



Studies on Molecular Interaction in Ternary Liquid Mixtures

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Abstract: Ultrasonic velocity, density and viscosity for the ternary liquid mixtures of cyclohexanone with 1-propanol and 1-butanol in carbon tetrachloride were measured at 303 K. The acoustical parameters and their excess values were calculated. The trends in the variation of these excess parameters were used to discuss the nature and strength of the interactions present between the component molecules.

Keywords: Molecular interaction, Ternary liquid mixtures, Excess parameters.

Introduction

In recent years, the measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular interaction in pure liquid mixtures. The presence of both proton donors and acceptors in a liquid (type III) system normally leads to self association of the molecules¹. The addition of molecules containing either donors only (type I) or acceptors only (type II) to the type III system results in the breaking up of the self association and formation of new *H*-bonding between the unlike molecules. When type I molecules are added to the type III system there will be a competition between the donors of the two liquids for the acceptor site in the later. Better understanding of the interactions between these two types of molecules can be achieved by diluting the self associated liquid by an inert solvent which contains neither donors nor acceptors. At sufficiently low concentrations, the type III molecules completely unassociated. The addition of an excess of molecules either type I or type II to this dilute solution provides a convenient technique for the investigation of *H*-bonding and other interactions present in the mixture. In the present work the following four ternary systems are studied. (i) Cyclohexanone + 1-propanol + carbon tetrachloride, (ii) cyclohexanone + 1-butanol + carbon tetrachloride.

Experimental

The ultrasonic velocities of the liquid and liquid mixtures were measured using a single crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz. While measurements, the temperature of the liquid samples were maintained constant at 303 K by water circulation from an electronically controlled constant temperature water bath having an accuracy of ± 0.01 K. An Oswald's viscometer calibrated with double distilled water was used for the measurement of viscosities in the mixtures. The values were accurate to ± 0.001 Nsm⁻². The densities of the mixture were measured using a specific gravity bottle and the accuracy in the measurement was 0.01 kg m⁻³. The adiabatic compressibility (β), free length (L_f), molar volume (V) and internal pressure (π_i) were calculated using the well known equations. The excess acoustical compressibility (β^E), free length (L_f^E) and internal pressure (π_i^E) were calculated using the well known equations. The excess acoustical parameters were calculated as,

$$A^E = A_{\text{exp}} - [X_1 A_1 + X_2 A_2 + X_3 A_3] \quad (1)$$

Where A is any acoustical parameter and X the mole fraction of the liquid component.

Results and Discussion

The measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) at 303 K and the excess values of acoustical parameters for the ternary liquid mixtures are furnished in the Table 1.

Table 1. Values of experimental density (ρ), viscosity (η) and ultrasonic velocity (u) and their excess acoustical parameters (β^E , L_f^E , V^E , π_i^E) of the ternary mixtures at 303 K.

Mole Fraction		ρ	η	U	$\beta^E \times 10^{-11}$	L_f^E	$V^E \times 10^{-7}$	π_i^E
X_1	X_2	kg m ⁻³	$\times 10^{-3}$ Nsm ⁻²	ms ⁻¹	N ⁻¹ m ²	$\times 10^{-12}$ m	m ³ mol ⁻¹	$\times 10^6$ Pa
(i) Cyclohexanone (X_1) + 1- Propanol (X_2) + Carbon tetrachloride (X_3)								
0.0000	0.6999	1069.33	1.7005	1032.9	1.201	0.426	1.059	-49.76
0.2004	0.4996	1087.25	1.5168	1094.3	-2.866	-0.819	-0.788	-92.14
0.3502	0.3498	1098.72	1.5496	1136.7	-4.166	-1.271	-1.720	-77.32
0.4000	0.2997	1101.85	1.5676	1150.2	-4.314	-1.355	-1.454	-70.01
0.5997	0.1007	1112.96	1.7276	1195.3	-3.292	-1.046	-1.109	-20.65
0.6998	0.0000	1118.20	1.8976	1213.8	-2.088	-0.658	-0.486	18.94
(ii) Cyclohexanone (X_1) + 1 – Butanol (X_2) + Carbon tetrachloride (X_3)								
0.0000	0.7000	11036.26	2.0498	1067.6	1.322	0.461	2.769	-36.03
0.2004	0.4997	1064.46	1.7148	1114.5	-1.823	-0.495	1.007	-74.92
0.3498	0.3502	1083.57	1.6627	1145.7	-2.763	-0.802	-1.274	-65.36
0.4000	0.3000	1087.79	1.6487	1157.9	-3.036	-0.905	-1.153	-62.17
0.5998	0.1002	1109.93	1.7536	1196.4	-2.780	-0.869	-1.054	-16.94
0.6998	0.0000	1118.20	1.8976	1213.8	-2.088	-0.658	-0.486	18.94

The results presented in Table 1 shows the non-ideal behaviour of the liquid mixture. If the mixtures are ideal, then all the excess values should have been zero. The deviations, either positive or negative, suggest the mixtures are non-ideal³.

