Ultrasonic Study on Molecular Interactions of Ternary Liquid Mixture of Alcohol, Formic Acid And Tri-Ethylamine At Three Different Temperatures

P J Thakare[1], J B Thakare[2], N G Belsare[3]
[1]Dr D Y Patil ACS college, Maharashtra
[2]S S S K R Innani Mahavidyalay, Karanja(Lad), Maharashtra
[3]Vidyabharti Mahavidyalay, Amravati, Maharashtra

Abstract - The free volume (V_f), excess free volume (V_f^E), relaxation time (τ), and specific acoustical impedance (Z) have been calculated from density, viscosity and ultrasonic velocity measurements for ternary liquid mixture of Alcohol + Tri-ethylamine (TEA) + Formic acid at three different temperatures 303, 308 and 313K. The nature of molecular interactions between component molecules is investigated through above parameters. The results are discussed in terms of hydrogen bonding and complexation between donor acids and acceptor amines.

Keywords - molecular interactions, hydrogen bonding, free length, internal pressure, ternary liquid mixtures.

Introduction

Ultrasonic velocity and related thermodynamic parameters help us for characterizing thermodynamic and physio-chemical aspects of binary and ternary liquid mixture like molecular association and dissociation. There is significant information of ternary liquid mixtures on the physio-chemical behaviour of ultrasonic wave propagation and has an influence on the physical properties of the medium. The sign and extent of nonlinear deviations ideal behaviour as a function of composition and temperature may be associated to the presence of strong or weak interaction between unlike molecules. Ultrasonic velocity variation and related parameters can shed much light upon the resulting structural changes associated with liquid mixtures of weakly or strongly interacting compounds[1,2]. For the present work ultrasonic investigations are carried out to detect the intermolecular interactions in ternary liquid mixture of carboxylic acids and amines.

Theory

Suryanarayana et al [3] have obtained formula for free volume in terms of the ultrasonic velocity and the viscosity of the liquid. Free volume in terms of Ultrasonic velocity (U) and the Viscosity of the liquid (η) can be expressed as[4],

$$V_f = [M_{eff}U/K\eta]^{1/2} \quad \text{(i)}$$

Where, $\mathbf{M_{eff}}$ is the effective molecular weight.
$\mathbf{M_{eff}} = \sum M_i f_i$, in which M_i and f_i are the molecular weight and the mole fraction of the corresponding constituents respectively.
'K' is a temperature independent constant and has value equal to 4.28×10^9 for all liquids.
The relaxation time can be calculated by formula,

$$\tau = \frac{4\eta}{3\rho U^2} \quad \text{(ii)}$$

Impedance is the property that determines the amount of reflection and is the characteristic of medium. It is very similar to electrical impedance. If there is no variation in impedance within the material then there is no reflection. It is given as[5] ,

$$Z = \rho U \quad \text{(iii)}$$

The Excess free volume V_f^E for the ternary mixture was calculated by using following equation,

$$V_f^E = V_{f\,mix} - V_{f1}f_1 + V_{f2}f_2 + V_{f3}f_3 \quad \text{(iv)}$$

Experimental work

In the present work density was measured by using density bottle (corning made certified 10 ml). Weight of bottle was taken by monopan balance (Model no. K15) supplied by K-Roy and Company, Varanasi. Its capacity is 100 gm with sensitivity of 0.01 mg. For the measurement of viscosity Ostwald viscometer was used. During measurement prepared sample was poured in to the viscometer and the time taken by the liquid sample to fall down from higher mark to lower mark. The liquids used for the work were of BDH AR grade. For the present work the chemicals used viz. Triethylamine(TEA), and Formic acid were procured SD fine Mumbai and from E Merk chemicals Ltd India. Samples of different concentration were prepared by mixing the component liquids in volume proportion. Every time 28ml of mixture was prepared for measurement of density, viscosity and ultrasonic velocity. In the present work ultrasonic velocity was measured by ultrasonic interferometer. A crystal controlled interferometer, model No. M8 15 supplied by Mittal enterprises, New Delhi, was used for measurement of ultrasonic velocity. Measurements are made at 2 MHz.

