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Ultrasonic Studies on Binary Liquid Mixtures of Tetrahydrofuran with Benzenes At 308.15 K

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ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of tetrahyrofuran with benzene, methyl benzene, ethyl benzene, chloro benzene, bromo benzene and nitro benzene have been measured at 308.15 K. The observed data have been utilized to calculate various acoustical parameters like isentropic compressibility (K_S), intermolecular free length (L_f) and acoustic impedance (Z). The various excess properties like excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E) and excess inter molecular free-length (L_f^E) were calculated and fitted to the Redlich-Kister equation. 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, Tetrahyrofuran, Benzenes, Excess isentropic compressibility, Excess inter molecular free-length, Excess acoustic impedance, Redlich-Kister equation.*

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 non-linear 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 [1-3].

Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids [4], binary and ternary mixtures [5-7]. 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 [8-10].

The present paper is part of ours on going research on thermodynamic properties of liquid-liquid mixtures [11-16]. This paper includes density and an ultrasonic behavior of binary mixtures of tetrahyrofuran (THF) with benzene and substituted benzenes over the entire composition range at 308.15 K.

THF, is a hetero cyclic organic compound with the formula ($(CH_2)_4O$). It is a colorless and low viscosity liquid with a smell similar to diethyl ether but is a much less potent anesthetic than diethyl ether. It is one of the most polar ethers (dipole moment, μ=1.75 D at 298.15 K) [17]. THF is the fully hydrogenated analogue of the aromatic compound furan. It is a moderately polar, aprotic solvent with a dielectric constant of 7.58 and unassociated liquid [11] that dissolves a wide range of non-polar and polar compounds. It is often used as a precursor to polymers in polymer science. The most widely used industrial application of THF is, its use in chemical process which involves the acid-catalyzed dehydration of 1, 4-butanediols, derived from condensation of acetylene with formaldehyde followed by hydrogenation [18].

THF has innumerable industrial applications. Thus, a study of physico-chemical property data on the binary liquid mixtures containing THF has attracted considerable interest in the literature [19-21]. Thermodynamic and transport properties of liquid mixtures of THF and benzene and substituted benzenes were not yet completely explored to study the departure of a real mixture from ideality. In addition, these properties have been widely used to

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study the intermolecular interactions between the various species present in the liquid mixture.

In view of the above the present research aims to measure densities and ultrasonic velocity of binary mixtures of THF with benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB) at 308.15 K and using this data excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_s^E) and excess inter molecular free-length (L_f^E) were calculated and fitted to the Redlich-Kister equation. The results were discussed in terms of intermolecular interactions between unlike molecules.

2. MATERIALS AND METHODS

THF, B, MB, EB, CB, BB and NB were purchased from E-Merck, Mumbai and used as purchased. Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system using Mettler balance with the precision of ±0.1 mg. 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 data (Table 1). The measurements were made with proper care in an AC room to avoid evaporation loss.

The densities (ρ) of liquids and their mixtures were measured using bicapillary 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 with in ±0.2 kg m^{-3}. The ultrasonic velocity (u) measurements were made by a single frequency (2 MHz) variable path interferometer with an accuracy of ±0.03%. A thermostatically controlled, well stirred constant temperature water bath, Schott Gerate (Model CT 050/2 made in Germany) whose temperature was controlled to ±0.02 K was used for all the measurements.

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 1-4 respectively and are incorporated in Table 2 for the binary systems under study.

$$K_S=1/u^2\,\rho \quad (1)$$

$$Z=\rho\, u \quad (2)$$

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

Where "K" is Jacobson's constant [31].

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

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

Where Y denotes u, Z, K_S and L_f respectively, X is the mole fraction of THF and suffixes 1 and 2 denotes the components 1 and 2 in binary mixtures and the values are given in Table 3.

The dependence of u^E, Z^E, K_S^E and L_f^E on the mole fraction of THF (X_{THF}) for all the six systems were fitted to the following Redlich-Kister equation by the least-squares method and the values are given in Table 4.

$$Y^E = x(1-X)\sum_i A_i(2x-1)^i \quad (6)$$

Where Y^E is u^E, Z^E, K_S^E and L_f^E parameters.

