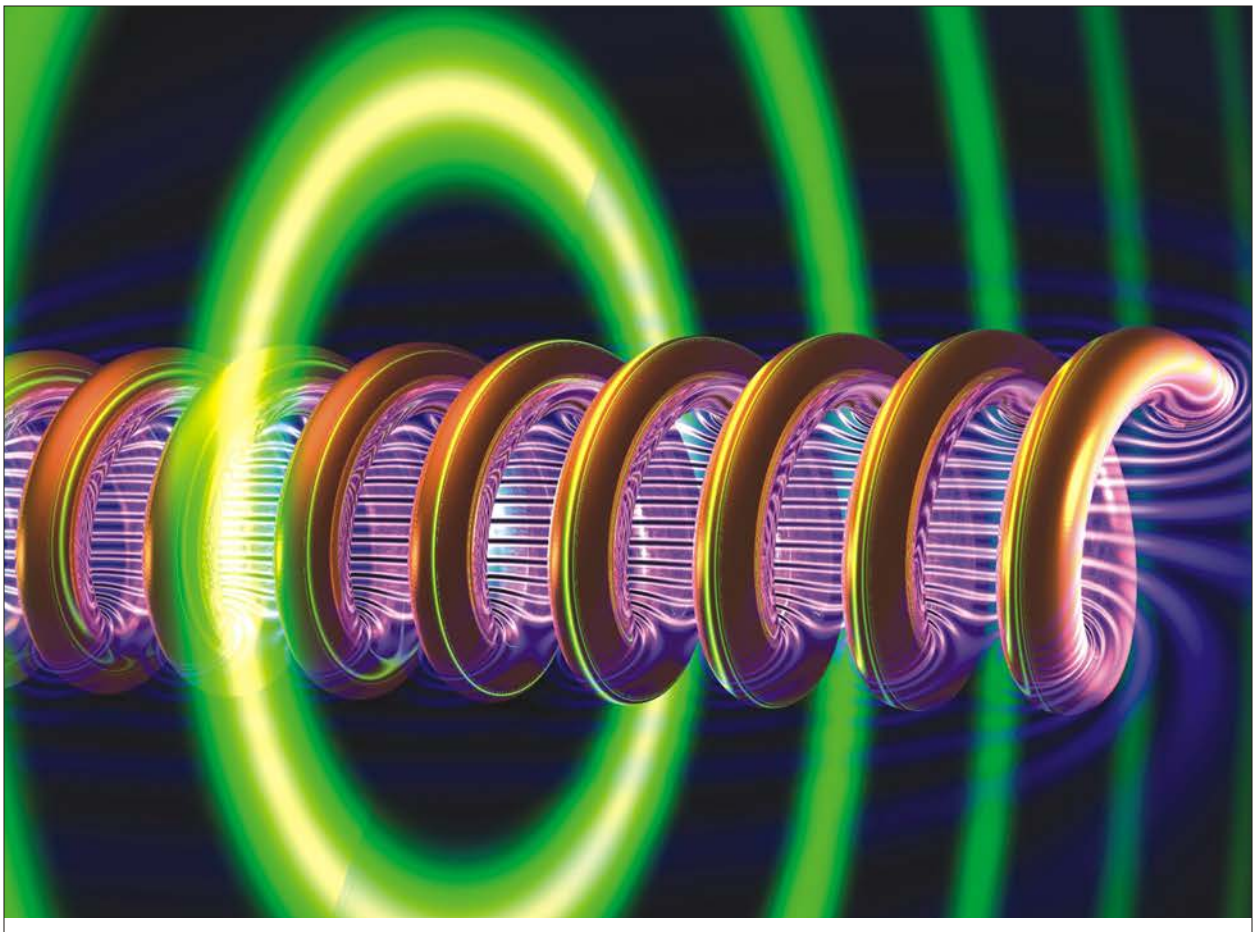

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Molecular Interactions of Aniline in Ternary Liquid Systems

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ABSTRACT

Sound velocity, density and viscosity values have been measured at 303 K in the ternary system of aniline+ethanol+toluene. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the components of the mixtures. Observed excess values in all the mixtures indicate dipolar and weak dispersive type interactions exist in the system.

