

Ultrasonic study of molecular interaction in ternary liquid mixtures at 293K

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Abstract: Densities and ultrasonic speeds of the ternary liquid mixture of diethyl amine with acetone and acetophenone in n-hexane at 293K over the entire composition range were measured. From these data, acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), internal pressure (π_i), excess velocity (U^E), excess adiabatic compressibility (β^E), excess intermolecular free length (L_f^E), excess acoustic impedance (Z^E) have been evaluated. These excess parameters have been used to discuss the nature and extent of interaction between the component molecules in the ternary mixtures. The ultrasonic speeds calculated according to Nomoto's relation, Rao's specific sound velocity theory and impedance dependence relation and are compared with those obtained experimentally.

Keywords: Ultrasonic speeds, Acoustic impedance, Intermolecular free length, Excess adiabatic compressibility.

I. Introduction

Measurements of ultrasonic investigations find extensive applications in predicting the physico-chemical behaviour of liquid mixtures [1-4]. Ultrasonic velocity in a liquid mixture is fundamentally related with the binding forces acting between the atoms or molecules present in the liquid systems [5].

. These studies can also be used to identify complexation and to calculate the stability constants of complexes [7-8]. The donor-acceptor complex formation is biologically important. Oxygen transfer in blood involves reversible complexation between haeme and oxygen. Electron-deficient carbons of carbonyl group can act as electrophiles. Basic groups like amino groups can interact with this group to form a complex and influence the properties of such compound [9]. In this paper, the results obtained in the study of molecular interaction between diethyl amine with acetone and acetophenone in n-hexane solvent have been reported over the entire composition at 293K. Molecular interactions among the components of the mixtures were inferred from the sign of the excess and deviation properties.

II. Experimental

Diethyl amine, Acetone and Acetophenone were Anal R grade. The solvent n-hexane was purified by distillation (b.p.69°C) before use. Densities, Viscosities and Ultrasonic Velocities were measured at 293K over a wide range of concentrations (0.02-0.2M). The densities of pure compounds and their solutions were measured accurately using Rudolph digital densitometer (accuracy ± 0.1). Viscosities of pure compounds and their mixtures were determined using Ostwald's Viscometer calibrated with double distilled water.

The ultrasonic velocity was measured by using variable path single crystal interferometer (Model F-81S, Mittal Enterprise, India) at fixed frequency 2 MHz with accuracy of $\pm 0.1 \text{ ms}^{-1}$. The temperature of the solution under study is maintained constant using the electronic Juloba thermostat. This thermostat is equipped with a heater, a stirrer, a thermometer and a regulator. The temperature was maintained with an accuracy of $\pm 0.1\text{K}$. Acoustical parameters such as adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) internal pressure (π_i), and relaxation time (τ) were calculated using standard equations [10].

$$\beta = 1/U^2\rho \quad (1)$$

$$L_f = k/\sqrt{U\rho} \text{ A}^0 \quad (2)$$

where, k is Jacobson's constant. This constant is a temperature dependent parameter whose value at any temperature (T) is given by $(93.875+0.345T) \times 10^{-8}$.

$$Z = \rho U \quad (3)$$

$$\pi_i = bRT(K\eta/U)^{1/2} (\rho^{2/3}/M_{\text{eff}}^{7/6}) \quad (4)$$

Where b is the cubic packing factor which is assumed to be 2 for all solutions, K is the temperature dependent constant whose value is 4.28×10^9 , R is the universal gas constant, T is the absolute temperature.

M_{eff} is the effective molecular weight which is expressed as

$$M_{\text{eff}} = (X_1M_1 + X_2M_2 + X_3M_3) \quad (5)$$

Where X and M are the mole fraction and molar weight of the individual constituent in the mixture respectively.

$$\tau = 4\eta / 3\rho U^2 \quad (6)$$

The strength of interaction between the component molecules of ternary mixtures is well reflected in the deviation of the excess functions from ideality [11]. The excess properties such as U^E , β^E , L_f^E and Z^E were calculated using the equation

$$Y^E = Y_{\text{mix}} - [X_1Y_1 + X_2Y_2 + X_3Y_3]$$

where Y^E is U^E or β^E or L_f^E or Z^E and X represents mole fractions of the component and subscript 1,2 and 3 for the components 1,2 and 3.