The parameters A_i, obtained by a nonlinear least squares polynomial fitting procedure, are also given in Table 4 together with the standard deviations (σ) values.

From the Table 2, it is observed that the values of u, Z, K_S and L_f varied with the mole fraction of THF (X_{THF}). This indicates the presence of interactions between

Table 1: Comparison of experimental density (ρ) and ultrasonic velocities (U) of pure liquids with literature values at 308.15.

Liquid	Density $\rho\times10^{-3}$ (kg m^{-3})		Ultrasonic velocity (u) (ms^{-1})	
	Experimental	Literature	Experimental	Literature
B	0.8629	0.8629 [22]	1238.2	1238.0 [26]
MB	0.8526	0.8529 [22]	1262.0	1262.0 [27,28]
EB	0.8387	0.8390 [23]	1277.0	1277.6 [29]
CB	1.0890	1.0907 [24]	1250.0	1250.0 [30]
BB	1.4739	1.4748 [24]	1122.0	1122.0 [27]
NB	1.1881	1.1885 [24]	1452.8	1423.0 [27]
THF	0.8714	0.8701 [25]	1222.1	1222.1 [25]

B=Benzene, MB: Methyl benzene, EB: Ethyl benzene, CB: Chloro benzene, BB: Bromo benzene, NB: Nitro benzene, THF: Tetrahyrofuran

Table 2: Values of density (ρ), ultrasonic velocity (u), acoustic impedance (Z), isentropic compressibility (K_S), intermolecular free-length (L_f) and relative association (R_A) for the binary liquid mixtures of Tetrahydrofuran (THF) with benzenes at 308.15 K.

Mole fraction of THF (X_{THF})	$\rho\times10^{-3}$ (Kg m^{-3})	u (m s^{-1})	$Z\times10^{-4}$ (Kg m^{-2} s^{-1})	$K_S\times10^{11}$ (m^2 N^{-1})	$L_f\times10^{12}$ (m)	Relative association (R_A)
Tetrahydrofuran (THF)+Benzene (B)						
0.0000	0.8629	1238.2	1.0684	75.5889	5.7580	1.0000
0.1084	0.8638	1236.6	1.0682	75.7078	5.7625	1.0015
0.2157	0.8647	1235.0	1.0679	75.8277	5.7671	1.0029
0.3162	0.8655	1233.4	1.0675	75.9515	5.7718	1.0043
0.4163	0.8664	1231.8	1.0672	76.0754	5.7765	1.0058
0.5165	0.8672	1230.2	1.0668	76.1994	5.7812	1.0072
0.6173	0.8681	1228.5	1.0665	76.3232	5.7859	1.0086
0.7154	0.8689	1226.9	1.0661	76.4492	5.7907	1.0101
0.8103	0.8698	1225.3	1.0657	76.5779	5.7955	1.0115
0.9012	0.8706	1223.7	1.0653	76.7095	5.8005	1.0128
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	1.0143
Tetrahydrofuran (THF)+Methyl benzene (MB)						
0.0000	0.8526	1262.0	1.0759	73.6464	5.6835	1.0000
0.1185	0.8546	1258.1	1.0752	73.9269	5.6943	1.0034
0.2408	0.8568	1254.0	1.0744	74.2225	5.7057	1.0070
0.3508	0.8588	1250.4	1.0739	74.4731	5.7153	1.0104
0.4611	0.8609	1246.5	1.0731	74.7611	5.7264	1.0139
0.5765	0.8632	1242.1	1.0721	75.0963	5.7392	1.0178
0.6579	0.8648	1238.5	1.0710	75.3899	5.7504	1.0207
0.7432	0.8664	1234.5	1.0695	75.7359	5.7636	1.0237
0.8090	0.8676	1231.5	1.0684	76.0008	5.7736	1.0260
0.9186	0.8697	1226.1	1.0664	76.4832	5.7919	1.0300
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	1.0331
Tetrahydrofuran (THF)+Ethyl benzene (EB)						
0.0000	0.8387	1277.0	1.0710	73.1159	5.6630	1.0000
0.1394	0.8430	1271.5	1.0718	73.3756	5.6731	1.0065
0.2709	0.8471	1266.0	1.0724	73.6526	5.6838	1.0129
0.3862	0.8507	1260.5	1.0724	73.9775	5.6963	1.0187
0.4945	0.8544	1255.0	1.0723	74.3033	5.7088	1.0247
0.5969	0.8580	1249.6	1.0721	74.6449	5.7219	1.0305
0.6881	0.8611	1244.1	1.0713	75.0331	5.7368	1.0357
0.7727	0.8642	1238.6	1.0704	75.4307	5.7520	1.0409
0.8540	0.8670	1233.1	1.0690	75.8617	5.7684	1.0458
0.9062	0.8687	1229.3	1.0679	76.1722	5.7802	1.0490
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	1.0543
Tetrahydrofuran (THF)+Chloro benzene (CB)						
0.0000	1.0890	1230.6	1.3402	60.6354	5.1571	1.0000
0.1311	1.0686	1229.9	1.3143	61.8616	5.2090	0.9814
0.2765	1.0438	1229.0	1.2828	63.4302	5.2746	0.9589
0.3985	1.0215	1228.1	1.2545	64.9042	5.3355	0.9386

