



Ultrasonic study of some polar and nonpolar binary liquid mixtures

K.Prasad^{1*}, Umakant Prasad²

¹University Department of Physics, T.M. Bhagalpur University, Bhagalpur-812 007, (INDIA)

²Department of Physics, T.N.B. College, Bhagalpur-812 007, (INDIA)

E-mail : k.prasad65@gmail.com

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ABSTRACT

Molecular interaction in three polar plus non-polar binary liquid mixtures (a) benzene + benzonitrile, (b) benzene + methyl propyl ketone (MPK) and (c) cyclohexane + MPK have been studied at 303.15K. Derived ultrasonic parameters isentropic compressibility (β), intermolecular free length (L_f), free volume (V_f), specific acoustic impedance (Z) and their respective excess parameters β^E , L_f^E , V_f^E and Z^E are computed. Relative association (RA), molar sound velocity (R) and solvation number (S_n) have also been computed. Hence the molecular interactions between the components of the three mixtures are studied, using the above parameters, over the entire composition range. It is found that the nature of interactions for the systems (a) and (b) are similar but different from that for system (c). The strength of interactions for the three systems is in decreasing order. Different ultrasonic parameters and excess values have been fitted by empirical equations with reliability better than 99%, in most of the cases.

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KEYWORDS

Ultrasonics;
Binary liquid mixture;
Molecular interaction;
Excess properties;
Ultrasonic parameters.

INTRODUCTION

Ultrasonic methods have been extensively used to study the physico-chemical behaviour of liquid systems. This is done by studying the ultrasonic velocity (U), density (ρ), viscosity (η) etc. in the pure liquids and their mixtures. A variation from linearity in the behaviour of ultrasonic velocity versus composition of mixture indicates presence of interactions between the components of the mixture. However, the study of only the observed parameters, such as, U, ρ and η etc. doesn't provide any information about the nature and relative strengths of these interactions. Such information are

provided by the investigation of derived parameters such as β , L_f , V_f , Z , RA, R, S_n , etc. and the excess values of some of these derived parameters.

The intermolecular interaction between polar and nonpolar components of binary liquid mixtures were studied in terms of non-ideality and excess molar volumes for the systems : (a) benzene + benzonitrile, (b) benzene + methyl propyl ketone (MPK) and (c) cyclohexane + MPK at 303.15°K^[1]. In the present work we have studied, to get better insight of the molecular interactions, for these systems in terms of β , L_f , V_f , Z , and their excess values as well as in terms of S_n , RA and percentage deviation of R over the entire composi-

tion range.

We have represented the observed and derived parameters and their excess values by accurate (> 99%) mathematical expressions using the method of polynomial fitting.

Theoretical

The different ultrasonic parameters are calculated using the relations below^[2-4]. The isentropic compressibility β is calculated using the equations of Newton and Laplace i.e.,

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

The distance covered by a sound wave between the surface of two molecules, called the intermolecular free length L_f , is given by

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

The effective volume accessible to the center of the molecule for movement is called the free volume per molecule V_f , given by

$$V_f = V_a - b \quad (3)$$

where K is a temperature dependent parameter and is equal to 631 at 303.15°K as given by Jacobson^[5,6]. V_a is the available volume and is calculated from the following expression obtained on combining the equations of Jacobson and Schaffs^[6,7].

$$V_a = (M/\rho)[1 - (U/U_\infty)] \quad (4)$$

where $U_\infty = 1600\text{ms}^{-1}$. The advantage of relation (4) over Kaulgud's thermodynamic relation^[8] is that it needs experimental ultrasonic velocity which can be measured with extreme precision. b , the van der Waal's parameter is given by

$$b = \frac{M}{\rho} \left[1 - \frac{R'T}{MU^2} \left\{ \sqrt{1 + \frac{MU^2}{R'T}} - 1 \right\} \right] \quad (5)$$

here R' is the gas constant and T is the absolute temperature. M is the molecular weight and for binary mixtures is replaced by M_{12} , where

$$M_{12} = X_1M_1 + X_2M_2 \quad (6)$$

here M_i is the molecular weight of the i th component of the mixture with mole fraction X_i . Specific acoustic impedance Z is given by

