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Molecular Interaction and Excess Thermodynamic Parameters In Binary Liquid Mixture Through Ultrasonic Measurements at 313.15 K

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ABSTRACT

Experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (u) have been measured for the binary liquid mixture toluene and 1,2 dichloroethane at 313.15K. From these data the thermodynamic parameters such as isentropic compressibility (β_s), intermolecular interaction (L_f), available volume (V_a), molar volume (V_m), nissan's parameter (d) and their excess values have been computed using the standard relations. The results are explained in terms of the existence of intermolecular interaction between the components in the binary liquid mixture.

Keywords: Binary mixture, ultrasonic velocity, excess values, acoustic properties.

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INTRODUCTION

The nature and extent of the patterns of molecular aggregation that exist in liquid mixture resulting from intermolecular interactions [1] have been investigated by ultrasonic technique. The physicochemical behavior and molecular interactions in a variety of liquid mixtures [2-3] have also been studied. The nature of relative strength of molecular interaction between the components of liquid mixture has been successfully investigated by ultrasonic methods [4]. Further the measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids. The interaction study between associated liquid and non-associated in inert media gives valuable information about solute – solute and solute – solvent interactions.

The study of pure liquids and their properties can not be altered continuously with in a reasonable range by varying the concentration till an optimum value of some desired parameter is attained. This is only possible by considering the liquid mixtures and solutions, which find direct applications in many chemical industries and technological processes. Further such studies as a function of concentration are useful in understanding the intermolecular interaction between the component molecules and more insight in to the structure and bonding of associated molecular complexes and other molecular processes. Since ultrasonic velocity is fundamentally related to the binding forces between the constituents of the medium, so it is highly sensitive to the structure and interactions present in the liquid system. The measurement of ultrasonic velocity of sound in liquids enables determination of some useful acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions. Hence these measurements are useful to study the strength of molecular interactions in liquid mixtures. The thermodynamic study of binary liquid mixture has attracted much attention of scientist and experimental data on a number system are available from review and publication [6-10]. Ultrasonic investigation of liquid mixtures consisting polar and polar components is of considerable importance in understanding intermolecular interaction between the component of the molecules and they find applications in several industrial and technological process. Many investigators [11-20] have been engaged in the task of collecting more and more data and explaining in terms of the properties of pure liquid.

In view of growing interest, the results of an ultrasonic velocity, density and viscosity to study the related thermodynamic properties that is molar volume (V_a), available volume (V_m), isentropic compressibility (β_s), inter molecular free length (L_f), and nissan's parameter and their excess values for the binary liquid mixture, Toluene and 1,2 dichloro ethane at 313.15 K have been

reported in the present paper. The excess functions are used to explain inter molecular interaction in the above binary liquid mixture.

MATERIALS AND METHOD

The toluene purity 99.5% [E – Merck] and 1,2 dichloroethane purity 99% [E – Merck]. Mixtures were prepared by mixing amounts of the pure liquids using chemical balance with the precision of $\pm 0.1\text{mg}$, mixture were allowed to stand for some time before every measurement, so as to avoid air bubbles. The purities of liquids were checked by recommended methods. The density of pure liquids and liquid mixtures was determined using a pycnometer with an accuracy of $\pm 0.053\%$ at 313.15K. An Ostwald's viscometer was used for the viscosity measurement of pure liquid and liquid mixtures. The flow of time of pure liquid and liquid mixtures were measured using an accurate stopwatch with a precision of ± 0.15 . Density and viscosity measurements were carried out using a thermostatically controlled well-stirred water bath to maintained temperature. The speed of sound waves were obtained by using ultrasonic interferometer model M – 84 at 2MHz frequency. All measurements were made in a thermostatically controlled water bath with temperature accuracy of $\pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION:

From the measured densities (ρ), ultrasonic velocity (u) and various acoustic parameters such as isentropic compressibility (β_s), inter molecular free length (L_f) and nissan's parameter were calculated using the following equations.

