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Ultrasonic Studies on Binary Liquid Mixtures of Benzene with Carbitols at 308.15 K

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ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of benzene with carbitols 2(2-methoxyethoxy)ethanol (methyl carbitol), 2(2-ethoxyethoxy)ethanol (ethyl carbitol), and 2(2-butoxyethoxy)ethanol (butyl carbitol), have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters such as isentropic compressibility (K_S), intermolecular free length (L_f), and acoustic impedance (Z). The various excess properties such as excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E), and excess intermolecular free length (L_f^E) were calculated. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

Key words: *Ultrasonic velocity, Benzene, Carbitols, Excess isentropic compressibility, Excess intermolecular free length, Excess acoustic impedance.*

1. INTRODUCTION

Ultrasonic wave propagation affects the physical properties of the medium and hence, can furnish information about molecular interactions of the liquid and liquid mixtures. The sign and magnitude of the nonlinear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules [1,2]. Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids [3], binary and ternary mixtures [4-6]. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess values with composition gives an insight into the molecular process [7,8]. The present paper is part of our research work on thermodynamic properties of liquid-liquid mixtures [9-15]. This paper includes density and ultrasonic behavior of binary mixtures of benzene (BEZ) with carbitols over the entire composition range at 308.15 K.

BEZ is a non-polar liquid with low dielectric constant (ε=2.28 at 298.15 K) and with zero dipole moment whereas carbitols are polar and associative in nature. It is interesting to study the molecular interactions involving the delocalized π-electrons cloud of BEZ with other molecules. Carbitols are of interest because of investigating the effect of simultaneous presence of ethereal and alcoholic oxygen atoms in the same molecule. The presence of etheric oxygen enhances the ability of the –OH group of the same molecule to form hydrogen bonds with other organic molecules [16-21]. The mixtures of BEZ with alcohols are interesting because of possibility weak hydrogen bonding (π ……. H-O) involving π-electrons of BEZ ring and hydroxyl group of carbitols. The best our knowledge, there has been no ultrasonic study reported on these binary mixtures. The effect of chain length in carbitols on the interactions between unlike molecules in these molecules will also examined.

2. EXPERIMENTAL

2.1. Materials

BEZ, methyl carbitol (MC), ethyl carbitol (EC), and butyl carbitol (BC) were purchased from E-Merck, Mumbai and used.

2.2. Methods

Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed

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system using Mettler balance with the precision of ±0.1 mg. The ultrasonic sound speeds in pure liquids and their binary mixtures were measured using the single - crystal variable – path ultrasonic interferometer operating at a frequency of 2 MHz and these were accurate up to ±0.03%. The densities (ρ) of liquids and their mixtures were measured using capillary pycnometer having a capillary diameter of 0.85 mm, which was calibrated using double distilled water. The necessary buoyancy corrections were applied. The density values were reproducible within ±0.2 kg.m^{-3}. Comparing the purity of compounds the measured values of density and ultrasonic velocity are those reported in literature and was found to be accurate up to ± 0.02 kg.m^{3}. The temperature was maintained constant during the period of measurement by a water circulation system from a thermostatically controlled and well stirred constant temperature water bath, Schott Garate whose temperature was controlled to ± 0.02 K was used for all measurements. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The purities of the liquids were checked by comparing the values of densities and ultrasonic velocities with literature. The measurements were made with proper care in an AC room to avoid evaporation loss.

3. RESULTS AND DISCUSSION

From the measured densities (ρ) and ultrasonic velocities (u) the various acoustical parameters such as K_S, Z, and L_f were calculated using the following equations 1, 2, 3, and 4, respectively, for the binary systems BEZ+MC, BEZ+EC, and BEZ+BC under study.

$$K_S=1/u^2\,\rho \tag{1}$$

$$Z=\rho\,u \tag{2}$$

$$L_f=K\,(K_s)^{1/2} \tag{3}$$

Where 'K' is Jacobson's constant [20].

The excess functions Y^E have been calculated using the relation:

$$Y^E=Y_{mix}-(X_1Y_1+X_2Y_2) \tag{4}$$

Where Y^E is u^E or Z^E or Ks^E or L_f^E and Y denotes u, Z, K_S, and L_f, respectively, X is the mole fraction of BEZ and suffixes 1 and 2 denotes the components 1 and 2 in binary mixtures and are incorporated in Table 1.