$$Z = \rho U \quad (7)$$

The ratio of experimental value L_f to the ideal value $(L_f)_{\text{ideal}}$ is a measure of the relative association RA and is given by^[9]

$$RA = L_f^M / (L_f^M)_{\text{ideal}} \quad (8)$$

The molar sound velocity R and the solvation number S_n are given, respectively, by

$$R = (M/\rho).U^{1/3} \quad (9)$$

$$S_n = (n_1/n_2)[1 - (\beta_S - \beta_1)] \quad (10)$$

Here, n_1 and n_2 are the number of moles of components 1 and 2 respectively. β_S and β_1 are, respectively, the isentropic compressibilities of the solution and the solvent. The excess values of the different parameters have been obtained by using the expression.

$$A^E = A_{\text{mix}} - A_{\text{ideal}} = A_{\text{exp}} - A_{\text{ideal}} \quad (11)$$

where

$$A_{\text{ideal}} = X_1A_1 + X_2A_2 \quad (12)$$

In equation (12) 'A' represents different ultrasonic parameters, such as, β , L_f , V_f , Z , etc. X_1 and X_2 are mole fractions of the first and second components in mixture with values A_1 and A_2 , respectively of the parameter A . A_{exp} stands for the experimentally determined value of the parameter A , for the mixture, with the help of experimental values of velocity and density. For our present study we have taken the experimental values of velocity and density, for the three systems, from literature^[10].

The measured parameters U and ρ and the derived parameters β , L_f , V_f and Z have been represented by an equation of the form :

$$P = \sum_{j=0} A_j X_1^j \quad (12)$$

The excess ultrasonic parameters A^E have been represented as a function of X_1 using equations of the Redlich-Kister form^[11].

$$A^E = X_1(1 - X_1) \sum_{n=0} B_n (1 - 2X_1)^n \quad (13)$$

Division by $X_1(1 - X_1)$ gives

$$\lambda A^E / X_1(1 - X_1) = \sum_{n=0} B_n (1 - 2X_1)^n \quad (14)$$

The right hand side of equations (12) and (14) are a simple power series in X_1 and $(1 - 2X_1)$, respectively, leading to easy evaluation of the coefficients a_j and B_n by the method of least squares.

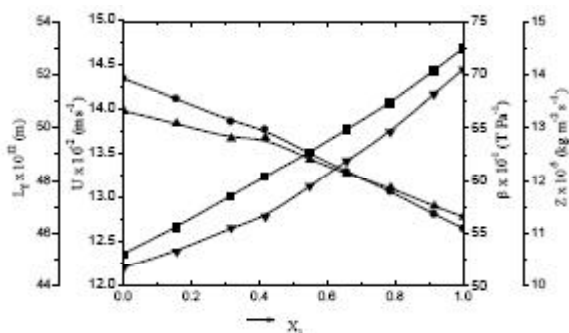
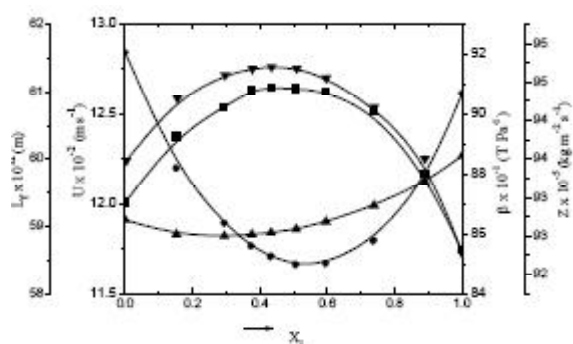
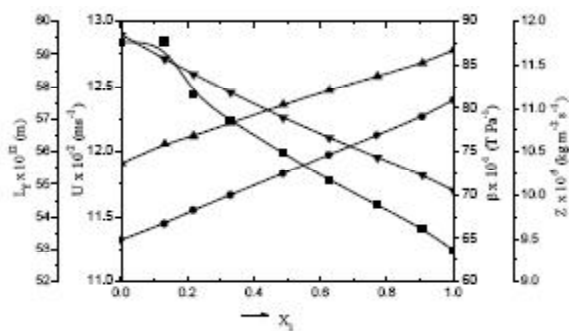
RESULTS AND DISCUSSION

