EXCESS THERMO ACOUSTIC PARAMETERS ON BINARY MIXTURE OF TETRAHYDROPYRAN WITH 1-PENTANOL

K.ANIL KUMAR[1*], SRINIVASU CH[2], T.S.KRISHNA[3] AND K.NARENDRA[4]

1. [*]Department of Physics, Sri Vani School of Engineering, Chevuturu (A P), India.
2. Department of Physics, Andhra Loyola College, Vijayawada-8 (A P), India.
3. Department of Physics, Nalanda group of institutions,Sattenapalli (A.P), India.
4. Department of Physics, V.R.Siddhartha Engineering College, Vijayawada-7 (A.P), India.

***Corresponding author: E.Mail: anilkumarkoneti@gmail.com**

ABSTRACT

Densities, speed of sound of binary mixture of Tetrahydropyran (THP) with 1-pentanol have been measured over the entire range of composition at five temperatures (T=298.15, 303.15, 308.15, 313.15 and 318.15 K) from the experimental values calculated the excess thermo acoustical parameters excess ultrasonic velocity (u^E), deviations in isentropic compressibility (ΔK_s), excess molar volumes (V_m^E), excess free length (L_f^E) and excess acoustic impedance (Z^E). Further, all the parameter's and there co-efficient have been fitted to Redlich-Kister polynomial equations for the study of inter molecular interactions.

KEYWORDS: Densities, Speed of sound, Thermo acoustical parameters, THP, 1-pentanol.

INTRODUCTION

The ultrasonic study finds extensive applications for characterizing aspects of physico-chemical behavior like nature of molecular interactions in pure liquids as well as liquid mixtures. In the recent years, the ultrasonic study of properties of liquid mixtures and solutions finds direct applications in chemical and biochemical industry. THP is a cyclic monoether. Attention will be fixed on excess thermo acoustical parameters such as excess ultrasonic velocity (u^E), deviations in isentropic compressibility (ΔK_s), excess molar volumes (V_m^E), excess free length (L_f^E) and excess acoustic impedance (Z^E). For the present work we selected equi-molar components of the mixture are of nearly equal. So, an alcohol of highly associated liquid, 1-pentanol (molecular weight 88.15) which is a very common substance in theoretical studies of hydrogen bonds and structural effects in excess thermodynamic properties is mixed with THP (molecular weight 88.13) which is used in polymerization processes, and also in the pharmaceutical industry as a reaction intermediate are considered.

EXPERIMENTAL DETAILS

Tetrahydropyran (THP), 1-pentanol are purchased from Sigma Aldrich chemical company (purities >0.998), the purity of the experimental liquids was checked by comparison their measured densities and speed of sound values at the range of 298.15 to 313.15 K (± 0.01 K) with those reported within the literature. Densities (ρ) and speeds of sound (u) of the pure liquids and their binary mixtures were measured using an Anton Paar vibrating-tube digital density and sound analyzer (model DSA 5000M) in the manner explained elsewhere. The measurements are based on measuring the period of oscillation of a vibrating U-shaped hollow tube filled with the liquid sample. The densimeter was calibrated at the measuring temperatures with air and freshly degassed quadruple distilled water. The mole fractions of the constituents of binary mixture were obtained with uncertainty of $1*10^{-4}$ from the measured apparent masses of the components. All the mixtures were weighed on precision balance Sartorius, model CP 225D, +/-0.01mg. The uncertainty and repeatability in the density and speed of sound measurements is $2*10^{-3}$ kg.m^{-3} and 0.1 ms^{-1} respectively, which is the same as claimed by the manufacturer, Anton Paar (Austria).

Table.1.Comparison of experimental sound velocity, densities of pure liquids with literature values at (T=298.15 to 318.15K)

Compound	T (K)	u (ms^{-1})		ρ (kgm^{-3})	
		Observed	Literature	Observed	Literature
THP	298.15	1269.3	1269.3 [4]	879.4	879.1 [5-6]
	303.15	1246.5	1246.8 [7]	874.3	-
	308.15	1223.9	1224.4 [7]	869.3	869.2 [8]
1-pentanol	298.15	1275.8	1275.2 [9]	811.3	810.8 [9]
	303.15	1258.9	1258.0 [10]	807.6	807.9 [11]
	308.15	1242.2	1243.6 [10]	803.9	803.4 [10]

RESULTS AND DISCUSSIONS

The measured values of speed of sound (u) and densities (ρ), and there excess thermo acoustic parameters *viz.*, excess ultrasonic velocity (u^E), deviations in isentropic compressibility (ΔK_s), excess molar volumes (V_m^E), excess free length (L_f^E) and excess acoustic impedance (Z^E) for the binary system of THP with 1-pentanol at five temperatures (T=298.15 to 318.15 K) are studied in this paper.

The close glance of the measured data shows that density increases and speed of sound of the mixture decreases with the increase in mole fraction of THP at all temperatures studied. The decrease in velocity is perhaps due to structural changes occurring within the mixtures, leading to weakening of intermolecular forces. The values of 'u' decrease with increase of temperature due to breaking of hetero and homo molecular clusters at high temperatures.

