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Molecular Interactions in Binary Mixture of Propylene Glycol and 1-Heptanol at 303K

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***Abstract*— Ultrasonic velocities (U), densities (ρ), viscosity (η) for the binary mixture of propylene glycol and 1-heptanol solution have been measured over the entire composition range at 303K. From the experimentally determined values, thermo-acoustic parameters such as excess isentropic compressibility (K_s^E), excess molar volume (V^E) and excess free length (L_f^E), excess Gibb's energy(G^E) and excess enthalpy (H^E) have been calculated.**
The results were interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ultrasonic velocity, Density, Excess Molar Volume, Isentropic Compressibility, Free Length, Excess Gibb's Energy, Propylene Glycol

1. INTRODUCTION

Studies on the viscosity and density of binary mixtures along with other thermodynamic properties are being increasingly used as tools for the investigation of the properties of pure components and the nature of intermolecular interactions between liquid mixture constituents [1]. Propylene glycol used as medical lubricant, moisturizer in medicines, tobacco products and cosmetics. Alkanol are interesting simple examples of biological and industrial important amphiphilic materials [2]. Several researchers [3-8] have measured the density, viscosity, and speed of sound for a wide range of binary mixtures containing alcohols as one of the components, and these properties were interpreted in terms of specific or nonspecific interactions. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. They are of great importance for their relevant role in chemistry, biology and studies on hydrogen bonding in liquid mixtures. Alcohols are also widely used as solvents. The molecules containing –OH group form associative liquids due to hydrogen bonding. The effect shown by the molecules with other functional groups on these molecules plays an important role in understanding the behavior of hydrogen bonding. The investigations regarding the molecular association in liquid mixtures having aromatic group as one of the components is of particular interest, since aromatic group is highly non-polar and can associate with any other group having some degree of polar attractions. Even though considerable work has been reported on alcohols as one of the component in binary and ternary mixtures, the data on binary mixtures of Heptanol with Propylene glycol at room temperature (303 K)variation is scanty.

The study of thermodynamic properties of multi component liquid mixtures and data on the analysis in terms of various models are important for industrial and pharmaceutical applications [9]. The excess thermodynamic functions [10] are sensitively dependent not only on the differences in intermolecular forces, but also on the differences in the size of the molecules. The signs and magnitudes of these excess values can throw light on the strength of interactions. So from the experimentally determined values of speed of sound density and viscosity, various thermo-acoustic parameters like excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibb's energy (G^E) and excess enthalpy (H^E) have been calculated. Here we report the results and discuss regarding the speed of sound, density and viscosity for the binary liquid mixtures of Propylene glycol with 1-heptanol at temperature 303 K.

II. EXPERIMENTAL DETAILS

a. Materials

The chemicals used in the present study are, Propylene glycol and 1-heptanol which are of AR grade obtained from Merck Co. Inc., Germany, with purities of greater than 99%. All the chemicals were further purified by standard methods [11] and only middle fractions were collected.

b. Measurements

All binary mixtures were prepared gravimetrically in air-tight bottles and adequate precautions have been taken to minimize evaporation losses. Before use, the chemicals were stored over 0.4nm molecular sieves approximately for 72 hours to remove water content and then degassed. The mass measurements were performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of $\pm 10^{-8}$ kg. The binary mixtures were prepared just before use. The uncertainty in mole fraction was estimated to be less than ±0.0001.

The viscosities were measured with Ostwald viscometer. The viscometer was calibrated at each temperature using redistilled water. The uncertainty in viscosity measurement is up to 0.001mPa-s. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stop watch with a precision of 0.01s. For all the pure components and mixtures, 3 to 4 readings were taken and the average of these values were used in all the calculations.

The densities of the pure compounds and their mixtures were determined accurately using 10 ml specific gravity bottles. The average uncertainty in the measured density was ±0.001 kg/m^3.

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The speed of sound was measured with a single-crystal variable path interferometer (Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz that had been calibrated with water and benzene. The uncertainty in the speed of sound was found to be ±0.1m/s.

c. Computational Details

The values of experimentally determined density and speed of sound for the binary mixtures of Propylene glycol with 1-heptanol at 303 K over the entire composition range.

In the present work the authors have calculated the excess values of isentropic compressibility and excess free length values to check the applicability of thermo dynamical ideality (the ideal mixing rules) to the components under study.

