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Study of Acoustic Parameters of Binary Mixtures of Cyclohexane with 2-Methoxyethanol.

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ABSTRACT

The interactions existing between components of the binary mixtures, namely cyclohexane and 2-methoxyethanol are found to be affected by the ultrasonic wave with a frequency of 2 MHz. Using the experimental data, some thermodynamic and acoustic parameters are computed at different temperatures over the entire composition range. Among the parameters are intermolecular free length (L_f), free volume (V_f), relaxation time (τ), acoustic impedance (Z), Rao's constant (R) and Wada's constant (W). Variations in these parameters at different concentrations of the components are non-linear and are explained based on structural changes taking place in the solutions. Variations in all the parameters play a significant role in arriving at the possible interactions existing between solute and solvent.

Keywords: Cyclohexane,2-Methoxyethanol; Ultrasonic velocity; Density; Free length, Free volume

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INTRODUCTION

Past two decades witnessed an extensive research work on study of interactions existing between different organic molecules in mixtures. Such interactions lead to physical properties of mixtures different from individual components present in mixtures. In view of several industrial applications, these studies have been proved to be very significant in molecular science. Molecular interaction studies can be carried out using various methodologies like ultrasonic measurements, infrared spectroscopic studies, measurements involving dielectric constants and nuclear magnetic resonance spectroscopic studies [1]. However, investigation of molecular interactions in liquid mixtures using ultrasonic studies has been proved to be versatile method due to its simplicity and accuracy [2–4].

There are numerous literature reports on molecular interaction studies of both binary mixtures and ternary mixtures containing simple to complex organic molecules, using ultrasonic method. The aim of all those reports was to throw light on the significant modifications occurring in physical properties resulted due to interactions, which in turn become significant in industrial processes. Among the literature reports, there are studies reported on cyclohexane as well as 2-methoxyethanol.

Narendra et al. reported ultrasonic study of a binary mixture containing cyclohexane and o-xylene [5]. In their study, they determined acoustical parameters like adiabatic compressibility, intermolecular free length, molar volume, enthalpy and internal pressure. It was concluded that there are induced dipole-induced dipole interactions between the component molecules of the mixture. Ultrasonic studies of binary liquid mixtures containing cyclohexane and carbitols was studied by Bahadur Alisha and co-workers [6]. The carbitols taken for the study are methylcarbitol, ethylcarbitol and butylcarbitol, and the parameters studied are isentropic compressibility, intermolecular free length and acoustic impedance. According to this report, with increase in chain length of alkoxy groups in carbitols, the extent of molecular interaction with cyclohexane increases.

In another study by SteeviFelixa and Rose Venis, the interaction existing between cyclohexane and 1-propanol as well as 1-butanol was reported [7]. This study involving measurement of density, viscosity, excess volume, free volume, free length, etc. inferred that there exists dipole-dipole type of interactions between the components of the mixtures. Vispute et al. in their study on molecular interactions between cyclohexane and protic/aprotic solvents considered ethanol, propan-1-ol, butan-1-ol, m-xylene, toluene, tetrahydrofuran, etc [8]. They concluded that compounds containing aromatic ring have interactions with cyclohexane due to donation of π-electrons of ring to cyclohexane. In case of mixtures containing alkanols and cyclohexane, addition of cyclohexane weakens the homo intermolecular hydrogen bond existing in them.

Molecular interaction studies of several organic compounds including 2-methoxyethanol in combination with water at 298.15 K were reported by Aminabhavi and Gopalakrishna [9]. The results obtained were fitted to Redlich-Kister polynomial equation to get the adjustable parameters. The observed parameters were compared with the available literature reports. In an study by Muhuri and Hazra, the molecular interactions existing between 2-methoxyethanol and propylene carbonate were determined through the measurement of density and viscosity [10]. The results obtained were explained on the basis of geometric effects and molecular interactions existing between components of the mixture.