The different observed and derived ultrasonic pa-

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TABLE 1: Polynomial equation (13) fitting coefficients for the measured and derived parameters for the three systems

Ultrasonic parameters	a_0	a_1	a_2	a_3	a_4	r^2
Benzene + Benzonitrile						
V_f	-84.8267	19.2657	-16.1203	35.1366	-19.9365	0.9980
Z	139293.99	-26989.105	22549.759	-51052.261	27606.91	0.9981
L_f	0.45036	0.07629	0.002433	-0.02885	0.03054	0.9999
β	51.5444	12.7559	-11.8251	36.6907	-18.9305	0.9968
ρ	996.2337	-106.1585	-27.4464	19.1333	-13.5852	1.0000
U	1397.8322	-108.2835	179.4989	-401.8918	211.3925	0.9945
Benzene + MPK						
V_f	-74.1472	11.8457	-16.4856	22.8389	-10.1741	0.9999
Z	94317.388	20097.248	-11540.065	11962.306	-4255.2498	0.9999
L_f	0.6338	-0.4241	1.0290	-1.21798	0.51681	0.9978
β	88.3146	-19.9015	-2.81796	11.5494	-6.3482	0.9999
ρ	796.3321	45.2786	108.6712	-164.0283	82.2354	0.9992
U	1191.4464	93.0876	67.2858	-219.6002	146.2901	0.9962
Cyclohexane + MPK						
V_f	-73.186995	-0.55075	-0.6796	-4.6621	2.3172	0.9998
Z	94477.561	-8152.3774	6391.4605	936.3159	423.97036	0.9999
L_f	0.59393	0.08071	-0.1462	0.15013	-0.09238	0.9963
β	89.3112	8.7456	-3.4477	-13.13899	5.4297	0.9999
ρ	796.68699	-53.20798	42.6786	-43.0042	25.7722	0.9999
U	1190.964	-79.5627	215.3536	-202.5608	102.7231	0.9999


Figure 1: L_f , U , β and Z as a function of mole fraction of benzene for the benzene + benzonitrile system.

Figure 3: L_f , U , β and Z as a function of mole fraction of benzene for the cyclohexane + MPK system

Figure 2: L_f , U , β and Z as a function of mole fraction of benzene for the benzene + MPK system

rameters are represented by equation (13). The coefficients of equation (13) along with r^2 , the coefficient of determination^[12], are given in TABLE 1. The represen-

tation are more than 99% reliable.

Figures 1, 2 and 3 show the variation of parameters U , β , L_f and Z as a function of X_1 for the three systems (a), (b) and (c), respectively. We find that in all the three systems U , β , L_f and Z exhibit nonlinear behavior, over the entire composition range, as a function of X_1 . This shows the presence of specific interactions in all the three systems.

From figure 1, we find that the intermolecular free length increases as a function of mole fraction of benzene for system (a). This change in intermolecular free length due to mixing affects the ultrasonic velocity U , the specific acoustic impedance Z , and the isentropic compressibility β of the mixture. If L_f decreases be-

TABLE 2 : Experimental U, ρ and calculated values of β^E , L_f^E , v_f^E , Z^E , RA and percentage deviations in R for the benzene + benzonitrile system

X_1	U ms ⁻¹	ρ Kg m ⁻³	$10^{-1} \times \beta^E$ TPa ⁻¹	$10^{10} \times L_f^E$ m	$10^6 \times v_f^E$ m ³ mole ⁻¹	$10^{-3} \times Z^E$ Kg m ⁻² s ⁻¹	RA	% deviation in R
0.0	1398	996.21	0.0	0.0	0.0	0.0	1.0	0.0
0.1557	1384	979.19	-0.692	-0.0021	-0.1256	6.5950	0.9863	0.0119
0.3161	1367	960.32	-1.127	-0.0026	-0.1726	9.5480	0.9837	0.0299
0.4169	1368	948.13	-2.346	-0.0032	-0.9687	22.3794	0.9805	0.2819
0.5481	1343	931.84	-1.694	-0.0042	-0.3311	13.9326	0.9750	0.0567
0.6567	1327	917.51	-1.427	-0.0038	-0.1677	10.7090	0.9774	0.0075
0.7856	1311	900.09	-1.301	-0.0040	-0.1805	9.7396	0.9768	0.0004
0.9143	1290	881.24	-0.464	-0.0017	-0.0167	2.9516	0.9899	-0.0335
1.0	1278	868.23	0.0	0.0	0.0	0.0	1.0	0.0