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Table 2: Continued

Mole fraction of THF (X_{THF})	$\rho\times10^{-3}$ (Kg m^{-3})	u (m s^{-1})	$Z\times10^{-4}$ (Kg m^{-2} s^{-1})	$K_S\times10^{11}$ (m^2 N^{-1})	$L_f\times10^{12}$ (m)	Relative association (R_A)
0.5081	0.9998	1227.3	1.2270	66.4041	5.3968	0.9189
0.6082	0.9781	1226.4	1.1996	67.9687	5.4600	0.8992
0.7021	0.9557	1225.5	1.1712	69.6712	5.5280	0.8788
0.7837	0.9347	1224.7	1.1447	71.3357	5.5936	0.8597
0.8595	0.9139	1223.8	1.1185	73.0572	5.6607	0.8408
0.9211	0.8960	1223.0	1.0958	74.6120	5.7207	0.8244
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	0.8020
Tetrahydrofuran (THF)+Bromo benzene (BB)						
0.0000	1.4739	1122.0	1.6537	53.8951	4.8620	1.0000
0.1953	1.4027	1149.0	1.6117	53.9998	4.8667	0.9442
0.3530	1.3362	1171.9	1.5658	54.4993	4.8892	0.8935
0.4809	1.2759	1189.0	1.5171	55.4348	4.9310	0.8491
0.5903	1.2163	1200.0	1.4597	57.0891	5.0040	0.8070
0.6838	1.1569	1207.1	1.3964	59.3268	5.1011	0.7660
0.7646	1.0968	1211.9	1.3292	62.0764	5.2180	0.7253
0.8345	1.0360	1215.1	1.2589	65.3766	5.3549	0.6845
0.8989	0.9733	1218.1	1.1856	69.2458	5.5111	0.6425
0.9500	0.9208	1220.1	1.1235	72.9519	5.6567	0.6075
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	0.5746
Tetrahydrofuran (THF)+Nitro benzene (NB)						
0.0000	1.1881	1452.8	1.7260	39.8795	4.1823	1.0000
0.1592	1.1688	1449.7	1.6944	40.7087	4.2256	0.9845
0.2966	1.1492	1437.7	1.6522	42.0995	4.2971	0.9707
0.4190	1.1261	1418.6	1.5975	44.1279	4.3994	0.9554
0.5294	1.0998	1397.5	1.5370	46.5539	4.5188	0.9378
0.6298	1.0715	1373.7	1.4718	49.4606	4.6577	0.9189
0.7188	1.0413	1348.8	1.4045	52.7896	4.8119	0.8985
0.7989	1.0078	1322.7	1.3331	56.7118	4.9874	0.8752
0.8697	0.9704	1295.0	1.2567	61.4466	5.1915	0.8487
0.9376	0.9237	1263.2	1.1667	67.8523	5.4554	0.8146
1.0000	0.8714	1222.1	1.0649	76.8367	5.8053	0.7770

the components in these binary liquid mixtures. The variation of u for the mixtures depends on the value of L_f. The observed decrease in u and the corresponding increase in L_f with mole fraction of THF (Table 2) for all the systems are in accordance with the view proposed by Eryring and Kincaid [32]. However, the excess functions which are a measure of the deviations from the ideal behavior are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters as explained above.