Thermoacoustical studies of binary mixtures containing 2-methoxyethanol and methyl acetate as well as ethyl acetate at different temperatures were reported [11]. Density and ultrasonic velocity were practically measured for the mixtures and various excess thermodynamic parameters were computed. From the results, the authors concluded that there is formation of hydrogen bonding between component molecules. Kemeakegha et al. studied volumetric behaviour of binary mixtures containing alkoxyethanols and amines [12]. In their study, the selected alkoxyethanols are 2-methoxyethanol and 2-ethoxyethanol. In their study, they observed that the excess molar volumes are negative in entire range of composition. This observation was attributed to formation of strong hydrogen bonds between unlike molecules. All the literature reports mentioned above indicate that there is interaction between cyclohexane and other organic molecules leading to changing trends in thermodynamic properties. Similarly, there are reports indicating such different thermodynamic properties when 2-methoxyethanol is combined with different organic compounds. Based on these inferences from various literature reports, the authors of the present study were interested in investigating the possible interactions occurring between the two molecules namely cyclohexane and 2-

methoxyethanol. To the knowledge of the authors, there are no literature reports showing the study of molecular interactions between the selected molecules using ultrasonic measurements.

Cyclohexane is a colourless liquid with a distinctive detergent-like odour, reminiscent of cleaning products. It is a non-polar organic solvent used in various fields. The main use of cyclohexane in industries is as a good solvent. 2- Methoxyethanol belonging to the group of cellosolves and amphiphilic compounds has both alcoholic –OH and partially etheric –O– in its structure, and is noted for its both donating and accepting ability, making it a potential candidate to form inter- and intra-molecular hydrogen bond. 2-alkoxyalkanols can be placed between protic and aprotic solvents. It is due to the fact that the physical and chemical properties of 2-alkoxyalkanols are due to their self association. 2-methoxyethanol in both pure form and aqueous solutions is used as a solvent of electrolytes, to some extent as an aprotic solvent and is often defined as a 'quasi-aprotic' solvent.

Molecular interactions can affect physico-chemical behaviour as well as hydrogen bonds and their strength. Study of thermoacoustical parameters is of much use in understanding these changes [13-15]. The authors of this paper are performing investigations on molecular interactions in various liquid mixtures [16-21]. As a part of it, the present article explores the results of work on thermodynamic and acoustic properties of liquid mixtures containing cyclohexane and 2-methoxyethanol at T=303.15, 308.15, 313.15 and 318.15 K. By using experimentally determined values, intermolecular Free length (L_f), Free volume (V_f), relaxation time (τ), acoustic impedance (z), Rao's constant (R) and Wada's constant (W)were calculated over the entire composition range. The derived acoustical parameters at different concentration of solute explained the structural changes in solutions.

MATERIALS AND METHODS

Cyclohexaneand 2-methoxyethanol (Sigma-Aldrich, USA, mass fraction purity 0.99) used in this study were AR grade and were purified by standard procedure [22]. The mixtures were stored in an air tight stoppered volumetric flasks. The flasks were allowed to attained thermal equilibrium. The ultrasonic velocities were measured by using a single-crystal variable-path multifrequency ultrasonic interferometer (Mittal Enterprises, India, model F-81) operating at 2MHz.The measurements of speeds of sound were reproducible within ± 0.67ms^{-1}.The temperature of the liquids during measurements was maintained to an accuracy of ±0.02K. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ±0.5%. Weights were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1mg. An average of 3 to 4 measurements was taken for each sample. Viscosities were measured at different temperatures using Ostwald's viscometer calibrated by using water and benzene. Once the mixture attains the bath temperature, the flow time has been measured. The flow measurements were made using an electronic stopwatch with a precision of 0.01s. The viscosity is determined by using the following relation.

$$\text{Viscosity}, \eta = k.\rho\ .t$$

Here k, ρ, and t are viscometric constant, density of liquid and time of efflux for a constant volume of liquid, respectively.