Observation Table

System-Alcohol + Tri-ethylamine + Formic Acid

ATemp. 303K

Mole Fraction of Formic acid	Density (gm/cm^3)	Viscosity (cp)	Velocity (cm/s)	Acoustical Impedance	Relaxation time (s) (Sec)	Free Volume V_f (cm^3/mole)	Excess Free Volume (cm^3/mole)
0.0000	0.9104	1.8136	130800	1.19E+05	1.55E-10	2.52E-05	-5.50E-04
0.1230	0.9675	2.1959	145920	1.41E+05	1.42E-10	2.16E-05	-4.43E-04
0.2294	0.9846	1.9290	142830	1.41E+05	1.28E-10	2.48E-05	-3.44E-04
0.3223	1.0027	1.6823	137550	1.38E+05	1.18E-10	2.81E-05	-2.57E-04
0.4042	1.0104	1.3997	131700	1.33E+05	1.06E-10	3.39E-05	-1.77E-04
0.4769	1.0239	1.1973	126450	1.29E+05	9.75E-11	3.96E-05	-1.06E-04
0.5418	1.0365	1.0623	122100	1.27E+05	9.17E-11	4.42E-05	-4.28E-05
0.6002	1.0494	0.8552	119700	1.26E+05	7.58E-11	5.84E-05	2.40E-05

Table No. 1

Temp 308 K

Mole Fraction of Formic acid	Density (gm/cm^3)	Viscosity (cp)	Velocity (cm/s)	Acoustical Impedance	Relaxation time (s) (Sec)	Free Volume V_f (cm^3/mole)	Excess Free Volume (cm^3/mole)
0.0000	0.9122	1.5337	129000	1.18E+05	1.35E-10	3.18E-05	-4.87E-04
0.1232	0.9648	1.9535	145710	1.41E+05	1.27E-10	2.57E-05	-3.96E-04
0.2297	0.9807	1.6695	141510	1.39E+05	1.13E-10	3.04E-05	-3.07E-04
0.3227	0.9967	1.5045	135840	1.35E+05	1.09E-10	3.26E-05	-2.31E-04
0.4047	1.0072	1.2808	130740	1.32E+05	9.92E-11	3.83E-05	-1.61E-04
0.4773	1.0172	1.1016	125520	1.28E+05	9.17E-11	4.44E-05	-9.71E-05
0.5423	1.0305	0.9611	120840	1.25E+05	8.52E-11	5.05E-05	-3.96E-05
0.6006	1.0456	0.9110	118020	1.23E+05	8.34E-11	5.20E-05	8.11E-06

Table no. 2

At 313K

Mole Fraction of Formic acid	Density (gm/cm^3)	Viscosity (cp)	Velocity (cm/s)	Acoustical Impedance	Relaxation time (s) (Sec)	Free Volume V_f (cm^3/mole)	Excess Free Volume (cm^3/mole)
0.0000	0.9060	1.3674	126600	1.15E+05	1.26E-10	3.67E-05	-4.65E-04
0.1233	0.9622	1.7431	144090	1.39E+05	1.16E-10	3.00E-05	-3.83E-04
0.2298	0.9777	1.4730	139440	1.36E+05	1.03E-10	3.58E-05	-3.01E-04
0.3228	0.9934	1.2986	135210	1.34E+05	9.53E-11	4.03E-05	-2.29E-04
0.4047	1.0043	1.1169	129060	1.30E+05	8.90E-11	4.62E-05	-1.64E-04
0.4774	1.0166	0.9585	123960	1.26E+05	8.18E-11	5.36E-05	-1.04E-04
0.5423	1.0285	0.8103	114240	1.17E+05	8.05E-11	6.00E-05	-5.13E-05
0.6006	1.0409	0.6691	126600	1.22E+05	6.21E-11	8.21E-05	1.28E-05

Table no. 3

Graphs:

