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Study of Acoustical and Physico-chemical Properties on the Binary Mixture of Chlorobenzene and p-Xylene at 298.15 K Temperature

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ABSTRACT: The study of liquid mixtures finds wide application in industrial and technological processes. In this work evaluated experimental densities (ρ) and ultrasonic velocities (U) for the pure liquids and liquid mixture of Chlorobenzene and p-Xylene using bicapillary pycnometer and single frequency variable path over the different concentration range at 298.15 K Temprature. The observed data had been utilized to calculate various acoustical parameters like Isentropic compressibility (K_S), Intermolecular free length (L_f) and acoustic impedance (Z). Excess ultrasonic velocities (U^E), Excess Isentropic compressibility (K_S^E), Excess Intermolecular free length (L_f^E) and Excess acoustic impedance (Z^E) were calculated using the measured values and correlated with the Redlich–Kister polynomial equation. The observed variations of the properties for the above mixture conclude that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the positive (U^E) and negative (K_S^E), (L_f^E) and (Z^E) values.

Keywords: Acoustic impedance, Density, Inter molecular free-Length, Isentropic Compressibility, Ultrasonic velocity.

I. INTRODUCTION

Acoustical and Physico-chemical properties of liquid mixtures and solutions are play very important role in understanding the nature of intermolecular interactions. Excess function, have been used as a qualitative and quantitative guide to predict the extent of complex formation in binary liquid mixtures. In recent years there has been considerable advancement in the theoretical and experimental investigation of the excess properties of simple liquid mixtures. In many industrial applications, liquid solutions rather than single component liquid systems, are used in processing and product formulations. Of the many properties to be considered in process and product design and optimization, Densities (ρ) and Ultrasonic velocities (U) important properties; thus, method for the prediction of these properties are of theoretical and practical interests.

Studies of thermodynamic properties of ternary mixture are of considerable interest in the fundamental understanding of the nature of interactions between the unlike molecules. In recent years, the theoretical and experimental investigations of excess and deviation functions are taken as interaction parameters to improve the results [1]. The measurement of acoustic and physico-chemical parameters have been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures [2]. The practical importance of liquid mixtures rather than single component liquid systems has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physico-chemical behavior of such systems [3-4]. These studies are very important because of their extensive use in textile industry, leather industry, pharmaceutical industry and in many others [5]. 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 [6-7] on volumetric, ultrasonic and transport properties of non aqueous binary liquid mixtures, here report the results of my study on density and ultrasonic velocity behaviour of binary mixture of Chlorobenzene with p- xylene over the entire composition range.

Villares *et al.,* reported [8] for the binary mixtures of (1,3-dioxolane or 1,4-dioxane) with (2-methyl-1-propanol or 2-methyl-2-propanol) at the temperatures (298.15 and 313.15) K. Excess volumes and excess isentropic compressibility coefficients were calculated from experimental data and fitted by means of a Redlich–Kister type equation. The ERAS model was used to calculate the excess volumes of the four systems at both temperatures. Bhatia *et al.*, [9] computed densities, speeds of sound, viscosities and refractive indices of binary mixtures of octan-2-ol with benzene, chlorobenzene and bromobenzene were measured over the entire range of composition at 298.15 and 303.15 K, and atmospheric pressure. From the experimental data, excess molar volumes VE, isentropic compressibilities KS, excess isentropic compressibilities , and deviations of speeds of sound , were calculated at 298.15 and 303.15 K. These excess functions were fitted to the Redlich–Kister polynomial equation. Papari *et al.,* [10] computed densities and speed of sound for three binary mixture with 2-phenylethanol with 1-butanol, 2-butanol and 2-methyl-1-propanol at six temperatures from 298.15 K. To 323.15 K. The results, were used to discuss the nature and strength of intermolecular interaction in these mixtures.

These studies are very important because of their extensive use in textile industry, leather industry, pharmaceutical industry and in many others. Acoustical parameters have proved useful in dealing with the problems of liquid structure and molecular interactions in liquid mixtures.

Chlorobenzene is a colorless, flammable aromatic organic compound and a widely used intermediate in the manufacture of other chemicals. Chlorobenzene is polar compound and this has been confirmed by the X-ray analysis which shows that the C-CI bond in chlorobenzene is 1.69 A^o . Its boiling point and melting point are 132°C and -45°C, respectively. The carbon-chlorine bond in Chlorobenzene is stronger than if it were a pure single bond. Chlorobenzene is insoluble in water and soluble in alcohol, benzene, xylene and ether. Chlorobenzene is more reactive because the chlorine atom is bonded with SP^3 hybridized carbon atom and consequently can be removed easily [11-12].

