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Ultrasonic Investigations of Molecular Associations in Binary Mixture of Trimethylamine with Non-polar Solvents

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Abstract- Ultrasonic propagation parameters yield valuable information regarding the behaviour of liquid systems. The intermolecular interactions and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity and its derived parameters. Ultrasonic velocity and density measurements for binary mixture: I trimethylamine + benzene II. trimethylamine + toluene III. trimethylamine + o- xylene at 298.15 K have been utilized to compute excess Isentropic compressibility, excess molar volume, free length and available volume. These values are reported as a function of mole fraction X_1 of trimethylamine β_s^E vs X_1 and V_m^E vs X_1 plots are explained in terms of specific/non-specific interactions between two like and unlike molecules.

Index Terms- Molecular interactions; Binary mixtures; trimethylamine

1. INTRODUCTION

Ultrasonic velocity and density measurements proved to be useful tools for gaining information on the dynamics of liquid systems[1-5]. Rao and Ragovramane [6] have explained the nature and strength of molecular interactions for the binary mixtures of triethylamine with benzene, toluene and o-xylene at 308.15K. Prakash et. al.[7] also measured ultrasonic velocity, density and viscosity of the binary mixtures of triethylamine with o-cresol, m- cresol, o- chlorophenol and benzyl alcohol at 308.15K. Thakur et.al.[8] studied binary liquid mixtures of trimethylamine with formic acid at different temperatures. Recently, an increasing number of thermodynamic studies in binary and ternary mixtures containing electrolytes and/or non-electrolytes are being performed which permit investigation in a wide range of solutions with suitable properties[8-14].

In the present study, the ultrasound velocity and density measurements have been made at 298.15K in binary mixtures: I trimethylamine + benzene II. trimethylamine + toluene III. trimethylamine + o-xylene. The parameters viz., β_s, β_s^E, L_f, V_m^E, V_a derived from experimental data have been presented and discussed.

2. EXPERIMENTAL

Ultrasonic velocity at 2 MHz has been measured by single crystal ultrasonic interferometer manufactured by M/s Mittal Enterprises. The accuracy of the velocity is ± 0.05%. The ultra-thermostat (Type U-10) was used to maintain the desired temperature. Water from ultra-thermostat was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket was well insulated and the temperature of the solution under study was maintained to an accuracy of $\pm 0.1^o$. Density measurement has been carried out

using pyknometer approximately 8.5 ml capacity, consisting of a small bulb with flat bottom and a graduated stem having well-fitted glass cap in order to prevent changes in composition due to evaporation of volatile liquids. The reproducibility of density values was found to be within ± 0.0002 gm/cm^3. All the chemicals used in the present work are from BDH (AR Grade). A thermostated paraffin bath was used to maintain the desired temperature during the measurements of density. The bath was made up of an immersion heater (1.5 KW), a stirrer, a check thermometer (Labotherm-N., German make), a contact thermometer and a relay [Jumo type, NT 15.0, 220 V ≅ 10A (German make)]. Thermal stability of the thermostat was found to be within $\pm 0.1^o$

3. RESULTS AND DISCUSSION:

Ultrasonic velocity (u) and density (d) have been experimentally determined for binary mixtures of trimethylamine alongwith benzene, toluene and o-xylene at 301.15K. The various acoustic parameters viz., Isentropic compressibility, molar volume, intermolecular free length and available volume were calculated using the following relations[15]

$\beta_s = 1/u^2d$ (1)
$V_m = M/d$ (2)
$L_f = k\sqrt{\beta_s}$ (3)
$V_a = V_m(1-u/u_\infty)$ (4)

where symbols have their usual meanings. The excess parameters β_s^E, and V_m^E was calculated as:

$\beta_s^E = \beta_s$ (mix.) - β_s (ideal) (5)
$V_m^E = V_m$ (mix.) - V_m (ideal) (6)

The experimentally determined ultrasonic velocity and density along with the calculated parameters are given in Table-1.

