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Ultrasonic Studies on Binary Liquid Mixture of Methyl acrylate with p-Xylene at 298 K

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ABSTRACT

Densities and ultrasonic velocities of binary liquid mixture of methyl acrylate with p-Xylene have been measured at 298 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),excessacoustic 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 result was discussed in terms of the existence of intermolecular interactions between the components in the liquid mixture under study.

Key words: Acoustic impedance, Inter molecular free-Length, Isentropic Compressibility, Ultrasonic velocity.

1.INTRODUCTION

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[1]. Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical, biochemical and kinetic studies[2]. 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 physicochemical 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[3]. 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[4]. 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. In continuation of our earlier work[5] 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 mixture of methyl acrylate with p- xylene 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, $\mu = 1.77$ D at 298 K) and strongly associated aprotic solvent [6] 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 [7].

Paraxylene is an aromatic hydrocarbon. p-xylene is a xylene with methyl groups at positions 1 and 4. p- xylene is predominantly an industrial chemical. Therefore, most opportunities for human exposure to p- xylene occur at the industrial facilities where it is handled. p- xylene is widely used as a feedstock (or "building block") to manufacture other industrial chemicals, notably terephthalic acid, purified terephthalic acid and dimethyl-terephthalate are used to manufacture polyethylene terephthalate polyesters, a kind of plastic[8].

The binary mixtures of methyl acrylate with aromatic acid will be interesting as these systems find applications in the studies of polymer phase diagrams and preferential interaction of polymers in mixed solvents[9]. 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[10]. Thermodynamic and transport properties of liquid mixture of methyl acrylate with p- xylene was 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 in the liquid mixture. In view of the above the present research aims to measure densities and ultrasonic velocity of binary mixtures of methyl acrylate with p- xylene at 298 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.

2.MATERIAL AND METHODS

Methyl acrylate and p- xylene were purchased from Sd fine chemicals India. Mixture was 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. The measurements were made with proper care in an AC room to avoid evaporation loss. The densities (ρ) of liquids and their mixture 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.

Table 1. Comparison of Experimental density (ρ) and ultrasonic velocity (U) of pure liquids with literature at 298 K

Liquid	Density (ρ) x 10^{-3} Kg m^{-3}		Ultrasonic velocity (U) m s^{-1}	
	Experimental	Literature	Experimental	Literature
Methyl acrylate	0.9363	0.9356	1142.0	1140.0
p- xylene	0.8571	0.8566	1290.3	1288.8

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 respectively and are incorporated in Table 2. for the binary system under study[11-15].

$$Ks = 1/u^2 \rho \qquad \dots (1)$$

$$Z = \rho u \qquad \dots (2)$$

$$Lf = K (Ks)^{1/2} \qquad \dots (3)$$

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

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

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 liquid 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 for liquid mixture were fitted to the following Redlich-Kister equation[16] by the least-squares method and the values are given in Table 4.

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

Where Y^E, U^E, Z^E, K_S^E and L_f^E is 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 methyl acrylate. This indicates the presence of interactions between the components in this binary liquid mixture. The variation of U for the mixture depend on the value of L_f. The observed decrease in U and the corresponding increase in L_f with mole fraction of methyl acrylate (Table 2) for the liquid mixture is in accordance with the view proposed[17]. 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 (ρ), ultrasonic velocity (U), acoustic impedance (Z), isentropic compressibility (K_S) and intermolecular free-length (L_f) for the binary liquid mixture of methyl acrylate with p-xylene at 298 K