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. In p-xylene, the resulting sigma complex has the positive charge distributed over carbon atoms. 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, purified terephthalic acid and dimethyl-terephthalate are used to manufacture polyethylene terephthalate polyesters, a kind of plastic [13].

In the literature of physical chemistry, physico-chemical and acoustical properties of liquids and liquid mixtures constitute an important area of research. The study of liquids and liquid mixtures has been exhaustive since the pioneering work of Vander Waal's around 1887, who suggested that the shape of the liquid molecules determine the intermolecular interactions. Since then, numerous research articles dealing with such studies have been published. This publication covered in textbooks, reviews and monographs.

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 [14]. Acoustical and Physico-chemical properties of liquid mixture of Chlorobenzene 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 mixture of Chlorobenzene with p- xylene at 298.15 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 molecules .

II. MATERIAL AND METHODS

Chlorobenzene 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. Mixture was 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 298.15 K [15-16].

Liquid	Density (ρ) × 10^{-3} Kg m^{-3}		Ultrasonic velocity (U) m s^{-1}	
	Experimental	Literature	Experimental	Literature
Chlorobenzene	1.1011	1.1009	1270.2	1271.0
p- Xylene	0.8569	0.8566	1289.4	1288.8

III. 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 3. for the binary system under study [17-20].

Table 2: List of symbols/Notations.

Sr.No.	Symbol/Notation	Description	Unit
1.	X	Mole fraction of liquid	—
2.	ρ	Density of mixture	Kg m^{-3}
3.	U	Ultrasonic velocity of mixture	m s^{-1}
4.	L_f	intermolecular free-length of mixture	M
5.	K_S	isentropic compressibility for the mixture	m^2 N^{-1}
6.	Z	acoustic impedance for the mixture	Kg $m^{-2}s^{-1}$
7.	U^E	excess ultrasonic velocity for the mixture	m s^{-1}
8.	$L_f{}^E$	excess intermolecular free-length for the mixture	M
9.	$K_S{}^E$	excess isentropic compressibility for the mixture	m^2 N^{-1}
10.	Z^E	excess acoustic impedance for the mixture	Kg m^{-2} s^{-1}
11.	K_T	Jacobson's constant	—
12.	Y^E	Redlich-Kister Polynomial equation	—
13.	A_i	Where $A_i = A_0, A_1, A_2, A_3, A_4$ are the coefficients obtained from Redlich-Kister polynomial equation	—

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

$$Z = \rho U \quad (2)$$

$$L_f = K_T (Ks)^{1/2} \quad (3)$$

Where 'K_T' is Jacobson's constant. It is temperature-dependent empirical constant, proposed by Jacobson in 1952 and given as $K_T = (93.87\ 5 + 0.375 \times T) \times 10^{-8}$ at temperature T [21]. The excess functions Y^E are 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 and suffixes 1 and 2 denotes the components 1 and 2 in binary liquid mixture and the values are given in Table 4. The dependence of U^E, Z^E, $K_S{}^E$ and $L_f{}^E$ on the mole fraction of Chlorobenzene for liquid mixture were fitted to the following Redlich-Kister equation [22] by the least-squares method and the values are given in Table 5.

$$Y^E = x (1- X) \sum i A_i (2x - 1)^i \quad (5)$$

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 5. together with the standard deviations (σ) values. From Table 3, it is observed that the values of U, Z, K_s and L_f varied linearly with the mole fraction of Chorobenzene. 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 Chlorobenzene (Table 3) for the liquid mixture is in accordance with the view proposed [23].

The present study was undertaken with binary liquid mixture Chlorobenzene with p- Xylene. Chlorobenzene and p-Xylene were chosen because they can interact with both polar and nonpolar components mixture [24]. 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 Chlorobenzene are examined. It is observed that The calculated values for the binary mixture of Chlorobenzene [25] and p-Xylene leads to positive devation in ultrasonic velocity and negative devation in excess isentropic compressibilities may be interpreted in terms of two opposing effects, namely loss of mutual dipolar association and difference in size and shape of unlike molecules, dipole induced dipole, electron-donor–acceptor interactions and interstitial accommodation of the non-common component in the p-Xylene lattice.

Table 3: 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 Chlorobenzene with p-xylene at 298.15 K.

