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Thermo-Acoustic and Excess Thermodynamic Studies of Organic Ternary Liquid Mixtures at 303.15K

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ABSTRACT

The observed experimental parameters such as density (ρ), viscosity (η) and ultrasonic velocity (U) of ternary liquid mixtures of 1-pertanol and 1-henanol with anisole in toluene have been measured at 303.15K. From the experimental data, the adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f) internal pressure (π_i) and acoustic impedance (Z) have been calculated. Also the excess thermodynamic parameters such as adiabatic compressibility (β^E), intermolecular free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E) and acoustic impedance (Z^E) were calculated. The observed variation of these parameters helps in understanding the nature of interaction and estimating the strength of interactions present in the mixtures.

Keywords: Ultrasonic velocity, Polar, Nonpolar, Excess values, Acoustic parameters.

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INTRODUCTION

Ultrasonic velocity measurements and other acoustical parameters of liquid mixtures are the powerful technique in understanding of chemical nature and the molecular interactions. Acoustical and thermo dynamical study of liquid mixtures provides enough knowledge about the association of molecular packing, molecular motion and strength of intermolecular interactions [1- 4].Ultrasonic wave propagation affects the physical properties of the medium and hence can furnish information about molecular interaction of the liquid and liquid mixtures. The sign and magnitude of the nonlinear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules [5].The study of the solution properties of liquid mixtures find applications in industrial and technological processes.

The study of molecular association in organic ternary mixtures having alcohol as one of the components is of particular interest, since alcohols are strongly self-associated liquid having a three dimensional network of hydrogen bond and can be associated with any other group having some degree of polar attraction [6]. Further such studies as function of concentration are useful in gaining insight into the structure and bonding of associated molecular components and other molecular processes.

Alcohols are of much importance in industries and it is a highly flammable and colorless liquid. The alcohols described above exist in associated form whereas, toluene has non associated structure in liquid state. Anisole and alkanols exist in associated and polar form whereas, toluene has non-associated and non-polar structure in liquid state. When a polar liquid is mixed with a non-polar liquid there may be three types of interactions namely dipole-dipole, dipole-induced dipole, induced dipole-induced dipole interactions. The structural arrangements and the charge in the physico chemical behavior of liquid mixtures are mainly due to the change in molecular orientation and charge in physical quantities. No attempts has been made to study the various ultrasonic and thermodynamic properties for the above binary mixtures with a polar liquid such as anisole.

MATERIALS AND METHODS

In the present work, we have used chemicals, which are analytical reagent (AR) and spectroscopic reagent (SR) grade of minimum assay of 99.9%. obtained from E-merk, Germany and Sd fine chemicals, India. The ternary liquid mixtures of different known composition were prepared by mole fraction basis. In all the mixtures, the mole fraction of the second component ie. toluene was (X_2 =

0.4) kept fixed, while the mole fractions of the remaining two were varied from 0.0 to 0.6 so as to have the mixtures of different compositions. The density of pure liquids and mixtures were determined using a specific gravity bottle by relative measurement method with reproducibility of ± 0.0001 gcm^{-3} (model SHIMADZU AX-200).

An Ostwald's viscometer 10 ml capacity was used for viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ± 0.1S. The speeds of sound waves were obtained by using an ultrasonic interferometer (Model-F81) supplied by M/S Mittal Enterprises, New Delhi having the frequency 3 MHz with an overall accuracy ±2 ms^{-1} has been used for velocity measurement. An electronically digital constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

THEORY

From the measured densities (ρ) and ultrasonic velocities (U) the following acoustical parameters have been calculated [6, 7].

