RESEARCH ARTICLE

ULTRASONIC STUDIES ON BINARY LIQUID MIXTURES OF METHYL ACRYLATE WITH BENZENES AT 308.15 K

[1]Vijaya Lakshmi, K., [1]Suhasini, D. M., [1]Jayachandra Reddy, N., [1]Ravi Kumar, K., [2]Chowdoji Rao, K. and *[1]Subha, M. C. S.

[1]Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu-515 003, A.P., India
[2]Department of Polymer Science, Sri Krishnadevaraya University, Anantapuramu-515 003, A. P., India

ABSTRACT

Densities and ultrasonic velocities of binary liquid mixtures of methyl acrylate (MA) with benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB) 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.

INTRODUCTION

Binary liquid mixtures due to their unusual behavior have attracted considerable attention (Ewing 1970). In chemical process industries, the materials are normally handled in fluid form and as a consequence, the physical chemical, and transport properties of fluids assume importance. Thus data on some of the properties associated with the liquids and liquid mixtures like density, viscosity and ultrasonic velocity, to find extensive application in solution theory and molecular dynamics (Mchaweh 2004). Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies (Kenart 2000). During the last two decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions through the study of the physico-chemical properties of such systems. Ultrasonic velocity and related data of liquid mixtures are found to be the most powerful tool in testing the theories of liquid state. In addition, ultrasonic velocity data can be utilized to deduce some useful properties of liquid mixtures which are not easily accessible by other means. The measurement of ultrasonic velocity has been adequately employed as a versatile tool for investigating the physical properties of matter-solid, liquid and gas. These studies are very important because of their extensive use in textile industry, leather industry, pharmaceutical industry and in many others. Ultrasonic velocity measurement has proved useful in dealing with the problems of liquid structure and molecular interactions in liquid mixtures.

Incontinuation of our earlier work (Vijaya Kumar Naidu *et al.*, 2003; Eswari Bai *et al.*, 2004; Bahadur Alisha *et al.*, 2007; Eswari Bai *et al.*, 2005) on volumetric, ultrasonic and transport properties of non aqueous binary liquid mixtures, here we report the results of our study on density and ultrasonic velocity behaviour of binary mixtures of methyl acrylate (MA) with benzene and substituted benzenes over the entire composition range. Methyl acrylate is a very important industrial chemical and is widely used commercially for the production of technically important high polymeric and latex compounds. It is polar (dipole moment, μ = 1.77 D at 298.15 K) (Dean 1956) and strongly associated aprotic solvent (Dean 1956) due to the presence of polar carbonyl group in the molecule and it is a versatile liquid which finds use as a monomer in the preparation of poly (methyl acrylate) which has innumerable industrial applications. Thus, a study of physico-chemical property data on the binary liquid mixtures containing methyl acrylate has attracted considerable interest in the literature, studied by Prausnitz (1986); Rowlilnson (1982) and Acree (1984). The

*Corresponding author: Subha, M. C. S.
Department of Chemistry Sri Krishnadevaraya University,
Ananthapuramu-515 003. A. P., India.

aromatic hydrocarbon molecules [benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB)] possess large quadrupole moments (Patterson 1994) causing an orientational order in these liquids. The binary mixtures of MA with aromatic hydrocarbons will be interesting as these systems find applications in the studies of polymer phase diagrams and preferential interaction of polymers in mixed solvents (Koningaveld 1977; Cowie 1968). The objective underlying the present work is to obtain information regarding molecular interactions in mixtures of a highly polar liquid with non-polar or weakly polar liquids. Thermodynamic and transport properties of liquid mixtures of methyl acrylate with 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 study the intermolecular interactions between the various species present in the liquid mixtures. In view of the above the present research aims to measure densities and ultrasonic velocity of binary mixtures of methyl acrylate (MA) 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 K_s, Z and L_f, excess functions like u^E, Z^E, K_s^E and L_f^E have been calculated and discussed the results in terms of molecular interactions present between unlike molecules and are presented here.

MATERIAL AND METHODS

Methyl acrylate (MA), benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB) were purchased from E-Merck and used as purchased. Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system by 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 and are given in Table 1.