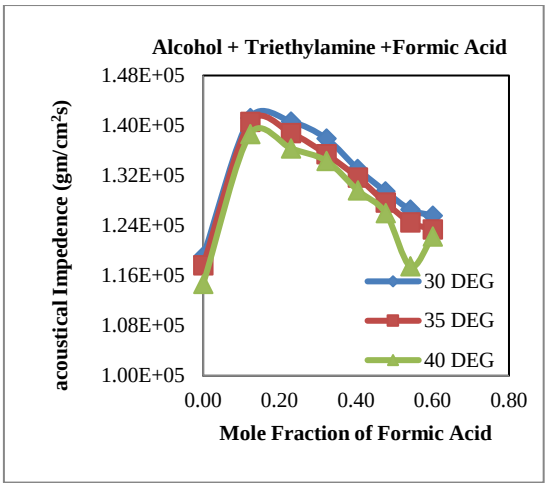

Fig no.1

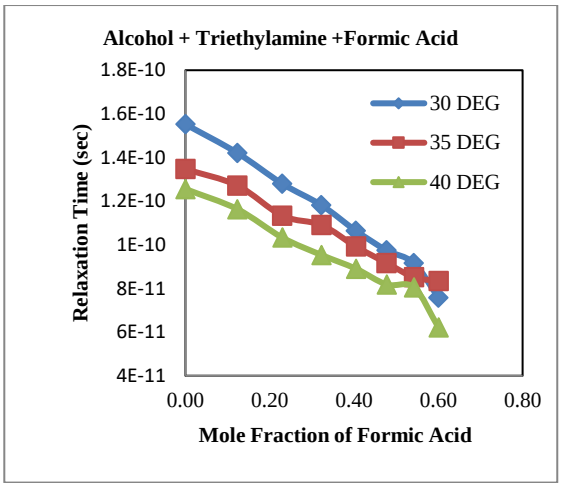

Fig no. 2

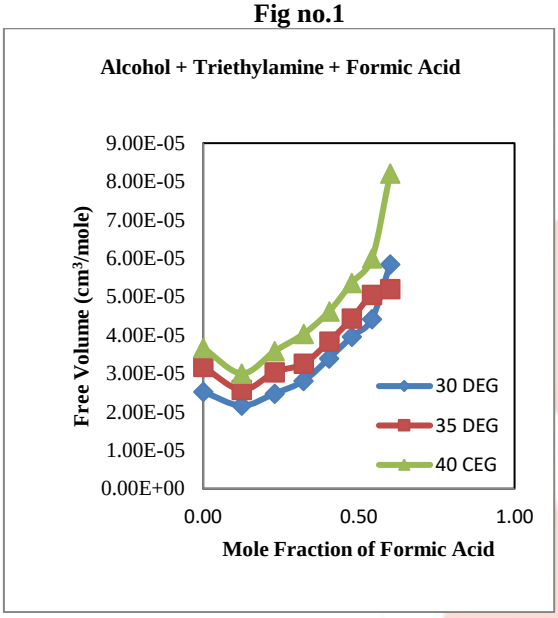

Fig no. 3

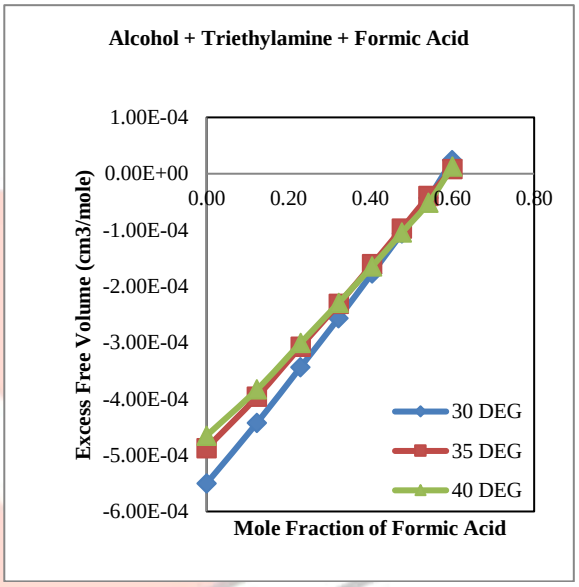

Fig no. 4

Results and Discussion:

Behavior of relaxation time depends on viscosity. Interestingly, almost similar pattern of behavior is seen in respect of relaxation time (τ), as that of viscosity. This similar change shows that, viscous forces play a dominant role in the relaxation process. The increasing trend of τ indicates the intermolecular interaction between the molecules of components. As the temperature increases relaxation time decreases.It is due to the instantaneous conversion of excitation energy to translational energy when temperature increased.

In the present investigation acoustic impedance increases with mole fraction of carboxylic acid up to certain maxima and decreases again at higher mole fraction of carboxylic acid. Such increasing values of acoustic impedance further support the possibility of strong molecular interactions due to H-bonding between amines and carboxylic acid molecules. After attaining maximum values the acoustic impedance decreases. Such decreasing trends of acoustic impedance further support the possibility of molecular interaction due to H-bonding and dipole-dipole interaction between amines and carboxylic acid. Senthamil Selvi et al (6) also observe same results. Further it is observed that as the temperature increases impedance value decreases. S P Poongothai et al also found the decrease in value of acoustic impedance with increase in temperature. 7

