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Note

Effect of aniline in methanol + benzene mixture – An ultrasonic study

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Sound velocity, density and viscosity values have been measured at 303 K in the ternary system of aniline + methanol + benzene. 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 dispersive type and dipole–induced-dipole interactions exist in the system.

Keywords: Mole fraction, measured parameters, calculated parameters, molecular interaction

During the last few decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions and investigating the physico-chemical behaviour of such. Thermodynamic and transport properties of liquid mixtures have been extensively used[1,2] to study the departure of a real liquid mixture from ideality. A departure from linearity in the velocity *versus* composition behaviour in liquid mixtures is taken as an indication of the existence of interaction[3, 4] between the different species. It is a well known fact that in the petrochemical industries during the separation of petrochemical intermediates from the crude oil or coal tar, mixtures of various alcohol-azeotropic combinations[5] exists as their relative volatility is very close to 1.00. To facilitate the separation process using extractive distillation process, extractive solvents are widely used. Further, aniline seems to be the unanimous extractive solvent used for the separation of alcohol azeotropes[6,7]. Thus, from the view point of molecular interaction, it becomes a ternary system.

Being a ternary mixture, contributions to molecular interactions can exist in various ways and the major contribution can be expected between aniline – benzene, aniline – alcohol, benzene – alcohol, among the components of ternary and also between them. Some more contributions are likely between azeotrope – aniline, amino-alcohol complex – benzene, ring (benzene + aniline) complexation – alcohol, and ternary complexes (in various formats such as ABC) with free components. Further the other chances of the redistribution of the components that can form minor contribution are also possible. Thus the molecular interactions existing between the components in various binary mixtures and ternary system have to be attempted. The very first member of the alcohol family, methanol is of interest here.

Benzene and aniline being aromatic, and aniline with amino group, behave as electron donors. Though the amino group is comparatively a strong electron-donor, the H atoms in the NH_2 group can also play the role of electron-acceptor centres[8]. Hence methanol with its hydrophobic and hydrophilic groups can interact with the other two components if the components behave as electron-donors. In this case, the hydrophobic group exhibits attractive type interactions and the hydrophilic shows repulsive type whereas repulsive interactions exist in between the two electron-donors, as a net effect the ternary system experiences a larger compressibility. In case if aniline behaves as electron-acceptor then it seems that donor-acceptor complexation of the two solutes exist in the alcohol medium wherein all are attractive type interactions that leads to a comparatively lower compressibility.

Thus it is of interest here to know what type of molecular situation exists inside the liquid mixtures. Hence, the present work deals with the measurement of ultrasonic velocity, density and viscosity and computation of related parameters at 303 K in the ternary mixture of aniline + methanol + benzene.

Experimental Section

The mixtures of various concentrations in mole fraction were prepared by taking purified AR grade samples at 303 K.

The ultrasonic velocities in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of ± 0.01 ms^{-1}. The density and viscosity are measured using a pycknometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-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[9-11]:

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

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

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

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

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

and

$$A_{id} = \sum x_i A_i \quad \ldots(6)$$

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, A_{exp} is the experimental value and A_{id} is the ideal value.

Results and Discussion

Measured values of density, viscosity and velocity at 303K for the ternary system of aniline + methanol + benzene are given in **Table I**. All the measured parameters increase with increasing mole fraction of aniline. Such non-linear variation indicates the presence of intermolecular interactions between the components[12].

Among the three components, aniline and methanol are expected to involve in strong interaction due to their polar nature[13]. Even though benzene is unsaturated, it behaves like a saturated compound ordinarily. Moreover, the presence of benzene molecules as electron donor will give higher stability to the carbocation of methanol and hence they cannot provide any strong interaction. As aniline is having a relatively higher dielectric constant (6.8012) than benzene (2.2620) and as both are electron donors, the interaction between the molecules of aniline with benzene is found to be stronger[14,15].

The perusal of **Table II** reveals that adiabatic compressibility, intermolecular free length and free volume are continuously decreases with increasing mole fraction of aniline whereas internal pressure is in increasing trend[16]. A reduction in adiabatic compressibility is an indication that component molecules are held close to each other. Thus, addition of aniline makes all the components to be more closer. This idea is supported by the decreasing trend of intermolecular free length.