Table 1. Comparison of Experimental density (ρ) and ultrasonic velocity (U) of pure liquids with literature at 308.15 K

Liquid	Density (ρ) x 10^{-3} Kg m^{-3}		Ultrasonic velocity (u) m s^{-1}	
	Exptl.	Lit.	Exptl.	Lit.
benzene	0.8629	0.86291[1]	1238.2	1238[5]
methyl benzene	0.8526	0.8529[1]	1262.0	1262[6 & 7]
ethyl benzene	0.8387	0.8390[2]	1277.0	1277.6[8]
chloro benzene	1.0890	1.0907[3]	1250.0	1250.0[9]
bromo benzene	1.4739	1.4748[3]	1122.0	1122.0[6]
Nitro benzene	1.1881	1.1885[3]	1452.8	1423.0[6]
Methyl acrylate	0.9367	0.9356[4]	1141.0	1140.0[10&11]

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 within ± 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 Gerrate (Model CT 050/2 made in Germany) whose temperature was controlled to ± 0.02 K was used for all the measurements.

Abeer (2011); Parthasarathi *et al.* (2011); Manapragada and Rajeev (2008); Patil Sujatha and Mirgane Sunil (2012); Munendra Kumar Gangwar *et al.* (2013); Thirumaran and Karthikeyan (2011); Bal Raj Deshwal *et al.* (2008); Wankhede (2012); Bala Karuna Kumar *et al.*, (2011); George *et al.* (2002); Sujatha and Sunil (2013)

RESULTS AND DISCUSSION

From the measured densities ( ) 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 respectively and are incorporated in Table 2 for the binary systems under study.

$$K_s = 1/u^2 \qquad \dots (1)$$
$$Z = \rho u \qquad \dots (2)$$
$$L_f = K (K_s)^{1/2} \qquad \dots (3)$$

Where 'K' is Jacobson's constant (Jacobson 1952).
The excess functions Y^E are calculated using the relation:

$$Y^E = Y_{mix} - (X_1 Y_1 + X_2 Y_2) \qquad \dots (4)$$

Where Y denotes u, Z, K_S and L_f respectively, X is the mole fraction and suffixes 1 & 2 denotes the components 1 & 2 in binary mixture 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 methyl acrylate (X_{MA}) 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.

$$Y^E = x(1-X)\sum_i A_i (2x-1)^i \qquad \dots (5)$$

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 Table 2, it is observed that the values of *u, Z, K_s and L_f* varied linearly with the mole fraction of MA (X_{MA}). This indicates the presence of interactions between the components in these binary liquid mixtures. The variation of u for the mixtures depend on the value of L_f. The observed decrease in u and the corresponding increase in L_f with mole fraction of MA (Table 2) for all the systems are in accordance with the view proposed by Eyring and Kincaid (1938). However, the excess functions which are a measure of the deviations from the ideal behaviour are relatively more sensitive to the intermolecular interactions between the unlike molecules of the mixture than the pure acoustical parameters.

Table 2. Values of density ( ), ultrasonic velocity (u), acoustic impedance (Z), isentropic compressibility (K_S) and intermolecular free-length (L_f) for the binary liquid mixtures of methyl acrylate (MA) with benzenes at 308.15 K