Free volume (V_f) is defined as the average volume in which the centre of a molecule can move due to the repulsion of the surrounding molecules. In the present investigation it is observed that free volume decreases with mole fraction of carboxylic acid, reaches to minimum value and increases again. The decrease in free volume is a result of various degrees of dispersive interactions and the coulombic interaction existing between the components molecules. Additionally, it also suggests the close packing of the molecules, which may be concluded as the increasing magnitude of the interaction [8,9] . Further,with rise in temperature the free volume increases. Thermal energy of the molecules increases with temperature, hence free volume is naturally expected to be more. The results discussed by M K Praharaj et al[10] in pyridine + N-N dimethylformamide +cyclohexane ternary liquid mixtures also supports the findings in the present investigation.

Excess free volume provides correct information about interaction. The perusal of table-1 provides a qualitative picture of excess free volume values for ternary liquid system. The sign of the V_f^E depends on the relative strength between the contractive forces and expansive forces. The chemical or specific intermolecular interactions and structural (interstitial accommodation) generally contributes negative values of V_f^E. The values of V_f^E become less negative with increase in concentration of carboxylic acid indicating the presence of weak molecular interaction [11, 12]. The negative values of V_f^E over the entire range of concentration predicts the association effects due to specific and favorable interaction between acids and amines in

polar solvents alcohol. Similar results are found by Steevi Felira et al[13]. This leads to contraction of volume during mixing. This may be due to formation of new bonds[14]. This nature is also supported by positive values of excess viscosity over the entire range of concentration[14].

Conclusion

From the behaviour of relaxation time, it is confirmed that molecular interactions are present in the component of the mixture. The increasing values of acoustical impedance predict the strong interactions present among the component molecules. As the thermal energy is increased due to increase in temperature, free volume increases. Donor acceptor type of interaction is majorly present in the present ternary system. The dipole-dipole interaction and dispersion forces are also present but the hydrogen bonding complexation between formic acid and tri-methylamine dominates the other two.

References:

1) Arul G., Palaniappan L., Indian J. Pure and Appl Phy 39(2001) 561.
2) Pandey J D., J Mol. Liquids, 81(1999) 123.
3) Suryanarayana, C V and Kuppusamy, T. (1976). Free volume and internal pressure of liquids from ultrasonic velocity. J. Acoust. Soc. Ind, 4, 75.
4) Schaff W, (1940), Z Phys, vol. 115,60.
5) Nigam R K, Dhillon M S, (1971), Ind J Chem vol. 8, 1260.
6) C Senthamil Selvi, S Ravichandran, C Thillaiyadi Valliammai, C Thenmozhi and V Kannappan, (2014), Acoustical studies of ternary mixtures at different temperatures, Rasayan J. Chem., vol. 7, 325-332.
7) S P Pongothai and S chidambra vinayagam, (2016), Ultrasonic studies on molecular interactions in ternary liquid mixtures at different temperatures, Journal of Chemical and Pharmaceutical Research, 8(11), 140-148.
8) P S Naidu and K Ravindra Prasad,(2002), Indian Journal of pure and Applied Physics, vol.40,264
9) A N Kannappan and V Ranjendran,(1999), Indian Journal of Pure and Applied Physics, vol. 73B.531.
10) M K Praharaj, A Satapathy, P Mishra and S Mishra, (2012), Ultrasonic studies of molecular interactions in pyridine + N-N dimethylformamide +cyclohexane ternary liquid mixtures at different temperatures, International Journal of Chemical and Pharmaceutical Sciences, vol. 3(3), 6.
11) Balija S, Oza S,(2002), Fliuid Phase Equilib, vol.200, 11
12) Rajendran V, Marikani A and Palaniappan L, (1994), Indian Journal of Pure Applied Ultrasonics, vol.16,16.
13) Steevi Felira, Uma Sivakami and Rose Venis, (2016), Molecular interactions in ternary liquid mixtures of 1,2-dichlorobenzene with cyclohexane and Toluene at 318 K, World Journal of Pharmacy and Pharmaceutical sciences,1602-1609.
14) Manoj Kumar Praharaj, (2016), Molecular interactions in ternary liquid mixture invoving toluene at different frequencies, Journal of chemical and pharmaceutical research, 8(1), 519-524.
15) R Venis, R Rajkumar, (2011), Densities and Ultrasonic velocities in ternary liquid mixture of anisole with cyclohexanone and 1-hexanol at 308.15K and 318.15K, Journal of Chemical and Pharmaceutical Research, vol. 3(2), 878.