The different theoretical ultrasonic velocity relations used in the present study are expressed as follows, Nomoto's relation [12].

$$U_{\text{NR}} = [(X_1R_1 + X_2R_2 + X_3R_3) / (X_1V_1 + X_2V_2 + X_3V_3)]^3$$

where X_1, X_2, X_3 are the mole fraction of the liquid mixtures. R_1, R_2, R_3 the molar sound velocity and V_1, V_2, V_3 are the molar volume of the components of ternary mixture.

Rao's specific sound velocity relation [13]

$$U_R = (\sum x_i r_i \rho)^3$$

where x_i is the mole fraction, r_i is the Rao's specific sound velocity = $u_i^{1/3} / \rho_i$, ρ is the density of the mixture, ρ_i is the density and u_i is the velocity of the i^{th} component of the mixture.

Impedance dependent relation [14]

$$U = (\sum X_i Z_i) / (\sum X_i \rho_i)$$

where X_i is the mole fraction, Z_i is the acoustic impedance and ρ_i is the density of the i^{th} component of the mixture.

III. Results and Discussion

The experimental densities and ultrasonic velocities at 293K of the pure liquids are presented in Table 1. The calculated values for various acoustical parameters such as β , L_f , Z and π_i are given in Table 2. Adiabatic compressibility (β) is a measure of intermolecular association or dissociation or repulsion. It also determines the orientation of the solvent molecules around the liquid molecule. The structural arrangement of the molecule affects the adiabatic compressibility. It is found that the adiabatic compressibility decreases with increasing concentration for both the system. This trend suggests that there is significant interaction between unlike molecules [15].

The free length is the distance between the surfaces of the neighbouring molecules. Generally, when the ultrasonic velocity increases, the value of the free length decreases [16]. The decrease in intermolecular free length indicates the interaction between the solute and solvent molecules due to which the structural arrangement in the neighbourhood of constituent ions or molecules gets affected considerably.

Sounds travels through materials under the influence of sound pressure. Since, molecules or atoms of a liquid are bound elastically to one another, the excess pressure results in a wave propagating through the liquid. Increasing trend of Z for both the systems is in agreement of increasing ultrasonic speed of the solutions.

The internal pressure is a measure of cohesive forces between the component molecules. The value of π_i increases for diethyl amine-acetone-n-hexane system due to the various degrees of dispersive interaction and the columbic interaction existing between the component molecules.

In order to highlight the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a physical property of the liquid mixtures from the ideal behaviour is a measure of the interaction between the molecules, which may be due to either adhesive or cohesive force.

Table 1 Experimental values of the Ultrasonic velocity and density of pure liquids.

Liquid	Ultrasonic Velocity (U) m.s ⁻¹	Density (ρ) kg.m ⁻³
Acetone	1185	790
Acetophenone	1468.8	1028
Diethyl amine	2081	707.4
Hexane	1099.8	658

Table 2 Values of U , ρ , β , L_f , Z and π_i of ternary system as a function of equimolar concentration of amine and ketone at 293K.