| Mole fraction of MA (X_{MA})	$\times 10^{-3}$ Kg m^{-3}	u m s^{-1}	Z X 10^{-4} Kg m^{-2} s^{-1}	K_S x 10^{11} m^2 N^{-1}	L_f x 10^{12} m
Methyl acrylate (MA) + Benzene (B)					
0.0000	0.8629	1238.2	1.0684	75.5889	5.7580
0.0898	0.8701	1229.1	1.0694	76.0775	5.7766
0.1842	0.8776	1219.4	1.0701	76.6384	5.7978
0.2801	0.8850	1209.6	1.0705	77.2232	5.8199
0.3778	0.8924	1199.8	1.0707	77.8410	5.8431
0.4761	0.8998	1190.1	1.0708	78.4708	5.8667
0.5775	0.9073	1180.2	1.0708	79.1267	5.8912
0.6734	0.9142	1171.2	1.0707	79.7506	5.9144
0.7837	0.9219	1160.9	1.0703	80.4822	5.9414
0.8941	0.9295	1150.8	1.0697	81.2336	5.9691
1.0000	0.9367	1141.0	1.0688	82.0027	5.9973
Methyl acrylate (MA) + Methyl benzene (MB)					
0.0000	0.8526	1262.0	1.0760	73.6438	5.6834
0.1042	0.8610	1250.3	1.0765	74.3011	5.7087
0.2031	0.8689	1239.0	1.0766	74.9653	5.7342
0.3118	0.8778	1226.4	1.0764	75.7518	5.7642
0.4175	0.8864	1213.9	1.0760	76.5604	5.7949
0.5081	0.8940	1203.0	1.0755	77.2909	5.8224
0.6184	0.9033	1189.6	1.0745	78.2311	5.8578
0.7133	0.9114	1177.8	1.0735	79.0952	5.8900
0.8103	0.9199	1165.6	1.0722	80.0117	5.9240
0.9051	0.9283	1153.3	1.0706	80.9906	5.9602
1.0000	0.9367	1141.0	1.0687	82.0053	5.9974
Methyl acrylate (MA) + Ethyl benzene (EB)					
0.0000	0.8387	1277.0	1.0710	73.1159	5.6630
0.1147	0.8481	1264.2	1.0721	73.7785	5.6886
0.2360	0.8586	1250.2	1.0734	74.5223	5.7172
0.3724	0.8708	1233.2	1.0738	75.5132	5.7551
0.4384	0.8770	1224.6	1.0739	76.0423	5.7752
0.5525	0.8879	1209.2	1.0736	77.0246	5.8124
0.6508	0.8977	1195.4	1.0732	77.9513	5.8473
0.7420	0.9073	1182.2	1.0726	78.8583	5.8812
0.8298	0.9170	1168.8	1.0718	79.8271	5.9172
0.9175	0.9271	1154.8	1.0706	80.8870	5.9564
1.0000	0.9367	1141.0	1.0688	82.0027	5.9973
Methyl acrylate (MA) + Chloro benzene (CB)					
0.0000	1.0890	1250.0	1.3613	58.7695	5.0771
0.1268	1.0742	1240.6	1.3326	60.4864	5.1507
0.2484	1.0586	1229.8	1.3019	62.4587	5.2341
0.3238	1.0484	1222.8	1.2819	63.7951	5.2897
0.4667	1.0281	1208.4	1.2423	66.6125	5.4053
0.5668	1.0129	1197.5	1.2129	68.8477	5.4952
0.6637	0.9972	1186.2	1.1829	71.2677	5.5910
0.7517	0.9824	1175.6	1.1549	73.6583	5.6840
0.8381	0.9672	1164.5	1.1263	76.2388	5.7827
0.9215	0.9520	1153.2	1.0978	78.9867	5.8860
1.0000	0.9367	1141.0	1.0688	82.0027	5.9973
Methyl acrylate (MA) + Bromo benzene (BB)					
0.0000	1.4739	1122.0	1.6537	53.8947	4.8620
0.1582	1.4202	1123.5	1.5956	55.7807	4.9463
0.3124	1.3665	1125.4	1.5379	57.7773	5.0341
0.4393	1.3127	1127.5	1.4800	59.9290	5.1270
0.5491	1.2590	1129.5	1.4220	62.2590	5.2257
0.6459	1.2053	1131.5	1.3638	64.8031	5.3314
0.7317	1.1516	1133.4	1.3052	67.5977	5.4451
0.8113	1.0979	1135.3	1.2464	70.6669	5.5674
0.8846	1.0441	1137.2	1.1874	74.0601	5.6995
0.9501	0.9864	1139.1	1.1236	78.1310	5.8540
1.0000	0.9367	1141.0	1.0688	82.0027	5.9973
Methyl acrylate (MA) + Nitro benzene (NB)					
0.0000	1.1881	1452.8	1.7261	39.8782	4.1822
0.1354	1.1792	1421.6	1.6764	41.9610	4.2901
0.2596	1.1698	1390.4	1.6265	44.2165	4.4039
0.3771	1.1516	1359.3	1.5653	46.9995	4.5403
0.4866	1.1310	1328.1	1.5021	50.1290	4.6891
0.5857	1.1086	1296.9	1.4377	53.6305	4.8501
0.6800	1.0822	1265.7	1.3698	57.6789	5.0298
0.7686	1.0541	1234.5	1.3013	62.2455	5.2251
0.8479	1.0259	1203.4	1.2345	67.3138	5.4337
0.9257	0.9928	1172.2	1.1637	73.3077	5.6704
1.0000	0.9367	1141.0	1.0688	82.0027	5.9973

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 methyl acrylate (MA) with benzenes at 308. 15 K