The excess values of isentropic compressibility K_s^E were calculated as follows,

$$K_s^E = K_s - K_s^{id} \quad (1)$$

Where K_s represent the calculated value of isentropic compressibility for the mixture

$$K_s = \frac{1}{\rho U^2} \quad (2)$$

K_s^E is its excess value, K_s^{id} is the ideal isentropic compressibility value, ρ is the density and U represents the speed of sound. K_s^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara [12, 13] and Douheret et al [14].

$$K_s^{id} = \sum \phi_i \left\{ K_{s,i}^o + \frac{TV_i^o(\alpha_i^o)^2}{C_{p,i}^o} \right\} - T\left(\sum x_i V_i^o\right)\left(\frac{\sum \phi_i \alpha_i^{o2}}{\sum x_i C_{p,i}^o}\right) \quad (3)$$

in which $K_{s,i}^o$, V_o^i, α_i^o, $C_{p,i}^o$ are the isentropic compressibility, molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i, *T* represents absolute temperature, ϕ_i is the volume fraction and x_i represents the mole fraction of i in the mixture.

The density values have been used to calculate the excess volumes, V^E, using the following equation,

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (4)$$

where ρ is the density of the mixture and x_1, M_1, and ρ_1 and x_2, M_2, and ρ_2 are the mole fraction, molar mass, and density of pure components 1 and 2, respectively.

The excess values of free length (L_f^E) and enthalpy (H^E) were calculated by using the expressions given in literature [15] as follows,

$$L_f^E = L_f - K_T(K_s^{id})^{1/2} \quad (5)$$

Where L_f represents the calculated value for the mixture and K_T represent a temperature dependent constant whose value is $K_T=(91.368+0.3565T)x10^{-8}$.

Where R represents gas constant, *T* is absolute temperature, ηis the viscosity of the mixture and η_1,η_2 are the viscosities of the pure compounds, *V* is the molar volume of mixture and V_1, V_2 are the molar volumes of the pure compounds,

Excess enthalpy H^E was calculated from usual relation.

$$H^E = H - (x_1H_1 + x_2H_2) \quad (6)$$

Where *H* represents the calculated value of enthalpy for the mixture and H_1, H_2 represent enthalpy of pure components 1 and 2, respectively.

III. RESULTS AND DISCUSSION

The values of density, viscosity and speed of sound for the binary liquid mixtures of propylene glycol and heptanol at temperatures of 303 K were determined and are given in Table 1.

$$\text{Density}: \rho_l = \frac{\rho_{wt}}{w_{wt}} wt_l$$

Viscosity (ŋ):Viscosity (ŋ): $\eta_l = \frac{\eta_{wt}}{t_w \rho_w} \rho_l t_l$

Ultra sonic velocity (U) = f.λ ms^{-1}

f=frequency of the generator = 2 x 10^6 hertz
λ= wavelength = 2d/n
Where d=average of taking oscillations.
n =no.of oscillations

Table 1:Density, Ultrasonic velocity and viscosity with mole fraction of propylene glycol.

Mole Fraction "x1"	Density ρ(Kg . m^{-3})	UltrasonicVelocity U($m.s^{-1}$)	Viscosity η (m.Pa.S)
0	0.8187	1336	5.6331
0.1703	0.8257	1354.6	6.693304
0.316	0.84406	1378.2	7.88338
0.4419	0.86838	1394	9.07077
0.5519	0.88716	1411.2	10.69656
0.6488	0.91866	1420.6	12.26575
0.7348	0.92958	1454.2	14.23121
0.81175	0.937198	1490.7	16.6242
0.8808	0.966179	1531.5	18.5445
0.9432	0.9909	1572.7	21.0247
1	1.0307	1604	23.1899

From these values, various thermo-acoustic parameters like a isentropic compressibility (K_s), free length (Lf), free volume (V_f), and enthalpy (H) have been determined and excess values like the excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibb's energy(G^E) and Excess enthalpy (H^E), have been calculated.

The values of thermo-acoustical parameters of intermolecular freelength (L_f), adiabatic compressibility (K_s),free volume (V_f), enthalpy (H) at temperatures T=303 K are given in Table 2and

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the values of excess thermo-acoustical parameters such as excess intermolecular freelength (L_f^E), excess adiabatic compressibility (K_s^E), excess free volume (V_f^E), excess enthalpy (H^E), , and excess Gibb's energy(G^E) at temperature T=303K are given in Table 3 . The variations of the above thermo-acoustical parameters at temperatures T=303 K with the mole fractions of propylene glycol are represented in the figures from Fig-1to Fig-9

