

## Molecular Interactions in Binary Mixture of Propylamine with Non-polar Solvents

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Ultrasonic velocity and density measurements for binary mixture: **I.** propylamine + benzene **II.** propylamine + toluene **III.** propylamine + *o*-xylene at 301.15 K have been utilized to compute excess adiabatic compressibility, excess molar volume, free length and available volume. These values are reported as a function of mole fraction  $X_1$  of propylamine  $\beta_s^E$  vs.  $X_1$  and  $V_m^E$  vs.  $X_1$  plots are explained in terms of dipole-dipole interactions between two like and unlike molecules.

**Key Words:** Molecular interactions, Binary mixtures, Propylamine.

### INTRODUCTION

Ultrasonic velocity and density measurements proved to be useful tools for gaining informations on the dynamics of liquid systems<sup>1-5</sup>. Rao and Regovramane<sup>6</sup> have explained the nature and strength of molecular interactions for the binary mixtures of triethyl amine with benzene, toluene and *o*-xylene at 308.15 K. Prakash *et al.*<sup>7</sup> also measured ultrasound velocity, density and viscosity of the binary mixtures of triethyl amine with *o*-cresol, *m*-cresol, *o*-chlorophenol and benzyl alcohol at 308.15 K. 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<sup>8-11</sup>.

In the present study, the ultrasound velocity and density measurements have been made at 301.15 K in binary mixtures: **I.** propylamine + benzene, **II.** propylamine + toluene, **III.** propylamine + *o*-xylene. The parameters *viz.*,  $\beta_s$ ,  $\beta_s^E$ ,  $L_f$ ,  $V_m^E$ ,  $V_a$  derived from experimental data have been presented and discussed.

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## 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  $\pm 0.05\%$ .

Density measurements has been carried out using pycnometer having well-fitted glass cap inorder to prevent changes in composition due to evaporation of volatile liquids. The accuracy in density measurements is within the range  $\pm 0.005$  g/mL. All the chemicals used in the present work are from BDH (AR grade).

## RESULTS AND DISCUSSION

Ultrasonic velocity ( $u$ ) and density ( $d$ ) have been experimentally determined for binary mixtures of propyl amine alongwith benzene, toluene and *o*-xylene at 301.15 K.

The various acoustic parameters *viz.*, adiabatic compressibility, molar volume, intermolecular free length and available volume were calculated using the following relations<sup>12</sup>

$$\beta_s = 1/u^2d$$

$$V_m = M/d$$

$$L_f = k\sqrt{\beta_s}$$

$$V_a = V_m(1-u/u_\infty)$$

where symbols have their usual meanings. The excess parameters  $\beta_s^E$  and  $V_m^E$  was calculated as:

$$\beta_s^E = \beta_s (\text{mix.}) - \beta_s(\text{ideal})$$

$$V_m^E = V_m (\text{mix.}) - V_m (\text{ideal})$$

The experimentally determined ultrasonic velocity and density along with the calculated parameters are given in Table-1 and Fig. 1. Both the experimentally determined ultrasonic velocity as well as density have been found to decrease with increasing mole fraction ( $X_1$ ) of propylamine.

The adiabatic compressibility values ( $\beta_s$ ) have been found to increase with the increase in mole fraction ( $X_1$ ) of propyl amine. An increase in  $\beta_s$  values with increasing  $X_1$  may be ascribed to two effects: *viz.*, (i) the decrease in density of the system and (ii) the dipole-dipole interaction between propylamine molecules.