TABLE 3 : Experimental U, ρ and calculated values of β^E , L_f^E , v_f^E , Z^E , RA and percentage deviations in R for the benzene + MPK system

X_1	U ms ⁻¹	ρ Kg m ⁻³	$10^{-1} \times \beta^E$ TPa ⁻¹	$10^{10} \times L_f^E$ m	$10^6 \times v_f^E$ m ³ mole ⁻¹	$10^{-3} \times Z^E$ Kg m ⁻² s ⁻¹	RA	% deviation in R
0.0	1191	796.69	0.0	0.0	0.0	0.0	1.0	0.0
0.1304	1206	802.28	0.7942	0.0087	-0.3231	-2.2790	1.0457	0.4390
0.2171	1212	810.93	-1.1710	-0.0021	-0.2481	-0.9078	0.9886	0.0379
0.3294	1222	818.56	-1.4640	-0.0028	-0.2898	-1.5319	0.9853	0.0365
0.4869	1236	829.42	-1.6380	-0.0027	-0.3329	-1.9688	0.9851	0.0575
0.6257	1247	839.34	-1.4160	-0.0022	-0.2568	-2.7774	0.9875	0.0418
0.7707	1258	849.87	-0.8992	-0.0007	-0.1402	-3.6122	0.9961	0.0401
0.9062	1268	860.07	-0.2325	0.0006	-0.0059	-3.6344	1.0039	0.0200
1.0	1278	868.33	0.0	0.0	0.0	0.0	1.0	0.0

cause of mixing then it results in increase of U as well as of Z, and in decrease of the isentropic compressibility β . Whereas if L_f increases as a result of mixing then U as well as Z should decrease and β should increase. This is what we find in figure 1.

Figure 2 shows that for the system benzene + MPK, L_f and β show a decreasing tendency with increasing mole fraction of benzene and U as well as Z have a reverse tendency. For the cyclohexane +MPK system, L_f and β show a concave downward variation with mole fraction of cyclohexane whereas U and Z have a concave upward nature. This is shown in figure 3. Here we find that velocity shows a minima and the compressibility a maxima. The complex formation in liquid mixtures can be detected by the presence of maximum or minimum or by any abrupt change from the normal behaviour in the physical properties^[13,14]. Therefore, in the present case, the behaviour of U and β as a function of mole fraction of cyclohexane indicate the formation of a complex. It is seen to be formed at 0.45 mole fraction of cyclohexane. The magnitude of strength of the complex is estimated to be 14.60 TPa⁻¹.

In order to investigate the relative interactions in

the three systems we have investigated the excess parameters β^E , L_f^E , v_f^E and Z^E , for these systems, over the entire composition range, as a function of X_1 . TABLES 2, 3 and 4 give these for the three systems. We find that β^E is negative throughout for system (a), is negative for all points except one for system (b) and is always positive for system (c). Increasing negative β^E indicates a greater interaction between the components of a mixture and a weak interaction is suggested by the positive values of β^E ^[15]. The magnitude of β^E determines the strength of interaction. Thus it implies that the strength of interaction between the components of the three systems are in the following order,

benzene + benzonitrile > benzene + MPK > cyclohexane + MPK

The decrease in isentropic compressibility as a result of mixing is a consequence of decrease in available free volume and thereby decrease in intermolecular free length. Thus, we expect behaviours of v_f^E and L_f^E , to be same as that of β^E . This is what we observe from the TABLES 2-4 and figure 4. Thus, negative values of β^E , v_f^E and L_f^E indicate the presence of strong interaction

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TABLE 4: Experimental U , ρ and calculated values of β^E , L_f^E , v_f^E , Z^E , RA and percentage deviations in R for the cyclohexane + MPK system

