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ULTRASONIC STUDY OF THE SELF–ASSOCIATION OF ANILINE IN ETHANOL-CYCLOHEXANE MIXTURES

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Abstract: *Sound velocity (U), density (ρ) and viscosity (η) values have been measured at 303 K in the ternary system of aniline+methanol+cyclohexane. From these data, acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume(V_f) and internal pressure(π_i) have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the components of the mixtures. Observed excess value in the mixture indicates the existence of dipole-induced dipole and dipole-dipole interactions in the system.*

Keywords: ultrasonic velocity, ternary system, molecular interactions

1. INTRODUCTION

The understanding of intermolecular interactions between polar and non-polar component molecules can be best made by ultrasonic investigations and they find applications in several industrial and technological processes.[1,2] Muhuri and co-workers[3] have evaluated the apparent molar volume and apparent molar compressibilities of tetraalkyl ammonium borates in 1,2-dimethoxyethane using sound velocity measurements and the presence of solute-solute and solute-solvent interactions were predicted in the system. Jayakumar et al.[4] have studied the molecular association and absorption on the electrolytic solutions of copper sulphate ($CuSO_4.5H_2O$) and nickel sulphate ($NiSO_4.7H_2O$) in water. They concluded the existence of solute-solvent interactions between the components of the system. Amalendu Pal et al.[5] have made an attempt to study the speed of sound and isentropic compressibilities of mixtures containing polyethers and ethyl acetate at 298.15 K and they discussed the dipole-dipole interactions between the components of the mixtures.

Ultrasonic and sonochemical reaction studies have been carried out by measuring ultrasonic velocities in the mixing of phenols such as cresol with esters such as ethyl acetate and *iso* amyl acetate as solvents by Renga Nayakulu et al.[6] They found that the reaction rate decreased due to the passage of sonic waves through the medium.

Such studies as a function of concentration are useful in gaining an insight into the structure and bonding of associated molecular complexes and other molecular processes. Further, they play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures.[7,8] Hence, the authors have performed a study on the molecular interaction existing in the mixtures of ethanol with cyclohexane and with aniline, using the sound velocity data. The present work deals with the measurement of U, ρ and η, and computation of related parameters at 303 K in the ternary mixture of aniline+ethanol+cyclohexane thereby the exact interactions between the component molecules have been identified.

2. EXPERIMENT DETAILS

The mixtures of various concentrations in mole fraction by weight were prepared by taking purified AR grade samples at 303 K. The purification was done as per standard procedures[9] and the purity was checked by comparing the ρ with those reported in literature[10] and found to be closer to first decimal. The U in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of ± 0.1 ms^{-1}. The ρ and η are measured using a pycknometer and an Ostwald's viscometer, respectively with an accuracy of 3 parts in 10^5 for ρ and 0.001 Nsm^{-2} for η. Using the measured data, the acoustical parameters such as β, L_f, V_f and π_i and their excess parameters have been calculated using the following standard expressions[11–13]

$$\beta = \left(U^2\rho\right)^{-1} \qquad \ldots (1)$$

$$L_f = K_T \beta^{1/2} \qquad \ldots (2)$$

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

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

$$A^E = A_{exp} - A_{id} \qquad \ldots (5)$$

$$\text{and } A_{id} = \sum x_i A_i \qquad \ldots (6)$$

where, K_T is the temperature dependent constant having a value 201.1209×10^{-8} in M.K.S. system, k is a constant equal to 4.28×10^9 in M.K.S. 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, where A_{exp} is the experimental value and A_{id} is the ideal value.

3. RESULTS AND DISCUSSION

The measured values of ρ, η and U for the system of aniline+ethanol+ cyclohexane are presented in the Table 1. All the three measured parameters increased monotonically but non-linearly. Any non-linear variation is a clear indication for the presence of interaction. The pure values for aniline are much greater than that of cyclohexane and the fixed component ethanol, and hence, an increasing trend appeared with increasing mole fraction of aniline. The increasing trend of η revealed that the addition of aniline increases the effective molecular area.[14] The increased in area due to the addition of a cyclic molecule (aniline) by replacing another cyclic molecule (cyclohexane) is quite peculiar. This may be due to the polar nature of the added component and is reflected in the observed trend of the measured parameters.