Conc. (M)	Ultrasonic velocity (U) m.s ⁻¹	Density (ρ) kg.m ⁻³	Adiabatic compressibility (β) $\times 10^{-9}$ m ² .N ⁻¹	Free length (L_f) $\times 10^{-10}$ m	Acoustic impedance (Z) $\times 10^6$ kg.m ⁻² .s ⁻¹	Internal pressure (π_i) $\times (10^{13})$ Pascal
Diethyl amine + Acetone + Hexane						
0.02	1062.4	658.0	1.350	0.0226	0.699	4.465
0.04	1060.2	660.0	1.347	0.0226	0.699	4.525
0.06	1058.4	662.3	1.347	0.0226	0.700	4.587
0.08	1057.0	664.0	1.347	0.0226	0.701	4.643
0.10	1056.0	667.0	1.344	0.0225	0.704	4.710
0.12	1054.3	669.3	1.344	0.0225	0.705	4.772
0.14	1052.4	671.0	1.345	0.0225	0.706	4.830
0.16	1051.0	673.4	1.344	0.0224	0.707	4.893
0.18	1049.5	675.0	1.345	0.0224	0.708	4.950
0.20	1049.0	677.0	1.342	0.0224	0.710	5.007
Diethyl amine + Acetophenone + Hexane						
0.02	1070.10	666.0	1.311	0.0224	712	4.171
0.04	1072.40	666.8	1.304	0.0223	715	4.160
0.06	1073.90	668.0	1.298	0.0223	717	4.154
0.08	1075.00	669.2	1.293	0.0222	719	4.149
0.10	1076.20	670.4	1.287	0.0222	721	4.144
0.12	1077.90	672.3	1.280	0.0221	724	4.143
0.14	1080.50	674.8	1.269	0.0220	729	4.144
0.16	1082.30	675.5	1.263	0.0220	731	4.135
0.18	1083.40	676.4	1.259	0.0219	732	4.128
0.20	1085.00	677.6	1.253	0.0219	735	4.123

Table 3 Excess values of ultrasonic velocity (U^E), adiabatic compressibility (β^E), intermolecular free length (L_f^E) and acoustic impedance (Z^E) of ternary mixtures at 293K

Conc.(M)	Excess ultrasonic velocity (U^E) m.s ⁻¹	Excess adiabatic compressibility (β^E) $\times 10^{-9}$ m ² .N ⁻¹	Excess intermolecular free length (L_f^E) $\times 10^{-10}$ m	Excess acoustic impedance (Z^E) $\times 10^6$ kg.m ⁻² .s ⁻¹
Diethyl amine + Acetone + n Hexane				
0.02	-51.2025	-0.00054	0.0010	-37737.647
0.04	-66.9215	-0.00054	0.0012	-49923.713
0.06	-81.9658	-0.00053	0.0014	-61274.897
0.08	-96.3436	-0.00053	0.0015	-72749.247
0.10	-110.0629	-0.00052	0.0017	-82343.378
0.12	-124.2313	-0.00052	0.0019	-92911.895
0.14	-138.3562	-0.00051	0.0020	-104022.36
0.16	-151.7446	-0.00051	0.0022	-113842.32
0.18	-165.0033	-0.00051	0.0024	-124357.73
0.20	-177.0389	-0.00050	0.0025	-133569.51
Diethyl amine + Acetophenone + n Hexane				
0.02	-46.2004	0.0755	0.0007	-29202.76
0.04	-60.2740	0.0888	0.0009	-44893.928
0.06	-75.0222	0.1033	0.0011	-60547.473
0.08	-90.0465	0.1185	0.0012	-76328.22
0.10	-104.8482	0.1335	0.0014	-91903.969
0.12	-119.0288	0.1457	0.0016	-106252.73
0.14	-132.1895	0.1546	0.0017	-119207.68
0.16	-146.0319	0.1688	0.0019	-134508.83
0.18	-160.4572	0.1840	0.0021	-149934.81
0.20	-174.2666	0.1974	0.0022	-164566.81

Table 3 presents that the value of U^E is negative which indicate the presence of weak interaction between the component molecules[17]. This supports our view that the interactions between the two ternary mixtures are weaker. The excess positive β^E values for diethyl amine + acetophenone + n-Hexane system represent the dispersion forces while the negative values for diethyl amine + acetone +n-Hexane interprets the charge transfer interaction between the unlike molecules [18].

The values of L_f^E are positive which indicates weak molecular interaction between the components of the mixtures, which results from dispersion force .The negative Z^E values in both ternary mixtures indicate the weakening of intermolecular interactions between the component molecules.

