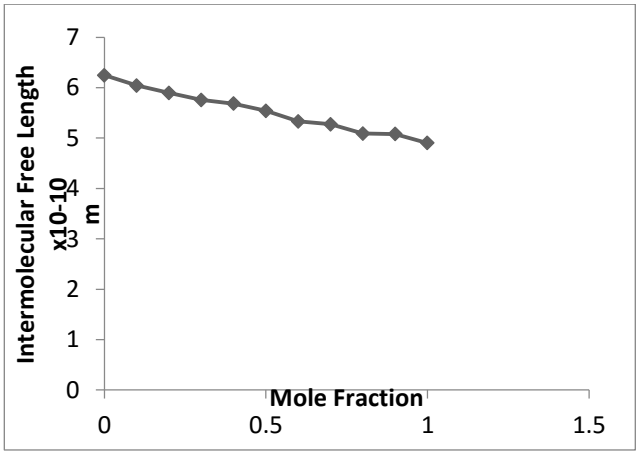

Fig: 5 Variation of intermolecularfree lengthwith Mole Fraction

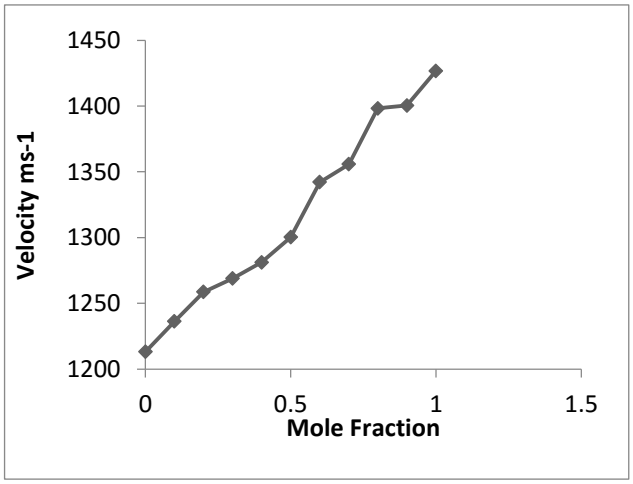

Fig 3 Variation of velocity with Mole Fraction

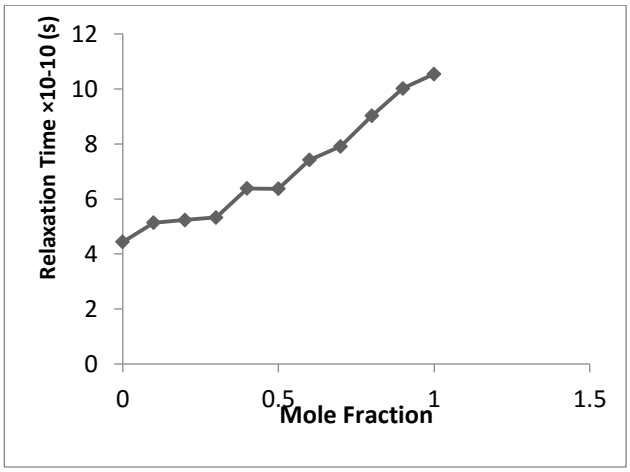

Fig: 6 Variation of Relaxation time with Mole Fraction

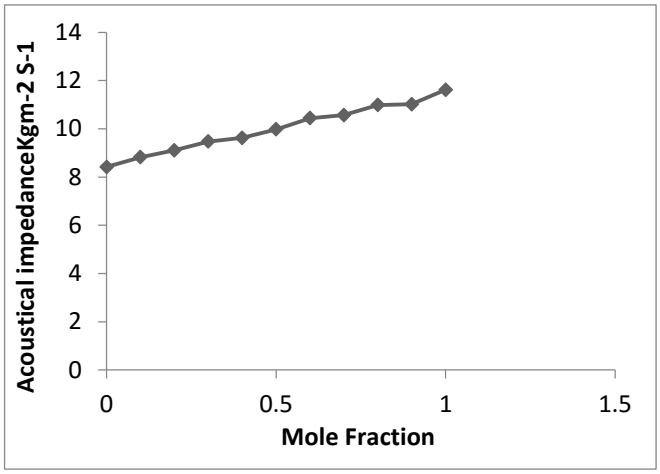

Fig: 7 Variation of Acoustical impedencewith Mole Fraction

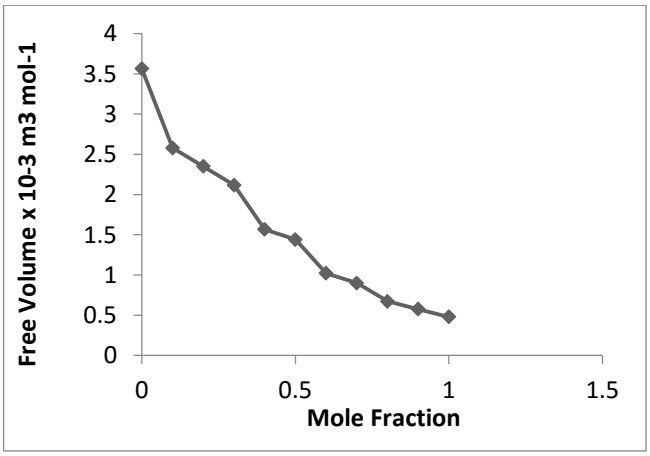

Fig: 8 Variation of free volume with Mole Fraction

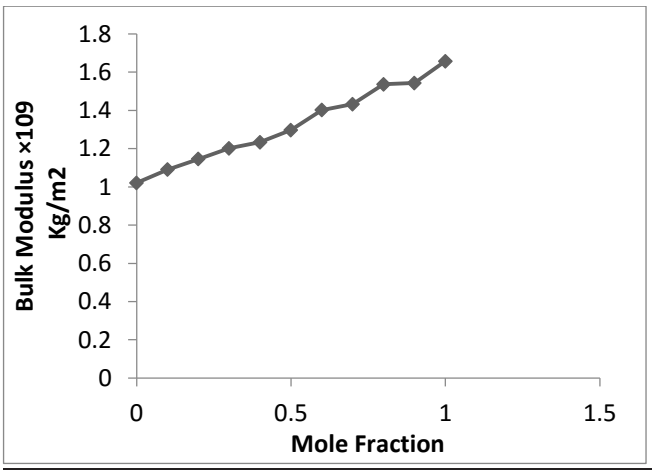

Fig: 9 Variation of Bulk modulus with Mole Fraction

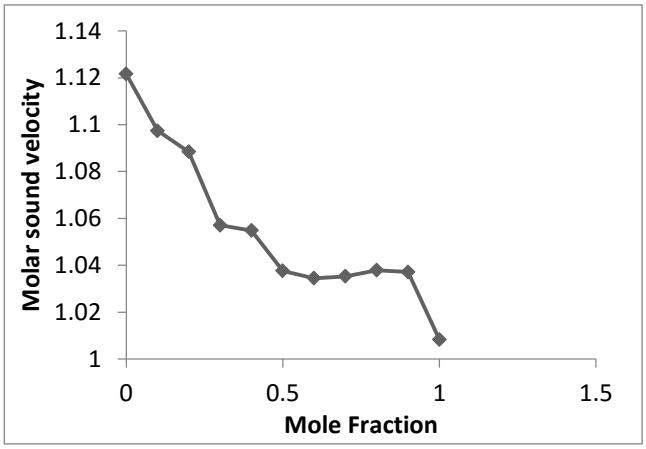

Fig: 10 Variation of molar sound velocity with Mole Fraction

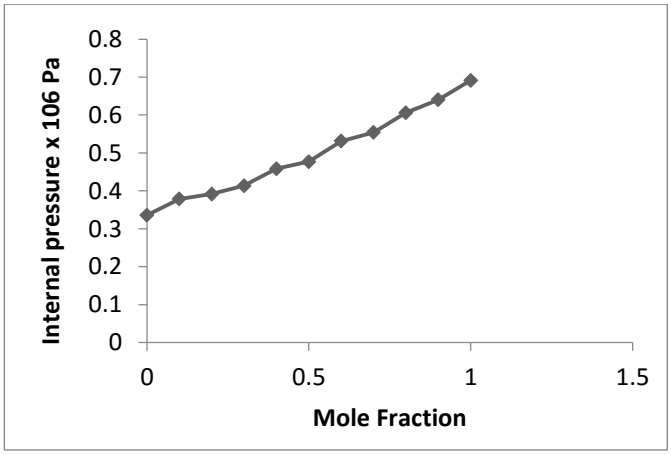

Fig: 11 Variation of Internal pressure withMole Fraction

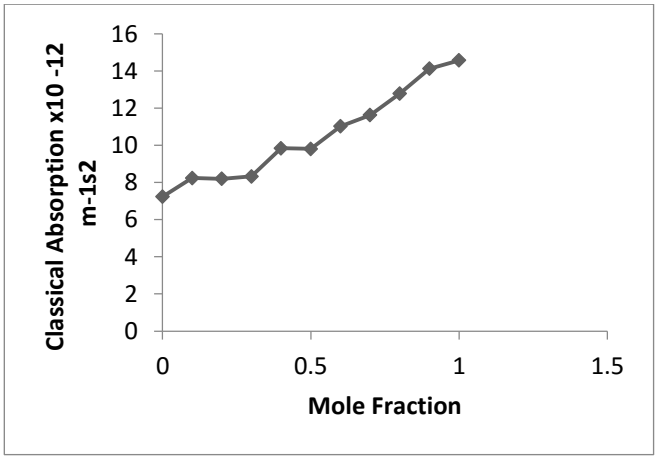

Fig: 12 Variation of Classical Absorption with Mole Fraction

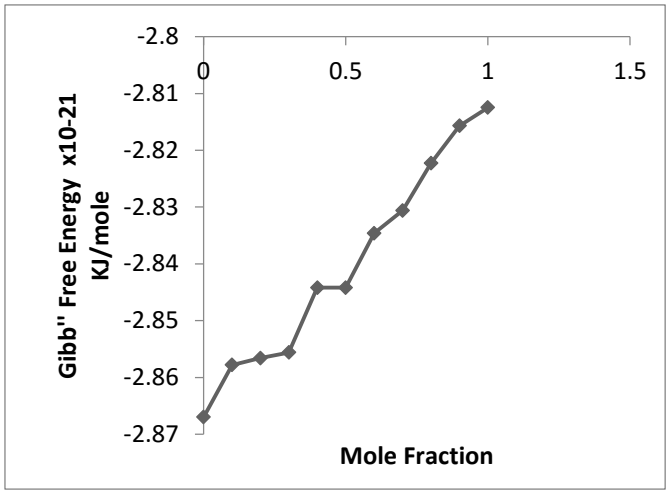

Fig: 12 Variation of Gibb's Free Energy with Mole Fraction

The experimental values of density, viscosity and speed of sound for 303.15k are presented in Table **1**.The thermo-acoustical parameters for 303.15k are given in table 1&2.In order to understand reaction kinetics of binary mixture, tabulated values of thermo-acoustical parameters are graphically represented in Figures **1-12**