Mole fraction of MA (X_{MA})	u^E m s^{-1}	Z^E X 10^{-4} Kg m^{-2} s^{-1}	K_S^E x 10^{11}m^2 N^{-1}	L_f^E x 10^{12} m
Methyl acrylate (MA) + Benzene (B)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.0898	-0.3714	0.0967	-0.0873	-0.0291
0.1842	-0.9458	0.1598	-0.1319	-0.0424
0.2801	-1.3393	0.1991	-0.1622	-0.0512
0.3778	-1.6578	0.2151	-0.1711	-0.0527
0.4761	-1.8521	0.2225	-0.1717	-0.0520
0.5775	-1.8470	0.2179	-0.1661	-0.0500
0.6734	-1.5955	0.1999	-0.1574	-0.0477
0.7837	-1.0884	0.1564	-0.1332	-0.0410
0.8941	-0.4735	0.0948	-0.0899	-0.0285
1.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate (MA) + Methyl benzene (MB)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.1042	0.8842	0.1236	-0.2140	-0.0741
0.2031	1.6141	0.2090	-0.3767	-0.1300
0.3118	2.0798	0.2722	-0.4991	-0.1713
0.4175	2.3895	0.3068	-0.5743	-0.1963
0.5081	2.4901	0.3178	-0.6014	-0.2050
0.6184	2.4264	0.3029	-0.5834	-0.1982
0.7133	2.0803	0.2651	-0.5129	-0.1736
0.8103	1.6873	0.2101	-0.4075	-0.1379
0.9051	0.8321	0.1149	-0.2212	-0.0743
1.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate (MA) + Ethyl benzene (EB)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.1147	2.7992	0.1384	-0.3566	-0.1274
0.2360	5.2710	0.2864	-0.6909	-0.2469
0.3724	6.8484	0.3665	-0.9122	-0.3240
0.4384	7.1964	0.3855	-0.9696	-0.3433
0.5525	7.3680	0.3870	-1.0013	-0.3529
0.6508	6.9088	0.3598	-0.9481	-0.3329
0.7420	6.1390	0.3281	-0.8516	-0.2986
0.8298	4.6848	0.2604	-0.6631	-0.2320
0.9175	2.5800	0.1609	-0.3826	-0.1336
1.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate (MA) + Chloro benzene (CB)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.1268	4.4117	0.8478	-1.2291	-0.4305
0.2484	6.8846	1.3277	-2.0820	-0.7164
0.3238	8.0590	1.5400	-2.4973	-0.8533
0.4667	9.2525	1.7586	-2.9999	-1.0127
0.5668	9.2716	1.7463	-3.0904	-1.0344
0.6637	8.5555	1.5757	-2.9216	-0.9686
0.7517	7.4957	1.3474	-2.5756	-0.8484
0.8381	5.8916	1.0215	-2.0025	-0.6564
0.9215	3.6435	0.6112	-1.1922	-0.3909
1.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate (MA) + Bromo benzene (BB)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.1582	-1.4794	3.4454	-2.5607	-0.9527
0.3124	-2.5105	6.6913	-4.8984	-1.8258
0.4393	-2.8925	8.3258	-6.3136	-2.3378
0.5491	-2.9329	8.9516	-7.0699	-2.5972
0.6459	-2.7721	8.7895	-7.2466	-2.6391
0.7317	-2.5023	7.9509	-6.8636	-2.4758
0.8113	-2.1147	6.7293	-6.0318	-2.1570
0.8846	-1.6074	5.1074	-4.6990	-1.6683
0.9501	-0.9519	2.5645	-2.4691	-0.8664
1.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate (MA) + Nitro benzene (NB)			
0.0000	0.0000	0.0000	0.0000	0.0000
0.1354	11.0377	3.9301	-3.6209	-1.3793
0.2596	18.5833	7.1099	-6.5973	-2.4957
0.3771	24.0398	8.7119	-8.7638	-3.2636
0.4866	27.0019	9.5828	-10.2470	-3.7639
0.5857	26.7213	9.6651	-10.9200	-3.9525
0.6800	24.9440	9.0652	-10.8439	-3.8669
0.7686	21.3895	8.0455	-10.0096	-3.5218
0.8479	14.9352	6.5777	-8.2818	-2.8756
0.9257	8.0133	4.6128	-5.5652	-1.9200
1.0000	0.0000	0.0000	0.0000	0.0000