The deviation in isentropic compressibilities can be explained by taking into consideration of the following factors:

(a) loss of dipole association and variations in size and shape of the component molecules which lead to decrease in velocity and an increase in compressibility;
(b) dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules which leads to increase in sound velocity and decrease of compressibility.

To understand this situation more clearly let us study about the following excess parameters V_m^E and ΔK_s. In the present work, plots of ΔK_s (fig 1) and V_m^E (fig 2) shows negative values over the entire composition range it suggests that the mixture prefers to have compact structure in the binary liquid system.

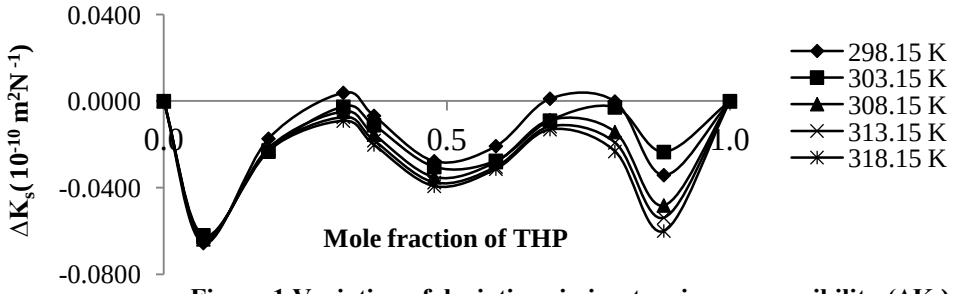

Figure.1.Variation of deviations in isentropic compressibility (ΔK_s) with mole fraction of THP + 1-pentanol system at different temperatures

The volume of the liquid mixture depends upon the structural arrangement in liquid as well as on the inter-molecular interactions. In a mixture of two liquids, the shapes of the molecules i.e. cluster geometry or macro-geometry, would thus, predominantly, decide an excess of molar volume. An increase in the strength of the hetero-molecular forces manifesting in a decrease in isentropic compressibilities 'K_s' of the mixture would tend to reduce the size of the cluster, hence decrease in total volume of the mixture.

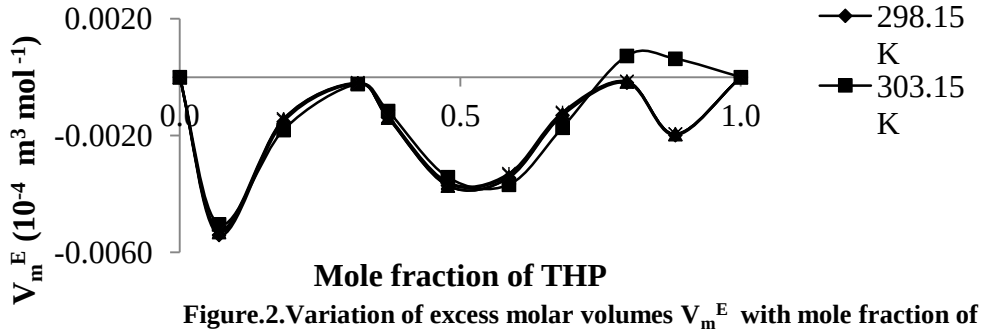

Figure.2.Variation of excess molar volumes V_m^E with mole fraction of THP + 1-pentanol system at different temperatures

The broad discussion given above regarding the variation of K_s^E and V_m^E shows that, these variations not only indicate the presence of hetero-molecular THP and 1-pentanol interactions in liquid mixtures, but also provide information on the relative strengths of homo-molecular THP-THP and pentanol-pentanol interactions. When THP-THP & pentanol-pentanol interactions in component liquids are of comparable strength and THP-pentanol interaction is slightly weaken then there won't be disruption of individual clusters but only gets loosened, i.e., loss of dipolar association. Here, if THP-THP & pentanol-pentanol interactions leading to an increase in the size of the respective clusters result in increase in volume of the mixtures. However when THP-pentanol interactions are stronger than the other, it causes disruption of the weaker clusters. Molecules released from the disrupted cluster may occupy interstitial spaces in the intact clusters leading to a concealment of free molecules, i.e. total volume of the liquid decreases.

The variation of L_f^E is plotted with the composition of THP with 1-pentanol. The L_f^E curves (Fig 3), show an initial decrease with the increase in the composition of THP in the mixture and a minimum L_f^E occurs at about 0.1 & 0.9 mole fraction of THP. The existence of minimum free length is an indication that the structural re-adjustment in the liquid mixtures are present in the direction of less compressible phase or close packing of molecules.

Variation of excess acoustic impedance is presented in fig 4, Z^E is positive at all the five investigating temperatures (except 0.3171 and 0.7968 mole fraction of THP). The mirror images like appearance of Z^E and V_m^E indicated clearly the presence of both loss of dipole association and dipole-dipole interactions present in the mixture. Also, as expected the observed deviations in Z^E is in opposite trend to that of behavior of ΔK_s over the entire range of systems investigated.

