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Study of Acoustical and Physico-chemical Properties for the Ternary Mixture of (Toluene+ Chlorobenzene + Cyclohexane) at 298.15 K Temperature

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Abstract

Ultrasonic velocity (U), density (ρ) for the ternary mixture of (Toluene + Chlorobenzene + Cyclohexane) in the various range of composition has been carried out at 298.15K. 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) have been calculated and using standard relations to the Redlich-Kister equation. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at temperature and the magnitude of intermolecular interactions among the constituents of the mixture always reflects the nature of substance. The variations in sign and values of these parameters are help us to know the interaction between component molecules and structural arrangement of the liquid mixture.

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

Introduction

In recent years acoustic and physico-chemical 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, eological natures in bio-fluids, oils, petroleum and etc, including both in experimental and theoretical approach[1-2]. 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., Cyclohexane 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 a acceptors[3-5]. The major advantages of liquids having some peculiar properties is attracted the attention to chemist, physicist and materials rescued. Physicochemical properties of pure and mixtures of organic liquids are having great importance in the field of science and industrial engineering. In particular density affects some important steps in the production process such as absorption on surface (adsorption) and separation from the mixtures (extraction)[6-8].

The increasing/decreasing trends with linearity of parameters are helpful to decide the type, strength and magnitude of interaction in the liquid mixtures. In this present work, reported some measured parameters such as adiabatic compressibility, free length, free volume, internal pressure, acoustical impedance, of ternary mixtures at three different temperatures[9-10].

The electronegativity of halogen atom which acts as an electron acceptor towards the π electrons of aromatic substituted ring. This is due to the fact that Substitute group of aromatic ring is an electron donating group through induction, enhances the π electrons density of the aromatic ring. This makes the donation of π electrons of aromatic ring for halogen atom easier, thus forming donor- acceptor complex between aromatic ring and neighbouring molecules[11-13].

Various efforts to understand the liquid mixture behavior based on theoretical and experimental considerations have been done[14-15]. Experimental studies of macroscopic and microscopic properties of liquid mixture and their interaction are required as they provide a way to test and verify theoretical study and give the useful physicochemical properties of the mixture[16-17]. Experimental study of molecular interaction and physicochemical properties of liquid mixture is reported by various spectroscopic methods such as optical, ultraviolet (UV) spectroscopy, X-ray diffraction (XRD), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), refractive index and dielectric studies, but to detect weak interaction in liquid mixture ultrasonic method of velocity measurement is very useful at low frequency range[18-22]. Ultrasonic velocity and density data of mixture give direct estimation of acoustic parameters which are not easily accessible by any other method[23]. In recent years, ultrasonic velocity measurement technique has been used as a probe to study the physicochemical parameter measurement, phase equilibria boundaries, charge complex formation and molecular interaction[24]. Variation in ultrasonic velocity and various thermo-acoustic parameters: adiabatic compressibility, free length, free volume, etc., of binary and ternary mixtures, has been investigated by some workers[25–26] in terms of molecular interactions between solute–solvent, solvent–solvent and solute–solute molecules.

In the present paper, I studied the acoustical and physico-chemical Properties for ternary liquid mixture (Toluene + Chlorobenzene + Cyclohexane) at 298.15K by analyzing the trend of excess acoustic and Physico-chemical parameters with different concentration. Toluene is nonpolar solvent, but due to its negative quadrupole moment it has some degree of polar attraction as well[27]. Chlorobenzene is a polar liquid belongs to the family of organic halogen compounds, which is a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements. Chlorine atom in Chlorobenzene is a electron withdrawing atom, tends to attract to π electrons of benzene ring, thereby and decreases the electron density of ring. As a result, the benzene ring in Chlorobenzene becomes relatively poor electron-donor towards the electron seeking proton of any groups[28]. *Cyclohexane* is a non-polar liquid and belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attractions[29]. I have reported the ultrasonic velocity

(U), density (ρ) and some excess acoustic parameters like excess adiabatic compressibility (K_s^E), excess intermolecular free length (L_f^E) and excess acoustic impedance (Z^E) and excess ultrasonic velocity(U^E) of the ternary liquid mixture of (Toluene + Chlorobenzene + Cyclohexane) in the various range of composition has been carried out at 298.15K temperature and 2 MHz frequency. The variation in these excess parameters is interpreted in terms of the interaction and structural arrangement of the ternary liquid mixture.

Materials and Methods

Toluene, Chlorobenzene and Cyclohexane were purchased from Sd fine chemicals, Mumbai India with on purity of 99.7% were used as such without further purification. 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 mixture of various concentrations in mole fraction were prepared by mass using a digital balance (manufactured by Aczet) with a precision of ± 1 mg. The masses of the component liquids required for preparing the mixture of known composition were calculated, and then a pseudo-ternary mixture of particular mole fraction was prepared. In the ternary liquid mixture, mole fraction of third component, Cyclohexane (X_3 = 0.3), was kept fixed, while mole fractions of other two (X_1: mole fraction of Toluene and X_2: mole fraction of the second component Chlorobenzene) were varied from 0.0 to 0.7, to have the mixture of different compositions. 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 correcti ons 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[7, 11, 16]

Liquid	Density (ρ) x 10^{-3} Kg m^{-3}		Ultrasonic velocity (U) m s^{-1}	
	Experimental	Literature	Experimental	Literature
Toluene	0.8623	0.8622	1303.9	1304.0
Chlorobenzene	1.1010	1.1009	1267.6	1271.0
Cyclohexane	0.7738	0.7739	1254.1	1254.0

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 ternary liquid system under study[12,16,26].