Table 4. Parameters of Eq. (5) and Standard deviations

Excess Property	A_0	A_1	A_2	A_3	A_4	
		Methyl acrylate (MA) + Benzene (B)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	0.10953	-22.68454	51.16041	-75.07245	46.16451	0.35174
$L_f^E \times 10^{12}$ m	-0.00075	-0.40351	1.1415	-1.4207	0.6826	0.00089
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	0.00052	1.26257	-2.60307	12.51853	-1.17958	0.00232
U^E m s^{-1}	0.00871	-4.26402	-8.60944	24.04214	-11.17769	0.03189
		Methyl acrylate (MA) + Methyl benzene (MB)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	-0.00013	-2.3016	2.37354	-0.61877	0.54933	0.00527
$L_f^E \times 10^{12}$ m	-0.00005	-0.80078	0.86174	-0.25578	0.19575	0.00194
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	0.00025	1.35665	-1.79782	0.96194	-0.522	0.00248
U^E m s^{-1}	-0.00047	9.65366	-9.65425	1.38186	-1.40559	0.05299
		Methyl acrylate (MA) + Ethyl benzene (EB)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	0.008120	-3.85031	4.44646	-2.4953	1.88423	0.01443
$L_f^E \times 10^{12}$ m	0.00305	-1.38733	1.65113	-0.93593	0.6642	0.0054
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	-0.00731	1.69935	-2.47673	1.88544	-1.09296	0.01313
U^E m s^{-1}	-0.004335	29.7451	-35.58501	17.62786	-11.73453	0.08.496
		Methyl acrylate (MA) + Chloro benzene (CB)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	0.00219	-11.20309	12.76523	-8.41389	6.82608	0.02915
$L_f^E \times 10^{12}$ m	0.00030	-3.95182	4.85258	-3.21211	2.30285	0.01061
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	0.00329	7.91662	-11.8729	8.09993	-4.13143	0.02527
U^E m s^{-1}	-0.00139	42.70621	-72.68309	66.27132	-36.17726	0.1552
		Methyl acrylate (MA) + Bromo benzene (BB)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	0.04329	-20.22719	22.80031	-34.97455	32.20724	0.16051
$L_f^E \times 10^{12}$ m	0.01541	-7.3666	7.11342	-9.68815	9.87406	0.05664
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	-0.0594	25.50031	-12.61913	-0.61242	-12.03449	0.20662
U^E m s^{-1}	0.02693	-13.01146	21.26977	-19.56395	11.16593	0.10046
		Methyl acrylate (MA) + Nitro benzene (NB)				
$K_s^E \times 10^{11}$ m^2 N^{-1}	0.09048	-35.08525	52.909	-78.25257	60.0504	0.3099
$L_f^E \times 10^{12}$ m	0.0319	-13.2048	18.76397	-24.41529	18.72374	0.39759
$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	-0.12927	40.7379	-67.6998	71.57947	-44.1277	0.39759
U^E m s^{-1}	0.02693	-13.0115	21.26977	-19.56395	11.16593	0.10046

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 the mole fraction of methyl acrylate (X_{MA}) are examined from the Figures. 1 to 4 respectively. It is observed from Figure. 1 that 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 (Vijaya lakshmi *et al.*, under press) this indicates the mixtures compressed more and it is natural to get positive excess ultrasonic velocities for these mixtures. The Figure. 2 shows variation of Z^E with composition of liquid mixtures which exhibit 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

MA + NB > MA + BB > MA + CB > MA + EB > MA + MB > MA + B
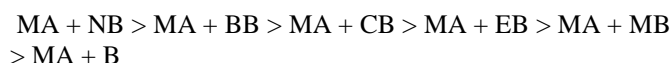
A similar observation was reported by Eswari Bai *et al.*, (2004) from their ultrasonic velocity studies of binary liquid mixtures of butoxy ethanol with some amines. Accordingly it is evident from the Figures. 3 and 4 that K_s^E and L_f^E are negative for all the systems over the whole mole fraction

range, both showing maxima at 0.5093 mole fraction of MA. The negative excess isentropic compressibility and excess intermolecular free length are attributed to the presence of molecular interactions, possibly through electron donar-acceptor interactions leading to complex formation between unlike molecules. The polar nature of the two components (MA with benzenes and substituted benzenes) leads to the interaction between the electron rich oxygen atom of carbonyl group of MA with the -electrons of aromatic ring of benzene and substituted benzenes, forming donor-acceptor complexes between the two component molecules in mixture which leads to a decrease in the intermolecular distances and increase in sound velocities, thereby decreasing the isentropic compressibility of the mixtures. The negative values obtained for the K_s^E and L_f^E are in the following order