Table 2: The values of thermo-acoustical parameters such as intermolecular freelength (L_f), adiabatic compressibility (K_s),free volume (V_f), enthalpy (H)in binary liquid mixtures containing propylene glycol and heptanol at temperatures T = 303 K

Mole Fraction "x_1"	Isentropic compressi-bility(K_s)	Free length (Lf)	Free volume (V_f)	Enthalpy (H)
0	6.84325E-10	5.216E-11	0.000274	35145.47
0.1703	6.60018E-10	5.1225E-11	0.000246	37399.05
0.316	6.23738E-10	4.9797E-11	0.000218	39494.29
0.4419	5.92604E-10	4.8538E-11	0.000196	41343.66
0.5519	5.66006E-10	4.7437E-11	0.000167	43966.61
0.6488	5.39388E-10	4.6308E-11	0.000145	46083.7
0.7348	5.08704E-10	4.4971E-11	0.000127	48599.33
0.81175	4.80162E-10	4.3692E-11	0.000109	51490.81
0.8808	4.41274E-10	4.1885E-11	9.97E-05	52889.96
0.9432	4.08017E-10	4.0276E-11	8.88E-05	54903.64
1	3.77102E-10	3.872E-11	8.14E-05	56165.9

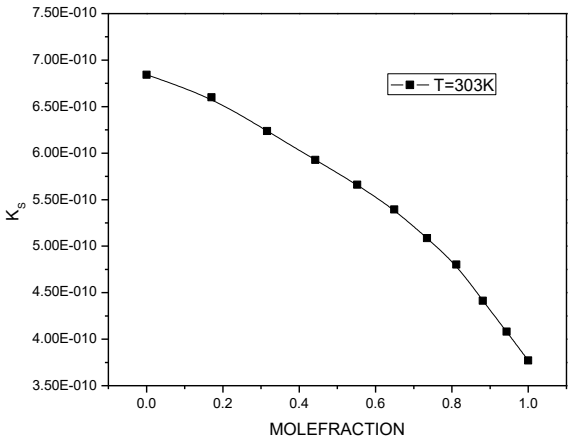

Fig.1

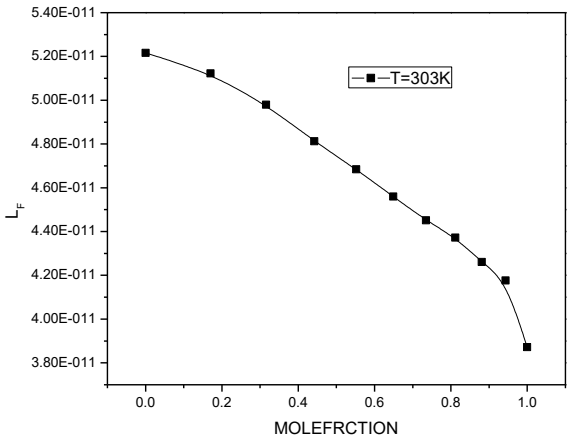

Fig.2

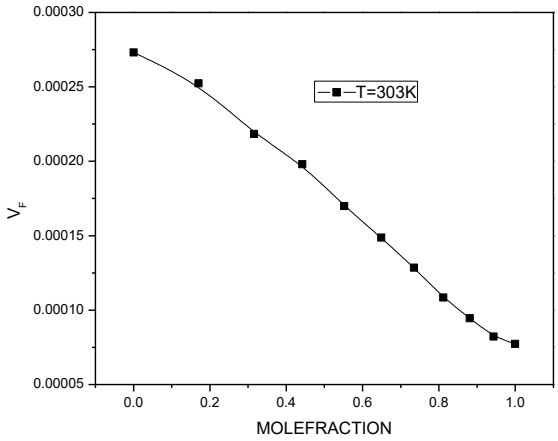

Fig.3

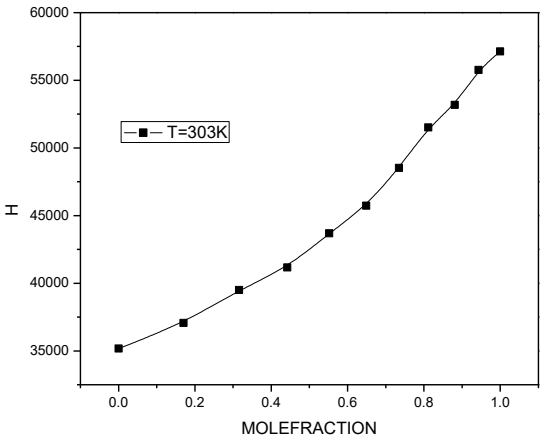

Fig.4

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The values of excess thermo acoustical parameters such as excess intermolecular freelength (L_f^E), excess adiabatic compressibility (K_S^E), excess free volume (V_f^E), excess enthalpy (H^E) excess Gibb's energy(G^E), and excess internal pressure(π_i^E)in a binary liquid mixture containing propylene glycol and heptanol at temperature T=303 K are given below in Table 3 and in figures 5-8.