Adiabatic compressibility (β)

$$\beta = \frac{1}{U^2 \rho} \qquad \ldots. (1)$$

Intermolecular free length (L_f)

$$L_f = K_T \sqrt{\beta} \qquad \ldots. (2)$$

Where K_T is a temperature dependent constant

Free volume (V_f)

$$V_f = \left(\frac{M_{eff}\, U}{K\eta} \right)^{3/2} \qquad \ldots. (3)$$

Where M_{eff} is the effective molecular weight ($M_{eff} = \sum m_i x_i$ in which m_i and x_i are the molecular weight and mole fraction of the individual constituents respectively) K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

Internal Pressure (π_i)

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad \ldots. (4)$$

Where K is a constant, b is a constant which is 2 for cubic packing, R the gas constant and T is the temperature in K.

Acoustic impedance (Z)

$$Z = U\rho \quad \ldots (5)$$

The excess parameters (A^E) has been calculated by using the relation

$$A^E = A_{\exp} - A_{id} \quad \ldots (6)$$

Where $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid components of i.

RESULTS AND DISCUSSION

The experimental values of density (ρ) viscosity (η) and ultrasonic velocity (U) at 303.15K are presented in Table 1. The values of adiabatic compressibility (β) free length (L_f) internal pressure (π_i) free volume (V_f) and acoustic impedance (Z) are listed in Table 2. The respective excess values of the above parameters have also been evaluated and presented in Figs. 1-5.

In the present investigation, it is found that for the systems I & II the density (ρ) and ultrasonic velocity (U) of the ternary liquid mixtures are decreasing with increasing mole fractions of 1-ols. Whereas, the viscosity increases as the mole fraction of 1-ols increases. The adiabatic compressibility (β) shows an inverse behavior compared to the ultrasonic velocity in all the mixtures with increase in concentration of 1-alkanols. The compressibility that charges with the structure and this lead to the change in ultrasonic velocity [8].

Table 1 Values of Density (ρ) viscosity (η) and velocity (U) of system I & II

Mole Fraction		ρ/(kg m^{-3})	η/(×10^{-3}Ns m^{-2})	U/(ms^{-1})
X_1	X_3			
System I: 1-Pentanol + Toluene + Anisole				
0.0000	0.6000	925.3	0.6717	1365.3
0.1000	0.5000	887.2	0.6964	1355.0
0.2000	0.4000	857.1	0.7066	1350.0
0.3000	0.3000	835.1	0.7181	1335.0
0.4000	0.2000	827.0	0.8090	1297.0
0.5000	0.1000	798.9	0.8540	1282.0
0.6000	0.0000	792.8	1.0000	1278.2
System II: 1-Hexanol +Toluene+ Anisole				
0.0000	0.6000	934.65	0.6820	1353
0.1000	0.5000	920.30	0.7696	1345
0.2000	0.4000	891.60	0.7843	1326
0.3000	0.3000	862.89	0.8101	1312
0.4000	0.2000	828.81	0.9383	1300
0.5000	0.1000	812.66	1.1226	1293
0.6000	0.0000	809.07	1.2415	1275

From the Table 2, it is noted that the free volume (V_f) decreases as the concentration of 1-alkanols increases whereas, the internal pressure (π_i) increases due to the various degree of dispersive interaction and columbic interaction existing between the component molecules [9]. The continuous decrease in free volume is due to the closer packing of the molecules inside a shield, resulting in cohesion between the molecules, which in turn decreasing the free volume.

Intermolecular free length (L_f) is found to be a predominating factor, which depends upon adiabatic compressibility (Table2). The observed ultrasonic velocity decreases and a corresponding free

length increase with increasing concentration of 1-ols in all the systems. According to the view proposed by Eyring and Kincaid[10] as a result of mixing of component liquids, the ultrasonic speed decreases with increase in free length and vice versa. This is observed in our systems.

