

Ultrasonic Study of Excess thermoacoustic Parameters in Binary Mixtures of Propylene Glycol and Hexanol

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ABSTRACT: Excess thermoacoustical parameters such as excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess enthalpy (H^E) have been measured for propylene glycol in Hexanol for various mole fractions at 303K temperature through ultrasonic study. These results have been explained on the basis of intermolecular interactions between the components in the liquid mixture and correlations among the parameters are discussed. The final results obtained have indicated that intermolecular hydrogen bond formation is stronger for (0.8Pg+0.2hex) molar ratio of the binary mixture liquid complex compare to that of other systems and hence this mixture is strongly recommended in therapeutical drugs, pharmaceutical industry and for the high heat transferability when needed

KEYWORDS: Excess Thermoacoustic parameters, binary mixture, intermolecular interactions, Hydrogen bond, Molar ratio.

I. INTRODUCTION

In recent years, ultrasonic investigations find extensive applications in characterizing of thermodynamic and physico-chemical aspects of binary and ternary liquid mixtures. Thermodynamic and transport properties of liquid mixtures provide important information with which to speculate the molecular liquid structure [1-3]. The excess thermodynamic functions are sensitively dependent not only on the differences in intermolecular forces, but also on the differences in the size of the molecules. Several researchers 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. The variation of these excess values with temperatures and composition for mixtures can throw light on the strength of interactions.

Excess values like the excess adiabatic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E) and Excess enthalpy (H^E) have been calculated. The thermo-acoustical and excess thermo-acoustical parameters play an important role in studying the nature of molecular interactions in liquid mixtures [4-6]. The excess thermo-acoustical parameters are defined as the difference between the experimental values and ideal mixture values. They give a measure of the non-ideality of the system as a consequence of associative or of other interactions [7]. 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 [6]. The excess thermodynamic functions [8] 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.

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Here we report the results of speed of sound, density and viscosity for the binary liquid mixtures of Propylene glycol with Hexanol at temperature 303K and calculated the excess thermoacoustic parameter which will information on molecular interactions.

II. EXPERIMENTAL DETAILS

The chemicals used in the present study are, Propylene glycol with Hexanol 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 and only middle fractions were collected. 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 72h 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 $\pm 0.001 \text{ kg/m}^3$.

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 $\pm 0.1 \text{ m/s}$.

The values of experimentally determined density and speed of sound for the binary mixtures of Propylene glycol with Hexanol 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,

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

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 [9] and Douheret et al [10].

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

in which $K_{s,i}^o$, V_i^o , 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 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,

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (4)$$

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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), Gibbs free energy (ΔG^{*E}) and enthalpy (H^E) were calculated by using the expressions given in literature [11] 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 $K_T = (91.368 + 0.3565T) \times 10^{-8}$.

Excess enthalpy H^E was calculated from usual relation.

$$H^E = H - (x_1 H_1 + x_2 H_2) \quad (6)$$

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 excess thermo-acoustical parameters such as excess intermolecular frelength (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess enthalpy (H^E) at temperatures $T=303.15K$ are given in Table 1 . The deviations observed in the excess parameters indicate the strength of interactions present between the component molecules of the binary mixtures under study [11]. The variations of the above excess thermo-acoustical parameters at temperatures $T=303.15 K$ with the mole fractions of propylene glycol are represented in the figures from Figure 1.

Table 1: The values of excess thermo-acoustical parameters : excess intermolecular frelength (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess enthalpy (H^E) at temperatures $T=303K$

Molefraction of Propylene glycol (X)	L_f^E	β^E	V_f^E	H^E
0.00000	0	0	0	0
0.14074	13.30968	26.41157	-9.33185	-19978.3604
0.26923	21.4606	41.02305	-5.50393	-11683.8167
0.38705	25.43682	46.63986	-2.39783	-4714.00295
0.49547	24.82695	42.58537	0.34902	1166.63015
0.59564	20.99806	32.7033	2.71898	6362.38312
0.68848	16.28118	22.61934	4.74302	10695.74629
0.77467	12.23226	15.51912	6.65703	15147.91591
0.85490	8.99189	11.22352	8.367	19632.73178
0.92986	2.75309	1.73688	10.03936	23281.57306
1.00000	0		0.0000	0