MA + B < MA+ MB < MA+ EB < MA + CB < MA + BB < MA + NB
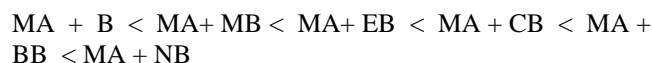
Ramamoorthy and Sastry (1983) and Palaniappan *et al.*, (1998) pointed out that, negative values of excess inter molecular free length (L_f^E) indicates that sound waves cover shorter distance due to decrease in intermolecular free length as a result of stronger donar-acceptor interactions between MA and benzene and substituted benzene molecules resulting in a large negative values of K_s^E and positive u^E values. Further, it is also observed from the experimental results that the negative contributions increase with increase in substitution in benzene (-H, -CH$_3$, -C$_2$H$_5$, -Cl, -Br and –NO$_2$). The variation of K_s^E and L_f^E are qualitatively similar to that of excess volumes as discussed from excess volume and excess viscosity studied by Vijaya lakshmi *et al.*, (under press) of these systems.
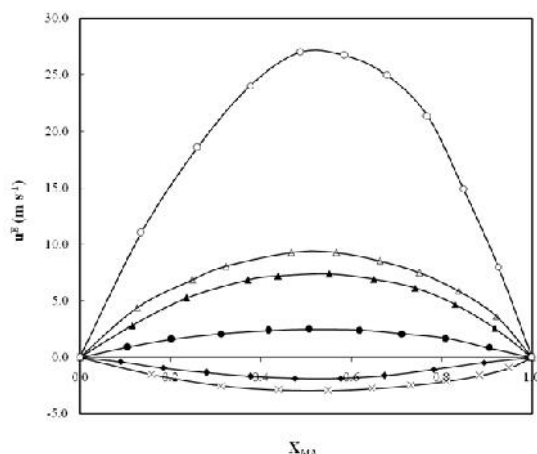
Fig. 1. Plots of excess ultrasonic velocity (u^E) vs mole fraction of methyl acrylate (X_{MA}) for binary mixtures of methyl acrylate (MA) with benzene (B, − −), methyl benzene (MB, − −), ethyl benzene (EB, − −), Chloro benzene (CB, − −), bromo benzene (BB, −×−) and nitro benzene (NB, − −) at 308.15 K.
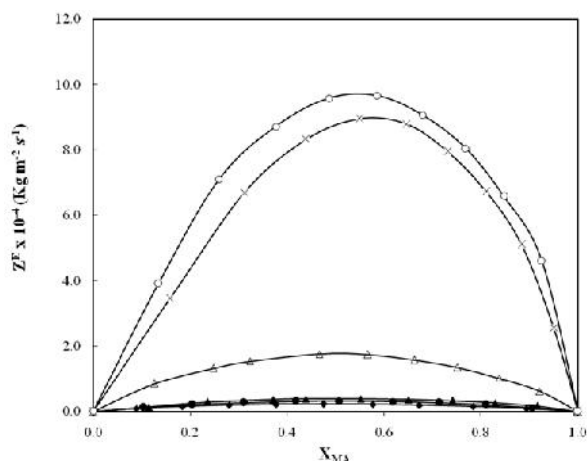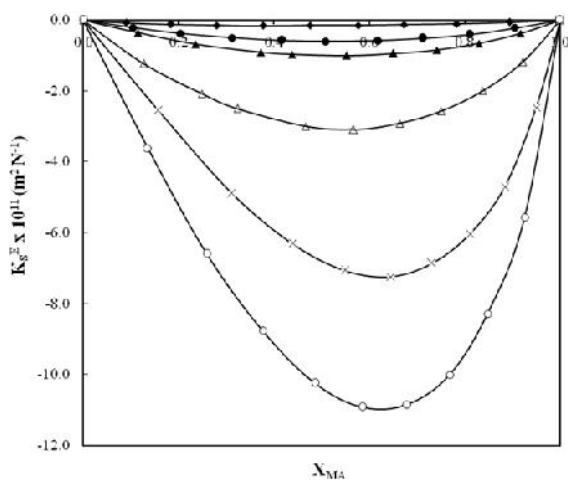

Fig. 2. Plots of excess acoustical impedance (Z^E) vs mole fraction of methyl acrylate (X_{MA}) for binary mixtures of methyl acrylate (MA)with benzene (B, − −), methyl benzene (MB, − −), ethyl benzene (EB, − −), chloro benzene (CB, − −), bromo benzene (BB, −×−) and nitro benzene (NB, − −) at 308.15 K.