With this view in mind, the variations in excess acoustical parameters, like the excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility K_S^E and excess intermolecular free-length (L_f^E) with mole fraction of THF (X_{THF}) are examined from the Figures 1-4 respectively. It is observed from Figure 1 that the u^E is positive for all the liquid mixtures under study. In general, if the media is dense the ultrasonic velocity value will be more and if the media is less dense the ultrasonic velocity value will be less. When we mix two liquids if they condense or compress more, ultrasonic velocity will be more. For these mixtures since the excess volume (V^E) values are negative [33], this indicates the mixtures compressed more and it is natural to get positive excess ultrasonic velocities for these mixtures. The Figure 2 shows the variation of Z^E with composition of liquid mixtures that exhibit

Table 3: Values of excess ultrasonic velocity (u^E), excess acoustic impedance (Z^E), excess isentropic compressibility (K_S^E) and excess intermolecular free-length (L_f^E) for the binary liquid mixtures of Tetrahydrofuran (THF) with benzenes at 308. 15 K.

Mole fraction of THF (X_{THF})	u^E (m s^{-1})	$Z^E \times 10^{-4}$ (Kg m^{-2} s^{-1})	$K_S^E \times 10^{11}$ (m^2 N^{-1})	$L_f^E \times 10^{12}$ (m)
Tetrahydrofuran (THF)+Benzene (B)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1084	0.1352	0.0091	−0.0164	−0.0061
0.2157	0.2528	0.0168	−0.0304	−0.0112
0.3162	0.2608	0.0172	−0.0320	−0.0117
0.4163	0.2624	0.0176	−0.0329	−0.0120
0.5165	0.2657	0.0186	−0.0340	−0.0124
0.6173	0.2785	0.0204	−0.0360	−0.0132
0.7154	0.2479	0.0187	−0.0324	−0.0119
0.8103	0.1658	0.0127	−0.0221	−0.0081
0.9012	0.0193	0.0017	−0.0039	−0.0013
1.0000	0.0000	0.0000	0.0000	0.0000
Tetrahydrofuran (THF)+Methyl Benzene (MB)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1185	0.8642	0.0514	−0.0976	−0.0362
0.2408	1.6279	0.1092	−0.1921	−0.0714
0.3508	2.4122	0.1774	−0.2924	−0.1092
0.4611	2.8841	0.2222	−0.3563	−0.1331
0.5765	3.0524	0.2519	−0.3893	−0.1454
0.6579	2.7562	0.2295	−0.3554	−0.1325
0.7432	2.1714	0.1785	−0.2815	−0.1046
0.8090	1.7631	0.1408	−0.2266	−0.0840
0.9186	0.7421	0.0546	−0.0939	−0.0346
1.0000	0.0000	0.0000	0.0000	0.0000
Tetrahydrofuran (THF)+Ethyl Benzene (EB)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1394	2.1631	0.1664	−0.2589	−0.0979
0.2709	3.8924	0.3063	−0.4712	−0.1780
0.3862	4.7324	0.3705	−0.5753	−0.2169
0.4945	5.1880	0.4331	−0.6525	−0.2457
0.5969	5.3198	0.4737	−0.6919	−0.2603
0.6881	4.8367	0.4453	−0.6431	−0.2416
0.7727	3.9912	0.4043	−0.5603	−0.2101
0.8540	2.9646	0.3195	−0.4318	−0.1618
0.9062	2.0634	0.2417	−0.3155	−0.1181
1.0000	0.0000	0.0000	0.0000	0.0000
Tetrahydrofuran (THF)+Chloro Benzene (CB)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1311	0.4473	0.1446	−0.8978	−0.3310
0.2765	0.7422	0.2817	−1.6849	−0.6173
0.3985	0.9281	0.3862	−2.1875	−0.7988

Contd...

