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Ultrasonic investigation of molecular association in binary mixtures of aniline with aliphatic alcohols

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Abstract

Sound velocity, density and viscosity values have been measured at 303 K in the three binary systems of aniline + methanol, ethanol and 1-propanol. 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 value in all the mixtures indicates that the molecular symmetry existing in the system is highly disturbed by the polar alcohol molecules' dipole−dipole and induced dipole−dipole type interactions that are existing in the systems. ***To cite this article: R. Thiyagarajan, L. Palaniappan, C. R. Chimie 10 (2007).***

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1. Introduction

Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules. In many industrial applications, liquid mixtures, rather than single component liquid system, are used in processing and product formulations. Thermodynamic and transport properties of liquid mixtures have been extensively used [1,2] to study the departure of a real liquid mixture from ideality. Further, these properties have been widely used to study the intermolecular interactions between the various species present in the mixture [3,4]. As alcohols are highly polar, they can be made to form azeotropes of binary complexes. Further, they play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures. Hence, the authors have performed a thorough study on the molecular interaction existing in the mixtures of methanol, ethanol and 1-propanol with aniline, using the sound velocity data. The present work deals with the measurement of ultrasonic velocity, density and viscosity, and computation of related parameters at 303 K in three non-ideal binary mixtures of aniline + methanol, aniline + ethanol and aniline + 1-propanol.

2. Experimental details

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

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at 303 K. The ultrasonic velocity (U) in liquid mixtures has been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of ± 0.1 ms^{-1}. The density, or the mass per unit volume (ρ) and viscosity (η) 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:

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

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

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

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

where, K_T and k are the temperature-dependent and independent parameters defined elsewhere [5,6] having a value 199.53×10^{-8} and 4.28×10^9 in S.I. system, respectively, $M_{\mathrm{eff}} = \sum x_i m_i$, where x is the mole fraction and m is the molecular weight of ith component, R is the universal gas constant; b is a dimensionless constant having a value of 2 for all liquids.

3. Results and discussion

The observed values for the system of aniline + alcohol are presented in Table 1. The values of density (ρ), viscosity (η) and ultrasonic velocity (U) show an increasing trend with increase in mole fraction of aniline in all the systems.

As ρ increases, the number of particles in a given region is increased and this leads to quick transfer of sound energy and thus velocity also increases [7,8]. As aniline is having a high boiling point, the energy between the molecules of aniline is so high that the molecular bonds of aniline cannot be ruptured, whereas for ethanol, it is not so. The increasing mole fraction of aniline supports non-rupturing of components and hence, increase in viscosity [9] is expected. All the observed parameters vary non-linearly and this indicates the existence of interactions in the medium. This is in line with the observations made by Jacek Glinski [10] in some binary systems.

The calculated values of adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f) and internal pressure (π_i) are given in Table 2. All these parameters invariably show a decreasing trend with increase in mole fraction of aniline except V_f in 1-propanol system. In 1-propanol system, unlike the other systems, V_f shows an increasing trend and all the other parameters, i.e., β, L_f, and π_i show a decreasing trend with increase in mole fraction of aniline irrespective of the alcohol type.

The compactness of the system with increase in mole fraction of aniline is indicated by reduced β values and the same is favoured by the decreasing trend of L_f. Such trends were noticed by Rajendran and Marikani [11] in some similar liquid systems. A continuous decrease in β or L_f is a clear evidence for the existence of strong interactions. Such strong interactions may be due to charge transfer, dipole–dipole, dipole–induced dipole, etc. It also reveals that both V_f and π_i exhibit similar trend [12], which is normally not so.

A monotonous non-linear decrease in V_f (or π_i) indicates that the chances for complex formation or charge transfer are overruled. The fluctuations in these

Table 1
Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of aniline (A) + methanol (B), ethanol (C), 1-propanol (D) at 303 K

Mole fraction of A	ρ kg m^{-3}			$\eta \times 10^3$ Ns m^{-2}			U ms^{-1}		
	B	C	D	B	C	D	B	C	D
0.0000	776.0	780.5	795.6	0.501	0.983	1.634	1103.0	1130.0	1193.0
0.1007	836.4	821.8	823.2	0.790	1.086	1.675	1208.7	1210.7	1238.7
0.1995	883.2	852.7	854.0	0.990	1.223	1.712	1301.0	1285.0	1289.6
0.2992	902.6	870.6	875.6	1.115	1.351	1.843	1356.5	1327.8	1325.6
0.4045	931.4	899.2	900.2	1.447	1.519	1.919	1432.3	1395.3	1379.3
0.5001	946.4	924.2	916.5	1.732	1.678	1.965	1496.2	1432.6	1407.3
0.6027	963.5	947.4	931.4	2.033	1.944	2.097	1515.3	1488.3	1467.0
0.7046	979.5	963.2	952.3	2.271	2.234	2.328	1549.2	1530.4	1514.5
0.8078	995.6	979.5	980.4	2.599	2.485	2.518	1569.6	1556.6	1544.3
0.9003	1004.3	992.1	993.6	2.856	2.732	2.814	1589.6	1576.2	1573.2
1.0000	1010.9	1010.9	1010.9	3.036	3.036	3.036	1614.0	1614.0	1614.0