THEORY

From the experimental data free length (L_f), free volume (V_f), relaxation time (τ), Rao's constant (R), Wada's constant (W) and acoustic impedance (z) were calculated using standard relations.

The values of free length L_f can be calculated by the following relation,

$$\text{Free length}, L_f = K_T \beta^{1/2}$$

Where, K_T is temperature dependent constant.

The values of acoustic impedance (z) can be calculated by the following relation

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Acoustic impedance z = u x ρ

Where, u is ultrasonic velocity and ρ is density.

Free volume (V_f) = $(\frac{Mu}{K\eta})^{3/2}$

Where, k is a constant= 4.28×10^9 , η =viscosity

The value of relaxation time is calculated using the following relation

Relaxation time (τ) = $\frac{4\eta}{3\rho u^2}$

Where, η is viscosity, ρ is density and u is ultrasonic velocity

Molar compressibility (W)or Wada's constant can be calculated by the fallowing relation

$W= \beta^{1/7}V$

Where, βa is adiabatic compressibility and V is Molar volume

The Molar sound velocity (R) or Rao's constant can be calculated by the fallowing relation

$R=u^{1/3}V$

Where, V is Molar volume and u is velocity

Table 1: Compounds considered for the study, with their sources, purification method, and purity.

Chemical name	Source	Purification method	Mass fraction purity	Analysis method
Cyclohexane	Sigma Aldrich	Vacuum distillation	≥0.99	GC*
2-methoxyethanol	Sigma Aldrich	Vacuum distillation	≥0.99	GC*

*GC = Gas chromatography

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocities, densities and viscosities for pure liquids are compared with those reported in literature [23-29], and it was found that they are in good agreement. The values of densities, ultrasonic velocities and viscosities for the binary liquid mixtures at different temperatures are given in Table-2.

The calculated values of acoustic parameters, viz., intermolecular free length (L_f), Free volume (V_f), relaxation time (τ), acoustic impedance (z), Rao's constant (R) and Wada's constant (W)and the variations of these parameters with the mole fraction of cyclohexane at different temperatures are given in Table- 3.

Table-2: Values of speed of sound, density and viscosity as a function of mole fraction of cyclohexane at T = (303.15, 308.15, 313.15 and 318.15) K.

Speed of sound, u/m.s^{-1}				
X_1	**303.15**	**308.15**	**313.15**	**318.15**
0.0000	1231.3	1205.8	1180.7	1163.4
0.0741	1241.5	1215.4	1190.1	1172.2
0.1526	1253.2	1228.3	1203.7	1186.1

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0.2358	1262.2	1238.8	1215.5	1198.3
0.3270	1273.9	1251.8	1229.5	1212.9
0.4187	1283.1	1261.8	1241.1	1225.2
0.5193	1291.7	1272.0	1252.1	1236.3
0.6269	1299.6	1280.6	1260.9	1245.1
0.7423	1308.1	1289.2	1269.5	1252.4
0.8663	1317.9	1299.0	1279.1	1261.6
1.0000	1323.1	1306.4	1288.8	1270.7
Density, $\rho x10^{-3}$/ kg.m^{-3}				
X_1	**303.15**	**308.15**	**313.15**	**318.15**
0.0000	768.9	764.2	759.4	754.6
0.0741	784.8	781.1	777.0	772.1
0.1526	802.9	798.9	795.0	790.7
0.2358	820.1	816.0	812.1	808.0
0.3270	837.3	833.1	829.0	824.7
0.4187	854.6	850.3	846.1	841.7
0.5193	872.4	868.1	864.2	859.9
0.6269	890.3	886.2	882.5	878.2
0.7423	910.2	906.4	902.9	898.8
0.8663	931.8	928.0	924.5	920.5
1.0000	955.7	950.8	946.3	941.4
Viscosity, η/ Ns.m^{-2}				
X_1	303.15K	308.15K	313.15K	318.15K
0.0000	1.0753	0.9699	0.8906	0.7997
0.0741	1.0284	0.9379	0.8498	0.7606
0.1526	0.9993	0.8963	0.8090	0.7197
0.2358	0.9580	0.8851	0.7805	0.6889
0.327	0.9206	0.8506	0.7488	0.6592
0.4187	0.8829	0.7975	0.7195	0.6260
0.5193	0.8458	0.7672	0.6836	0.5992
0.6269	0.7980	0.7374	0.6415	0.5713
0.7423	0.7639	0.6999	0.6121	0.5419
0.8663	0.7255	0.6590	0.5822	0.5287
1.0000	0.6821	0.6431	0.5498	0.5122