Mole fraction of Chlorobenzene (X)	$\rho \times 10^{-3}$ Kg m-3	U m s^{-1}	$Z \times 10^4$ Kg $m^{-2}s^{-1}$	$K_S \times 10^{-11}$ m^2 N^{-1}	$L_f \times 10^{-11}$ m
0.0000	0.8569	1289.4	1.1048	70.1931	4.2548
0.1024	0.8415	1278.6	1.0759	72.6903	4.3687
0.2085	0.8326	1267.4	1.0552	74.7715	4.4945
0.3088	0.8398	1253.2	1.0524	75.8199	4.5465
0.4102	0.8265	1246.4	1.0301	77.8829	4.6754
0.5069	0.8201	1234.7	1.0125	79.9853	4.8021
0.6124	0.8147	1223.1	0.9964	82.0499	4.9245
0.7154	0.8102	1212.8	0.9826	83.9130	5.0254
0.8107	0.8097	1201.2	0.9726	85.5943	5.2587
0.9059	0.8024	1189.7	0.9546	88.0509	5.4578
1.0000	0.8007	1176.5	0.9420	90.2290	5.6897

On the other hand, both excess isentropic compressibility (K_S^E) and excess intermolecular free-length (L_f^E) are negative for the liquid mixture over the whole mole fraction range, both showing maxima at mole fraction of Chlorobenzene. The nature of the two components (Chlorobenzene and p- Xylene) leads to the interaction between the electron chlorine atom of Chlorobenzene with the π-electrons of aromatic ring of p- Xylene, forming donor-acceptor complexes between the two component molecules in mixture [26] which leads to a decrease in the intermolecular distances and increase in molecular interaction there by decreasing the isentropic compressibility of the mixture [27]. Negative values of excess inter molecular free length (L_f^E) increase [28] with increasing molar concentration of Chlorobenzene indicate significant interactions between Chlorobenzene and p-Xylene molecules forming dipole induced dipole interaction. On the other hand, there is possibility of the electron donor acceptor (charge-transfer) type interactions [29-30] between highly electronegative halogen atom of >Cl of Chlorobenzene (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 Chlorobenzene 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.

Table 4: 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 Chlorobenzene with p- Xylene at 298.15 K.

Mole fraction of Chlorobenzene (X)	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}	$L_f^E \times 10^{-11}$ m
0.0000	0.0000	0.0000	0.0000	0.0000
0.1024	4.2385	-0.8578	-2.8579	-0.9857
0.2085	4.8970	-0.8987	-3.5870	-1.0252
0.3088	5.6254	-0.9356	-3.9658	-1.1258
0.4102	6.0250	-0.9778	-4.2578	-1.2587
0.5069	6.7581	-1.0412	-4.8569	-1.2983
0.6124	7.2654	-1.2120	-5.0250	-1.3203
0.7154	7.9980	-1.3875	-5.6857	-1.3784
0.8107	8.5485	-1.4757	-5.9902	-1.4025
0.9059	9.2354	-1.5983	-6.4521	-1.4756
1.0000	0.0000	0.0000	0.0000	0.0000

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

Excess Property	A_0	A_1	A_2	A_3	A_4	σ
$K_S^E \times 10^{-11}$ m^2 N^{-1}	-0.00018	-2.5255	-2.4680	-1.2587	0.9857	0.0231
$L_f^E \times 10^{-11}$ m	-0.00023	-0.8789	1.5872	-0.4521	-1.2012	0.0187
$Z^E \times 10^4$ Kg m^{-2} s^{-1}	0.00036	1.5475	-2.3586	-2.0325	0.8548	0.0086
U^E m s^{-1}	-0.00053	9.2582	-11.258	2.5874	-2.0124	0.0254

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 (–CH_3) in aromatic hydrocarbon molecule. The aromatic derivation setup an interaction between the π electron cloud and (–CH_3) group. Though, the interaction is minor intensity but they can lead to the formation of intermolecular complexes. The contribution due to structural effects which must be taken into account which may result in decrease values of K_s^E and L_f^E.

IV. CONCLUSION

In the present research work calculated various excess parameters like Ultrasonic velocity (U^E), Isentropic compressibility (K_S^E), Intermolecular free length (L_f^E), acoustic impedance (Z^E) of Chlorobenzene and p-Xylene liquid mixture and investigation on the acoustical and physico-chemical Properties. It is observed from the measured data that the value of U^E is positive and the values of K_S^E, L_f^E, Z^E are negative in the mixture and the variation of the properties of the mixture studied supports the view that the interactions between molecules predominate over the dissociation effects in the individual components and nature, molecular geometry, concentration of mixture. Chlorobenzene and p-Xylene molecules show dipole induced dipole interaction is predominant and characterized by the negative and positive values.

V. FUTURE SCOPE

The acoustical and physico-chemical parameters are important data assessment tools set into simplest and usable form to effectively convey the information to general public, policy makers and decision makers. The purpose of the present work should focus on future the theoretical values of acoustical and physico-chemical parameters of this binary liquid mixture have been compared with experimental data to verify the applicability studied.

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Conflict of Interest. The author declare that he has no conflict of interest.

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