For the system of binary mixtures of Diethylamine+n-Butanol, adiabatic compressibility, intermolecular free length, relaxation time, acoustical impedance free volume and bulk modulus, molar sound velocity, internal pressure, absorption coefficient Gibb's free energy are calculated at the constant temperature of 303.15k. For the system of binary mixtures of Diethylamine+n-Butanol the ultrasonic velocity increases with increase in concentration this may be due to strong molecular interaction between molecules. Figure (3) shows the variation of ultrasonic velocity with concentration of Diethylamine+ n-Butanol. The value of density increasing trend with increasing molality of Diethylamine + n-Butanol increases the particles in the medium and so the values of sound velocity also increases. The increasing density values increases the frictional resistance between the constituents of the mixture it tend to increases the coefficient of viscosity of the mixture. The density and viscosity indicates that the existence of interaction between the constituents of the mixture. From the table 1, the value of adiabatic compressibility (β_a) values are positive and the value is decreases with increases in mole faction. Inter molecular free length, shows same behaviour as adiabatic compressibility. Relaxation time depends on viscosity and adiabatic compressibility of Diethylamine + n-Butanol mixture. From this the time decreases with increases in concentration of Diethylamine + n-Butanol. Relaxation time is directly proportional to adiabatic compressibility and viscosity. This supports the view that viscous force play a dominate role in relaxation time .The mathematical relation for specific acoustic impedance $z=u\rho$, adiabatic compressibility $\beta_a=1/u^2\rho$ shows that the behaviour is positive. Specific acoustic impedance is the complex ratio of the effective sound pressure at a point to the effect particle velocity at that point. The free volume plays a important role in ultrasonic wave propagation in liquids found that the free volume of liquid molecules depends on the particular temperature of the liquid at which is measured. The bulk modulus increases with increasing concentration this may be due to contraction governed by compressibility , which depends a inter molecular forces resulting increases in bulk modulus with increases concentration. The molar sound velocity is decreases with increasing concentration and it shows there is weak interaction between molecules. The internal pressure gives information regarding the nature of strength of force existing between the molecules. The absorption coefficient is increases with increasing concentration of liquid mixture. The Gibb's Free energy decreases with increase in concentration of Diethylamine + n-Butanol which confirms the hydrogen bonding formation in binary liquid mixtures.