Table 3: Continued.

Mole fraction of THF (X_{THF})	u^E (m s^{-1})	$Z^E \times 10^{-4}$ (Kg m^{-2} s^{-1})	$K_S^E \times 10^{11}$ (m^2 N^{-1})	$L_f^E \times 10^{12}$ (m)
0.5081	1.0088	0.5082	−2.4632	−0.8962
0.6082	1.0123	0.6055	−2.5204	−0.9130
0.7021	0.8678	0.6958	−2.3391	−0.8421
0.7837	0.7115	0.7851	−1.9967	−0.7146
0.8595	0.5057	0.8604	−1.5033	−0.5351
0.9211	0.2717	0.9322	−0.9464	−0.3351
1.0000	0.0000	0.0000	0.0000	0.0000
Tetrahydrofuran (THF)+Bromo Benzene (BB)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1953	7.4505	7.2995	−4.3758	−1.7951
0.3530	14.5147	11.9934	−7.4942	−3.0581
0.4809	18.8919	14.6569	−9.4929	−3.8467
0.5903	18.9510	15.3501	−10.3484	−4.1483
0.6838	16.6016	14.5340	−10.2558	−4.0591
0.7646	13.3935	12.5685	−9.3599	−3.6526
0.8345	9.5366	9.6477	−7.6633	−2.9428
0.8989	6.1001	6.1117	−5.2715	−1.9885
0.9500	2.9950	2.9119	−2.7377	−1.0149
1.0000	0.0000	0.0000	0.0000	0.0000
Tetrahydrofuran (THF)+Nitro Benzene (NB)				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1592	33.6574	7.3668	−5.0544	−2.1513
0.2966	53.2856	12.2278	−8.7415	−3.6655
0.4190	62.4533	14.8437	−11.2367	−4.6290
0.5294	66.8526	16.1004	−12.8908	−5.2277
0.6298	66.1649	16.2164	−13.6946	−5.4679
0.7188	61.7872	15.3653	−13.6548	−5.3704
0.7989	54.2362	13.5196	−12.6928	−4.9148
0.8697	42.8298	10.5637	−10.5747	−4.0237
0.9376	26.6743	6.0551	−6.6784	−2.4868
1.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Parameters of Eq. (6) and standard deviations.

Excess property	A0	A1	A2	A3	A4	σ
Tetrahydrofuran (THF)+Benzene (B)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	−0.00066	−0.17026	0.24905	−0.13045	0.05518	0.0043
$L_f^E \times 10^{12}$ (m)	0.00026	−0.06293	0.09445	−0.05279	0.02262	0.00164
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	0.00049	0.09158	−0.13660	0.08402	−0.04136	0.00281
U^E (m s^{-1})	0.00478	1.45321	−2.30076	1.27216	−0.45311	0.03605
Tetrahydrofuran (THF)+Methyl benzene (MB)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	−0.00526	−0.34159	−3.36358	6.58179	−2.86820	0.01092
$L_f^E \times 10^{12}$ (m)	−0.00200	−0.12078	−1.29329	2.52162	−1.10438	0.00414

Contd...