Table 2
Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of aniline (A) + methanol (B), ethanol (C), 1-propanol (D) at 303 K

Mole fraction of A	$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{11}$ m			$V_f \times 10^7$ m^3 mol^{-1}			$\pi_i \times 10^{-8}$ Pa		
	B	C	D	B	C	D	B	C	D	B	C	D
0.0000	10.592	10.033	8.831	6.545	6.370	5.976	0.699	0.435	0.328	10.38	9.44	8.80
0.1007	8.183	8.009	7.917	5.703	5.641	5.608	0.505	0.431	0.336	10.25	8.85	8.40
0.1995	6.689	7.102	7.040	5.151	5.309	5.286	0.500	0.426	0.342	10.06	8.32	8.05
0.2992	6.020	6.515	6.499	4.885	5.083	5.077	0.490	0.423	0.349	9.12	8.21	7.90
0.4045	5.233	5.710	5.839	4.551	4.756	4.809	0.475	0.419	0.357	8.97	7.80	7.75
0.5001	4.720	5.272	5.509	4.319	4.567	4.670	0.449	0.416	0.362	8.66	7.57	7.65
0.6027	4.520	4.765	4.988	4.225	4.340	4.442	0.435	0.412	0.367	8.44	7.50	7.54
0.7046	4.253	4.432	4.578	4.098	4.184	4.253	0.423	0.410	0.373	8.06	7.45	7.43
0.8078	4.076	4.213	4.276	4.010	4.078	4.109	0.415	0.405	0.380	7.89	7.41	7.39
0.9003	3.940	4.057	4.066	3.942	4.001	4.005	0.403	0.399	0.385	7.64	7.31	7.31
1.0000	3.797	3.797	3.797	3.919	3.919	3.919	0.393	0.393	0.393	7.25	7.25	7.25

parameters, even though non-linear, follow the same trend, which reveals that there would be no induced dipoles. As both the components are polar molecules, the existing strong interactions are supposed to be of dipole–dipole type. Further, in such cases, as they are strong and mostly of attractive nature, chances for reduction in π_i are possible. The observed trend in π_i confirms this view.

The increasing trend of V_f observed only in 1-propanol system with the aniline mole fraction may be due to the larger chain length of 1-propanol molecule [13]. Of course this is reflected in the viscosity variations also. The addition of aniline makes the medium to have more and more ring structured molecule that restricts the movement of linear chain molecules and thus free volume is found to increase with aniline mole fraction. This is not conflicting with the decreasing trend observed for other two alcohols as methanol is small in size, whereas for ethanol, the hydrocarbon chain has hydrophobic nature [14]. In the 1-propanol system, it is observed that V_f shows a monotonous increase, whereas a reverse trend is observed in π_i values with increase in mole fraction of aniline. A continuous increase in V_f indicates that the components are packed in a cage-like structure; however, no complex formation is suspected. This compactness of the medium reduced the effective adhesive forces and thus π_i shows a decreasing trend [15,16].

To ascertain these conclusions, excess values of these parameters have been evaluated using the standard relations:

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

and

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

where A^E stands for excess property of any given parameter, A_{exp} is the experimental value and A_{id} is the

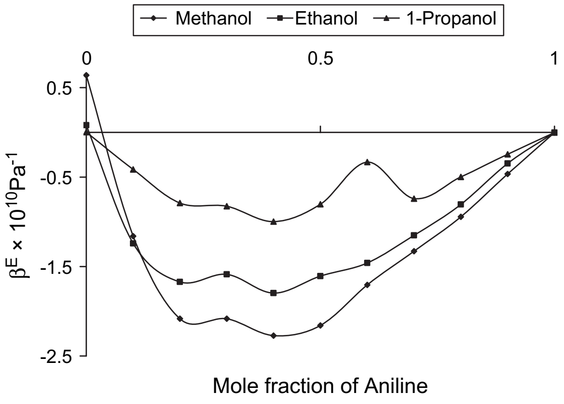

Fig. 1. Mole fraction vs. excess adiabatic compressibility at 303 K.