Key words: Sound velocity, free length, free volume, adiabatic compressibility, mole fraction, molecular interaction

INTRODUCTION

The molecular interactions existing between the components of liquids and their mixtures reflect the structural arrangement and their functional aspects. The review of literature has shown that such analyses have been made for hundreds of binary, ternary, quaternary organic and inorganic mixtures, electrolytic solutions, bio-liquids (Velusamy and Palaniappan, 2011), petroleum products etc., using ultrasonic characterizations. For assessing the nature of molecular interactions and investigating the physic-chemical behavior or such mixtures, ultrasonic studies have been mostly used in modern trend. The presence of solute-solute and solute-solvent interactions of tetra alkyl ammonium borates in 1, 2-dimethoxy ethane have been evaluated by Muhuri *et al.* (1996) using the sound velocity measurements and by evaluation of apparent molar volume and apparent molar compressibilities. The existence of solute-solvent interaction between the components of the copper sulphate ($CuSO_4.5H_2O$) and nickel sulphate ($NiSO_4.7H_2O$) in water was studied by Jayakumar *et al.* (2001). The dipole-dipole interaction between the components of the mixtures containing poly ethers and ethyl acetate at temperature 298.15 K was attempted by Pal *et al.* (2000) using the ultrasonic study.

Nayakulu *et al.* (2006) have carried out ultrasonic and sonochemical reaction studies in the mixtures of *ortho*-cresol with ethyl acetate and isoamyl acetate. They found that the reaction rate decreases due to the passage of sonic wave through the medium. Venkatesu *et al.* (2006) evaluated the ultrasonic sound velocity and densities for the ternary mixtures of N, N-dimethylformamide (DMF) and cyclohexanone with ethanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15 K and they predicted the possible molecular interaction between the unlike molecules.

Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture from ideality (Awasthi and Shukla, 2003; Pandey and Kumar, 1994; Nikam *et al.*, 1996). A departure from linearity in the velocity versus composition

behaviour in liquid mixtures is taken as an indication of the existence of interaction between the different species (Fort and Moore, 1965). The present study deals with the measurement of ultrasonic velocity, density and viscosity and computation of related parameters and their excess values at 303 K in the ternary mixture of aniline+ethanol+toluene.

MATERIALS AND METHODS

Experimental details: The mixtures of various concentrations in mole fraction were prepared by taking purified AR grade samples at 303 K and the mixtures were analyzed for their purity as done by Farooq *et al.* (2008). The ultrasonic velocities in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of ±0.1 m sec^{-1}. The density and viscosity are measured using a pycnometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.001 nsec m^{-2} for viscosity.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions (Ali and Nain, 2002; Peters, 1982):

$$\beta = (U^2\rho)^{-1} \tag{1}$$

$$L_f = K_T\beta^{1/2} \tag{2}$$

$$V_f = \left[\frac{M_{eff}U}{\eta k}\right]^{3/2} \tag{3}$$

$$\pi_i = bRT\left[\frac{k\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right] \tag{4}$$

$$A^E = A_{exp} - A_{id} \tag{5}$$

and:

$$A_{id} = \sum x_i A_i \tag{6}$$

where, K_T is the temperature dependent constant having a value 201.1209×10^{-8} in MKS system, k is a constant equal to 4.28×10^9 in MKS system, independent of temperature for all liquids, $M_{eff} = \sum x_i m_i$ where, x is the mole fraction and m is the molecular weight of i^{th} component and A^E stands for excess property of any given parameter, A_{exp} is the experimental value and A_{id} is the ideal value.

RESULTS AND DISCUSSION

Measured values of density, viscosity and velocity at 303 K for the ternary system of aniline+ethanol+toluene are given in Table 1. All the measured parameters increase with increasing mole fraction of aniline (Eliel, 1985). Such non-linear variation indicates the presence of intermolecular interactions between the components (Srivastava *et al.*, 2010; Sako *et al.*, 2010; Narendra *et al.*, 2011).