Table 4: Continued

Excess property	A0	A1	A2	A3	A4	σ
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	0.00431	0.01150	3.01828	−5.39864	2.36145	0.00900
U^E (m s^{-1})	0.03577	4.13028	21.66508	−46.83934	20.99534	0.07749
Tetrahydrofuran (THF)+Ethyl benzene (EB)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	0.00153	−2.18020	2.05424	−1.47209	1.59369	0.01004
$L_f^E \times 10^{12}$ (m)	0.00058	−0.82451	0.77721	−0.54093	0.58662	0.00382
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	−0.00160	1.48366	−1.96140	2.51004	−2.02733	0.00968
U^E (m s^{-1})	−0.00513	17.30741	−9.81674	−7.48951	0.00714	0.06468
Tetrahydrofuran (THF)+Chloro Benzene (CB)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	−0.00389	−7.18505	3.31390	1.26756	2.60743	0.01051
$L_f^E \times 10^{12}$ (m)	−0.00181	−2.62974	1.11909	0.83207	0.68078	0.00451
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	−0.03865	3.99039	−18.48990	34.84254	−20.16804	0.15157
U^E (m s^{-1})	−0.00146	1.63560	−2.93916	4.22285	−2.91631	0.01401
Tetrahydrofuran (THF)+Bromo benzene (BB)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	−0.00944	−22.19663	−1.24754	3.66829	19.88750	0.08717
$L_f^E \times 10^{12}$ (m)	−0.00608	−8.62536	−4.00723	9.46134	3.22681	0.04215
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	0.04944	32.29252	36.81370	−96.85887	27.40038	0.27320
U^E (m s^{-1})	0.02469	10.48038	206.09632	−390.62699	174.11715	0.26040
Tetrahydrofuran (THF)+Nitro benzene (NB)						
$K_S^E \times 10^{11}$ (m^2 N^{-1})	0.11580	−47.09058	100.59809	−170.82342	116.79627	0.41813
$L_f^E \times 10^{12}$ (m)	0.04015	−19.32123	37.92443	−59.61776	40.84162	0.14002
$Z^E \times 10^{-4}$ (K g m^{-2} s^{-1})	−0.08457	61.86998	−99.18661	118.57413	−80.99035	0.24881
U^E (m s^{-1})	−0.39990	297.59145	−566.95869	670.43291	−399.12865	1.52040

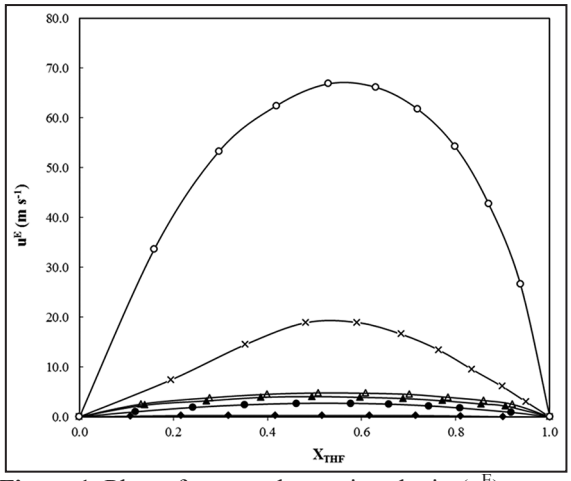

Figure 1: Plots of excess ultrasonic velocity(u^E) versus mole fraction of tetrahydrofuran (X_{THF}) for binary mixtures of tetrahydrofuran (THF) with benzene (−♦−), methyl benzene (−●−), ethyl benzene (−▲−), chloro benzene (−Δ−), bromo benzene (−×−) and nitro benzene (−○−) at 308.15 K.

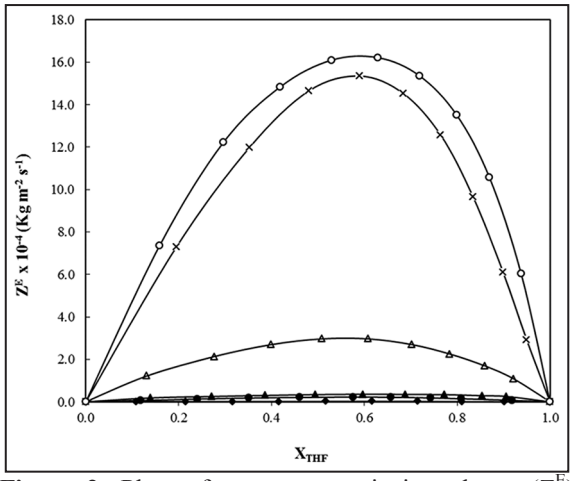

Figure 2: Plots of excess acoustic impedance (Z^E) versus mole fraction of tetrahydrofuran (X_{THF}) for binary mixtures of tetrahydrofuran (THF) with benzene (−♦−), methyl benzene (−●−), ethyl benzene (−▲−), chloro benzene (−Δ−), bromo benzene (−×−) and nitro benzene (−○−) at 308.15 K.

positive deviations as expected as per the equation (2) for Z^E calculation.