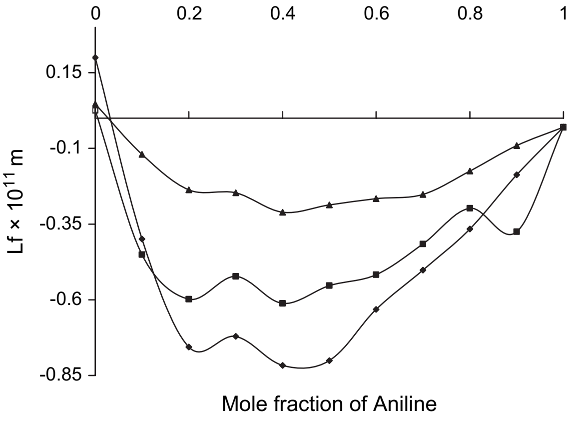

Fig. 2. Mole fraction vs. excess intermolecular free length at 303 K.

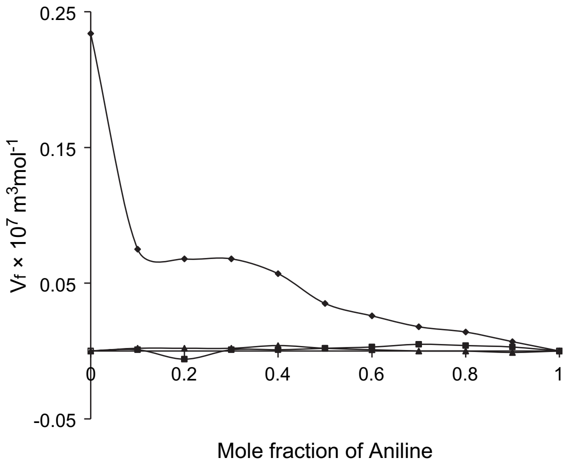

Fig. 3. Mole fraction vs. excess free volume at 303 K.

ideal value and x and A refers to the mole fraction and the relevant property of the ith component, respectively. The trends shown by the calculated values are depicted in Figs. 1–4. The perusal of these figures indicates that β^E and L_f^E in the mixture are fully negative, which confirms the existence of strong interactions. V_f^E and π_i^E are positive, but V_f^E shows a decreasing trend with increasing the mole fraction of aniline, whereas π_i^E values are highly fluctuating. The positive but decreasing V_f^E suggests that the dipole–dipole interactions need not to be of fully attractive type [17,18]. The existence of polar-like interactions is also reflected in the π_i^E values.

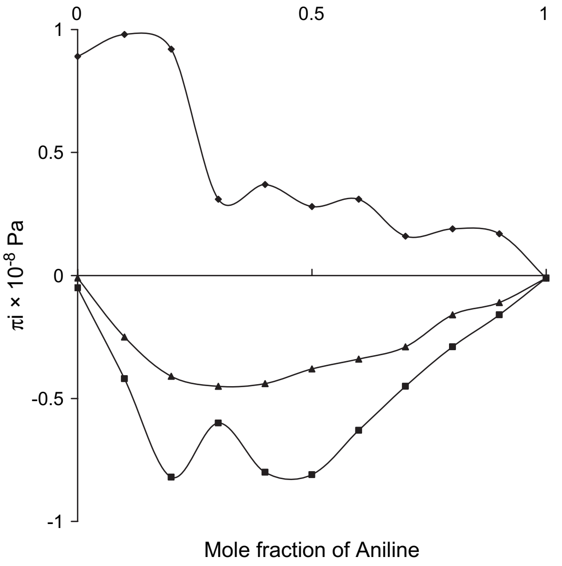

Fig. 4. Mole fraction vs. excess internal pressure at 303 K.

All the three alcohols are having one hydroxyl group with increasing number of methyl group. The hydrophilic hydroxyl group in all the three alcohols can interact with the amino group of aniline and thus dipole–dipole interactions are evident in all the three systems. In case of ethanol, the hydrocarbon chain acts as hydrophobic, whereas in other two alcohols such properties are not evident. This hydrophobic tendency needs a non-polar group to interact. 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 [19] and hence the hydrophobic nature of ethanol can create temporary dipoles in the amino group of aniline molecule and thus dipole–induced dipole interactions are additionally existing in the ethanol system. The formations of these temporary dipoles are reflected in the observed fluctuations in the trend of V_f^E in the ethanol system.

In these ethanol system, V_f^E values are observed to be positive and fluctuating, whereas π_i^E values are negative and have haphazard variations. These fluctuations in the considered binary mixture reflect the possibility of new induced dipoles. Thus, dipole–dipole and dipole–induced dipole types are confirmed in the system.

4. Conclusion

1. Presence of interactions is confirmed in all the systems.
2. Existing interactions are strong in magnitude irrespective of the alcohol chain length.
3. In addition to the unanimous existence of dipole–dipole interactions, dipole–induced dipole types are additionally present in the ethanol system.

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