Fig. 3. Plots of excess isentropic compressibility (K_S^E) vs mole fraction of methyl acrylate (mixtures of methyl acrylate (MA)− −), chloro benzene (CB, − −), bromo benzene(BB, −×−) and nitro benzene (NB, − −) at 308.15 K
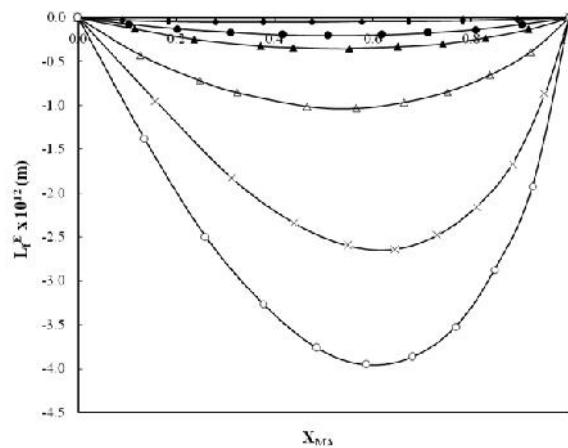

Fig. 4. Plots of excess intermolecular free-length (L_f^E) vs mole fraction of methyl acrylate (X_{MA}) for binary mixtures of methyl acrylate (MA)with benzene (B, − −), methyl benzene (MB, − −), Ethyl benzene (EB, − −), chloro benzene (CB, − −), bromo benzene (BB, −×−) and nitro benzene (NB, − −) at 308.15 K.

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 MA are polar (Riddick *et al*., 1986) and those of the aromatic hydrocarbons [benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB)] have large quadrupole moment by Patterson (1994), which causes molecular order in the pure state. MA 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 (Yang *et al*., 2002) between highly electronegative oxygen atom of >C=O group of MA (acting as a donor) and the -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 MA and aromatic hydrocarbon molecules in these mixtures. Recently, Yang *et al*., (2002) reported similar type of donor-acceptor interactions between the oxygen atom of sulpholane and -electrons of the aromatic hydrocarbons (benzene, methyl benzene, ethyl benzene, o-xylene, m-xylene and p-xylene) and Ali *et al*., (2006) also reported similar interactions between the oxygen atom of DMSO and -electrons of the aromatic hydrocarbons (benzene, methyl benzene, ethyl benzene, 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 ethyl benzene. 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 methyl benzene and ethyl benzene, 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 MA with CB, BB and NB the K_s^E and L_f^E values at equimolar concertration of these at 0.5093 mole fraction was formed to follow the negative values in the following order

NB > BB > CB > B

When a halogen atom is introduced into the aromatic ring, it brings about a change (decrease) in the -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 over all volumetric effects in the mixtures. Bromo benzene 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 negative contribution to K_s^E and L_f^E is expected as compared to the mixtures containing chloro benzene. A similar effect can also be expected in case of high electro negative group of nitro benzene also. However it is observed that K_s^E and L_f^E for the binary mixtures containing nitro benzene and bromo benzene are more negative than those containing chloro benzene thereby indicating the presence of strong intermolecular interactions. The decrease in K_s^E and L_f^E on going from benzene to chloro benzene to bromo benzene to nitro benzene appears to be a consequence of increased polarizability of the molecule due to the introduction of a halogen atom or nitro group in the aromatic ring. For the binary mixtures of cyclohexane with benzene, chloro benzene and bromo benzene in use of thermo physical property studies, a similar behaviour has been reported by Stokes *et al.* (1970); Letcher (1972); Kohler and Rott (1954).

Conclusion

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 functions from the rectilinear dependence on composition of these mixtures suggest the presence of molecular interactions between the components of binary mixtures. The interactions are primarily due to the electron donor-acceptor interactions existing between the components of the mixtures.

REFERENCES

Abeer K. Shams, *J. of Al-Nahrain University*, 14(2), (2011) 75.

Acree, W. E. (Jr.), *Acadamicress,* New York. (1984).

Ali, A., Nain, A. K., Chand, D., Ahmad, R., *Bull. Chem. Soc. Jpn.*, 79, (2006) 702.

