THERMO ACOUSTICAL STUDIES OF MOLECULAR INTERACTION IN THREE COMPONENT LIQUID SYSTEM AT 303, 308 AND 313 K

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ABSTRACT

The ultrasonic velocity (U), density (ρ) and viscosity (η) measurements have been carried out in three ternary liquid mixtures of tetrahydrofuran (THF) + hexane + decane, tetrahydrofuran (THF) + heptane + decane and tetrahydrofuran (THF) + octane + decane at 303, 308, 313 K. The experimental data have been used to calculate some acoustical and thermodynamical parameters such as adiabatic compressibility, freelength, specific acoustic impedance, free volume, internal pressure, viscous relaxation time and Gibb's free energy. The results of these parameter have been explained on the basis of molecular interaction among the components of the mixture.

Keywords: Ultrasonic velocity, freelength, viscous relaxation time and Gibb's free energy

INTRODUCTION

In recent years the measurements of ultrasonic velocity have been employed to understand the nature of molecular interaction in pure liquids and liquid mixtures[1-3].The acoustics and thermo dynamics study of ternary liquid mixtures of non-electrolytes have not received as much attention as that of the acoustics and thermodynamics study of binary liquid mixtures. It is therefore, interesting to estimate acoustical and thermodynamical deviations for systems with more than two components. The objective of this paper is to present the results of acoustical and thermodynamical study on the molecular interaction in ternary mixtures containing tetrahydrofuran (THF) with Pseudo binary mixtures of n-alkanes. The n-alkanes and THF have been studied extensively in view of their importance in the petrochemical industries, particularly in the light of present day trends toward heavier feed stocks[4-5], A knowledge of thermophysical properties of mixtures of the organic liquids is of great importance in various fields of petro-chemical industry and technology. In contrast to the mixtures of n-alkanes, which have been studied comprehensively, the mixtures of n-alkanes and THF substituents are less well understood.

Tetrahydrofuran (THF), commercially known as cellosolves is considered as a good industrial solvent. It figures prominently in the high energy battery industry and has found its application in the organic synthesis as manifested from medium[6]. THF + n-alkanes binary mixtures are also important owing to hydrogen bonding between n-alkanes and tetrahydrofuran. Hence, the present investigation has been undertaken to provide better understanding

of the nature of the THF with binary mixtures of n-alkanes system and to throw light on molecular interaction.

MATERIALS AND METHODS

All the chemicals used in this present research work are analytical reagent(AR)and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merck Germany and Sdfine chemicals India as such used without further purification. Fresh conductivity water was used throughout the investigation. The purities of the above chemicals were checked by density determination at 303, 308, 313 K ± 0.1K which showed an accuracy of ± $1x10^{-4}$ gcm^{-3} with the reported values[7-8]. The ternary liquid mixtures of different known compositions were

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prepared in stopper measuring flasks. The density, viscosity and velocity were measured as a function of composition of the ternary liquid mixture at 303, 308 and 313 K for several Pseudo binary systems in which THF was added to a binary mixture of components 2(hexane nC_6, heptane nC_7, and octane nC_8) and 3 (decane nC_{10}), having the fixed mole ratios x_2/x_3. For this purpose, binary mixtures with $x_2/x_3 \cong 0.3$ was prepared by weighing. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kgm^{-3}. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An Ostwald's viscometer (10 ml) was used for the viscosity measurement and the efflux time was determined using a digital chronometer to within ±0.01s. An ultrasonic interferometer having the frequency of 3 MHz with an overall accuracy of ± 2 ms^{-1} was used for ultrasonic velocity measurement. An electronically digital operated constanttemperature bath (Raaga Industries) was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.1 K.

THEORY AND CALCULATIONS

Various acoustical and thermodynamical parameters are calculated from the measured data such as Adiabatic Compressibility $\beta = \frac{1}{U^2\rho}$ …(1)

Intermolecular free length $L_f = K\sqrt{\beta}$ …(2)

where K is a temperature dependent constant. Its values are 631×10^{-6}, 636×10^{-6} and 642×10^{-6} respectively at 303, 308 and 313 K.

Specific acoustic impedance can be calculated using the following relation $Z = U\cdot\rho$ …(3)

Where U is the ultrasonic velocity and ρ is the density.

Free volume $V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{3/2}$ …(4)

where M_{eff} is the effective molecular weight (=$\Sigma m_i x_i$, in which m_i and x_i are the molecular weight and the 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 …(5)

where b is the cubic packing which is assumed to be 2 for all liquids and solutions, η the viscosity, R is a gas constant and T absolute temperature.

The Gibb's energy can be estimated from the following relation.…(6)

Where K is the Boltzmaan's constant (1.23×10^{-23} JK^{-1}), T the absolute temperature, 'h' the Planck's constant and τ is the relaxation time ().

