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THERMO PHYSICAL PROPERTIES OF TERNARY MIXTURES OF 1-HEXANOL/1-OCTANOL CONTAINING N-N-DIMETHYLFORMAMIDE AND TOLUENE AT 303.15 K

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ABSTRACT In the present work, ultrasonic velocity (u), viscosity (η) and density (ρ) of ternary mixtures of 1-hexonal and 1-octanol with dimethylformamide in toluene at 303.15 K have been measured over the entire composition range. From the experimental data, acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), acoustic impedance (Z), excess adiabatic compressibility (β^E), excess free length (L^E_f), excess free volume (V^E_f) and excess acoustic impedance (Z^E) have been computed. The variation of these properties with composition are discussed in terms of molecular interactions between unlike molecules of the mixtures.

KEYWORDS : Ultrasonic velocity, molecular interaction, adiabatic compressibility, excess parameters, N-N-dimethyl formamide.

INTRODUCTION

The study of molecular interaction in binary and ternary liquid mixtures plays an important role in molecular sciences. In recent years ultrasonic technique has become a powerful tool in providing information about the physico chemical properties of liquid system [1-2]. Ultrasonic has acquired the status of an important method for the study of structure of molecule and properties of matter. These of ultrasound is one of the famous and familiar approaches for the study of molecular interaction in fluids.

The studies of ultrasonic velocities are being increasingly used as tool for investigation of properties of pure components and the nature of intermolecular interaction between the liquid mixture constituents. The ultrasonic studies are extensively used to estimate the thermodynamic properties and to predict the intermolecular interactions.

The physical or chemical nature and the corresponding strength of the molecular interaction between the components of the ternary liquid mixtures have been successfully investigated by the ultrasonic method [3]. The ultrasonic velocity of a liquid is fundamentally related to the binding forces between atoms or molecules and it has been successfully employed in understanding the nature of molecular interaction in pure liquids as well as binary and ternary mixtures [4,5].

The studies of molecular association in organic ternary mixtures having alcohol as one of the components is of particular interest, since alcohols are strongly self-associated liquids having a three dimensional network of hydrogen bond and can be associated with any of other group having some degree of polar attraction [6].

In view of growing interest, the results of various acoustical parameters and their excess values of ternary mixtures containing 1-hexanol and 1-octanol with the binary mixtures of dimethyl formamide and toluene have been presented.

Experimental Details:

In the present work, the chemicals which have been used are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-merk Germany and Sd fine chemicals, India. The speeds of sound waves was obtained by using ultrasonic interferometer, (Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± 2ms $^{-1}$. An electronically digital operated constant temperature bath (RAAGA Industries, Madras – 61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement was 0.1K. The density was measured using pycnometer of capacity 5 ml and gave an estimated reproducibility of 0.0001 g cm^{-3}. The viscosity was measured using an Ostwald's viscometer having time efflux 0.01s and the accuracy was found to be ± 3 ×10^{-6} Nm^{2}s. The temperature around the viscometer was maintained with 0.1K in an electronically controlled thermostatic water bath. For preparing various concentration mixtures, the mole fraction of second component toluene was kept constant (x_2 = 0.3) and mole fraction of other two components were varied from 0.0 to 0.7.

Theory:

The various acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) acoustic impedance (Z) and their excess values were determined using the following equations [7,8]:

$$\beta = \frac{1}{u^2 \rho}$$

$$L_f = k_T \beta^{1/2}$$

$$V_f = \frac{Meff\ U}{\eta k}$$

$$Z = U\rho$$

where K_T is the temperature dependent constant, M_{eff} is the effective molecular weight of the solution, k is the temperature independent constant (k = 4.28 10^9), b is a constant which is 2 for cubic packing.

The excess parameters (A^E) of all the acoustic parameters were computed by the relations.

$$A^E = A_{exp} - A_{id}$$

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

RESULTS AND DISCUSSION:

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for the ternary mixtures at 303.15K are presented in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume((V_f) and acoustic impedance (Z) are presented in Table 2. The excess function such as β^E, L_f^E, π_I^e and Z^E are presented in Figs. 1-4.

It is found that the adiabatic compressibility increases with increase in mole fraction of 1-alkanols. The adiabatic compressibility shows an inverse behaviour compared to the ultrasonic velocity in all the mixtures with increase in concentration of 1-alkanols. The compressibility that changes with the structure and this lead to the change in ultrasonic

velocity [9].

