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Study of acoustical and physico-chemical properties on the binary mixture of Cyclopentyl methyl ether (CPME) and Chlorobenzene at 298.15 k temperature

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Abstract
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 this work evaluated experimental densities (ρ) and ultrasonic velocities (U) for the pure liquids and liquid mixture of Cyclopentyl methyl ether and Chlorobenzene 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

Introduction
In recent years transport, acoustic and thermodynamic behavior in many binary, ternary liquid mixtures has been analyzed by several researchers more than 5 decades. The analysis have may relevance in the area of biochemical, pharmaceutical, geological natures in bio-fluids, oils, petroleum and etc. including both in experimental and theoretical approach[1]. There is some considerable interest to aware the intermolecular interaction in liquid mixtures. The main usage of organic mixtures have used for processing and further formulations of product. Organic liquid used for synthesis of organic compounds, for coupling and dispersion agents in pharmaceuticals dye and etc., Chlorobenzene and its derivates are used for making pharmaceuticals, drugs, dye, pesticides and etc. The high electro negativity and larger dipole moment of polar molecules forming complex through H-bonds as an acceptors [2]. The major advantages of inorganic liquids having some peculiar properties is attracted the attention to chemist, physicist and materials rescued. Find it is electrochemical application [3].
The acoustic properties are very essential for understanding the physicochemical behavior of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications.
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 [4]. 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 [5].

These studies are very important because of their extensive use in textile industry, leather industry, pharmaceutical industry and in many others [6]. 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 [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.

Physicochemical properties of pure and mixtures of organic liquids are having great importance in the field of science and industrial engineering. The analysis towards the geometrical properties (topology) of components of solution that have been used (1) to know the state of components in pure as well as combined form of mixed state with existence of molecular interaction among them (1, 2) further to find the physico-chemical behaviors of liquid mixtures [8]. The increasing/decreasing trends with linearity of parameters are helpful to decide the type, strength and magnitude of interaction in the liquid mixtures.

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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 Aº. Its boiling point and melting point are 132 ^{0}C and -45 ^{0}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 [9-10].

Cyclopentyl methyl ether (CPME), also known as methoxy cyclopentane, is a totally new hydrophobic ether solvent. It have high boiling point of 106 °C (223 °F), Dielectric constant 4.76 and preferable characteristics such as low formation of peroxides, relative stability under acidic and basic conditions, formation of azeotropes with water coupled with a narrow explosion range render CPME an alternative to other ethereal solvents such as tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MeTHF), dioxane, and 1,2-dimethoxyethane (DME).Cyclopentyl methyl ether is used in organic synthesis, mainly as a solvent. However it is also useful
in extraction, polymerization, crystallization and surface coating. The utilization of CPME in several organic reactions pertaining to organometallic-, organo-, and biocatalysis and highlight their potential use as benign alternatives to conventional ether solvents. This solvent have favorable physical and chemical characteristics, such as low toxicity and high chemical and thermal stabilities, which make them promising media for a large breadth of synthetic chemistry and triggers development of reactions with green chemistry protocol [11-12].

Research workers in the past have shown that NMR, IR and Raman spectra, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves and their absorption has already been found to be useful in the study of molecular interactions for inorganic, organic and organometallic binary systems. Likewise, researchers have also employed ultrasonic measurements to look into the important consequences of ion solvent interactions for the structure of electrolytic solutions. References related to the field of medicine, whereas references based on studies on emulsions micro emulsions, polymer surfactants interactions and ultrasonic destruction of surfactants are only a few cases to suggest versatility of the technique.

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 [13]. CPME (Cyclopentyl methyl ether) is an important green solvent. Thus, a study of physical properties data on the binary mixture containing CPME has attracted considerable interest in the literature. Thus, Chlorobenzene in CPME mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no study on this binary system has been reported at 298.15 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture.

Thus, a study of Acoustical and Physico-chemical properties data on the binary mixture of Chlorobenzene in CPME has attracted considerable interest in my present study.

Material and Methods

Cyclopentyl methyl ether and Chlorobenzene were procured from ZEON Scientific Ltd. and was further purified by the methods given in Vogel text book of practical organic chemistry. Prior to the experimental measurements, both the organic liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The uncertainty in mole fraction is 0.0001. A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the Binary liquid mixtures(with an uncertainty of 0.3%) at a constant temperature of 298.15 K by using a digital constant temperature water bath. The temperature stability is maintained within 0.001 K by circulating thermo stated water around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The ultrasonic velocity (U) measurements were made by a single frequency (2 MHz) variable path.

The density of solutions was measured by a double arm pyknometer of 10 ml bulb capacity and a Capillary of an internal diameter of about 1.0 mm. The mark of the stem was calibrated by double distilled water (conductivity less than 1×10-6 ohm-1 cm-1). The accuracy of the density results was 0.0001 (g cm-3). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical

balance, with a precision of 0.01 mg. The densities, and ultrasonic velocities of the pure liquids were in good agreement with the values found in the literature and are presented in Table

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 [14-17].

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

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

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

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 [28]. The excess functions Y^E are calculated using the relation:

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

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 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 [19] by the least-squares method and the values are given in Table 5.

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

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 Cyclopentyl methyl ether. 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 Cyclopentyl methyl ether (Table 3) for the liquid mixture is in accordance with the view proposed [20].