From Table 1 it is observed that the decrease in u and corresponding increase in L_f with X_{BEZ} in the systems under study is in accordance with the view proposed by Eyring and Kincaid [20], and observed that u, Z, and R_A for the systems BEZ+MC, BEZ+EC, and BEZ+BC decrease nonlinearly with increase in X_{BEZ}, while Ks and L_f exhibit reverse trends, which suggest, the presence of molecular interactions between the component molecules [15,22]. The excess functions which are a measure of the deviations from ideal behavior are relatively more sensitive to the intermolecular interactions between unlike molecules, with this view u^E, Z^E, K_S^E, and L_f^E have been calculated using experimental data with the help of equation 4, and these excess functions u^E, Z^E, K_S^E, and L_f^E versus X_{BEZ} have been shown in Figures 1-4.

In general, K_S^E and L_f^E depend on two factors (i) increase in free length, defined by Jacoson [20], due to loss of dipolar association and breaking up hydrogen bonding [23] and differences in size and shapes of

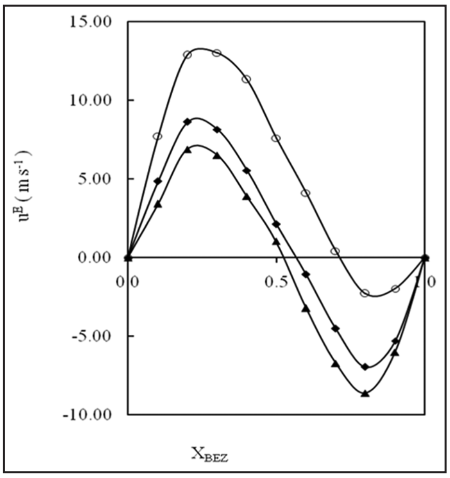

Figure 1: Plots of excess ultrasonic velocity (u^E) versus mole fraction of benzene (BEZ) (X_{BEZ}) at 308.15 K for the binary mixtures of BEZ with methyl carbitol (−♦−), ethyl carbitol (−○−), and butyl carbitol (−▲−).

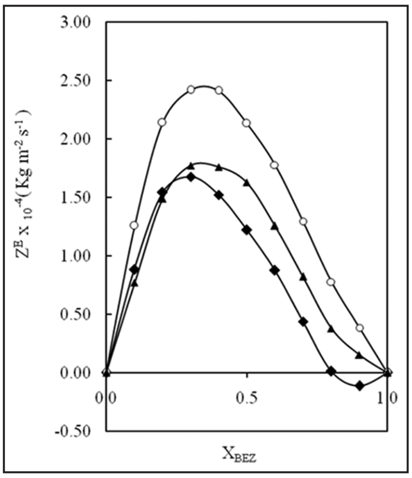

Figure 2: Plots of excess acoustic impedance (Z^E) versus mole fraction of benzene (BEZ) (X_{BEZ}) at 308.15 K for the binary mixtures of BEZ with methyl carbitol (−♦−), ethyl carbitol (−○−), and butyl carbitol (−▲−).

Table 1: Values of density (ρ), ultrasonic velocity (u), excess ultrasonic velocity (u^E), acoustic impedance (Z), excess acoustic impedance (Z^E), isentropic compressibility (K_S), excess isentropic compressibility (K_S^E), intermolecular free length (L_f), excess intermolecular free length (L_f^E), and relative association (R_A) for the binary liquid mixtures of BEZ with carbitols at 308.15 K.