The values of free length (L_f) increases (Table 2) with increase in mole fraction of 1-ols. Intermolecular free length is found to be a predominating factor, which depends upon adiabatic compressibility and shows a similar behaviour as that of compressibility. On the basis of a model for propagation of sound proposed by Eyring and Kincaid (1938) [10], ultrasonic velocity should decrease if the intermolecular free length increases and vice-versa. This is an accordance with the expected increase in free length following a decrease in ultrasonic velocity in nature.

This increase in L_f is due to dominating effect of mutual dissociation of the component molecules in the mixture, which in not compensated by the hydrogen bonding between unlike molecules [11]. The free volume decreases with increase in concentration of 1-ols in both the systems. 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 decrease the free volume. This indicates the specific interaction between the components of the mixtures [9].

Further mixing of such DMF with 1-alkanols causes dissociation of hydrogen bonded structure of 1-ols and subsequent formation of H-bond between the oxygen atom of C=0 group of DMF and hydrogen atom of OH-group of 1-alkanol molecules. This dissociation effect leads to an decrease in volume and hence an increase in adiabatic compressibility. The values of acoustic impedance decrease with molar concentration.

The excess parameters play a major role in understanding the nature of molecular interactions in liquid mixtures. Generally the excess functions depend upon several contribution arising from physical, chemical and structural effects. The physical contribution consists of dispersion forces or weak dipole-dipole interaction leading to positive values of βE L_f^E and whereas, the geometric fitting of molecules of two different sizes into each other structure results in negative βE L_f^E and values. Chemical contribution include breaking up of the molecular association present in the pure liquids resulting in positive βE and L_f^E values and specific interaction such as formation of new hydrogen bonds results in negative βE and L_f^E [12].

The observed negative values of β^E and L_f^E in system-I indicates the presence of strong interaction between the component molecules [13]. The positive deviation in B^E and L_f^E in system-II may be attributed to the presence of weak interaction between the component molecules in the mixture [12].

The excess free volume $\left(V_f^E\right)$ are negative in both the systems. This negative values are the indication of the existence of strong interaction between the component molecules [14]. The presented excess parameters for the ternary system reveals that Z^E values are positive for system-I and negative for system-II.

The positive values of Z^E indicates the presence of strong interaction and negative values corresponds the existence of dispersive forces [15]. The trends in Z^E further supports our conclusion drawn from the variation of B^E and L_f^E for both the systems.

CONCLUSION:

The observed changes in the acoustic parameters and their excess function derived for ultrasonic velocity, density and viscosity suggest the presence of intermolecular interaction in the ternary liquid mixtures of 1-alkanols with DMF and toluene at 303.15K. It is concluded that there is a formation of hydrogen bonding between DMF and 1-alkanols and the strength of associative interaction between the unlike molecules weakens with the increase in chain length of 1-alkanols and the order of interaction is as follows: 1-hexanol > 1-octanol.

Table 1 Values of Density (ρ) viscosity (η) and velocity (U) of system I & II at 303.15K

Mole Fraction		ρ/(kg m^{-3})	η/(×10^{-3}Ns m^{-2})	U/(ms^{-1})
X_1	X_3			
System I: 1-Hexanol+Toluene+Dimethylformamide				
0.0000	0.7000	908.34	0.6631	1471.2
0.1000	0.6000	899.05	0.7911	1395.0
0.2000	0.5000	889.76	0.8717	1375.5
0.3000	0.4000	880.48	0.9523	1354.1
0.4000	0.3000	865.62	1.0918	1341.1
0.5000	0.2000	850.76	1.2477	1323.3
0.6000	0.1000	843.33	1.4965	1308.4
0.7000	0.0000	832.18	1.8569	1299.7
System II: 1-Octanol +Toluene+ dimethylformamide				
0.0000	0.7000	902.77	0.7011	1499.6
0.1000	0.6000	893.48	0.8072	1380.0
0.2000	0.5000	874.90	0.9787	1363.0
0.3000	0.4000	867.47	1.1539	1341.4
0.4000	0.3000	854.47	1.3533	1323.6
0.5000	0.2000	847.04	1.5758	1311.1
0.6000	0.1000	841.47	1.8131	1303.2
0.7000	0.0000	828.46	2.1320	1295.0

Table 2 Values of Adiabatic compressibility (β), Free length (L_f), Free volume (V_f) and Acoustic Impedance (Z) of system-I&II at 303.15K