Table 1. Experimental Values of ultrasonic velocity, density, Isentropic compressibility, intermolecular free length, Available volume and excess molar volume for binary mixture: I trimethylamine + benzene II. trimethylamine + toluene III. trimethylamine + o- xylene at 298.15 K

Mole Fraction of Trimethylamine (X_1)	Ultrasonic Velocity (u)(ms^{-1})	Density (d) (g/mL)	Isentropic Compressibilty (β_s) x 10^{12} (cm^2/dyne)	Intermolecular free length (L_f)	Molar Volume (Excess) (V_m^E) (mL/mol)	Available Volume (V_a) (mL.mol)
(I) Trimethylamine + Benzene at 298.15 K						
0.0000	1280	0.8444	72.28	0.5365	0.00	18.51
0.0892	1283	0.8190	74.18	0.5435	-0.32	18.49
0.1805	1286	0.7928	76.27	0.5511	-0.56	18.49
0.2741	1289	0.7659	78.58	0.5594	-0.75	18.50
0.3700	1292	0.7385	81.12	0.5683	-0.89	18.53
0.4684	1295	0.7104	83.94	0.5781	-0.95	18.57
0.5692	1297	0.6823	87.09	0.5889	-1.00	18.67
0.6727	1300	0.6536	90.53	0.6004	-0.97	18.74
0.7790	1301	0.6241	94.59	0.6137	-0.83	18.93
0.8880	1303	0.5939	99.20	0.6285	-0.52	19.15
1.0000	1306	0.5628	104.17	0.6440	0.00	19.30
(II) Trimethylamine + Toluene at 298.15 K						
0.0000	1292	0.8601	69.65	0.5266	0.00	20.62
0.1032	1291	0.8291	72.34	0.5367	0.11	20.65
0.2056	1293	0.7982	74.99	0.5464	0.23	20.55
0.3074	1296	0.7674	77.58	0.5558	0.35	20.30
0.4084	1298	0.7370	80.54	0.5663	0.45	20.14
0.5087	1299	0.7068	83.85	0.5778	0.53	20.05
0.6083	1300	0.6774	87.35	0.5897	0.50	19.94
0.7073	1302	0.6484	90.97	0.6018	0.43	19.76
0.8055	1303	0.6197	95.04	0.6152	0.31	19.63
0.9031	1304	0.5912	99.47	0.6293	0.16	19.50
1.0000	1306	0.5628	104.17	0.6440	0.00	19.30
(III) Trimethylamine + O-Xylene at 298.15 K						
0.0000	1350	0.8552	64.16	0.5054	0.00	19.37
0.1159	1355	0.8210	66.34	0.5139	0.73	18.76
0.2278	1360	0.7878	68.63	0.5227	1.35	18.15
0.3359	1365	0.7557	71.02	0.5318	1.83	17.54
0.4403	1370	0.7247	73.51	0.5410	2.15	16.93
0.5413	1375	0.6948	76.12	0.5505	2.32	16.32
0.6390	1380	0.6666	78.78	0.5601	2.21	15.69
0.7336	1385	0.6393	81.55	0.5698	1.93	15.05
0.8252	1390	0.6130	84.43	0.5798	1.46	14.41
0.9140	1395	0.5876	87.46	0.5901	0.81	13.77
1.0000	1306	0.5628	104.17	0.6440	0.00	19.30

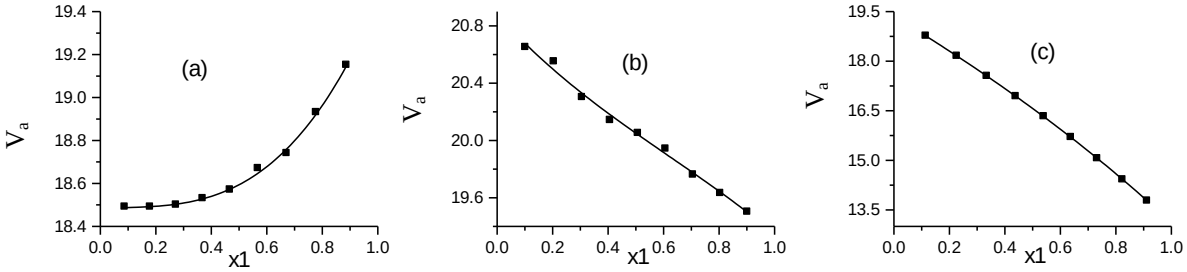

Figure1 Available Volume vs mole fraction (a) Trimethylamine + Benzene (b) Trimethylamine + Toluene (c) Trimethylamine + o-Xylene