Table 3: Free volume, V_f , Acoustic impedance, Z, Free length, L_f, Rao's constant, R, and Wada's constant, W, values as a function of mole fraction of cyclohexane at T = (303.15, 308.15, 313.15 and 318.15) K.

$V_f x\ 10^{-5}$					$L_f x10^{-11}$				
x_1	303.15	308.15	313.15	318.15	x_1	303.15	308.15	313.15	318.15
0.0000	0.7973	0.8216	0.8468	0.8652	0.0000	5.074	5.199	5.330	5.468
0.0741	0.7761	0.7978	0.8201	0.8367	0.0741	6.029	6.233	6.443	6.621
0.1526	0.7533	0.7715	0.7903	0.8036	0.1526	6.017	6.215	6.420	6.595
0.2358	0.7355	0.7499	0.7651	0.7755	0.2358	5.845	6.033	6.226	6.392
0.3270	0.7175	0.7281	0.7397	0.7473	0.3270	5.742	5.918	6.101	6.259
0.4187	0.7032	0.7103	0.7179	0.7225	0.4187	5.631	5.797	5.969	6.120
0.5193	0.6913	0.6938	0.6974	0.6992	0.5193	5.534	5.692	5.853	5.998
0.6269	0.6824	0.6803	0.6802	0.6792	0.6269	5.440	5.588	5.741	5.880
0.7423	0.6743	0.6674	0.6634	0.6601	0.7423	5.353	5.493	5.641	5.778
0.8663	0.6671	0.6550	0.6469	0.6403	0.8663	5.259	5.396	5.539	5.678
1.0000	0.6663	0.6466	0.6322	0.6226	1.0000	5.159	5.293	5.433	5.570
R					W				

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x_1	303.15	308.15	313.15	318.15	x_1	303.15	308.15	313.15	318.15
0.0000	117.3	117.2	117.1	117.3	0.0000	111.9	111.8	111.7	111.9
0.0741	114.4	114.2	114.0	114.1	0.0741	109.4	109.2	109.0	109.1
0.1526	111.4	111.2	111.0	111.0	0.1526	106.8	106.6	106.4	106.5
0.2358	108.4	108.3	108.1	108.1	0.2358	104.2	104.1	104.0	104.0
0.3270	105.5	105.5	105.3	105.4	0.3270	101.7	101.7	101.6	101.6
0.4187	102.7	102.7	102.6	102.7	0.4187	99.3	99.2	99.2	99.2
0.5193	99.8	99.8	99.7	99.8	0.5193	96.7	96.7	96.6	96.7
0.6269	97.0	96.9	96.8	96.9	0.6269	94.2	94.2	94.1	94.1
0.7423	93.9	93.9	93.7	93.7	0.7423	91.5	91.4	91.3	91.3
0.8663	90.8	90.7	90.6	90.6	0.8663	88.7	88.7	88.6	88.5
1.0000	87.4	87.5	87.5	87.5	1.0000	85.7	85.8	85.8	85.8