It can be observed from the Figure 1 that the β^E values are initially positive for the two systems of alcohols diluted with carbon tetrachloride and with zero concentration of cyclohexanone. The addition of carbon tetrachloride to the self associated alcohols breaks the self association and almost all the dipoles are freed due to the rupture of *H*-bonding. This results in an increase in volume and so greater compressibility for the systems. When cyclohexanone is added to these systems the dipoles of cyclohexanone interact with the free dipoles of alcohols. These will be dipole - dipole interaction as well as formation of new *H*-bonds

between the unlike molecules. These facts are clearly evident from Figure 1, which exhibits decreasing trend in β^E values as the concentration of cyclohexanone increases. Further due to polar nature of cyclohexanone and alcohols dipole –dipole interaction prevail in these systems. Similar results were reported by Venkatesu and Prabhakar Rao³ in the ternary mixtures of *N,N*-dimethylformamide + cyclopentanone +1- alkanols.

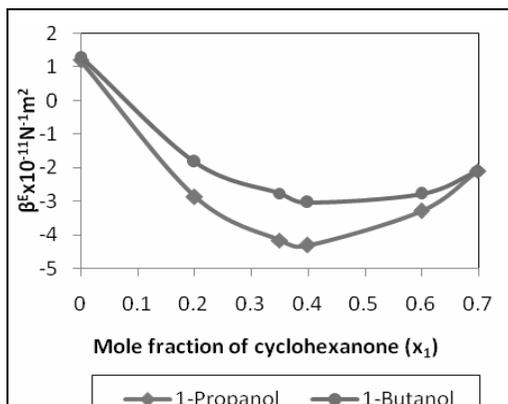


Figure 1. Variation of excess adiabatic compressibility *versus* mole fraction of cyclohexanone (X_1)

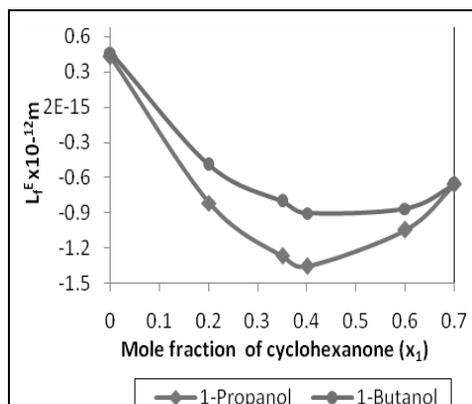


Figure 2. Variation of excess free length *versus* mole fraction of cyclohexanone (X_1).

The β^E values are also negative for the ternary systems containing 1- propanol and 1- butanol. In the systems studied, as the concentration of cyclohexanone increases, β^E values become less negative indicating the weak molecular interaction between the molecules of the system⁴. Similar results were reported by Rajendra Naidu and Ramachandra Naidu⁵ for the ternary systems of methyl ketone and 1-alkanols in *n*-nonane. Since L_f is directly related to the β values similar trends are observed for L_f^E , in the systems as shown in Figure 2.

It can be observed from Figure 3, the V^E values shows less variation with the increase in concentration of cyclohexanone .The negative values of V^E in all the systems may be attributed to the presence of dipole-dipole interaction. The values of π_i^E are almost negative as shown in Figure 4 for the systems studied .This suggests that dipole and dispersive forces are operative in these systems^{6,7}.

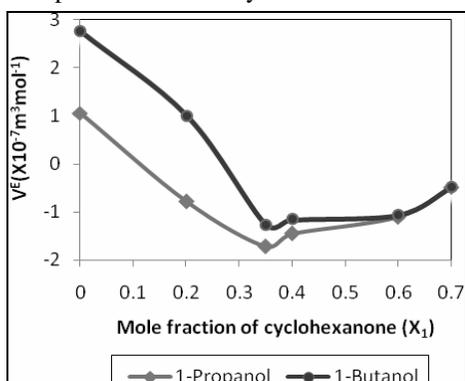


Figure 3. Variation of excess molar volume *versus* mole fraction of cyclohexanone (X_1).

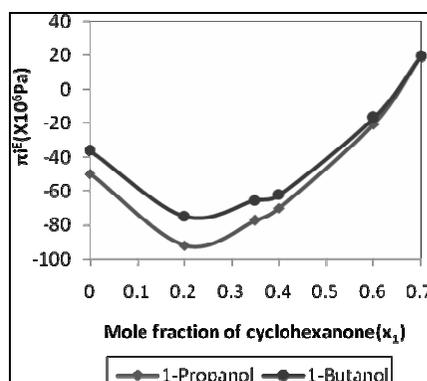


Figure 4. Variation of excess internal pressure *versus* mole fraction of cyclohexanone (X_1).

Conclusion

From the observed trends in the variation of excess values of the different acoustical parameters it may be concluded that dispersive and weak interactions are present in the systems studied.

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