Mole fraction of THF (X_{TEA})	$\rho\times10^{-3}$ (kg m^{-3})	U (m s^{-1})	u^E (m s^{-1})	$Z\times10^{-4}$ (kg m^{-2} s^{-1})	$Z^E\times10^{-4}$ (kg m^{-2} s^{-1})	$K_S\times10^{11}$ (m^2 N^{-1})	$K_S^E\times10^{11}$ (m^2 N^{-1})	$L_f\times10^{12}$ (m)	$L_f^E\times10^{12}$ (m)	Relative association (R_A)
BEZ+MC										
0.0000	1.0073	1382.7	0.0000	1.3928	0.0000	51.93	0.0000	4.7724	0.0000	1.0000
0.1008	0.9969	1374.1	4.8467	1.3698	0.8801	53.13	−1.0516	4.8272	−0.3941	0.9917
0.2004	0.9857	1364.6	8.6334	1.3451	1.5423	54.48	−1.9226	4.8884	−0.7140	0.9829
0.3009	0.9734	1350.7	8.1401	1.3148	1.6768	56.31	−2.3383	4.9698	−0.8397	0.9739
0.3999	0.9604	1334.9	5.5467	1.2820	1.5222	58.43	−2.4290	5.0625	−0.8380	0.9647
0.5001	0.9464	1318.1	2.1133	1.2474	1.2199	60.82	−2.2822	5.1648	−0.7519	0.9546
0.5999	0.9316	1301.6	−1.0733	1.2126	0.8759	63.36	−1.9695	5.2717	−0.6166	0.9437
0.7001	0.9158	1284.8	−4.5067	1.1766	0.4373	66.15	−1.4185	5.3865	−0.4056	0.9317
0.8002	0.8990	1269.0	−6.9533	1.1408	0.0118	69.07	−0.7304	5.5043	−0.1638	0.9184
0.9003	0.8813	1257.3	−5.3000	1.1081	−0.1120	71.78	−0.2621	5.6110	−0.0325	0.9031
1.0000	0.8627	1249.3	0.0000	1.0778	0.0000	74.27	0.0000	5.7075	0.0000	0.8859
BEZ+EC										
0.0000	0.9748	1345.3	0.0000	1.3114	0.0000	56.68	0.0000	4.9861	0.0000	1.0000
0.1012	0.9680	1343.3	7.7152	1.3003	1.2559	57.25	−1.2115	5.0111	−0.4807	0.9935
0.1997	0.9605	1339.0	12.8712	1.2861	2.1366	58.07	−2.1256	5.0468	−0.8344	0.9869
0.3002	0.9518	1329.5	13.0192	1.2654	2.4155	59.44	−2.5218	5.1060	−0.9670	0.9803
0.4002	0.9422	1318.2	11.3192	1.2420	2.4107	61.08	−2.6410	5.1759	−0.9889	0.9731
0.4999	0.9318	1304.9	7.5904	1.2159	2.1298	63.03	−2.4473	5.2578	−0.8896	0.9657
0.6001	0.9204	1291.8	4.1096	1.1890	1.7774	65.11	−2.1282	5.3439	−0.7513	0.9571
0.7002	0.9079	1278.5	0.4192	1.1608	1.2938	67.38	−1.6118	5.4365	−0.5470	0.9473
0.8001	0.8942	1266.2	−2.2904	1.1322	0.7763	69.75	−1.0006	5.5312	−0.3206	0.9360
0.9002	0.8791	1256.9	−1.9808	1.1049	0.3854	72.00	−0.5091	5.6198	−0.1569	0.9225
1.0000	0.8627	1249.3	0.0000	1.0778	0.0000	74.27	0.0000	5.7075	0.0000	0.9071

(Contd...)

Table 1: (*Continued*).

Mole fraction of THF (X_{TEA})	$\rho\times10^{-3}$ (kg m^{-3})	U (m s^{-1})	u^E (m s^{-1})	$Z\times10^{-4}$ (kg m^{-2} s^{-1})	$Z^E\times10^{-4}$ (kg m^{-2} s^{-1})	$K_S\times10^{11}$ (m^2 N^{-1})	$K_S^E\times10^{11}$ (m^2 N^{-1})	$L_f\times10^{12}$ (m)	$L_f^E\times10^{12}$ (m)	Relative association (R_A)
BEZ+BC										
0.0000	0.9397	1325.3	0.0000	1.2454	0.0000	60.59	0.0000	5.1550	0.0000	1.0000
0.1002	0.9358	1321.1	3.4152	1.2363	0.7696	61.23	−0.7309	5.1822	−0.2820	0.9969
0.1998	0.9315	1317.0	6.8848	1.2268	1.4890	61.89	−1.4274	5.2103	−0.5511	0.9934
0.3001	0.9265	1309.0	6.5076	1.2128	1.7705	62.99	−1.7027	5.2563	−0.6455	0.9900
0.3999	0.9208	1298.8	3.8924	1.1959	1.7579	64.38	−1.6787	5.3139	−0.6203	0.9865
0.4992	0.9143	1288.4	1.0392	1.1780	1.6272	65.89	−1.5287	5.3758	−0.5498	0.9822
0.5999	0.9067	1276.5	−3.2076	1.1574	1.2569	67.69	−1.1095	5.4486	−0.3781	0.9770
0.6997	0.8980	1265.4	−6.7228	1.1363	0.8224	69.55	−0.6150	5.5230	−0.1858	0.9705
0.7998	0.8879	1255.9	−8.6152	1.1151	0.3786	71.40	−0.1253	5.5963	−0.0054	0.9620
0.9001	0.8762	1250.9	−5.9924	1.0960	0.1523	72.94	0.0355	5.6561	0.0381	0.9506
1.0000	0.8627	1249.3	0.0000	1.0778	0.0000	74.27	0.0000	5.7075	0.0000	0.9363