The positive deviations in u^E and Z^E (Figures 1 and 2) for all the systems under study are observed over the entire range of composition. These trends for these systems again support our view that the interactions between unlike molecules are quite possible, and these values are in the following order:

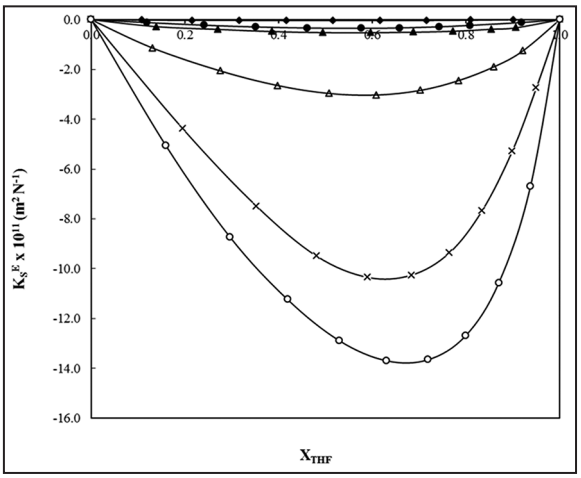

Figure 3: Plots of excess isentropic compressibility (K_s^E) versus mole fraction of tetrahydrofuran (X_{THF}) for binary mixtures of tetrahydro furan (THF) with benzene (−♦−), methyl benzene (−●−), ethyl benzene (−▲−), chloro benzene (−Δ−), bromo benzene (−×−) and nitro benzene (−○−) at 308.15 K.

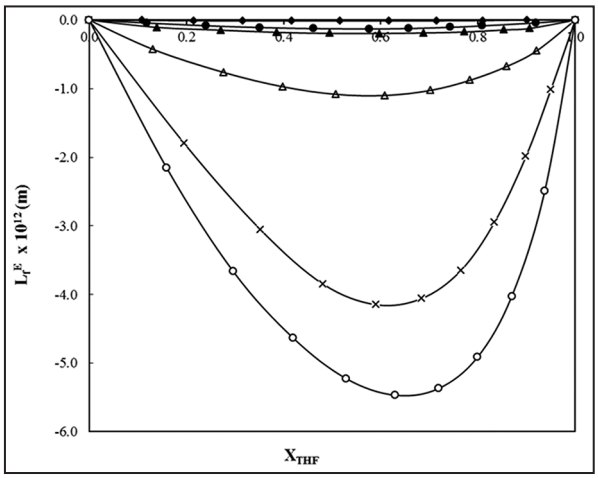

Figure 4: Plots of excess intermolecular free-length (L_f^E) versus mole fraction of tetrahydrofuran (X_{THF}) for binary mixtures of tetra hydrofuran (THF) with benzene (−♦−), methyl benzene (−●−), ethyl benzene (−▲−), chloro benzene (−Δ−), bromo benzene (−×−) and nitro benzene (−○−) at 308.15 K.

THF+NB>THF+BB>THF+CB>THF+EB>THF+MB>THF+B

A similar observation was reported by Bai et al., [12] from their ultrasonic velocity studies of binary liquid mixtures of butoxy ethanol with some amines.

Accordingly it is evident from the Figures 3 and 4 that K_S^E and L_f^E are negative for all the systems over the whole mole fraction range, both showing maximum at 0.5 mole fraction of THF. The negative excess isentropic compressibility and intermolecular free length are attributed to the presence of molecular interactions, possibly through electron donar-acceptor interactions leading to complex formation between unlike molecules.

In general, K_S^E values depend upon two factors, (i) Increase in free-length, defined by Jacobson [31] due to loss of dipolar association, breaking up of hydrogen bonding [32] and difference in size and shapes of the component molecules and (ii) decrease in free-length as a result of dipole-dipole interactions, hydrogen bonding association [32] and complex formation between the component molecules [33].

