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 (βs), intermolecular interaction (Lf), available volume (Va), molar volume (Vm), 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 (Va), available volume (Vm), isentropic compressibility (βs), inter molecular free length (Lf), 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 ± 0.1mg, 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 ±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 ± 0.1°C.

RESULTS AND DISCUSSION:

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

The molar volume of binary liquid mixture is given by

\[ V_m = [X_1 M_1 - X_2 M_2] - \rho \] \[1\]

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 \( \rho \) is the density of the liquid.

The isentropic compressibility (βs) and intermolecular free length (Lf) are calculating using following methods.

\[ \beta_s = \frac{1}{u^2 \rho} \] \[2\]

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

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

Nissan’s parameter (d) = \( \ln \frac{\eta^E}{X_1 X_2} \) \[4\]

Where \( \eta^E \) 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 (βs), intermolecular free length (Lf), 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 η 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 (Vm), excess isentropic compressibility (βs), excess available volume (Va) and excess intermolecular free length (Lf) 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 (βs) and excess intermolecular free length (Lf) 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 + 1,2 dichloro ethane at 313.15 K

| Mole fraction of Toluene $X_1$ | Isentropic compressibility (exp) $\text{cm}^2/\text{dyne} \times 10^{12}$ | Isentropic compressibility (add) $\text{cm}^2/\text{dyne} \times 10^{12}$ | Excess isentropic compressibility $\text{cm}^2/\text{dyne} \times 10^{12}$ | 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 $\eta^E$ 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) $\eta$ | Viscosity (add) $\eta$ | Excess Viscosity $\eta$ | Ln$\eta^E$ | ‘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 |
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 ($\beta_s^E$) 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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REFERENCE:

1. S. Bahadur Alisha, S. Nafeesa Banu, et al, “Ultrasonic studies on binary liquid mixtures of tri ethyl amine with carbitols at 308.15K” Indian Journal of advances in chemical science 5 (3), (2017), 148-15
2. Zareena Begaum et al, thermodynamic, ‘ultrasonic studies of binary liquid mixtures of anisaldehyde with alkoxy ethanols at different temperatures’. Journal of molecular liquids, 178, 2013, 99 -112.
3. K. Rajgopal and S.Chenthilnath, “molecular interaction studies and theoretical estimation of ultrasonic speeds of toluene with nitriles at different temperatures”. Thermo chimica Acta ,498 (1-2), 2010, 45 -5
4. Thanuja B., Charles Kangam, et al “studies on intermolecular interactions on binary mixture of methyl orange – water system, excess molar functions of ultrasonic parameters at different temperatures” Journal of ultrasonic sonochemistry, 18, 2011,1274-1278.
5. Nithiyanantham S. and Palaniappan “physicochemical studies on some di saccharides in aqueous media at 29815K” Chemical science transaction. 2 (1), 2013,
6. D.Bala Karuna Kumar, Y. Subba Reddy et al, “Study of intermolecular interactions in industrially useful binary liquid mixtures of N- methyl-2 pyrrolidone with the help of scaled particle theory” Journal of chemical and pharmaceutical research, 9(5), (2017), 294-299.
7. Ravi M. Jumle and Usha Wasnic , “ A study of acoustical behavior of terbunafine in binary liquid mixture at 303K” International Journal of researches in biosciences agriculture and technology, 2(5), (2017),1040-1043.
8. Rajgopal K, Chenthilnath S. Excess parameters studies on binary liquid mixtures of 2-methyl 2 – propanol with aliphatic nitriles at different temperatures. Journal of Molecular Liquids. 160(2):2011; 72-80
9. Padmanaban R.et al, “ A study of comparative analysis poly propylene glycol, “International Journal of current research and review” 9(10), (2017), 89-91.
10. Jagdish G. Baragi, Seema Maganur, et al. Excess of molar volumes and efractive indices of binary liquid mixtures of acetyl acetone with n- nonane, n-decane at 25oC,30oC,35oC. Journal of Molecular Liquid. 178, 2013, 175-177
11. Raj kumar and Singh Y.P., “ Intermolecular interaction in binary liquid mixture by ultrasonic measurements” International journal of research in applied „natural and social sciences” 5(6), (2017), 31-38.
12. M.V. Ratnam, Reema T.Sayed etal. Molecular interaction study of binary mixtures of methyl benzoate, viscometric and ultrasonic study. Journal of Molecular Liquids.166, 2012, 9-16 .
13. Gyan Prakash Dubey, Kishan Kumar. Thermodynamic properties of binary liquid of diethylene tri amine with alcohols at different temperatures. Journal of Thermochimica. Acta mixtures. 524 (1-2) 2011,7
14. Kumar S, Jeevandham P. Densities, viscoties and excess properties of aniline and o-anisidine with 2 – alkoxy ethanols at 303.15oK. Journal of Molecular Liquids. 174, 2012, 34–41.
15. Anil Kumar Nain. Ultrasonic study of molecular interactions in binary mixtures of methyl, acrylate with 1- alkanols at different temperatures. Journal of Chemical Thermodynamics. 59 -2013; 49-64.
16. Rajgopal K, Chenthilnath S. Molecular interaction studies and theoretical estimation of ultrasonic speeds in binary mixtures of toluene with nitriles at different temperatures. Journal of Thermochemica Acta. 498(1), 2010, 45-53.

17. Lovely Sarkar and Mahendra Nath Rao. Density, viscosity and ultrasonic speed of binary mixtures of 1,3 dioxane with 2, methoxy methanol. Journal of Chemical Engineering data. 54(12), 2009; 3307-3312

18. Riyazuddin and Sadaffarin. Ultrasonic velocities and densities of phenyl alanine with aqueous NaNO₃ solution at (298.15 – 328.15) K. Journal of Chemical Engineering data. 55(7), 2010; 2643–26

19. Bedare GR, Bhandakkar VD, et al. Ultrasonic study of molecular interactions in binary mixtures 1,4-dioxan with methanol at 308K. European Journal of Applied Engineering and Scientific Researches. 1(1), 2012, 1-4

20. Saxena Chandra Mohan, et al, “Ultrasonic study and molecular interactions of binary liquid mixture of ethylamine and benzyl alcohol at 313.15K” Research Journal of chemical sciences, 3(5), 2013, 10-13.