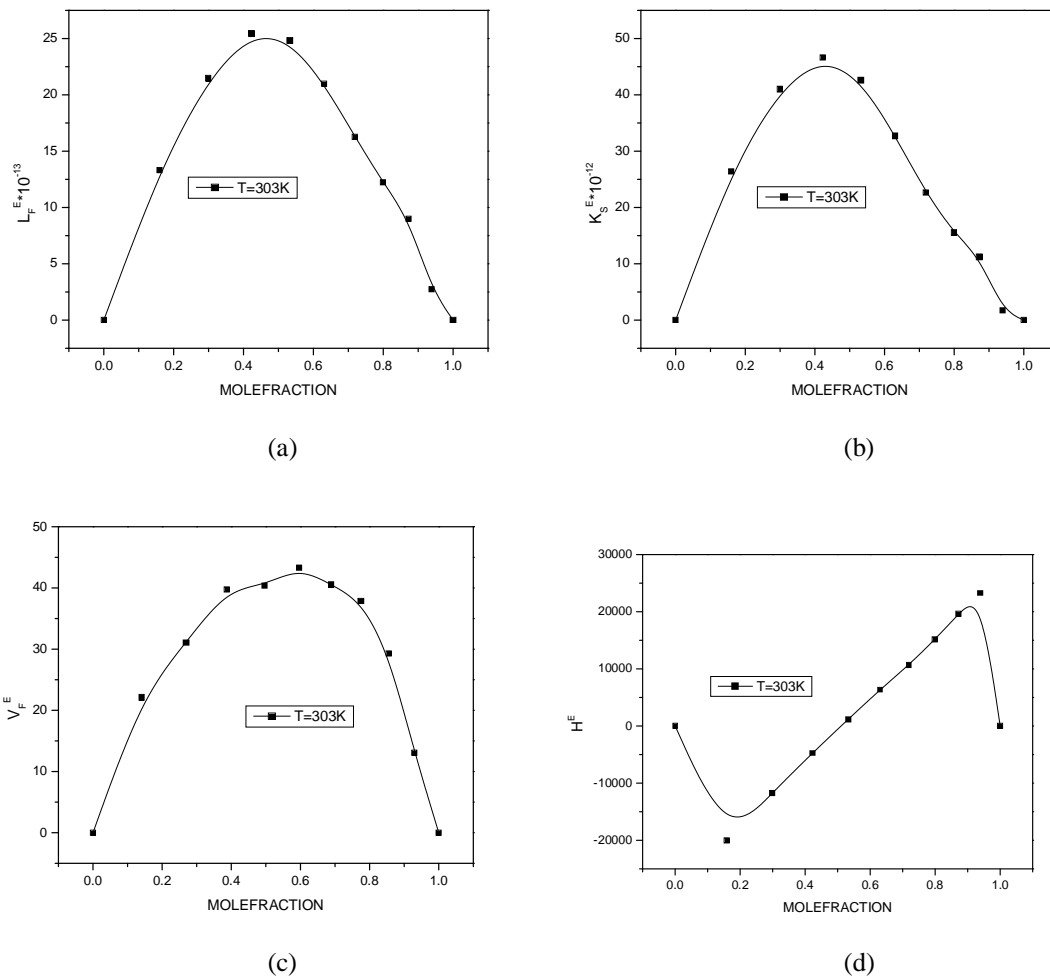


Figure 1. Variations of excess thermo-acoustical parameters, (a) excess intermolecular frelength (L_f^E); (b) excess adiabatic compressibility (β^E); (c) excess free volume (V_f^E); (d) excess enthalpy (H^E)

The variation of excess molar volume (V^E), with respect to mole fraction, x_1 , is given in Fig. 1 (c) over the entire composition range and at T 303K. The strength of the intermolecular interactions in binary liquid mixtures can be explained using the sign and magnitude of the V^E values. The V^E values are negative mostly in case of Hexanol but the trend changed to positive as the molar ratio of PG increases. This suggests that the sign and magnitude of the V^E values are sensitive to the molar ratio of PG. This kind of behaviour of V^E can attributed to the formation of H-bonds, disruption of alcohol self-associations and the structural characteristics like geometrical fitting of one component into the other as a result of the increase in difference of size and shape of the component molecules. It is clear from Fig. 1(a). The expansion in molar volume can be attributed to the presence of weak intermolecular forces of attraction [12]. Similar results were reported by Garcio et al. [13]. The negative values of V^E indicate that there is more compact packing of the molecules which implies that the molecular interactions are strong whereas the positive values indicate a loose packing of molecules in the binary mixture compared to those in the pure component. The negative values of V^E decrease for the binary liquid mixtures under study as the interactions between unlike molecules become weaker as the molar ratio of PG increases. This confirms the predictions drawn from the values of β^E . Similar results were observed by

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Vol. 6, Issue 3, March 2017

earlier workers [14] It can be observed from Fig. 1(b & c) that the L_f^E values have a negative trend similar to what we have observed in case of the β^E at temperature under study. The negative values of L_f^E suggest that specific interactions are present between unlike molecules in these binary systems [15]. These positive values indicate the existence of strong intermolecular interaction through hydrogen bonding between the component molecules of the liquid mixtures under study. From Fig. 1(d), it is clear that the excess values of enthalpy (H^E) are negative with respect to the mole fraction, x_1 , over the entire composition range. The negative values of H^E insist on the fact that there are strong specific interactions between unlike molecules in these liquid mixtures [16]. The negative H^E values also suggest the existence of inter molecular hydrogen bond.

IV. CONCLUSION

The values of excess free length, excess isentropic compressibility and excess enthalpy are found to be negative and the excess molar volume values changed from negative to positive for all the binary systems over the entire range of composition and at given temperatures considered in the present study. This is a clear indication for the presence intermolecular interactions due to hydrogen bonding between the component molecules.

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