Z x 10^{-6}

x_1	303.15	308.15	313.15	318.15
0.0000	0.9467	0.9215	0.8967	0.8778
0.0741	0.9744	0.9493	0.9247	0.9051
0.1526	1.0061	0.9813	0.9570	0.9379
0.2358	1.0351	1.0109	0.9870	0.9682
0.3270	1.0666	1.0428	1.0193	1.0003
0.4187	1.0965	1.0729	1.0500	1.0313
0.5193	1.1269	1.1042	1.0821	1.0631
0.6269	1.1570	1.1349	1.1128	1.0935
0.7423	1.1906	1.1686	1.1463	1.1256
0.8663	1.2280	1.2054	1.1825	1.1613
1.0000	1.2645	1.2421	1.2196	1.1962

Figure 1: Variation of excess free volume V_f^E with mole fraction (x_1)in the binary liquid mixtures of cyclohexane with 2-MEat T = (303.15, 308.15, 313.15 and 318.15) K.

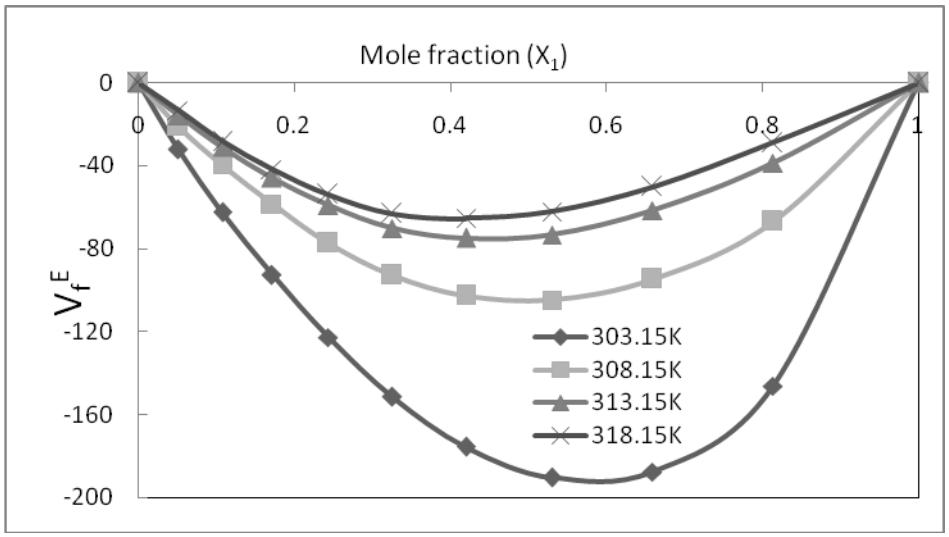

Figure 2: Variation of excess free length L_f^E with mole fraction (x_1)in the binary liquid mixtures of cyclohexane with 2-MEat T = (303.15, 308.15, 313.15 and 318.15) K.

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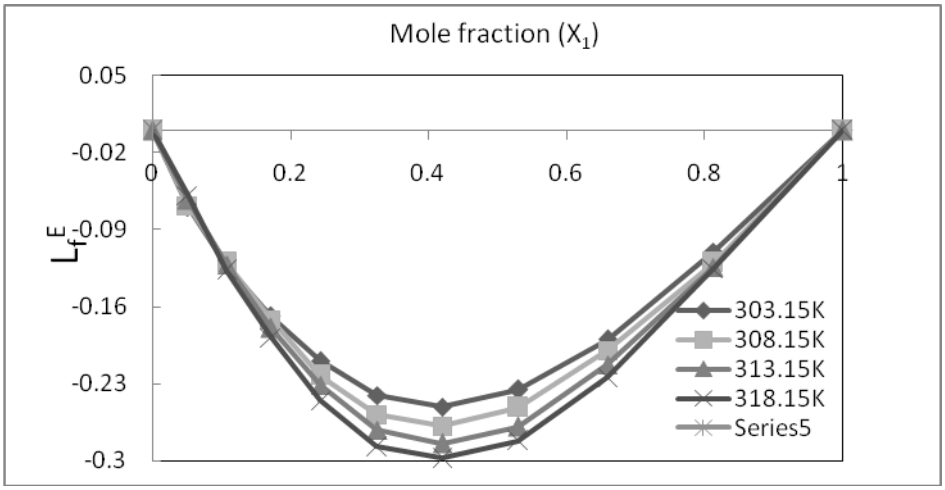