Mole fraction of methyl acrylate(X)	ρ x 10^{-3} Kg m-3	U m s^{-1}	Z x 10^{-4} Kg $m^{-2}s^{-1}$	KS x 10^{11} m^2 N^{-1}	Lf x 10^{12} m
0.0000	0.8571	1290.3	1.0850	74.2542	5.8578
0.1035	0.8612	1281.4	1.0802	75.0215	5.9875
0.2142	0.8708	1263.2	1.0785	76.1240	6.0220
0.3020	0.8824	1255.7	1.0720	76.9887	6.1025
0.4102	0.8930	1238.9	1.0714	77.6587	6.1878
0.5087	0.9002	1215.6	1.0625	78.2546	6.2741
0.6102	0.9093	1208.2	1.0580	79.1200	6.3300
0.7121	0.9127	1192.1	1.0524	80.0010	6.4802
0.8104	0.9204	1175.9	1.0468	80.8578	6.5200
0.9056	0.9365	1153.0	1.0398	81.5226	6.5882
1.0000	0.9422	1145.8	1.0302	82.9855	6.6011

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 mixture of methyl acrylate with p- xylene at 298 K

Mole fraction of methyl acrylate (X)	U^E m s^{-1}	Z^E x 10^{-4} Kg m^{-2} s^{-1}	KS ^{E} x $10^{11}m^2$ N^{-1}	Lf ^{E} x 10^{12} m
0.0000	0.0000	0.0000	0.0000	0.0000
0.1120	0.9588	0.1652	-0.2321	-0.0825
0.2030	1.5245	0.1957	-0.3425	-0.1200
0.3120	1.7882	0.2654	-0.4102	-0.1536
0.4201	1.8236	0.3058	-0.5243	-0.1785
0.5010	1.9104	0.3182	-0.6821	-0.2053
0.6145	1.7420	0.2945	-0.5002	-0.1854
0.7013	1.3406	0.2147	-0.4130	-0.1625
0.8147	1.0182	0.1876	-0.2864	-0.1235
0.9089	0.9747	0.1402	-0.2015	-0.0814
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	σ
K_S^E x 10^{11} m^2 N^{-1}	-0.00014	-2.5487	2.5258	-0.6254	0.5592	0.0061
L_f^E x 10^{12} m	-0.00008	-0.9587	0.95820	-0.2622	0.1982	0.0021
Z^E x 10^{-4} Kg m^{-2} s^{-1}	0.00028	1.4582	-1.5879	0.9785	-0.5478	0.0028
U^E m s^{-1}	-0.00049	9.8540	-9.7587	1.3956	-1.4524	0.0574

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 are examined. It is observed that U^E is positive for liquid mixture 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. Since the excess volume (V^E) values are negative this indicates the mixtures compressed more and it is natural to get positive excess ultrasonic velocities for this mixture. The variation of Z^E with composition of liquid mixture which exhibit positive deviations as expected as per the equation (2) for Z^E calculation. The positive deviations in U^E and Z^E for the liquid mixture under study are observed over the entire range of composition.

K_s^E and L_f^E are negative for the liquid mixture over the whole mole fraction range, both showing maxima at mole fraction of methyl acrylate. 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 (methyl acrylate and p-xylene) leads to the interaction between the electron rich oxygen atom of carbonyl group of methyl acrylate with the π-electrons of aromatic ring of p-xylene, 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, there by decreasing the isentropic compressibility of the mixture.

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 methyl acrylate and p- xylene 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 (-CH3). 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 of this liquid mixture. 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. Methyl acrylate 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 [18-20] between highly electronegative oxygen atom of >C=O group of methyl acrylate (acting as a donor) and the π-electrons of ring of p- xylene 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 methyl acrylate and p- xylene molecules in this mixture. It is observed that K_s^E and L_f^E becomes more negative as the number of – CH3 group in the benzene ring. This is due to the fact that methyl group (–CH3) 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 be decrease. Resulting in this liquid mixture increased donor-acceptor interaction between unlike molecules with increase in size of substituted group (–CH3) 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. For the binary mixture containing methyl acrylate with p- xylene the K_s^E and L_f^E values at equimolar concertration were formed to follow the negative value in the liquid mixture.

4.CONCLUSION

The dependence of ultlrasonic velocity on composition of the mixture 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 this mixture suggest the presence of molecular interactions between the components of binary mixture. The interactions are primarily due to the electron donor-acceptor interactions existing between the components of the mixture.

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