Table 2 Values of Adiabatic compressibility (β), Free length (L_f),Internal pressure(π_i), Free volume(V_f), and Acoustic Impedance (Z) of system – I & II

Mole Fraction		β/(×10^{-10}Pa^{-1})	L_f/(x10^{-10}m)	π_i/(x10^6 Pa)	$_{Vf}$/(x10^{-7}m^3 mol^{-1})	Z/(x10^5 kg m^{2}s^{-1})
X_1	X_3					
System I: 1-Pentanol + Toluene + Anisole						
0.0000	0.6000	5.797	4.804	316.595	3.359	12.634
0.1000	0.5000	6.138	4.943	324.448	3.053	12.022
0.2000	0.4000	6.401	5.048	325.189	2.794	11.571
0.3000	0.3000	6.719	5.172	331.880	2.681	11.148
0.4000	0.2000	7.187	5.349	363.939	2.080	10.726
0.5000	0.1000	7.615	5.506	376.894	2.069	10.242
0.6000	0.0000	7.721	5.544	417.006	1.387	10.133
System II: 1-Hexanol +Toluene+ Anisole						
0.0000	0.6000	5.844	4.823	322.64	3.238	12.645
0.1000	0.5000	6.006	4.890	342.57	2.654	12.378
0.2000	0.4000	6.378	5.039	343.38	2.503	11.822
0.3000	0.3000	6.732	5.177	345.66	2.325	11.321
0.4000	0.2000	7.139	5.331	366.36	1.823	10.774
0.5000	0.1000	7.360	5.413	399.38	1.369	10.507
0.6000	0.0000	7.603	6.501	424.70	1.142	10.315

It is observed that the acoustic impedance (Z) decreases with increasing mole fraction of 1-alkanols. The decrease in acoustic impedance with increase in mole fraction indicates significant interaction between the component molecules. The same trend is observed in Anwar Ali and Anil Kumar Nain 2001[11].

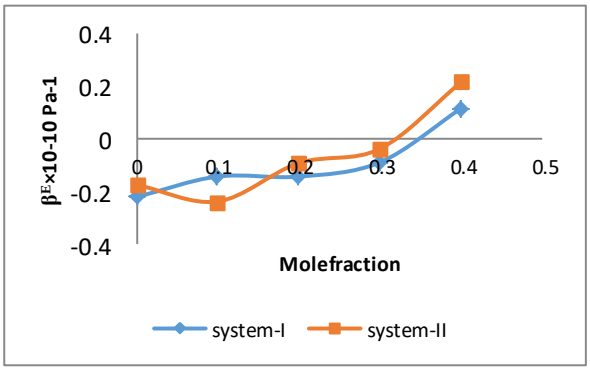

Fig.1 Excess Adiabatic compressibility Vs mole fraction of 1-ols.