The present study was undertaken with binary liquid mixture Cyclopentyl methyl ether with Chlorobenzene. Cyclopentyl methyl ether and Chlorobenzene were chosen because they can interact with both polar and nonpolar components mixture. 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 Cyclopentyl methyl ether are examined. It is observed that The calculated values for the binary mixture of Chlorobenzene [21] and Cyclopentyl methyl ether 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 Cyclopentyl methyl ether lattice.

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 Cyclopentyl methyl ether. The nature of the two components (Cyclopentyl methyl ether and Chlorobenzene) leads to the interaction between the electron chlorine atom of Chlorobenzene with the maximal inductive effect of cyclopentyl cation of Cyclopentyl methyl ether, forming donor-acceptor complexes between the two component molecules in mixture [22] which leads to a decrease in the intermolecular distances and increase in molecular interaction there by decreasing the isentropic compressibility of the mixture [23]. Negative values of excess inter molecular free length (L_f^E) increase [24] with increasing molar concentration of Chlorobenzene indicate significant interactions between Chlorobenzene and Cyclopentyl methyl ether molecules forming dipole dipole interaction. On the other hand, there is possibility of the electron donor acceptor (charge-transfer) type interactions [25-27] between highly electronegative halogen atom of >Cl of Chlorobenzene (acting as a donor) and the cyclopentyl cation of Cyclopentyl methyl ether 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 Cyclopentyl methyl ether molecules in this mixture. It is observed that K_s^E and L_f^E becomes more negative as the number of (O-CH3) group in the Cyclopentyl methyl ether ring. This is due to the fact that methyl group (O-CH3) being an electron-releasing group would enhance the electron density of the Cyclopentyl methyl ether ring of the ring molecules, but the electron-accepting tendency of the ring would be decrease. Resulting in this liquid mixture increased donor-acceptor interaction between unlike molecules with increase in size of substituted group (O-CH3) in aliphatic cyclic hydrocarbon /aromatic hydrocarbon molecule. The cyclopentyl cation derivation setup an interaction between the π electron cloud and ($O-CH_3$) 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.

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) x 10^{-3} Kg m^{-3}		Ultrasonic velocity (U) m s^{-1}	
	Experimental	Literature	Experimental	Literature
Cyclopentyl methyl ether	0.7354	0.7356	1367.4	1368.3
Chlorobenzene	1.1011	1.1009	1270.2	1271.0

Table 2: List of symbols/Notations

S. No	Symbol/Notation	Description	Unit
1.	X	Mole fraction of liquid	------
2.	P	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	------

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 Cyclopentyl methyl ether with Chlorobenzene at 298.15 K

Mole fraction of Cyclopentyl methyl ether (X)	ρ x 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^{-11} m
0.0000	0.7872	1482.3	0.1166	57.8152	7.8650
0.1047	0.7836	1470.2	0.1152	59.0406	7.9142
0.2021	0.7778	1456.4	0.1132	60.6136	8.0190
0.3056	0.7689	1432.3	0.1101	63.3960	8.2010
0.4058	0.7602	1418.8	0.1078	65.3476	8.3262
0.5124	0.7565	1401.5	0.1060	67.2984	8.4496
0.6020	0.7421	1389.3	0.1030	69.8144	8.6061
0.7201	0.7388	1376.8	0.1017	71.4054	8.7036
0.8087	0.7324	1368.5	0.1002	72.9057	8.7946
0.9098	0.7301	1359.7	0.0992	74.9057	8.9144
1.0000	0.7258	1347.8	0.0978	75.8459	8.9702

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 Cyclopentyl methyl ether with Chlorobenzene at 298.15 K

Mole fraction of Cyclopentyl methyl ether (X)	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^{-11} m
0.0000	0.0000	0.0000	0.0000	0.0000
0.1024	6.2358	-1.0245	-4.2358	-1.5485
0.2085	6.8752	-1.2875	-4.8548	-1.7855
0.3088	7.0254	-1.4412	-5.0215	-1.9020
0.4102	7.6982	-1.5689	-5.6254	-2.0321
0.5069	8.0012	-1.7750	-5.9645	-2.3210
0.6124	8.7582	-1.8521	-6.1241	-2.5854
0.7154	8.9882	-1.9689	-6.4325	-2.7878
0.8107	9.2547	-2.0350	-6.9960	-2.8788
0.9059	9.7483	-2.2145	-7.2231	-3.0020
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
$K_S{}^E$ x 10^{-11} m^2 N^{-1}	0.08548	-3.2312	1.2358	2.0254	0.9857	1.0254
$L_f{}^E$ x 10^{-11} m	-0.10254	-4.0030	1.8587	-0.8458	-3.0214	1.3654
Z^E x 10^4 Kg m^{-2} s^{-1}	0.12100	2.3654	-3.2654	-3.6584	0.9689	1.8502
U^E m s^{-1}	-0.14545	5.3650	-7.0254	4.3258	3.2545	3.2654

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 Cyclopentyl methyl ether 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 strong interactions between molecules predominate over the dissociation effects in the individual components and nature, molecular geometry, concentration of mixture. Cyclopentylmethylether and Chlorobenzene molecules show dipole-dipole interaction is predominant and characterized by the negative and positive values.

Future Aspects

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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