Table 1: Values of ρ, η and U in aniline (x_1) + ethanol(x_2) + cyclohexane (x_3) at 303 K.

Mole fraction		ρ	$\eta\times10^3$	U
x_1	x_3	kgm^{-3}	Nsm^{-2}	ms^{-1}
0.0000	0.7070	750.8	0.788	1184.6
0.0998	0.6040	802.0	0.908	1217.0
0.1964	0.5022	835.9	1.017	1248.5
0.3032	0.4041	851.5	1.151	1288.0
0.4039	0.3005	885.1	1.292	1338.0
0.5072	0.2008	907.4	1.475	1386.0
0.6040	0.0943	938.0	1.795	1459.0
0.7100	0.0000	963.2	2.234	1530.4

Table 2 lists the calculated parameters of β, intermolecular L_f, V_f and π_i. A rapid decreasing nature of β is observed with increased in the mole fraction of aniline. As the system gets more and more replaced by polar molecules, interaction of increasing magnitude arises and hence β decreased.[15,16] The same behavior is reflected in intermolecular L_f values. The closeness of components revealed that system is well-packed.

Table 2: Values of β, L_f, V_f and π_i in aniline (x_1) + ethanol (x_2) + cyclohexane (x_3) at 303 K.

Mole fraction		$\beta \times 10^{10}$	$L_f \times 10^{11}$	$V_f \times 10^7$	$\pi_i \times 10^{-8}$
x_1	x_3	Pa^{-1}	m	m^3mol^{-1}	Pa
0.0000	0.7070	9.491	6.147	1.298	4.70
0.0998	0.6040	8.418	5.789	1.103	5.14
0.1964	0.5022	7.674	5.527	0.986	5.46
0.3032	0.4041	7.079	5.308	0.880	5.68
0.4039	0.3005	6.310	5.012	0.795	5.98
0.5072	0.2008	5.736	4.779	0.705	6.10
0.6040	0.0943	5.008	4.465	0.570	6.86
0.7100	0.0000	4.432	4.200	0.412	7.50

V_f is found to decrease with the increasing mole fraction of aniline whereas the π_i increased. These variations may be attributed to two reasons: (i) enormous number of component molecules is formed due to splitting of a major component or (ii) the enlargement of existing molecules due to the added component. The contribution due to first reason will make the net inward chaos to be more and hence the π_i increases. Also the enlargement of the molecules reduces the available volume between the components and it weakens the surface layer that is reflected as the increased of π_i.

The perusal of Table 2 showed that π_i is in increasing trend, thus revealing that the reduction of V_f is not due to splitting of components but is of enlargement. Thus, aniline is bound to combine with the other components.[17] This happens at all mole fractions of aniline, thus conveying that aniline can combine with polar ethanol as well as with non-polar cyclohexane.

The respective excess parameters have been calculated and are given in Figures 1 to 4 which indicate that the parameters are negative over a wide range of mole fraction. Being the excess values, these parameters revealed the extent of non-ideality at the respective mole fractions. On observing the trend shown by the graphs, it seems that a straight line (linear) or curve linear nature is found to exist if the values would be smoothened. But such smoothening mislead that the non-ideality of the system follows a definite relation which cannot be in practice. Thus the inspection of the excess parameters has been made as such with the experimental values without any smoothening.

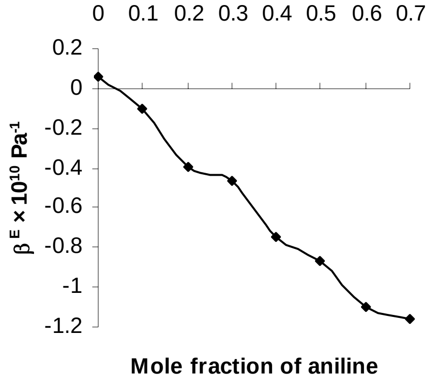

Figure 1: Mole fraction *vs.* excess β at 303 K.