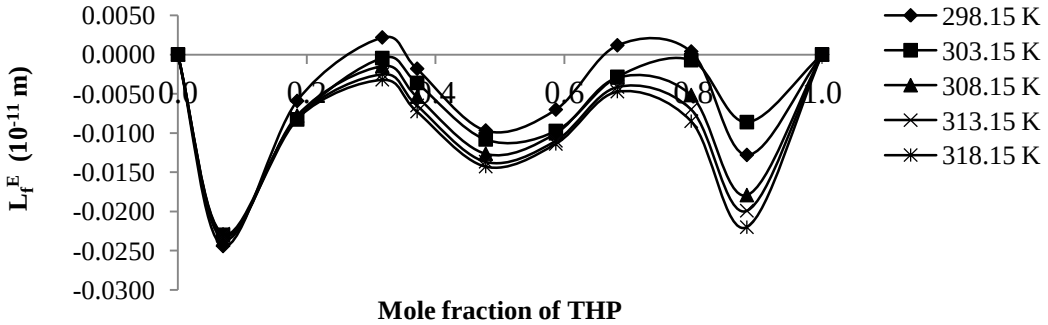

Figure.3.Variation of excess free length L_f^E with mole fraction of THP + 1-pentanol system at different temperatures

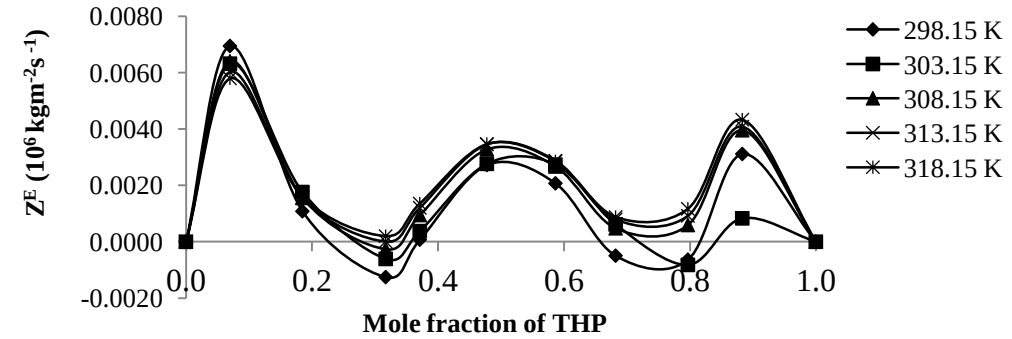

Figure.4.Variation of excess acoustic impedance (Z^E) with mole fraction of THP + 1-pentanol system at different temperatures

From the Figures $\Delta K_s, V_m^E$, L_f^E and Z^E it's understood that presence of significant specific interactions of strong nature of loss of dipole association with dipole-dipole interactions with in the equi molar liquid mixture considered over entire composition range of THP at different temperatures.

Basing on deviation in isentropic compressibility as well as excess ultrasonic velocity (fig 5) are both positive and negative which shows the existence association and dissociation of molecules and hence moderate interactions are present in this mixture. Also, the positive values of 'u^E' increases with increase in temperature, which indicates the increase of strength of interactions with temperature in all the mixtures.

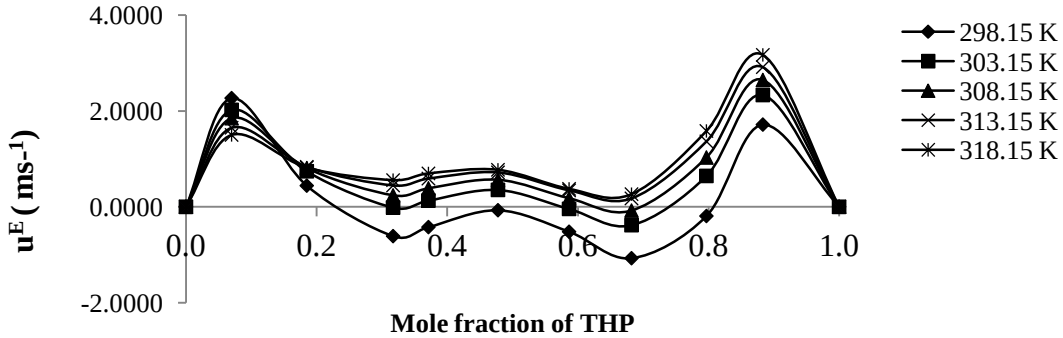

Figure.5.Variation of excess ultrasonic velocity (u^E) with mole fraction of THP + 1-pentanol system at different temperatures

CONCLUSION

In the present study, it can be inferred that presence of significant specific interactions of strong nature of loss of dipole association with dipole-dipole interactions in the equi molar liquid mixture present over entire composition range of THP at different temperatures studied.

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