The first effect contributes to an increase in inter space between molecules in mixtures, consequently sound waves cover smaller distances in mixtures than in pure components. This would result in negative deviation in ultrasonic velocity and positive deviation in isentropic compressibility. The second effect contributes to a decrease in inter space between molecules in mixtures consequently sound waves cover larger distances in mixtures than in pure components. This would result in positive deviation in ultrasonic velocity and negative deviation in isentropic compressibility. The actual values of K_S^E would depend upon the balance between the two opposing effects. The experimental values indicate that the negative contributions predominate in these mixtures.

The behavior of K_S^E and L_f^E with the composition of the mixture can be qualitatively examined by considering the nature of the component molecules in the pure state and in the mixture. The molecules of THF are polar [8] and those of the aromatic hydrocarbons (B, MB, EB, CB, BB and NB) have large quadrupole moment [32], which causes molecular order in the pure state. THF on mixing with the aromatic hydrocarbons, would induce a decrease in the molecular order in the latter, resulting in an expansion in volume, and hence, may lead to positive K_S^E and L_f^E values. On the other hand, there is possibility of the electron donor-acceptor (charge-transfer) type interactions [33,34] between highly electronegative oxygen atom of >C=O group of THF (acting as a donor) and the π-electrons of ring of aromatic hydrocarbon molecules (acting as a acceptor), resulting in negative K_S^E and L_f^E values. The observed negative K_S^E and L_f^E values suggest the presence of significant donor-acceptor interactions between THF and aromatic hydrocarbon molecules in these mixtures. Recently, Yang et al., [35] reported similar type of donor-acceptor interactions between the oxygen atom of sulfolane and π-electrons of the aromatic hydrocarbons (B, MB, EB, o-xylene, m-xylene and p-xylene) and Ali et al., [36] also reported similar interactions between the oxygen atom of dimethyl sulfoxide and π-electrons of the aromatic hydrocarbons (B, MB, EB, o-xylene, m-xylene, p-xylene and mesitylene) from their physico-chemical studies of binary liquid mixtures.

It is observed that K_S^E and L_f^E becomes more negative (Figures 3 and 4) as the number of $–CH_3$ group in the benzene ring increase from benzene (devoid of $–CH_3$ group) to EB. This is due to the fact that methyl group ($–CH_3$) being an electron-releasing group would enhance the electron density of the benzene ring of the aromatic molecules, but the electron-accepting tendency of the aromatic ring would however decrease, as we move from benzene to MB and EB, resulting in increased donor-acceptor interaction between unlike molecules with increase in size of substituted group i.e., from methyl group ($–CH_3$) to ethyl group in aromatic hydrocarbon molecule, causing decrease in the value of K_S^E and L_f^E of the mixture. This would be responsible for more negative K_S^E and L_f^E values, in the sequence, B<MB<EB.

For the binary mixtures containing THF with CB, BB and NB the K_S^E and L_f^E values at equimolar concertration of these were formed to follow the negative values in order.

NB>BB>CB>B

When a halogen atom is introduced into the aromatic ring, it brings about a change in the π-electron density around the aromatic ring and also a change in the shape and size of the resultant molecule. Both these factors are likely to contribute to the overall volumetric effects in the mixtures. BB makes the molecule more asymmetric, resulting into a higher free volume in solution and in view thereof a relatively larger free volume in solution and in view thereof a relatively larger positive contribution to K_S^E and L_f^E is expected as compared to the mixtures containing CB. However, it is observed that K_S^E and L_f^E for the binary mixtures containing BB are more negative than those containing CB indicating the presence of strong intermolecular interactions. The decrease in K_S^E and L_f^E on going from benzene to CB to BB appears to be a consequence of increased polarizability of the molecule due to the introduction of a halogen atom in the aromatic ring. For the binary mixtures of cyclohexane with benzene, CB and BB a similar behavior has been reported [37-39].

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 ultlrasonic 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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