Acoustical and Thermodynamical properties of Ternary liquid mixtures of 1- pentanol/1- Hexanol + Benzene + Dibutylether at 303.15K.

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ABSTRACT

Densities (ρ), viscosities (η)and ultrasonic velocities (U) of ternary liquid mixtures of 1- pentanol, 1-hexanol with dibutylether in Benzene have been measured at 303.15K. The experimental data have been used to calculate the various acoustical parameters namely adiabatic compressibility (β), free length (L_f). Internal pressure(πi), free volume (V_f) and the excess values of the above parameters are also evaluated to study the intermolecular interaction between the component molecules of the mixture.

Key words: Ultrasonic Velocity, Adiabatic Compressibility, Ternary System, Excess Parameters

I. INTRODUCTION

Ultrasonic wave propagation affects the physical properties of medium, and hence, can furnish information about molecular interactions of the liquid and liquid mixtures. The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with compositions are attributed to the difference in molecular size and strength of interaction between unlike molecules. [1-3]. Ultrasonic methods find extensive applications for characterizing aspects of physiochemical behavior such as the nature of molecular interactions in pure liquids as well as liquid mixtures. [4-5]. The physical and chemical properties of liquid mixtures are influenced by the intermolecular forces [6-8]. Knowledge of density and viscosity is essential in the design of processes involving chemical separations, equipment design, solution theory, heat transfer, fluid flow and molecular dynamics [9]. Several researches [10-14] 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 non specific interactions. Alcohols are strongly associated in solution because of dipole- dipole interaction and hydrogen bonding. Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interaction, present in binary and ternary liquid mixtures. In this paper, an attempt has been made to investigate the ultrasonic studies of ternary mixtures of n-alcohols like 1-pentanol, 1- hexanol in benzene with dibutylether at 303.15 K.

II. EXPERIMENTAL DETAILS

In all the mixtures, the mole fraction of the second component benzene (x_2=0.4) was 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. All the chemicals used were of Analytical Reagent (AR) and spectroscopic Reagent (SR) grades with minimum assay of 99.9%. 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 10ml capacity was used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ± 0.01s. 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 of 3 MHZ with an overall accuracy of ±2 ms^{-1}. An electronically digital operated constant temperature bath (RAGAA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

III. THEORY

The acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (πi) and free volume (V_f) were determined using observed values of velocity, density and viscosity from the following equations:

i. $\beta = 1/\rho U^2$ ——— (1)

ii. $L_f = K_T \beta^{1/2}$ ——— (2)

iii. $\Pi i = bRT\,[K\eta/U]^{1/2}\,[\rho^{2/3}/M_{eff}^{7/6}]$ ——— (3)

iv. $V_f = [M_{eff}\,U/K\eta]^{3/2}$ ——— (4)

Where K_T is the temperature dependent constant, K the temperature independent constant (K =4.28 X 10^9), b a constant which is 2 for cubic packing. R the gas constant and T is the temperature in K . M_{eff} and U are molecular effective weight and velocity of liquids. The excess parameters (A^E) of all the acoustic parameters were computed by the relation

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

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

IV. RESULTS AND DISCUSSION

The experimentally measured values of density, viscosity and ultrasonic velocity of the ternary liquid mixtures at 303.15K are presented in Table 1. The values of adiabatic compressibility (β) free length (L_f) internal pressure (πi) and free volume (V_f) are presented in Table 2. The values of density, viscosity and velocity increases with increasing mole fraction of 1-alkanol in both the systems. Adiabatic compressibility (β) is a powerful thermodynamic parameter in sensing the molecular interactions in liquid mixtures [15].

The deviation in adiabatic compressibility can be explained by taking into consideration of the following factors.

(1) Loss of dipolar association and difference in size and shape of the component molecules lead to decrease in velocity and increase in compressibility [16].
(2) Dipole – dipole interaction or hydrogen bonded complex formation between unlike molecules leads to increase in sound velocity and decrease of compressibility, the actual deviation depends on the resultant effect.

The decrease in adiabatic compressibility for the systems I & II indicates, there is significant interaction between unlike molecule. On the basis of a model for propagation of sound proposed by Eyring and Kincaid (1938), [17] ultrasonic velocity should decreases while the intermolecular free length increases and vice-versa. This is an accordance with the expected decrease in compressibility following a increase in ultrasonic velocity in these mixtures. The decrease in free length is due to the decreased adiabatic compressibility which brings the molecules to a closer packing. The values of free volume (V_f) decreases whereas internal pressure(πi) increases with increase in mole fraction of 1- alkanols. This is due to the various dispersive interaction and the columbic interaction between the components of mixture. [18]

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 excess adiabatic compressibility β^E (Fig 3.1) excess free length L_f^E (Fig 3.2) are positive in systems I & II indicating the weak interactions between the components of mixtures [19]

In the study of liquid mixtures, the variations of the excess internal pressure πi^E may give some information regarding the nature of force existing between the molecules. The negative sign of excess internal pressure indicate the weak interaction while the positive sign of excess internal pressure indicate the strong interaction between the component molecules. The observed negative sign of πi^E (Fig 3.4) in these systems may be attributed to the weak interaction in the liquid mixtures [20-21]