Fig 1 shows the variation of available volume with mole fraction of Trimethylamine. The plots of available volume vs mole fraction of trimethylamine indicates the least interaction in the system containing benzene. In the light of the above results, it seems that the interactions present in the systems under investigation are due to electron releasing nature of trimethylamine. The experimentally determined ultrasonic velocities have been found to increase whereas densities have been found to decrease with increasing mole fraction(X_1) of trimethylamine. The Isentropic compressibility values (β_s) have been found to increase with increase in mole fraction (X_1) of trimethylamine. An increase in β_s values with increase in mole fraction may be ascribed to two effects: viz., (i) the decrease in density of the system and (ii) the dipole-dipole interaction between trimethylamine molecules. The dependence of excess Isentropic compressibility upon the mole fraction of trimethylamine has been examined by least square fitting the β_s^E values to a polynomial equation

$$\beta_s^E = A_0 + A_1X_1 + A_2X_1^2 \qquad (7)$$

The curve fit parameters along with standard deviations are listed in Table-2 and Fig.2.

Table- 2 CURVE FIT PARAMETERS FOR β_s^E

(I) Trimethylamine + Benzene at 298.15 K		
A0	0.29995916	0.13785
A1	-14.020345	0.65646
A2	13.466295	0.65709
(II) Trimethylamine + Toluene at 298.15 K		
A0	0.64788420	0.12293
A1	-15.250753	0.55893
A2	14.322070	0.5413
(III) Trimethylamine + O-Xylene at 298.15 K		
A0	0.15047245	0.07096
A1	-23.267500	0.31122
A2	9.3103516	0.29369

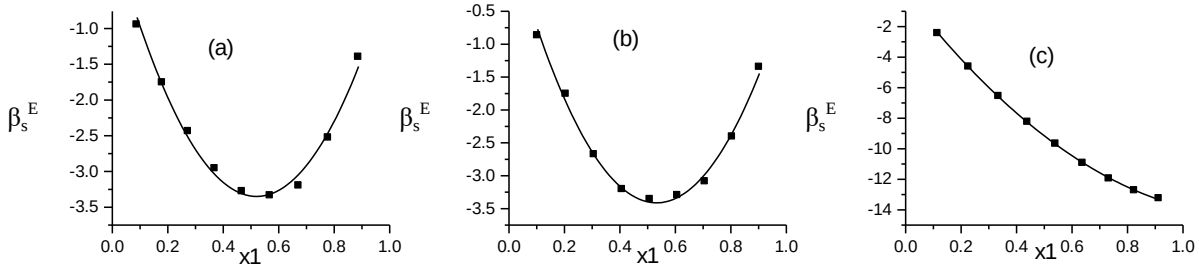

Figure 2 β_s^E vs x_1 (a) Trimethylamine + Benzene (b) Trimethylamine + Toluene (c) Trimethylamine + o-Xylene

The excess isentropic compressibility values have been found negative for all the systems under investigation. The negative excess Isentropic compressibility values, however, suggests dipole-dipole interaction between the molecules of binary mixtures. The extent of negativity is maximum in o-xylene. The negative excess values decide the non-specific interaction between the liquid molecules due to dispersion forces. The specific interaction will be due to dipole-dipole interaction, dipole-induced dipole

interaction and also associating nature of like molecules which is due to the hydrogen bonding. The increase in free-length values with decreasing ultrasonic velocity seems to be due to solute-solute interaction. Although Trimethylamine is strong polar, electron donating compound therefore it interact more with the other non-polar electron deficient molecules like benzene and toluene while compounds like o-xylene are polar to some extent. Therefore, it is expected that the computed excess isentropic compressibility must be negative. Dipole- dipole, Dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values [16-22].

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