Mole Fraction		β/(×10^{-10} Pa^{-1})	L_f/(x10^{-10}m)	V_f/(x10^{-7} m^3 mol^{-1})	Z/(x10^5 kg $m^{-2}s^{-1}$)
X_1	X_3				
System I: 1-Hexanol+Toluene+Dimethylformamide					
0.0000	0.7000	5.0863	0.4510	2.6109	1.3363
0.1000	0.6000	5.7156	0.4781	1.9497	1.2541
0.2000	0.5000	5.9402	0.4874	1.7363	1.2238
0.3000	0.4000	6.1941	0.4977	1.5599	1.1922
0.4000	0.3000	6.4231	0.5068	1.3134	1.1608
0.5000	0.2000	6.7123	0.5181	1.1034	1.1258
0.6000	0.1000	6.9266	0.5263	0.8636	1.1034
0.7000	0.0000	7.1137	0.5334	0.6460	1.0815
System II: 1- Octanol +Toluene+ dimethylformamide					
0.0000	0.7000	4.9257	0.4438	2.4714	1.3537
0.1000	0.6000	5.8770	0.4848	1.9616	1.2330
0.2000	0.5000	6.1524	0.4960	1.5909	1.1924
0.3000	0.4000	6.4066	0.5062	1.3303	1.1636
0.4000	0.3000	6.6802	0.5169	1.1197	1.1309
0.5000	0.2000	6.8679	0.5241	0.9536	1.1105
0.6000	0.1000	6.9974	0.5290	0.8276	1.0966
0.7000	0.0000	7.1976	0.5365	0.6923	1.0728

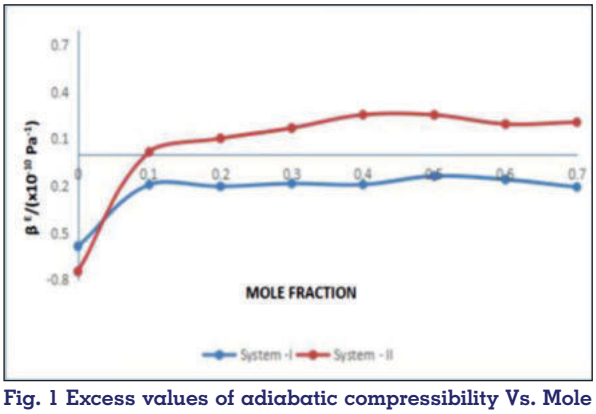

Fig. 1 Excess values of adiabatic compressibility Vs. Mole fraction of 1-ols.

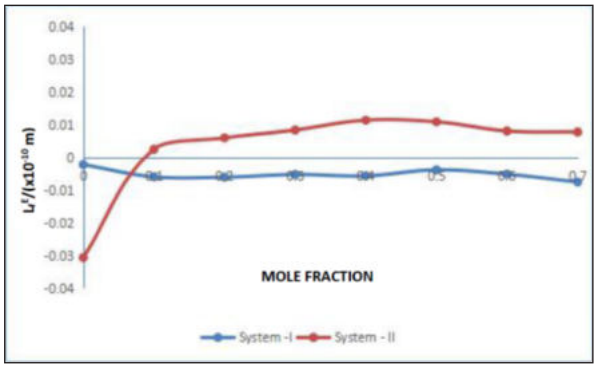

Fig. 2. Excess values of Free length Vs. Mole fraction of 1-ols

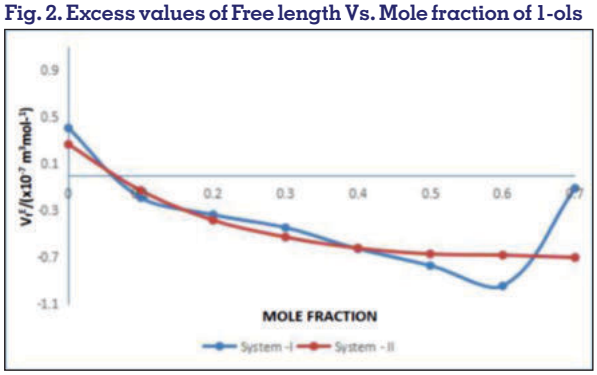

Fig. 3. Excess values of free volume Vs. mole fraction of 1-ols

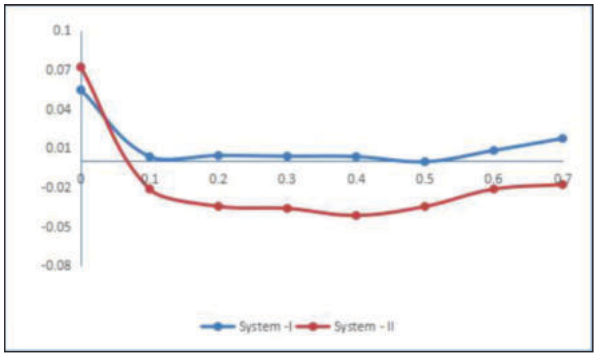

Fig. 4. Excess values of Acoustic impedance Vs. mole fraction of 1-ols

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