The values of excess free volume V_f^E (Fig 3.3) are positive at lower mole fraction and decreases with increase in concentration of 1- alcohol. The value of the excess function β^E, L_f^E depend upon several physical and/or chemical contribution. The physical contribution consists of dispersion forces or weak dipole-dipole interaction that leads to positive values β^E and L_f^E. Another factor, which involves a physical contribution, is the geometrical effect allowing the fitting of molecules of two different sizes into each other's structure resulting in negative β^E & L_f^E values. Chemical contribution include breaking up of the associates present in pure liquids, resulting in positive β^E & L_f^E. The observed positive values of β^E, L_f^E are due to the breaking of interactions and the corresponding distruption which of molecular order in the pure components which may due to the dispersive force that show weak interaction between the unlike molecules. [22]

The excess ultrasonic velocity U^E are negative for all the two systems. The negative deviations in U^E(Fig3.5) from linear dependence suggest that the presence of weak interaction between the component molecule, which supports our earlier conclusion that the presence of weak interaction between the component molecules. [23-24]

TABLE -1

Values of Density (ρ), Viscosity (η) and Velocity (U) of systems I & II

Mole Fraction		ρ/(Kgm^{-3})	η/(×10^{-3}Nsm^{-2})	U/(ms^{-1})
X_1	X_3			
System I: 1-Pentanol+Benzene+Dibutylether				
0.0000	0.6000	783.96	0.5257	1182.2
0.1000	0.5000	791.13	0.5617	1185.0
0.2000	0.4000	800.10	0.6249	1216.0
0.3000	0.3000	801.90	0.6738	1220.0
0.4000	0.2000	803.69	0.7799	1223.0
0.5000	0.1000	809.07	0.9383	1231.0
0.6000	0.0000	825.22	1.1393	1238.0
System II :1-Hexanol+Benzene+Dibutylether				
0.0000	0.6000	785.75	0.5331	1174.0
0.1000	0.5000	792.93	0.5630	1181.4
0.2000	0.4000	800.10	0.6501	1196.0
0.3000	0.3000	805.48	0.7308	1214.0
0.4000	0.2000	807.28	0.9808	1228.0
0.5000	0.1000	810.87	0.9851	1250.0
0.6000	0.0000	828.81	1.3110	1275.0

TABLE- 2

Values of Adiabatic compressibility (β), Free length (L_f) Internal pressure (π_i) and Free volume (V_f) of Systems I & II

Mole Fraction		β/(×10^{-10}pa^{-1})	L_f/(×10^{-10} m)	Π_i/(×10^6 pa)	V_f/(×10^{-7} m^3 mol^{-1})
X_1	X_3				
System I: 1-Pentanol+Benzene+Dibutylether					
0.0000	0.6000	9.126	0.6027	247.65	4.357
0.1000	0.5000	9.001	0.5986	269.31	3.732
0.2000	0.4000	8.452	0.5800	296.32	3.110
0.3000	0.3000	8.378	0.5775	323.32	2.618
0.4000	0.2000	8.318	0.5754	366.46	1.974
0.5000	0.1000	8.156	0.5698	424.90	1.409
0.6000	0.0000	7.906	0.5610	501.49	0.987
System II :1-Hexanol+Benzene+Dibutylether					
0.0000	0.6000	9.233	0.606	250.65	4.222
0.1000	0.5000	9.035	0.599	266.29	3.777
0.2000	0.4000	8.737	0.589	295.16	2.978
0.3000	0.3000	8.423	0.579	322.16	2.453
0.4000	0.2000	8.214	0.571	384.07	1.538
0.5000	0.1000	7.892	0.560	395.81	1.502
0.6000	0.0000	7.422	0.543	475.04	0.9642