X_1	U ms^{-1}	ρ Kg m^{-3}	$10^{-1} \times \beta^E$ TPa^{-1}	$10^{10} \times L_f^E$ m	$10^6 \times v_f^E$ $\text{m}^3 \text{mole}^{-1}$	$10^{-3} \times Z^E$ $\text{Kg m}^{-2} \text{s}^{-1}$	RA	% deviation in R
0.0	1191	796.69	0.0	0.0	0.0	0.0	1.0	0.0
0.1525	1183	789.40	2.3540	0.0109	0.7120	-14.1751	1.0562	0.0024
0.2942	1182	783.94	3.4390	0.0163	1.0022	-20.6238	1.0847	0.0249
0.3752	1183	780.86	3.8150	0.0193	1.0633	-23.0768	1.1010	0.0791
0.4326	1184	779.02	3.9980	0.0201	1.1172	-24.1646	1.1057	0.0822
0.5075	1186	776.84	4.1030	0.0205	1.1566	-24.7884	1.1078	0.0789
0.5951	1190	774.34	3.9660	0.0208	1.0852	-24.1836	1.1093	0.1157
0.7377	1199	770.98	3.2930	0.0186	0.8534	-20.4741	1.0980	0.1434
0.8891	1212	769.02	1.9090	0.0106	0.5127	-12.0105	1.0552	0.0801
1.0	1227	768.92	0.0	0.0	0.0	0.0	1.0	0.0

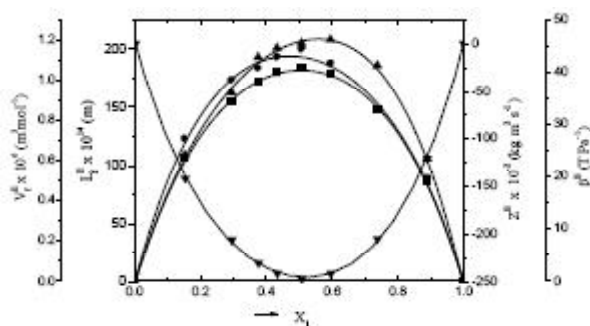


Figure 4: β^E , L_f^E , v_f^E and Z^E as a function of mole fraction of cyclohexane for the cyclohexane + MPK system

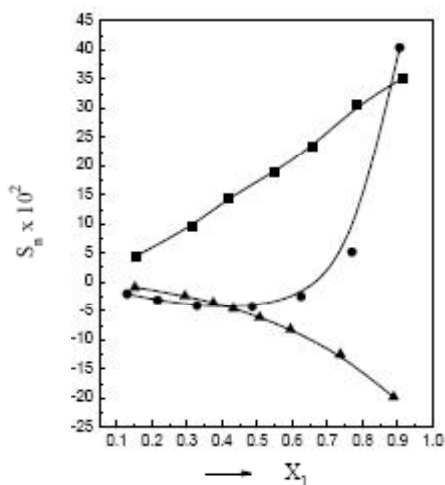


Figure 5: Solvation number S_n for the three systems as a function of mole fraction of all the first component

between the molecules. Also on physical grounds the behaviour of Z^E is expected to be opposite to those of β^E , v_f^E and L_f^E . This we find for the systems (a) and (c). However, for the system benzene + MPK, Z^E has similar behaviour, though with very small magnitude, as

those of β^E , v_f^E and L_f^E . Such kind of mixed behaviour are sometimes shown^[16,17]. From these observation we may also imply that the investigations of intermolecular free length and specific acoustic impedance and their excess values are very much useful in the study of interaction between components of a mixture at par with other thermodynamical investigations.

From TABLES 2-4, we also find that the behaviour of different excess parameters are similar in systems (a) and (b) but are different from that in system (c). These imply that the types of interaction in the systems (a) and (b) are similar but these are different from that in system (c). Dipolar stabilisation of polar components in benzene solution may be responsible for the nature of interaction in benzene + benzonitrile and benzene + MPK solutions. The decrease in self association of polar molecules by addition of cyclohexane seems to be responsible for the type of interaction in cyclohexane + MPK liquid mixture.