Figure 3: Variation of acoustic impedance Z^E with mole fraction (x_1)in the binary liquid mixtures of cyclohexane with 2-MEat T = (303.15, 308.15, 313.15 and 318.15) K.

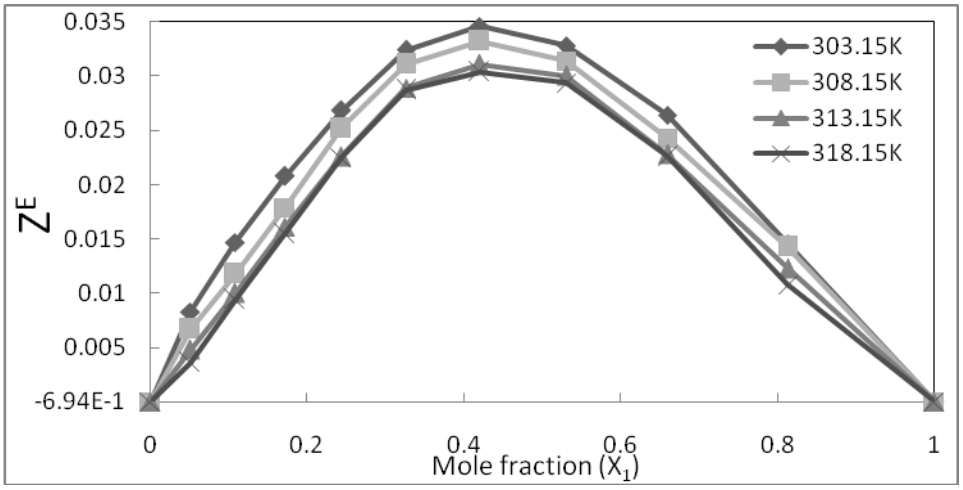

Fig. 1 indicates that V_f^E values decrease with increase in mole fraction, reaches a minimum value and then increase gradually. Interestingly, this trend is observed to be the same at all the temperatures considered in the present study. The negative trend decreases with increase of temperature. The negative values of excess free volume may be attributed to the packing effect and ion-dipole interaction of solvent molecules with cyclohexane in these mixtures [30]. From **Fig. 2,** it can be observed that the L_f^E values are negative for the entire mole fraction range and at all four temperatures. The negative values of L_f^E suggest that there exist strong interactions between the component molecules of the mixture as supported by Kerr effect [31].**Fig. 3** shows that the excess values of acoustic impedance are all positive in the over the entire composition range and at all the four temperatures studied. The positive excess values of Z^E support the interpretation of strong molecular interactions existing between the molecules present in the liquid mixtures [32].

CONCLUSION

Densities, speeds of sound and viscosity values of pure cyclohexane and 2-methoxyethanol as well as the binary mixtures containing these compounds at temperatures T = (303.15 to 318.15) K at the atmospheric pressure 0.1MPa, are reported. Values of the excess free volume (V_f^E), excess free length (L_f^E), excess acoustic impedance (Z^E), Rao's constant (R) and Wada's Constant (W) were obtained from experimental values of densities, speeds of sound and viscosity. Values of V_f^E, and L_f^E are observed to be negative while the values of Z^E are observed to be positive. The overall negative behaviour of V_f^E and L_f^E and positive values of Z^E may be attributed to the strong interactions existing between the molecules of the mixtures. The present work infers that investigation of liquid mixtures using ultrasonic study is one of the best ways in the analysis of molecular interactions existing among the components of liquid mixtures.

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