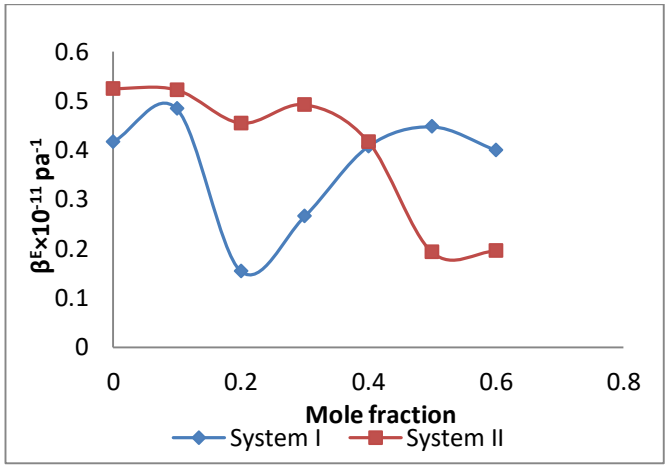

Fig.3.1: Excess values of Adiabatic compressibility Vs mole fraction of 1-ols

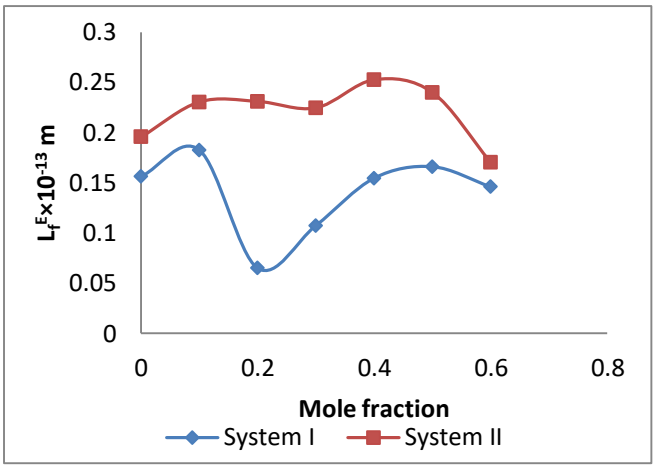

Fig.3.2: Excess values of Free length Vs mole fraction of 1-ols

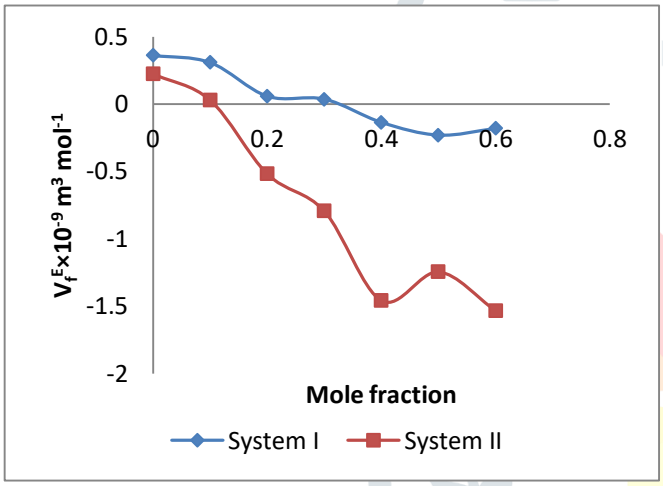

Fig.3.3 : Excess values of Free volume Vs mole fraction of 1-ols

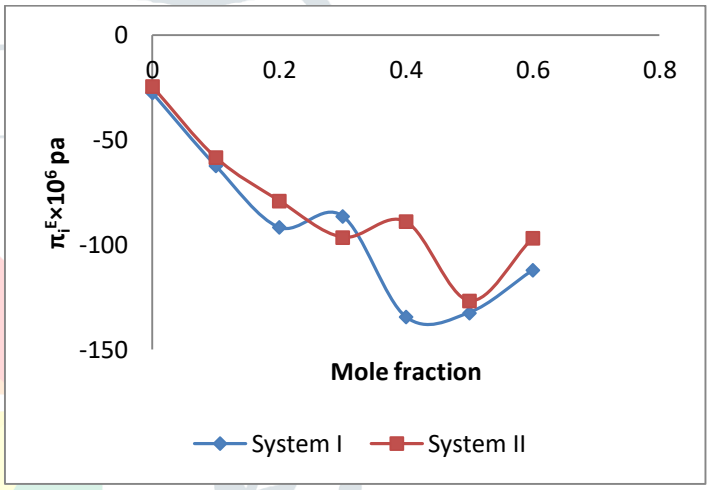

Fig.3.4:Excess values of Internal pressure Vs mole fraction of 1-ols

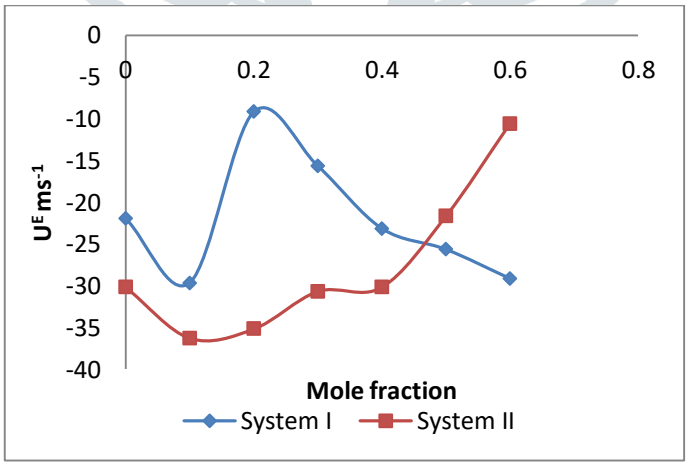

Fig.3.5: Excess values of Velocity Vs mole fraction of 1-ols

V. CONCLUSION

From the variations of ultrasonic velocity, density, viscosity, the calculated acoustical parameters and the sign and magnitude of excess functions like the positive values of β^E, $L_f{}^E$ and the negative values of v_f^E, Πi^E and U^E in the ternary mixtures suggest that the presence of weak dipolar and dispersive interaction between the component molecules in the mixtures. The average degree of cross-association of mixtures gradually decreases as the chain length of alkan – 1-ol is increases. Thus the

larger the chain length of 1-ol, the greater is the decrease in the average degree of association. The existence of molecular interaction in the mixture is in the order of 1- hexanol <1-pentanol. Hence there exists a weak molecular interaction between unlike molecules.

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