Table 4 Theoretical ultrasonic velocities calculated using Nomoto's relation, Rao's specific sound and Impedance dependence relation velocity theory along with experimental values and the percentage error for two ternary systems at 293K

Concentration	Expt.	Ultrasonic Velocity, U, ms^{-1}			% Deviation		
		Nomoto	Rao	Impedance	Nomoto	Rao	Impedance
Diethyl amine + Acetone + n-Hexane							
0.02	1062.4	1035.8	1023.2	1114.8	2.5003	3.6905	-4.9285
0.04	1060.2	1046.1	1030.4	1129.3	1.3289	2.8151	-6.5162
0.06	1058.4	1056.2	1039.0	1143.4	0.2039	1.8337	-8.0302
0.08	1057.0	1066.2	1044.9	1157.1	-0.8735	1.1473	-9.4702
0.1	1056.0	1076.1	1057.0	1170.4	-1.902	-0.0923	-10.8357
0.12	1054.3	1085.8	1065.8	1183.4	-2.9879	-1.0952	-12.2435
0.14	1052.4	1095.4	1071.9	1196.0	-4.0845	-1.8544	-13.644
0.16	1051.0	1104.8	1081.4	1208.3	-5.1226	-2.8931	-14.9626
0.18	1049.5	1114.2	1087.1	1220.2	-6.1613	-3.5835	-16.265
0.20	1049.0	1123.4	1094.8	1231.8	-7.0888	-4.3660	-17.4293
Diethyl amine + Acetophenone + n-Hexane							
0.02	1070.1	1038.0	1058.7	1119.4	2.9996	1.0646	-4.6075
0.04	1072.4	1050.6	1058.0	1138.6	2.0338	1.3435	-6.1714
0.06	1073.9	1063.2	1059.2	1157.3	0.9981	1.3686	-7.7705
0.08	1075.0	1075.8	1060.4	1175.7	-0.0722	1.3552	-9.3686
0.1	1076.2	1088.4	1061.7	1193.7	-1.1312	1.3492	-10.9171
0.12	1077.9	1101.0	1066.3	1211.3	-2.1405	1.0786	-12.3753
0.14	1080.5	1113.6	1073.8	1228.5	-3.0608	0.6246	-13.7004
0.16	1082.3	1126.2	1072.7	1245.4	-4.0535	0.8901	-15.0716
0.18	1083.4	1138.8	1072.6	1262.0	-5.1108	1.0007	-16.4820
0.20	1085.0	1151.4	1073.9	1278.2	-6.1168	1.0234	-17.8046

Theoretical evaluation of ultrasonic speeds in liquid mixtures offers a simple and convenient method [19] for the study of the nature of molecular interactions in these mixtures. The theoretical values of ultrasonic speeds, evaluated using Nomoto's relation, impedance dependence relation and Rao's specific sound velocity theory along with the experimental values and percentage deviation in the calculated values are presented in Table 4 for comparisons. On comparison, the results indicate that for both the systems, diethyl amine + acetone + n-Hexane mixtures, minimum deviations are observed in case of Rao's specific sound velocity theory followed by Nomoto's relation and impedance dependence relation shows the maximum deviation.

IV. Conclusion

The results of the present study indicate that the thermodynamic parameters are sensitive to the molecular interactions present in the liquid mixtures. The positive values of L_r^E and the negative values of U^E , Z^E indicates the presence of weak dipolar and dispersive interactions between the component molecules over the entire composition range of both ternary mixtures. The charge transfer interaction between diethyl amine and acetone is clearly revealed by negative β^E values for diethyl amine + acetone + n-Hexane system. The theoretical values of ultrasonic velocities are calculated by using Nomoto's relation, Rao's specific sound velocity theory and impedance dependence relation. Among the three theories taken up for the prediction of sound velocity, a good agreement in experimental and theoretical values of velocity is observed in case of Rao's specific sound velocity theory for both ternary systems.

Acknowledgements

One of the authors (SH) is thankful to the Director of Dr. Mrs. Ira N. Nimdeokar P.G. and Research centre for Chemistry, Hislop College, Nagpur for providing laboratory facilities.

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