3. CONCLUSION

The variation in ultrasonic velocity, density and viscosity evaluated parameters suggests the presence of molecular interaction in the binary mixtures. Ultrasonic velocity measurements can be employed to detect and assess weak and strong molecular interaction present in binary liquid mixtures. Ultrasonic method is a powerful probe for characterizing the physical and chemical properties of liquids. These conclusions high light the importance of ultrasonic method in detecting strong molecular interactions between the components of liquid mixtures.

4. REFERENCES

[1]. Ashok kumarDassh and Rita Paikary, 2014 International journal of Advance Science and Technology, Vol 66,pp 89-104.

[2]. P.Vasantha Rani, L.Bala and R.EzhilPavai , 2009 Global Journal of Molecular Sciences, 4(1),48-49.

[3]. S.ThiruMurugan and D.Priya ,2013 Indian Journal of Pure and Applied Physics, Vol 51 pp 413-420.

[4]. Harish Kumar and Deepika,2012 International Journal of Research in Physical Chemistry, 2(3), 20-29.

[5]. S.Ajitha, A.Hemamalini and V.N.meena Devi, 2013 Research Journal of Pharmaceutical, Biological and Chemical Sciences, Vol 4 pp 218-222.

[6]. A.A.Mistry, V.D.Bhandakkar and O.P.Chimankar, 2013 Advanced in Applied Science Research, 4(2) 54-59.

[7]. Rose Venis and Rosario Raj Kumar, 2011 Journal of Chemical Pharmacy Research, 3(2) 878-885.

[8]. Mishra Sujatha and Paikary Rita, 2013 Research Journal of Physical Science, Vol 1(4) 15-21.

[9]. A.N.Kannapan, S.Thirumaran and R.Palani, 2009 Journal of Physical Science, Vol 2(20) 97-108.

[10]. V.D.Bhandakkar, 2014 International Journal of Advanced Research in Physical Science, Vol 1(5) pp 1-5.

[11]. S.Thirumaran and J.Earnest Jayakumar,2009 Indian Journal of Pure and Applied Physics, Vol 47 pp 265-272.

[12]. R.Palani and K.Meenakshi, 2007 Indian journal of Chemistry, Vol 46A pp 252-257.

[13]. M.Pushpalatha, C.H. Srinivasu and K.Narendar, 2013 International journal of Research in Pharmacy and Chemistry, 3(1) 129-131.

[14]. P.Kumar,S.Kumar,S.Singh and R.S.Gangwar, 2011 Oriental Journal of Chemistry, 27(2) 639-644.

[15]. S.Nagaraj, M.C.S SubhaC.Nagamani and K.ChowdojiRao, 2016 World Journal of Pharmacy and Pharmaceutical Sciences, 5(1) 1423-1441.

BOOKS

1. Riddick,J.A., Bunger,W.B., Sanako,T.K., 1986, Physical properties and methods of purification, John Willy & Sons ,New York.

2. Hirschfelder ,J.O , Curtio,and Byron bird .R., 1950,Molecular theory of gases and Liquids, John Willy & Sons, New Yark.