Bahadur Alisha, S., Surendra Babu, N., Subha, M. C. S., *J. Pure Appl. Ultrason.* 29 (2007) 60.

Bal Raj Deshwal, Anusharma, Krishna Chandu Singh, Chinese *J. of Chem. Eng.*, 16(4), (2008) 599.

Bala Karuna Kumar, D., Rayapa Reddy, K., Srinivasa Rao, G., Rama Rao, G. V., Rambabu, C., *J. Chem. Pharm. Res.*, 3(5), (2011) 274.

Cowie, J. M. G., *J. Polym. Sci. Part C.*, 23, (1968) 267.

Dean, J. A., *Lange's Hand book of chemistry, McGraw Hill*, New York, (1956).

Eryring, H., Kincaid, J. F*., J. Chem. Phys.*, 6, (1938) 620.

Eswari Bai, M., Neerajakshi, K. G., Krishna Rao, K. S. V., Narayana Swamy, G., Subha, M. C. S., *J. Indian Chemical Society* ,82 (2005) 25.

Eswari Bai, M., Subha, M. C. S., Narayana Swamy, G., Chowdoji Rao, K., *J. Pure and Appl. Ultrasonics,* 26 (2004) 79.

Ewing, M. B., *J. of Chem. Thermodyn.*, 2, (1970) 689.

George, J., Sastry, N. V., Patel, S. R., Valand, M. K., *J. Chem. Eng. Data*, 47, (2002) 262.

Jacobson, B., Acta Chem. Scand., 6, (1952) 1485; *J. Chem. Phys.*, 20, (1952) 927.

Kenart, C. M., *Phys. and Chem. Of Liq.*, 38, (2000) 155.

Koningaveld, R., Stepto, R. F. T., *Macromolecules*, 10, (1977) 1166.

Letcher, T. M., *J. Chem. Thermodyn.*, 4, (1972) 59.

Manapragada V. Rathnam, Rajeev Kumar R. Singh, *J. Chem. Eng. Data*, 53, (2008) 265.

Mchaweh, A., *Fluid Phase Equilibria.*, 224, (2004) 157.

Munendra Kumar Gangwar, Ashisk Kumar Saxena, Rajeev Agarwal, *Adv. in Appl. Sci. Res.*, 4(2), (2013) 29.

Palaniappan, P. L. R. M., Pichaimuthu, A., Kannappan, K. N., *Ind. J. Phys.*, 72B, (1998) 175.

Parthasarathi, S., Saravanakumar, K., Baskaran, R., Kubendran, T. R., *Int. J. of Sci. and Tech.*, 1, (2011) 2.

Patil Sujatha S., Mirgane Sunil R., *Int. J. of Res. in Chem. and Envir.*, 2(1), (2012) 166.

Patterson, D., *J. Sol. Chem.*, 23, (1994) 105.

Prausnitz, J. M., Lichenthalar and Azevedo, E. G., Second edition, *Prentice-Hall Inc., Englewood Cliffs, N. J.,* (1986).

Ramamoorty, M., Sastry, D. S., *Ind. J. Pure Appl. Phys.*, 21, (1983) 579.

Riddick, J. A., Bunger, W.B., Sakano, T., *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed. Wiley Interscience, New York, (1986).

Rowlinson, J. S., Swinton, F. L., *Butterworth Scientific, London, Third edition*, (1982).

Stokes, R. H., Levien, B. J., Marsh, K. N., *J. Chem. Thermodyn.*, 2, (1970) 43.

Sujatha S. Patil, Sunil R. Mirgane, *Avd. Appl. Sci.Res.*, 4(3), (2013) 329.

Thirumaran, S., Karthikeyan, N., *Int. J. of Chem. Res.*, 3(3), (2011) 83.

Vijaya Kumar Naidu, B., Chowdoji Rao, K., Subha, M. C. S., *J. Chem. Eng. Data*, 48, (2003) 625.

Vijaya Lakshmi, K., Suhasini, D., Jayachandra Reddy, M., Ravi, C., Subha, M. C. S., Chowdoji Rao, K., *Ind. J. of Adv. in Chem. Sci.* (under press)

Wankhede, D. S., *J. of the Korean Chem. Soc.*, 56, (2012) 1

Yang, C., Ma, P., Zhou Q., *J. Chem. Eng. Data*, 49, (2002) 262.

****