The dependence of excess adiabatic compressibility upon the mole fraction of propylamine has been examined by least square fitting the  $\beta_s^E$  values to a polynomial equation

$$\beta_s^E = A_0 + A_1X_1 + A_2X_1^2$$

TABLE-1

Mole fraction propylamine ( $X_1$ )	Ultrasonic velocity (u) ( $\text{ms}^{-1}$ )	Density (d) (g/mL)	Isentropic compressibility ( $\beta_s \times 10^{12}$ ) ( $\text{cm}^2/\text{dyne}$ )	Intermolecular free length ( $L_f$ )	Molar volume ( $V_m^E$ ) (mL/mol)	Available volume ( $V_a$ ) (mL/mol)
(I) Propylamine + benzene						
0.0000	1297.3	0.8597	69.11	0.5229	0.00	17.19
0.1316	1268.2	0.8463	73.47	0.5391	-0.93	18.50
0.2613	1250.6	0.8215	77.83	0.5549	-0.54	19.41
0.3890	1230.0	0.7921	83.45	0.5746	0.42	20.61
0.5148	1219.8	0.7765	86.55	0.5852	-0.21	20.88
0.6388	1204.8	0.7478	92.13	0.6037	0.72	21.75
0.7610	1188.3	0.7254	97.63	0.6215	0.91	22.66
0.8813	1171.4	0.7170	101.64	0.6341	-0.60	23.46
1.0000	1157.5	0.6911	108.00	0.6537	0.00	23.61
(II) Propylamine + toluene						
0.0000	1286.3	0.8510	71.02	0.5300	0.00	21.22
0.1535	1266.7	0.8348	74.66	0.5435	-0.49	21.74
0.2973	1244.3	0.8113	79.61	0.5612	-0.04	22.52
0.4323	1217.5	0.7912	85.27	0.5808	-0.40	23.48
0.5593	1210.3	0.7639	89.37	0.5946	0.88	23.45
0.6790	1193.7	0.7508	93.47	0.6081	0.02	23.58
0.7920	1179.0	0.7368	97.64	0.6215	-0.71	23.52
0.8988	1167.1	0.7152	102.65	0.6373	-0.51	23.59
1.0000	1157.5	0.6911	108.00	0.6537	0.00	23.61
(III) Propylamine + <i>o</i> -xylene						
0.0000	1342.5	0.8792	63.11	0.4997	0.00	19.40
0.1703	1314.2	0.8582	67.47	0.5167	-0.39	20.39
0.3239	1271.3	0.8310	74.46	0.5428	0.08	22.44
0.4630	1247.0	0.8122	79.18	0.5597	-0.55	22.88
0.5897	1240.3	0.7803	83.31	0.5741	0.51	22.55
0.7055	1216.8	0.7690	87.83	0.5895	-1.01	22.69
0.8117	1191.7	0.7423	94.86	0.6126	-0.60	23.32
0.9095	1173.2	0.7207	100.81	0.6315	-0.79	23.41
1.0000	1157.5	0.6911	108.00	0.6537	0.00	23.61

The curve fit parameters along with standard deviations are listed in Table-2 and Fig. 2. The excess adiabatic compressibility values are found to be negative, although smaller in magnitude. The negative values, however, suggests dipole-dipole interaction between the molecules of binary mixtures. The strength of interaction is much weaker in propyl amine and benzene system, which may be attributed to the non-polar nature of benzene.