We have also investigated the solvation number S_n for the three systems as a function of X_1 . This is shown in figure 5. S_n is positive for system (a) and negative for system (c). For system (b) it is mostly negative. Comparing with figures 1-3 we find that this behaviour of S_n is similar, in general, to that of L_f and ρ . The TABLES 2-4 also give RA and percentage deviation in R for the three systems over the entire composition range. We find that values of RA for the three mixture systems (a), (b) and (c) are always less than 1, mostly less than 1 and always greater than 1, respectively. From these again the same conclusions about interaction between the components of different mixtures are drawn (as above). We also observe the absence of linearity in R for all the

TABLE 5 : Redlich-Kister equation (15), n=2, fitting coefficients for different excess parameters for three systems

Excess Parameters	B ₀	B ₁	B ₂	r ²
Benzene + Benzonitrile				
β ^E	-7.46293	-1.02691	3.35332	0.29761
Z ^E	6425.0928	-266.76259	-3551.9603	0.29515
L _f ^E	-0.01501	-0.005449	-0.006992	0.79172
V _f ^E	-1.93665	0.34895	2.41212	0.32034
Benzene + MPK				
β ^E	-12.1946	-5.59698	22.70688	0.64856
Z ^E	-566.76002	-1252.0014	-3798.8943	0.94192
L _f ^E	-0.02045	-0.026105	0.087886	0.58862
V _f ^E	-1.17056	1.30164	-0.31342	0.78669
Cyclohexane + MPK				
β ^E	16.14906	0.35757	4.62803	0.96811
Z ^E	-9788.7058	-550.3149	-3130.5507	0.9821
L _f ^E	0.082859	0.015008	0.022464	0.98277
V _f ^E	4.45078	-0.37834	1.58991	0.89791

TABLE 6 : Redlich-Kister equation (15), n=5, fitting coefficients for different excess parameters for three systems

Excess parameters	B ₀	B ₁	B ₂	B ₃	B ₄	B ₅	r ²
Benzene + Benzonitrile							
β ^E	-8.73776	8.98476	31.13523	-86.56428	-58.60761	130.31215	0.89376
Z ^E	7941.7681	-11432.125	-35850.428	96079.655	67358.514	-144738.53	0.88375
L _f ^E	-0.01505	-0.005175	0.00333	-0.04581	-0.03133	0.091014	0.97105
V _f ^E	-3.01140	8.00298	24.19092	-61.81353	-44.26662	91.19132	0.86240
Benzene + MPK							
β ^E	-9.989796	-40.68283	-9.8529	-238.91943	67.23642	-313.31561	0.95218
Z ^E	-929.73261	-445.81728	1075.6271	-5810.0833	-8160.5038	8551.1849	0.99507
L _f ^E	-0.006368	-0.016279	-0.119465	0.259028	0.3839122	-0.5692128	0.98944
V _f ^E	-1.33988	0.68017	2.36474	-2.98639	-5.28225	8.72160	0.99962
Cyclohexane + MPK							
β ^E	16.35391	0.606415	0.834441	-1.82577	6.58556	1.66734	0.99937
Z ^E	-9903.7844	-496.92149	-855.33091	-730.31311	-4132.1397	1706.9533	0.99997
L _f ^E	0.082984	0.0064044	0.013112	0.088622	0.026466	-0.139449	0.99503
V _f ^E	4.55739	0.13177	-0.09770	-4.46430	2.55967	6.18712	0.98947

three systems. This implies the presence of molecular association in the three binary mixtures^[18-20]. The magnitude of maximum percentage deviations in R for the three systems are, respectively, 0.2819, 0.4390 and 0.1434. This may again imply the order of strength of interaction between the components of the three mixtures to be the same as obtained above. Our present conclusions are in agreement with those of our earlier work^[1].

Using eqn.(15) most of the workers have been representing different excess values by terminating the series at n=2. We find that the reliability of such representation, in general, is poor. Thus, for a better representation of the excess ultrasonic parameters we have included higher terms in the series. TABLES 5 and 6 represent the coefficients of eqn.(15) along with r², the coefficient of determination, for different excess parameters for the three systems, for n=2 and 5, respectively. The coefficients a_j and B_n have the same unit and prefix as the respective parameters which they represent. We find that keeping terms upto n=5 in eqn. (15) vastly improves the reliability of representation of different excess parameters. For most cases it is between 95 to 99 per cent.

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