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

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

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

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

$$Y^E = Y_{mix} - (X_1Y_1 + X_2Y_2 + X_3Y_3) \quad (4)$$

Where Y denotes U, Z, K_S and L_f respectively, X is the mole fraction and suffixes 1, 2 & 3 denotes the components X_1, X_2 & X_3 in ternary liquid mixture and the values of X_1 and X_2 are given in Table 3 & 4. The

dependence of U^E, Z^E, $K_S{}^E$ and $L_f{}^E$ on the mole fraction of Toluene, Chlorobenzene and Cyclohexane for liquid mixture were fitted to the following Redlich-Kister equation[16] 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 Toluene, Chlorobenzene and Cyclohexane. This indicates the presence of interactions between the components in this ternary 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 (Table 3) 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 parameters.

Table 2. List of symbols / Notations

S.No	Symbol / Notation	Description	Unit
1.	X_1, X_2, X_3	Mole fractions of liquids	----
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	------

Table 3. Values of density (ρ), ultrasonic velocity (U), acoustic impedance (Z), isentropic compressibility (K_S) and intermolecular free-length(L_f) for the ternary liquid mixture of Toluene, Chlorobenzene and Cyclohexane at 298.15 K

Mole fraction of Toluene (X_1)	Mole fraction of Chlorobe-nzene (X_2)	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	0.7000	0.7486	1338.5	0.1002	74.5612	4.2457
0.1000	0.6000	0.7514	1326.3	0.0997	75.6563	4.0375
0.2000	0.5000	0.7729	1313.7	0.1015	76.1717	4.3554
0.3000	0.4000	0.7804	1291.2	0.1017	76.7703	4.5021
0.4000	0.3000	0.7946	1274.8	0.1013	76.8591	4.6854
0.5000	0.2000	0.8145	1258.3	0.1024	77.5426	4.8674
0.6000	0.1000	0.8253	1245.5	0.1027	78.1089	4.9654
0.7000	0.0000	0.8326	1232.9	0.1027	79.0147	5.2027

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 ternary liquid mixture of Toluene, Chlorobenzene and Cyclohexane at 298.15 K

Mole fraction of Toluene(X_1)	Mole fraction of Chloro benzene (X_2)	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	0.7000	0.9857	-2.1425	-0.8541	-0.0720
0.1000	0.6000	0.9588	-2.0857	-0.8025	-0.0685
0.2000	0.5000	1.0245	-2.5025	-0.8724	-0.0854
0.3000	0.4000	1.0583	-2.8690	-0.8972	-0.0895
0.4000	0.3000	1.0354	-3.0202	-0.9114	-0.0947
0.5000	0.2000	1.0875	-3.4101	-0.9242	-0.1054
0.6000	0.1000	1.1012	-3.7548	-0.9486	-0.1120
0.7000	0.0000	1.1011	-3.7498	-0.9404	-0.1106

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}	-0.00321	-4.5438	3.2587	-0.8757	0.8945	0.0085
L_f^E x 10^{-11} m	-0.00875	-1.2386	0.9587	-0.3654	0.2012	0.0037
Z^E x 10^4 Kg m^{-2} s^{-1}	0.00654	1.8580	-1.2154	0.9878	-0.7487	0.0042
U^E m s^{-1}	-0.00245	8.8540	-9.2358	1.5487	-1.3254	0.0687

With this view in mind, the variations in excess 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 Toluene, Chlorobenzene and Cyclohexane 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 I mix three liquids if they condense or compress more ultrasonic velocity will be more. Since the excess acoustic impedance (Z^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 deviations as expected as per the equation (2) for Z^E calculation. The positive deviations in U^E while the positive values are due to strong attractive forces between unlike molecules in 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 Toluene, Chlorobenzene and Cyclohexane. 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 Chlorobenzene leads to the interaction between Toluene and Cyclohexane. The electron rich chloro atom of Chlorobenzene with the π-electrons of aromatic ring of Toluene and axial position of Cyclohexane, forming donor-acceptor complexes between the three component molecules in mixture which leads to a decrease in the intermolecular

distances and increase in sound velocities and increase force of attraction 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 Chlorobenzene with Toluene and Cyclohexane 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 (-CH_3) and (-H). 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. Chlorobenzene on mixing with the aromatic and aliphatic non polar hydrocarbons, would induce a decrease in the molecular order. On the other hand, there is possibility of the electron donor acceptor (charge-transfer) type interactions[13, 15-17, 27] between highly electronegative chlorine atom of $>X^-$ group of chloro-benzene (acting as a donor) and the π-electrons of ring of Toluene and axial interaction of cyclohexane 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 with Toluene and Cyclohexane molecules in this mixture. It is observed that K_s^E and L_f^E becomes more negative due to – CH_3 group in the benzene ring . 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 be decrease and size of volume change due to axial interaction of Cyclohexane form dipole induced dipole inetraction. 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 and increase axial interaction in aliphatic hydrocarbon, 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 ternary liquid mixture containing Chlorobenzene with Toluene and Cyclohexane the K_s^E and L_f^E values at equimolar concertration were formed to follow the negative value in the liquid mixture.

Conclusion

The dependence of parameters 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 ternary mixture may be affected by the nature, molecular geometry and concentration. The interactions are primarily due to the electron donor-acceptor interactions and dipole induced dipole inetraction existing between the components of the ternary liquid mixture.

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 ternary liquid mixture have been compared with experimental data to verify the applicability studied.

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