Table 3 : Excess thermo-acoustical parameters

Mole Fraction "x1"	Excess Adiabatic compressibility $K_S^{E*10-12}$ ($m^2.N^{-1}$)	Excess Intermolecular free length $L_f^{E}*10^{-13}$/m	Excess Free volume V^E(m^3.mol^{-1})	Excess Enthalpy H^E (J.mol^{-1})	Excess Gibb's free energy (G^E)
0	0	0	0	0	0
0.1703	26.29307	13.56392	-29.9011	14704.4	19.4117
0.316	33.30448	18.86377	-15.2414	-9636.72	152.3733
0.4419	39.57862	23.19348	-3.79907	-5218.85	337.8748
0.5519	45.66413	26.956	6.37703	-351.77	761.1068
0.6488	47.83806	28.68797	13.4091	3742.185	1079.814
0.7348	42.70621	26.87903	21.6698	8012.309	1584.709
0.8117	37.02861	24.42072	29.2796	12473.65	2144.692
0.8808	18.65677	15.63242	33.3703	15281.5	2438.241
0.9432	3.940431	7.924411	37.2680	18568.2	2818.436
1	0	0	0	0	0

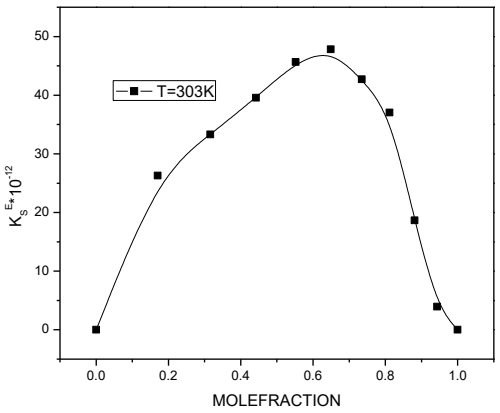

Fig.5

From Fig-5 represents the variations of excess adiabatic compressibility (K_S^E) in binary liquid mixtures containing propylene glycol and heptanol over the entire mole fraction range of propylene glycol at temperature T= 303 K.

It is observed that the excess adiabatic compressibility (K_S^E) values are negative. This indicates that the attractive forces between the molecules of components are stronger [16] than the intra-molecular attractions in each component. According to Fort and Moore [17], a negative excess compressibility is an indication of strong hetero-molecular interaction in the liquid mixtures which is attributable to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between unlike components. In the present study, the excess compressibility is negative and it suggests the existence of strong intermolecular interactions in the binary liquid mixture.

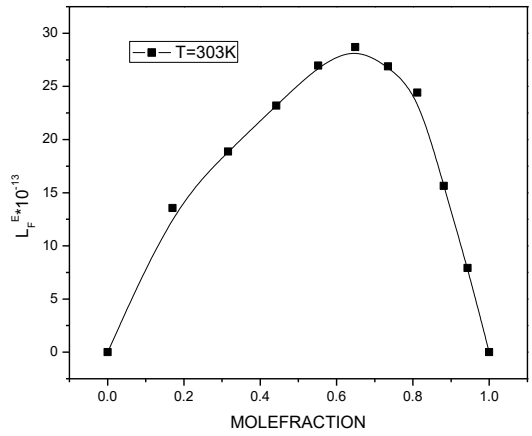

Fig. 6

From Fig-6, it is observed that the excess intermolecular freelength values are negative for the entire mole fraction range. The negative values of excess intermolecular free length suggest that there exist strong interactions between the components of liquid mixture [18]

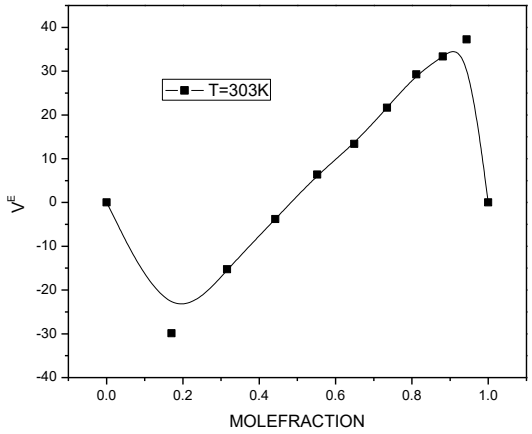

Fig.7

The variation of excess free volume (VfE) with the mole fraction of propylene glycol is represented in Fig-7. It is observed from Fig-7 values are negative over the entire composition range. This suggests that the component molecules are more close together in the liquid mixture than in pure liquids forming the mixture, indicating that strong attractive interactions[19].