The molar volume of binary liquid mixture is given by

$$V_m = [X_1M_1 + X_2M_2] / \rho \quad [1]$$

Where V_m is molar volume, M_1 and M_2 are molecular weight of pure components, X_1 and X_2 are mole fraction of the component 1 and 2, and ρ is the density of the liquid. The isentropic compressibility (β_s) and intermolecular free length (L_f) are calculating using following methods.

$$\beta_s = 1/u^2 \rho \quad [2]$$

$$L_f = K / u \rho^{1/2} \quad [3]$$

Where 'K' is temperature constant, 'u' is speed of sound and 'ρ' is the density of liquid.

$$\text{Nissan's parameter (d)} = \ln \eta^E / X_1X_2 \quad [4]$$

Where η^E is the excess value of viscosity and X_1 and X_2 are mole fraction of the component 1 and 2, Experimentally determined density and ultrasonic velocity were used to calculate isentropic compressibility (β_s), intermolecular free length (L_f), available volume and their excess values

using the standard relations with accuracy up to second decimal digit. The variation of these thermodynamic parameters with entire concentration range of toluene with 1,2 di chloro ethane are shown in Table [1 – 4]. Deviation in the properties computed demonstrated that their exist a molecular interaction between the liquid mixture of unlike molecules. These may be attributed to the change the adhesive and cohesive forces. The experimental values of ultrasonic velocities, densities, molar volumes and their excess values for the system toluene and 1,2 di chloro ethane are shown in Table -1 at 313.15 K. The Table -2 shows isentropic compressibility; inter molecular free length and their excess values for the entire system. Table -3 shows available volume and their excess values and Table – 4 shows the viscosity, their excess values, $\ln \eta^E$ and Nissan's parameter (d) have been calculated for the system toluene and 1,2 di chloro ethane at 313.15 K.

In Toluene + 1,2 di chloro ethane mixture the ultrasonic velocity, molar volume available volumes, isentropic compressibility increase with increase in mole fraction. However the density, viscosity decreases under similar condition. Excess molar volumes (V_m^E), excess isentropic compressibility (β_s^E), excess available volume (V_a^E) and excess intermolecular free length (L_f^E) are all positive under all condition of composition and temperature. In the table -4 shows the excess viscosity and Nissan's parameter 'd' are negative. With this view in mind, the variations in excess acoustical parameters like the excess isentropic compressibility (β_s^E) and excess intermolecular free length (L_f^E) with mole fraction of toluene are examined respectively. 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.

Table 1: Ultrasonic velocities, Densities, Molar volumes and their excess values for the system Toluene + 1,2 di chloro ethane at 313.15 K

Mole fraction of toluene X1	Ultrasonic velocity m/sec	Density g/ml	Molar Volume (exp)	Molar Volume (add)	Excess Molar Volume
0.0000	1134	1.2232	80.90	80.90	0.00
0.1000	1136	1.1738	83.72	83.64	+0.08
0.2015	1141	1.1271	86.58	86.42	+0.16
0.3011	1150	1.0837	89.38	89.15	+0.23
0.4007	1161	1.0422	92.33	91.88	+0.45
0.5000	1170	1.0039	95.17	94.60	+0.57
0.5981	1181	0.9690	97.91	97.29	+0.62
0.7020	1192	0.9353	100.68	100.14	+0.54
0.8002	1204	0.9068	103.11	102.83	+0.28
0.8995	1219	0.8783	105.68	105.55	+0.13
1.0000	1236	0.8507	108.31	108.31	0.00

Table 2: Isentropic compressibility's, intermolecular free length and their excess values for the system Toluene + 1,2dichloro ethane at 313.15 K