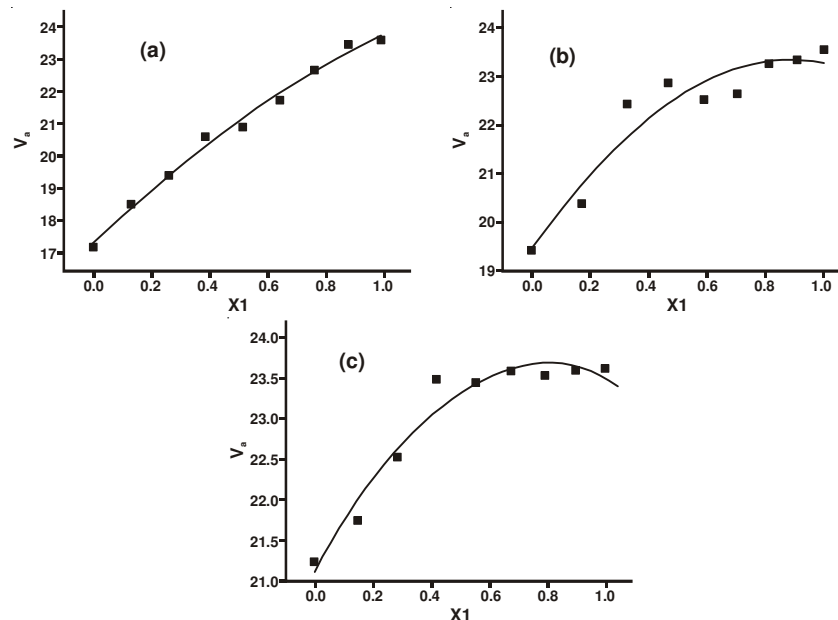


Fig. 1. Available volume ( $V_a$ ) vs. mole fraction ( $X_1$ ); (a) propylamine + benzene (b) propylamine + toluene (c) propylamine + *o*-xylene

TABLE-2  
CURVE FIT PARAMETERS FOR  $\beta_s^E$

(I) Propylamine + benzene		
A0	0.081256427	0.50766
A1	-7.114539200	2.34730
A2	6.714295500	2.25219
(II) Propylamine + toluene		
A0	-0.20674678	0.50854
A1	-9.57536420	2.29862
A2	9.96202410	2.18703
(III) Propylamine + <i>o</i> -xylene		
A0	0.52959338	1.06476
A1	-23.73502100	4.72729
A2	22.02892300	4.47285

The increase in free-length values with decreasing ultrasonic velocity seems to be due to solute-solute interaction.

The plots of available volume vs. mole fraction of propylamine also 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 is due to electron releasing nature of propylamine.

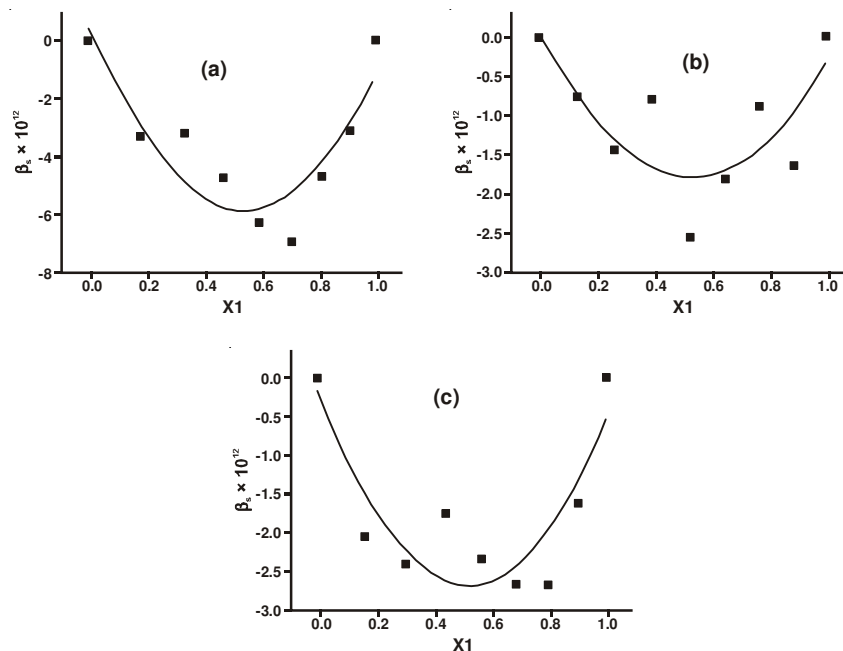


Fig. 2. Excess adiabatic compressibility ( $\beta_s^E$ ) vs. mole fraction ( $X_1$ );  
 (a) propylamine + benzene (b) propylamine + toluene  
 (c) propylamine + *o*-xylene

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