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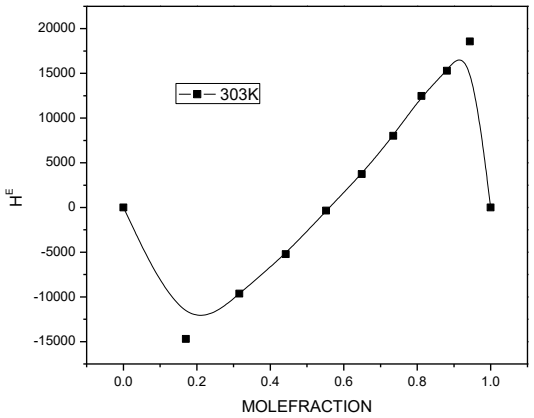

Fig. 8

the variation of excess enthalpy in the present binary system is as shown in Fig-8 it is observed that H^E values are negative over the entire composition range of propylene glycol. The negative values of H^E suggest strong interactions [21].

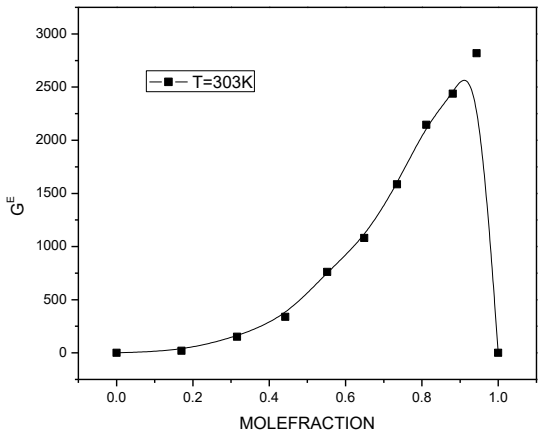

Fig. 9

Figs. 9 represent the excess Gibb's free energy of activation (ΔG*E) with respect to mole fraction x1, over the entire composition range and at T = 303 K. It can be observed that the ΔG*E values are positive at 303K and over the entire range of mole fraction. These positive values indicate the existence of strong intermolecular interact hydrogen bonding between the component molecules of the liquid mixtures under study. Similar results were observed by earlier workers [21]
. The maximum deviation is observed for propylene glycol+ heptanol system indicating the strength of bond formation in this system0.8 +0.2 is more compared to that of other system.
the variations of adiabatic compressibility (K_S) with respect to the mole fraction at temperatures T= 303 K. It is observed from table 2 the value of adiabatic compressibility decreases with increase in mole fraction. These types of variations indicate that there exist strong molecular interactions between the component molecules of liquid mixture and also interactions become weaker with increase of temperature. The variations of intermolecular free length (L_f) with mole fraction at temperatures T=303 K is represented and it is observed that, the value of intermolecular free length decreases with increase in mole fraction. The decrease in intermolecular free length with mole fraction indicates strong intermolecular interactions between the component molecules of the liquid mixture .

The variations of excess intermolecular free length (L_f^E) with the mole fraction of propylene glycol ranging from 0 to 1 at temperatures T=303 K in the binary liquid mixtures containing propylene glycol and heptanol is at 303K is as shown is negative. Therefore the molecular interactions are observed and may due to formation hydrogen bond between the constituent molecules.

IV. CONCLUSIONS

The excess parameters are calculated from the experimentally determined. The formation of hydrogen bond in the mixture is identified by studying the variations in these parameters through molecular interactions between the two moieties.

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REFERENCES

[1] Yang C, Xu W, Ma P: Thermodynamic properties of binary mixtures of p-xylene with cyclohexane, heptane, octane, and n-methyl-2-pyrrolidone at several temperatures. Journal of Chemical & Engineering Data 2004; 49: 1794-1801.