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of the system: aniline+ethanol+toluene at 303 K

Mole fraction				
x_1	x_3	ρ (kg m^{-3})	$\eta \times 10^3$ (Nsec m^{-2})	U (m sec^{-1})
0.0000	0.7000	836.8	0.602	1240.3
0.0990	0.6006	851.0	0.682	1279.0
0.1983	0.5010	874.5	0.815	1318.3
0.2977	0.4012	903.2	0.955	1349.6
0.3974	0.3012	920.0	1.138	1391.0
0.5015	0.2010	935.1	1.398	1436.3
0.5974	0.1006	955.7	1.938	1500.3
0.7100	0.0000	963.2	2.234	1530.4

Table 2: Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of the system: aniline+ethanol+toluene at 303 K

Mole fraction					
x_1	x_3	$\beta \times 10^{10}$ (Pa^{-1})	$L_f \times 10^{11}$ (m)	$V_f \times 10^7$ ($m^3 mol^{-1}$)	$\pi_i \times 10^{-8}$ (Pa)
0.0000	0.7000	7.768	5.561	2.314	3.97
0.0990	0.6006	7.183	5.347	2.017	4.21
0.1983	0.5010	6.579	5.118	1.612	4.61
0.2977	0.4012	6.078	4.919	1.310	5.03
0.3974	0.3012	5.617	4.729	1.064	5.47
0.5015	0.2010	5.183	4.542	0.820	6.03
0.5974	0.1006	4.648	4.301	0.537	7.04
0.7100	0.0000	4.432	4.200	0.412	7.50

Among the three components, aniline and ethanol are expected to involve in strong interaction due to their polar nature (Dean, 1987). Even though toluene is unsaturated, it behaves like a saturated compound ordinarily. Moreover, the presence of toluene molecules as electron donor will give higher stability to the carbocation of ethanol and hence they cannot provide any strong interaction. As aniline is having a relatively higher dielectric constant (6.8012) than toluene (2.362) and as both are electron donors, the interaction between the molecules of aniline with toluene is found to be stronger (Deshpande and Bhatgadde, 1968; Palaniappan, 2001, 2012).

The calculated values of **β**, L_f, V_f and π_i for the present system are given in Table 2. As expected, **β** and L_f are continuously decreasing with increasing mole fraction of aniline (Palaniappan *et al.*, 2003). The inspection of these trends reveals a unanimous higher **β** (and L_f) that reveals that the present system can provide some compactness and the observed trend of L_f confirms this view. Thus, the existence of strong interactions due to dipolar type is evident.

Considering V_f and π_i values, they are behaving mutually opposite to each other. Decreasing V_f and increasing π_i values with increasing mole fraction of aniline is noticed, as observed in other liquid systems by Palaniappan (2002). Further, the gradual increase in π_i indicates that the adhesive forces between the components are much more enhanced than the cohesive forces within the component. All these observations are fully supporting the existence of dipolar type interaction, especially at higher mole fractions of aniline.

To confirm the existence of interactions in the system, it is customary to calculate the excess values of the parameters considered in the work. These values represent the deviation of the ideal