Mole fraction of Toluene X ₁	Isentropic compressibility (exp) cm ² /dyne X10 ¹²	Isentropic compressibility (add) cm ² /dyne X 10 ¹²	Excess isentropic compressibility cm ² /dyne X10 ¹²	Inter molecular Free length (exp) A ⁰	Inter molecular Free length (add) A ⁰	Excess inter molecular Free Length A ⁰
0.0000	63.57	63.57	0.00	0.5118	0.5118	0.0000
0.1000	66.01	64.90	+ 1.11	0.5216	0.5169	+ 0.0047
0.2015	68.15	66.26	+ 1.89	0.5299	0.5214	+ 0.0085
0.3011	69.77	67.60	+ 2.17	0.5362	0.5271	+ 0.0091
0.4007	71.18	68.93	+ 2.25	0.5416	0.5323	+ 0.0093
0.5000	72.71	70.25	+ 2.46	0.5474	0.5374	+ 0.0100
0.5981	73.92	71.57	+ 2.35	0.5519	0.5423	+ 0.0096
0.7020	75.24	72.96	+ 2.28	0.5568	0.5477	+ 0.0091
0.8002	76.07	74.27	+ 1.80	0.5599	0.5527	+ 0.0072
0.8995	76.62	75.60	+ 1.02	0.5619	0.5579	0.0040
1.0000	76.94	76.94	0.00	0.5631	0.5631	0.0000

Table 3: Available Volumes and their Excess Values for the System Toluene + 1,2 Di chloro ethane at 313.15K

Mole fraction of Toluene X ₁	Available volume (exp) ml /mole	Available volume (add) ml / mole	Excess available volume ml /mole
0.0000	23.65	23.65	0.00
0.1000	24.27	23.74	+ 0.53
0.2015	24.83	23.85	+ 0.98
0.3011	25.13	23.93	+ 1.20
0.4007	25.33	24.04	+ 1.29
0.5000	25.55	24.14	+ 1.41
0.5981	25.61	24.23	+ 1.38
0.7020	25.67	24.33	+ 1.34
0.8002	25.51	24.43	+ 1.18
0.8995	25.16	24.53	+ 0.63
1.0000	24.64	24.64	0.00

Table 4 : Viscosity and their excess values, Ln η^E and Nissan's parameter (d) for the system Toluene + 1, 2 Di chloro Ethane at 313.15 K

Mole fraction of Toluene X ₁	Viscosity (exp) Cp	Viscosity (add) Cp	Excess Viscosity Cp	Lnη ^E	'd'
0.0000	0.696	0.696	0.000	0.000	0.000
0.1000	0.674	0.676	- 0.002	- 0.001	-0.011
0.2015	0.651	0.755	- 0.004	- 0.002	- 0.015
0.3011	0.635	0.642	- 0.007	- 0.004	- 0.019
0.4007	0.614	0.624	- 0.010	- 0.007	- 0.029
0.5000	0.595	0.607	- 0.012	- 0.010	- 0.040
0.5981	0.577	0.590	- 0.013	- 0.012	- 0.049
0.7020	0.561	0.571	- 0.010	- 0.010	- 0.047

0.8002	0.546	0.553	- 0.007	- 0.005	- 0.031
0.8995	0.532	0.536	- 0.004	- 0.004	- 0.044
1.0000	0.518	0.518	0.000	0.000	0.000

CONCLUSION:

Ultrasonic method is a powerful probe for characterizing the physico chemical properties and existence of molecular interaction in the mixture. The density, ultrasonic velocity, viscosity and the derived acoustical parameters provide evidence of confirmation. Thus it can be concluded from these studies of ultrasonic speed, density and viscosity measurements the negative values of excess viscosity and Nissan's parameter shows different molecular size attributed to the presence of dispersive forces between the mixing components and suggest the presence of specific and weak intermolecular interactions. While the positive value of excess molar volumes (V_m^E), excess available volume (V_a^E), excess isentropic compressibility (β_s^E) and intermolecular free length (L_f^E) shows the presence of weak molecular interaction between the unlike molecules of the binary liquid mixture (Toluene and 1,2 di chloro ethane) at the temperature 313.15K.

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