Free volume and internal pressure are behaving opposite to each other. Free volume shows a decreasing trend with increasing mole fraction of aniline[17]. Since the π and σ electrons of benzene are readily

Table I — Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of the system: Aniline + Methanol + Benzene at 303K

Mole fraction x_1	Mole fraction x_3	ρ kgm^{-3}	$\eta \times 10^3$ Nsm^{-2}	U ms^{-1}
0.0000	0.7110	835.4	0.577	1223.3
0.0959	0.6077	873.8	0.669	1268.0
0.2004	0.4995	890.5	0.830	1318.0
0.3021	0.4051	906.0	1.005	1370.0
0.4007	0.3033	932.7	1.194	1408.6
0.4983	0.2006	953.4	1.476	1455.6
0.6111	0.0960	967.5	1.895	1506.3
0.7046	0.0000	979.5	2.271	1549.2

Table II — Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of the system: Aniline + Methanol + Benzene at 303

Mole fraction x_1	Mole fraction x_3	$\beta \times 10^{10}$ Pa^{-1}	$L_f \times 10^{11}$ m	$V_f \times 10^7$ m^3mol^{-1}	$\pi_i \times 10^{-8}$ Pa
0.0000	0.7110	7.999	5.643	1.818	4.88
0.0959	0.6077	7.117	5.323	1.720	5.22
0.2004	0.4995	6.464	5.073	1.362	5.63
0.3021	0.4051	5.880	4.838	1.111	5.96
0.4007	0.3033	5.403	4.638	0.928	6.26
0.4983	0.2006	4.950	4.439	0.735	6.95
0.6111	0.0960	4.555	4.258	0.546	7.56
0.7046	0.0000	4.253	4.115	0.423	8.06

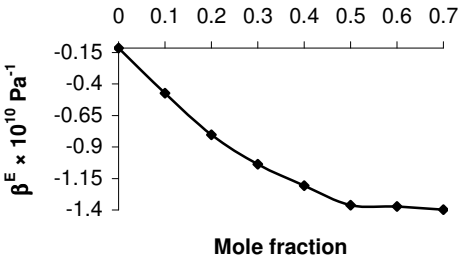

Figure 1 — Mole fraction of benzene *Vs.* excess adiabatic compressibility at 303 K.

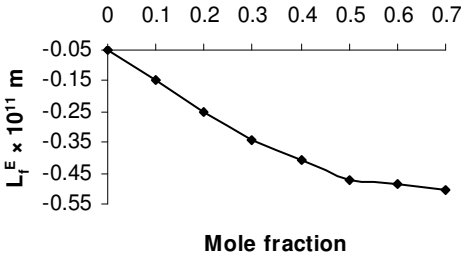

Figure 2 — Mole fraction of benzene *Vs.* excess intermolecular free length at 303 K.

available for an electrophile, it leads to a suggestion that dispersive types as well as dipole–induced dipole type interactions are dominant between benzene and other polar molecules.

The addition of aniline with a mixture leads to a compact structure due to the presence of dipolar type interaction. This contributes to the decrease in free volume values. However, as these can easily form complex structures, internal pressure shows an increasing trend[18].

The estimated excess values are illustrated in **Figures 1** to **4**. All the excess values are negative over the entire mole fraction range. The observed excess adiabatic compressibility and excess intermolecular free length values reflect the same idea as obtained above and the negative value clearly confirms the presence of strong interactions between the components. V_f^E and π_i^E are also negative whereas both are behaving in a similar manner[19,20]. A dip is formed around 0.3 mole fraction of aniline in the trend of V_f^E and π_i^E. The reduction of V_f^E with the increasing mole fraction of aniline becomes the maximum at 0.3 mole fraction of aniline. This clearly confirms that the maximum number of component molecules get into complexation at this mole fraction.

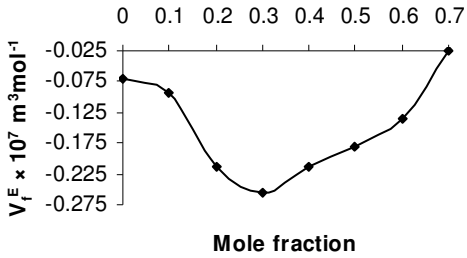

Figure 3 — Mole fraction of benzene *Vs.* excess intermolecular free volume at 303 K.

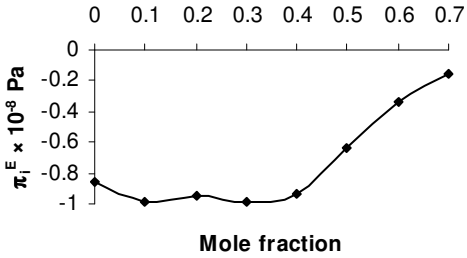

Figure 4 — Mole fraction of benzene *Vs.* excess internal pressure at 303 K.

Conclusion

Dispersive and dipole–induced dipole type interactions are found in the system, and aniline, on adding with the methanol + benzene is able to associate with other free components as well as with the binary complexes.

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