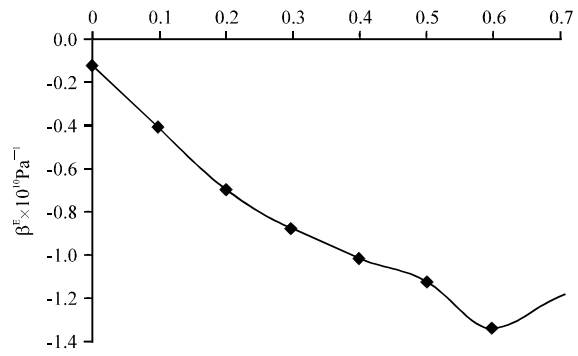

Fig. 1: Mole fraction of toluene vs. excess adiabatic compressibility at 303 K

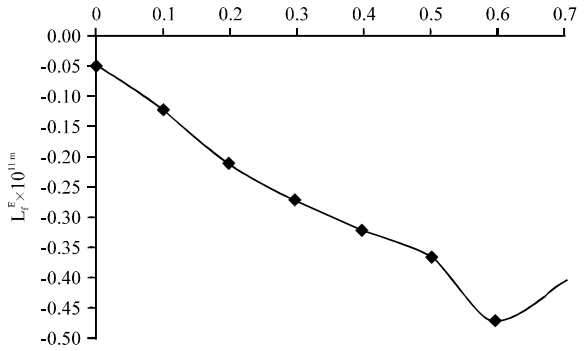

Fig. 2: Mole fraction of toluene vs. excess intermolecular free length at 303 K

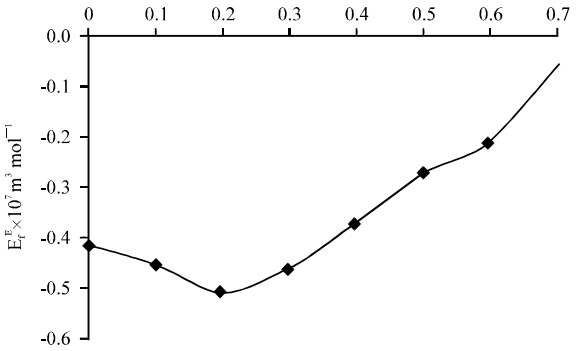

Fig. 3: Mole fraction of toluene vs. excess intermolecular free volume at 303 K

value from that of the observed value of the respective parameter. The ideal values were calculated using the additivity rule which is applicable only for linear variations. Thus any non-zero value in the excess parameter is a measure of non-linearity and is the confirmation for the existence of interaction in the system (Thirumaran and Thenmozhi, 2010).

In the present work, the respective excess parameters have been calculated and are illustrated in Fig. 1-4. All these values for ternary mixture are negative. The negative β^E and negative β^E shows a continuous increase in magnitude with a dip at 0.3 mf of aniline and confirms that the strong interactions are enhanced as aniline mole fraction is increased. The trend of V_f^E exhibit a dip at 0.3 whereas for π_f^E at 0.6 mole fraction of aniline further, the variations noticed on either

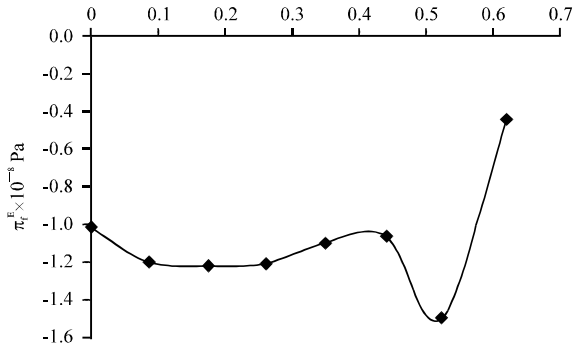

Fig. 4: Mole fraction of toluene vs. excess internal pressure at 303 K

side of this dip are more haphazard (Sundharam and Palaniappan, 2005; Palaniappan, 1988). These observations support that all the added aniline are in the cluster formation with the toluene+ethanol binary complexes at this mole fraction.

CONCLUSION

Followings conclusions were obtained from the above discussions:

- Presence of specific strong dipolar type interactions is noticed
- Weak dispersive interaction in small magnitude exists at lower mole fractions and
- Aniline, at 0.3 mole fraction, serves the best combinational ratio for this system, as all the component molecules get completely engaged in the interaction process

REFERENCES

Ali, A. and A.K. Nain, 2002. Ultrasonic study of molecular interaction in binary liquid mixtures at 30°C. Pramana, 58: 695-701.

Awasthi, A. and J.P. Shukla, 2003. Ultrasonic and IR study of intermolecular association through hydrogen bonding in ternary liquid mixtures. Ultrasonics, 41: 477-486.

Dean, J.A., 1987. Lange's Handbook of Chemistry. 13th Edn., McGraw Hill Int., New York, pp: 186-188.

Deshpande, D.D. and L.G. Bhatgadde, 1968. Sound velocities, adiabatic compressibilities and free volumes in aniline solutions. J. Phys. Chem., 72: 261-266.

Eliel, E.L., 1985. Stereochemistry of Carbon Compounds. 9th Edn., Tata McGraw Hill, New Delhi, pp: 95-97.

Farooq, R., S.F. Shaukat, A.K. Khan and U. Farooq, 2008. Ultrasonic induced decomposition of methidathion pesticide. J. Applied Sci., 8: 140-145.