[2] Sk. Md Nayeem D. Krishna Rao. "Comparative analysis of molecular interactions between drugs of aqueous propylene glycol with certain alkahols at 308.15k: an insight from density and viscosity studies *IJPSR, 2015; Vol. 6(9): 3961-3974*

[3] E. Zorebski, E. Waligora. "Densities, Excess Molar Volumes, and IsobaricThermal Expansibilities for 1,2- Ethanediol + 1-Butanol, or 1-Hexanol, or 1-Octanol in the Temperature Range from (293.15 to 313.15) K". J. Chem. Eng. Data.53 (2008) p.591-595.

[4] A. Boruń, M.,.Żurada, A Bald, "Densities and excess molar volumes for mixtures of methanol with other alcohols at temperatures (288.15–313.15 K)" J Therm. Anal. Calorim. 100 (2010) p. 707-715.

[5] S.S Sastry, Babu S, T. Vishwam, K Parvateesam, H.S Tiong. "Excess parameters for binary mixtures of ethyl benzoate with 1-propanol, 1-butanol and 1-pentanol at T=303, 308, 313, 318, and 323 K". Phys B. 420 (2013) p. 40-48.

[6] R.F Checoni. "Excess molar enthalpy for methanol, ethanol, 1-propanol, 1-butanol + n-butylamine mixtures at 288.15 and 308.15 K at atmospheric pressure". J Therm.Anal. Calorim.101 (2010) p.349-57.

[7] S.Sreehari Sastry, Shaik.Babu, T.Vishwam, Ha.SieTiong. Study of molecular interactions in the mixtures of some primary alcohols with equimolar mixture of 1-propanol and alkylbenzoates at T = 303.15 K. J. Chem. Thermodynamics, 68 (2014) p.183-192.

[8] S.SreehariSastry, S.M.Ibrahim, L.Tanuj Kumar,Shaik.Babu, Ha.SieTiong. Excess thermodynamic and acoustic properties for equimolar mixture of ethyl benzoate and 1-alkanols with benzene at 303.15 K. International Journal of Engineering Research & Technology, 4 (2015) p.315-324.

[9] J.M Resa, C. Gonzalez , JM Goenaga, M. Iglesias. "Influence of temperature on ultrasonic velocity measurements of ethanol+ water+1-propanol mixtures". J Therm Anal Calorim. 87 (2007) p.237-245.

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ISSN: 2278-0181
Vol. 7 Issue 05, May-2018

[10] S. Sharma, B Jasmin, J.Ramani, R Patel. "Density, excess molar volumes and refractive indices of β-pinene with o, m, p-xylene and toluene at 303.15, 308.15 and 313.15K". Phys. Chem. Liq. 49 (2011) p.765-76.

[11] A.I Vogel. "Text book of organic chemistry". 5th ed. New York: John wiley; 1989.

[12] O. Kiyohara ,G.C.Benson."Ultrasonic speeds and Isentropic compressibilities of n-alkanol + n-heptane mixtures at 298.15 K". J. Chem. Thermodyn. 11 (1979) p.861-873.

[13] G.C Benson, O. Kiyohara. "Evaluation of excess is entropic compressibilities and isochoric heat capacities: .J.Chem. Thermodyn. 11 (1979) p.1061-64.

[14] G.Douheret, A .Pal A, M.I Davis. "Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K".J.Chem.Thermodyn. 22 (1990) p.99-108.

[15] K. Narendra K, Ch. Srinivasu, Ch. Kalpana, P. Narayanamurthy. "Excess thermo dynamical parameters of binary mixtures of toluene and mesitylene with anisaldehyde using ultrasonic technique at different temperatures". J. Therm. Anal. Calorim.107 (2012) p.25-30.

[16] A. George. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, 1997

[17] R.J Fort, W.R Moore. "Adiabatic compressibilities in binary liquid mixtures". Trans. Faraday Soc. 61 (1965) p.2102–2110

[18] K.BjørnAlsberg, M.AndrewWodward, K. Michael Winson, Rowland and Douglas B. Kell *Analyst,*122(1997) p.645-652

[19] S. Sreehari Sastry, Suriya Shihab Sk., Sie Tiong Ha, Temperature Dependence of Excess Parameters for Binary Mixtures of 1-4Butanediol and 1-Alkanols by Ultrasonic Technique, IJERT 4 (2015) p. 611-621

[20] M. Gondran, M. Minoux Linear Algebra and it Applications, 282 (1998) p. 47-61

[21] Ch.Sowjanya ,S.Sreehari Sastry "Ultrasonic ,density,viscosity studies in binary mixtures of propylene glycol and 1-pentanol at room temperature" . International Journal of Engineering Research & Technology 6 (2017) p.17-22.