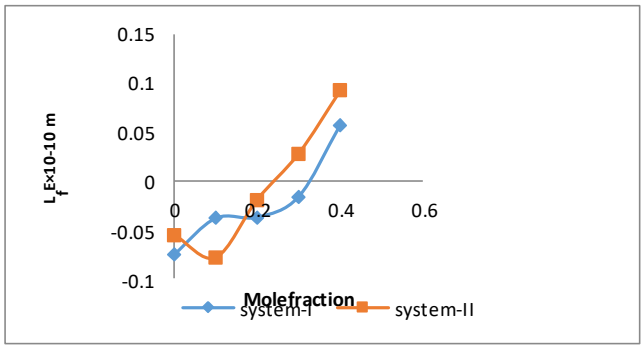

Fig.2 Excess Free length of Vs mole fraction of 1-ols

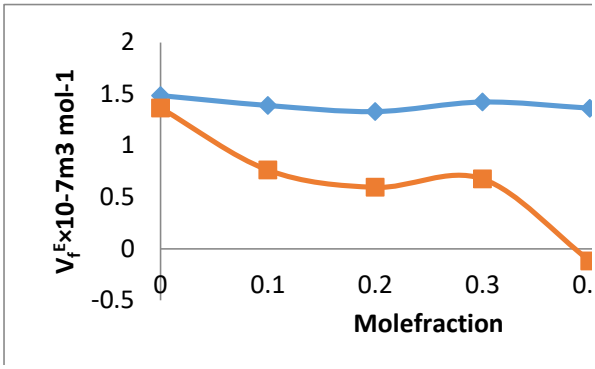

Fig.3 Excess Free volume Vs mole fraction of 1-ols

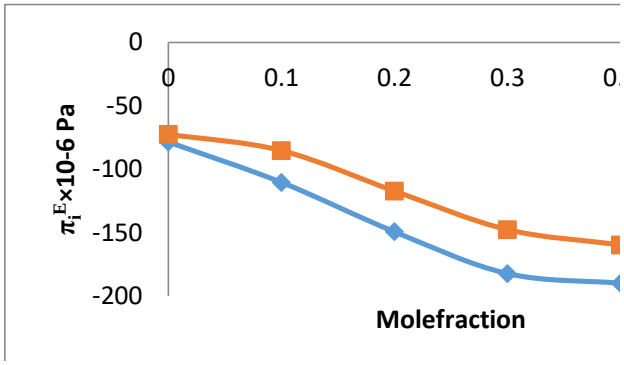

Fig.4 Excess Internal pressure Vs Mole fraction of 1-ols

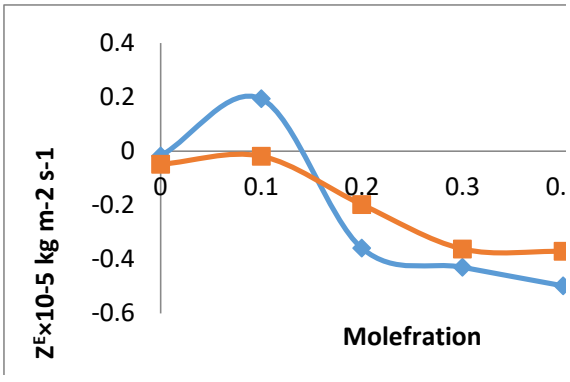

Fig. 5 Excess Acoustic impedance Vs mole fraction of 1-ols

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. The study of excess properties of liquid mixtures provides useful information regarding the nature and strength of molecular interaction. The deviation of the physical property of the liquid mixtures from the ideal behavior is the measure of interaction between the molecules, which is attributed to either adhesive or cohesive forces.

The variation of excess adiabatic compressibility (β^E) against composition of alcohols in all the ternary systems is shown in Fig.1. It can be observed that the excess compensability is negative at lower mole fraction and it becomes positive at higher mole fraction in both 1-pentanol and 1-heranol systems, suggested that the negative excess compressibility has been due to a closed packed molecules, while positive excess values are due to weak interaction [12] between unlike molecules. Also the negative values of compressibility indicate the formation of hydrogen bond between unlike molecules.

The values of excess intermolecular free length L_f^E follow the same tread as that of β^E. It exhibits both positive and negative values for 1-pentarol and 1-hexanol systems. Fig 3 give the values of the excess free volume for the ternary systems. The excess values are found to be almost positive in all the systems studied, which indicates the existence of weak molecular interaction in the liquid mixtures [13].

In the study of liquid mixtures the variation of the excess internal pressure $\left(\pi_i^E\right)$ may give some information regarding the nature and force existing between the molecules. It is observed from the Fig.4 the values of π_i^E are negative in all the systems studied. According to Deshphande *et al* (1968)[14] the negative sign of excess internal pressure indicate the weak interaction, which the positive sign of excess internal pressure $\left(\pi_i^E\right)$indicates the strong bonding between molecules in all composition [15]. The observed negative values of π_i^E confirms only weak molecular interactions are present in our systems studied. It is observed that the values of Z^E are negative over the entire composition range for the systems under study. The negative deviations in Z^E suggests that dispersive forces are operative [16] which further supports our early view.

CONCLUSION

The trends in the variation of parameters derived from ultrasonic velocity and the sign and magnitude of the excess function suggest the presence of weak dipolar interactions and dispersive forces between the unlike molecules in all the systems studied. It is concluded that the strength of associative interaction between the unlike molecules weaken with the increase in chain length of the 1-alcohols and

the order of interaction is as follows 1-pentanol > 1-hexanol ie. interaction decreases with increase in alkyl chain length in 1-alkanol molecules, probably due to less proton donating tendency to higher alcohols.

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