Fort, R.J. and W.R. Moore, 1965. Adiabatic compressibilities of binary liquid mixtures. Trans. Faraday Soc., 61: 2102-2111.

Jayakumar, S, S.G. Ram, N. Karunanidhi and V. Kannappan, 2001. Polarisability and acoustical studies of electrolytic solutions. J. Pure. Applied Ultrason., 23: 31-38.

Muhuri, K., K. Prakash, D. Bijan and D.K. Hazra, 1996. Apparent molar volumes and apparent molar compressibility's of some symmetriced tetra alkylammonium bromites in 1, 2-dimethoxy ethane. Indian J. Chem., 35A: 288-294.

Narendra, K., P. Narayanamurthy and C. Srinivasu, 2011. Refractive indices of binary liquid mixture at different temperatures. Asian J. Applied Sci., 4: 535-541.

Nayakulu, S.V.R., S. Venkateswar, C.S. Reddy and D.L. Reddy, 2006. Ultrasonic and sonochemical reaction studies of o-cresols in different solvent mixtures. Phys. Chem. liquids, 44: 269-273.

Nikam, P.S., M. Hasan and R.B. Pathak, 1996. Densities and speeds of sound for aniline+aliphatic alcohols (C_1-C_4) at different temperatures. J. Pure Appl. Ultrason., 18: 19-25.

Pal, A., S. Sharma and A. Kumar, 2000. Speeds sound and isentropic compressibility`s of mixtures containing polyesters and ethyl acetate at temperature 298.15 K. Indian J. Pure Applied Phys., 38: 174-179.

Palaniappan, L., 1988. Ultrasonic study of ternary mixtures, rock specimens diabetes mellitus. Ph.D. Thesis, Annamalai University.

Palaniappan, L., 2001. Ultrasonic study of 2-butanol in cyclohexane with toluene. Indian J. Phys., 75: 515-518.

Palaniappan, L., 2002. Thermo acoustical studies of some iso-alcohols in cyclohexane with toluene. Indian J. Pure Applied Phys., 40: 828-830.

Palaniappan, L., D. Devadoss and M. Thairiyaraja, 2003. Molecular interactions studies in the ternary mixtures of 1-hexanol+acetonitrile+toluene. Indian J. Phys., 77B: 679-682.

Palaniappan, L., 2012. Ultrasonic analysis of intermolecular interaction in the mixtures of benzene with methanol, ethanol, 1-propanol. Asian J. Mater. Sci.

Pandey, J.D. and A. Kumar, 1994. Ultrasonic velocity in pure liquids. J. Pure Applied Ultrason., 16: 63-68.

Peters, E.I., 1982. Introduction to Chemical Principles. 3rd Edn., CBS College Publishing, Philadelphia, pp: 324-326.

Sako, A., A. Memeledje and P. Assamoi, 2010. Measurement of the viscosity of mousse myoblasts modified with the αβ cristalline through the technique of micromanipulation by the means of micropipette. Asian J. Applied Sciences, 3: 250-261.

Srivastava, R., A.R. Saksena and A. Gupta, 2010. Viscometric studies on the molecular association of biomolecules based on thermodynamic parameters supported by UV spectra. Asian J. Applied Sciences, 3: 13-24.

Sundharam, N. and L. Palaniappan, 2005. Molecular interaction studies in the ternary mixture of methanol+benzene+cyclohexane. Indian J. Phys. Proc. Indian Assoc. Cultivat. Sci., 79: 1173-1178.

Thirumaran, S. and P. Thenmozhi, 2010. Study of molecular interaction in ternary liquid mixtures by ultrasonic velocity measurements. Asian J. Applied Sci., 3: 153-159.

Velusamy, V. and L. Palaniappan, 2011. Compositional analysis α-lactalbumin. Am. J. Biochem. Mol. Biol., 1: 106-120.

Venkatesu, P., G.C. Sekhar and M.V.P. Rao, 2006. Ultrasonic studies of N,N-dimethylformamide+cyclohexane+1-alkanols at 303.15 K. Phy. Chem. Liquids, 44: 287-291.