BEZ: Benzene, MC: Methyl carbitol, EC: Ethyl carbitol, BC: Butyl carbitol

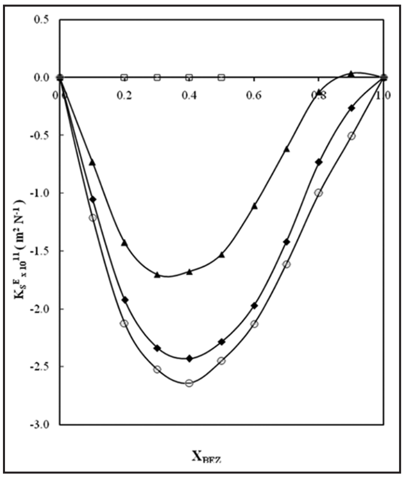

Figure 3: Plots of excess isentropic compressibility (K_S^E) versus mole fraction of benzene (BEZ) (X_{BEZ}) at 308.15 K for the binary mixtures of BEZ with methyl carbitol (−♦−), ethyl carbitol (−○−), and butyl carbitol (−▲−).

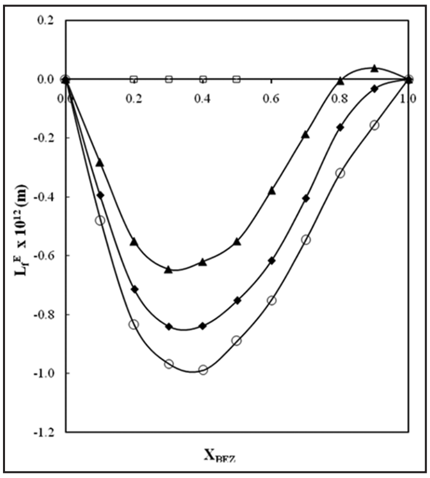

Figure 4: Plots of excess intermolecular free length (L_f^E) versus mole fraction of benzene (BEZ) (X_{BEZ}) at 308.15 K for the binary mixtures of BEZ with methyl carbitol (−♦−), ethyl carbitol (−○−), and butyl carbitol (−▲−).

the component molecules and (ii) decrease in free length as a result of dipole–dipole interactions lead to hydrogening association [23] complex formation between the component molecules [9]. The first effect decreases the ultrasonic speed in the solution as a result of which, its isentropic compressibility increases. The second effect increases the sound speed so that the isentropic compressibility of the solution decreases. The observed K_S^E and L_f^E values are the net results of these effects. A similar observation was made by Pal and Das [22] from their ultrasonic velocity studies for the binary liquid mixtures. Figures 3 and 4 show that K_s^E and L_f^E are negative over the whole composition range except for the system BEZ+BC, which exhibits smaller positive value at ~0.9 X_{BEZ}.

The negative values of K_s^E and L_f^E for all these systems indicate that the combination of several contributions like those from (i) specific interactions between delocalized π-electron cloud of BEZ molecules, (ii) closer molecular arrangement, and (iii) depolymerization of associated entities of pure carbitols. The negative K_s^E and L_f^E values (Figures 3 and 4) for these mixtures suggest that contributions from first two factors outweigh the contributions from the third factor, thus the addition of BEZ to carbitols results in enhancing the structure of these mixtures. By the close observation of these figures, the K_s^E and L_f^E values for BEZ+BC system are found positive at extremely BEZ rich region that is at ~0.9 X_{BEZ}. This might be due to the predominance of the third factor over the first two factors as discussed above. The negative values of K_s^E and L_f^E for all the systems under study fall in the following order:

BEZ+BC<BEZ+MC<BEZ+EC

This order suggests that the strength of intermolecular interactions increase with an increase in chain length of alkoxy group of carbitols, except in the case of BEZ+BC. This might be attributed to the dominance of steric effect due to the bulky nature of BC molecules. This conclusion receives support from the work of Aminabhavi *et al.* [23].

It is noticed from Figure 1 that an inversion of sign in u^E is observed from positive to negative for all the systems under study. A positive u^E variation at lower $X_{BEZ,}$ whereas a slight negative deviation at higher X_{BEZ} for all the mixtures is observed. It is also observed from Figure 2 that Z^E values are positive over the entire range of mole fraction. From these variations of u^E and Z^E, it is concluded that the specific interactions are present between the unlike molecules which support our earlier conclusions drawn from K_s^E and L_f^E. It again supports our view regarding the presence of molecular interactions of these mixtures under study [24].

4. CONCLUSIONS

Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interaction in the mixture. In addition, the density, ultrasonic velocity and the derived excess acoustical parameters provide evidence of confirmation. It is concluded that the dependence of ultrasonic velocity on composition of the mixtures is satisfactorily explained. The trends in the variation of the parameters derived from ultrasonic velocity and the sign and extent of deviation of the excess function from rectilinear dependence on composition of these mixtures suggest the presence of molecular interaction between the components of binary mixtures. The interactions are primarily due to the electron donor-acceptor interactions existing between the components of the mixtures.

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***Bibliographical Sketch**

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