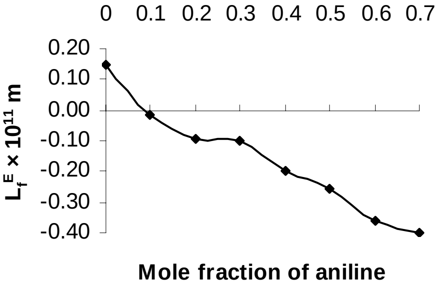

Figure 2: Mole fraction *vs.* excess intermolecular L_f at 303 K.

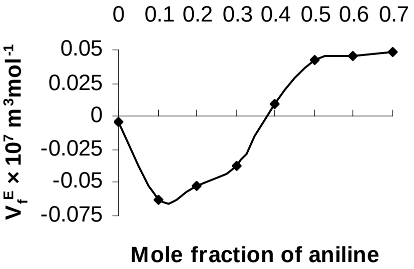

Figure 3: Mole fraction *vs.* excess intermolecular V_f at 303 K.

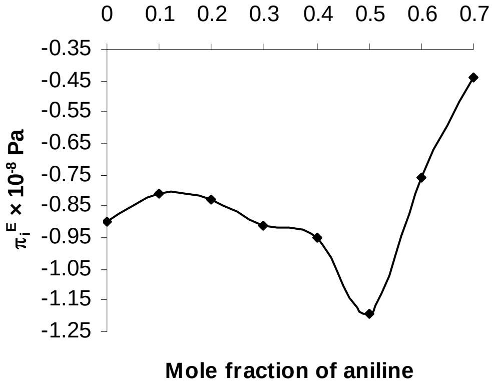

Figure 4: Mole fraction *vs.* excess π_i at 303 K.

The magnitudes of negative excess β and excess intermolecular L_f are continuously decreasing with increasing mole fraction of aniline. Thus, the strong interaction existing between the components were confirmed. Excess V_f values were negative up to 0.3 mole fraction of aniline and then it became positive whereas excess π_i was negative at all mole fractions. A dip in excess V_f exists at 0.1 mole fraction of aniline showed the non-ideality of the components. The addition of aniline is indicated by this dip, which indicates that all the added aniline molecules completely get into the complex structure and there would be no free aniline component.

Among the three components, aniline (1.13 D) and ethanol (1.68 D) are strong polar whereas cyclohexane is very weak or nonpolar (0.10 D)[10] but ethanol is an excellent solvent which contains one hydrophilic (OH) group and one hydrophobic (CH_3) group. The hydrophilic group can dissolve the polar component (aniline) while the hydrophobic group can dissolve the nonpolar components (cyclohexane). As the mole fraction of ethanol remain unchanged, the association of ethanol with the other two components are possible in the entire mole fraction range. Thus dipole-dipole interactions are formed between the hydrophilic group of ethanol and the amino group of aniline whereas weak dispersive interactions are formed between the conforming cyclohexane rings and the hydrophobic group of ethanol. These weak dispersive interactions can manifest as induced dipole-dipole interactions in many instances.[18,19] It is evident that dipole-dipole type is stronger than the other interactions existing in the system. This is reflected in the positive excess V_f at higher mole fraction of aniline.

Further, the positive excess V_f indicates that the formation of aniline+ ethanol complexes predominates that of aniline+ethanol+cyclohexane. This clearly revealed that 0.3 mole fraction was the maximum limit of aniline to be added with this system. Excess π_i values changes randomly that indicates the drastic variations due to the fluctuating induced dipoles in the cyclohexane molecule.[20–22]

4. CONCLUSION

Presence of specific strong interactions were confirmed and identified as dipole-dipole and dipole-induced dipole type. Aniline was found to readily influence the component molecules as well as cyclohexane+ethanol complexes, even at 0.1 mole fraction.

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