RESULTS AND DISCUSSION

The experimental values of density, viscosity and ultrasonic velocity for the three ternary mixtures viz., THF + hexane + decane, THF + heptane + decane and THF + octane + decane at 303, 308, 313 K are summarized in Table-1. The acoustical and thermodynamical parameters such as adiabatic compressibility(), intermolecular free length (L_f), specific acoustic impedance (Z), free volume (V_f), internal pressure (π_i), viscous relaxation time (τ) and Gibb's free energy (ΔG) are presented in Tables 2-3.

In all the three systems (Table-1) the values of density and viscosity increases with increase in concentration of THF, but it decreases with increase in temperature. The density increases with increase in concentration of THF suggest, a strong electrolytic nature in which the THF tends to attract the alkanes mixtures. The measurement of viscosity in ternary mixtures provides some reliable information in the study of molecular interaction. The gradual increase in density and viscosity with increasing the concentration of THF at all temperatures suggest the strong molecular interaction between the mixtures.A rise in temperature leads to less ordered structure and more spacing between the molecules. The decrease in density and viscosity with temperature indicates decrease in intermolecular forces due to increase in the thermal energy of the systems, which causes increase in volume expansion and hence increase in free path length.The ultrasonic velocity (Table-1) decreases with increase in the concentration of THF as well as with rising of temperature. Decrease in ultrasonic velocity may be attributed to the strong interaction and also due to increase in the mobility of THF. The increase of thermal energy weakens the molecular forces and hence the decrease in velocity is expected.

From Table-2 it is found that the adiabatic compressibility and free length increases with increasing

the concentration of THF as well as temperature in all the three systems studied. The increase in free length and compressibility implies that there is enhanced molecular interaction in these systems(Fort et.,al, 1965), as the new entities (Formed due to molecular interaction) become compact and less compressible. The increase in temperature, however, makes the free length to increase, as expected due to the thermal expansion of the liquids. Hence it is well clear that the intermolecular free length is the determining factor to the nature of variation of ultrasonic velocity in the mixtures.The decrease in velocity and increase in compressibility were attributed to the formation of hydrogen bonds between THF and alkane mixtures. Table-2 shows the values of specific acoustic impedance and it increases with increasing the concentration of THF, however it is found to decrease with rise of temperature. The observed decreasing behaviour can be explained on the basis of lyophobic interaction between the components of mixture, which increases the intermolecular distance, making relatively wider gap between the molecules, with elevations of temperatures and becoming responsible for the propagation of ultrasonic waves(Mehrotra et., al 1988).The following observations have been made from the Table-3. (i) the values of free volume decreases with increasing the concentration of THF in all systems studied, but, however, it is found to increase with rising of temperatures; (ii) the values of internal pressure increases with increasing of THF, as well as with rising of temperatures in all systems; (iii) the values of viscous relaxation time and Gibb's energy increases with increase in concentration of THF and temperature too.

The magnitude of free volume is lesser in system III than the other two systems which reveals a strong molecular interactions between the components of the mixture. The continuous decrease in free volume leads to a closer packing of the molecule inside a shield which may be brought about by the increase in the magnitude of interaction(Srinivasalu et., al 1995).The increasing behaviour of internal pressure suggest the strengthening of cohesive forces, and perhaps due to making up the structure of alkane mixtures. The viscous relaxation time which is in the order of 10^{-10} s is due to structural relaxation process . The observed behaviour of viscous relaxation time shows the presence of molecular interaction with addition of THF concentration. This is further confirmed by Gibb's free energy parameter. The increasing positive values of Gibb's free energy suggest that the closer approach of unlike molecules is due to hydrogen bonding. Recently Ali(Ali et., al 2000) attributed the increasing positive values of ΔG in few ternary liquid mixtures, to hydrogen bond formation between unlike molecules, which supports the present investigation.

CONCLUSIONS

Ultrasonic method is a powerful probe for characterising the physico-chemical behaviour and existence of molecular interactions in the mixture. In addition, the density, viscosity and the computed acoustical and thermodynamical parameters provide evidence of confirmation. Hence, it is concluded that the appreciable molecular interactions exist in these mixtures which may be due to the presence of hydrogen bonding between THF and alkane mixtures. From the magnitude of free volume, the existence of molecular interactions in the mixture is in the order: THF + hexane+decane < THF + heptane + decane < THF + octane + decane. The interaction tends to be weaker due to the presence of weak intermolecular forces and thermal dispersion forces with elevation of temperatures.

Table 1. Values of density (ρ),viscosity (η) and ultrasonic velocity (U) at 303, 308 and 313 K.

Mole fraction	*ρ/(kgm^{-3})*			*η/(×10^{-3} Nsm^{-2})*			*U/(ms^{-1})*		
x_1	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System-I : tetrahydrofuran (x_1) + hexane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	673.7	671.5	667.7	0.4241	0.4203	0.3980	1136.0	1099.2	1047.0
0.1	678.2	676.6	675.8	0.4055	0.4018	0.3850	1176.3	1135.7	1075.8
0.2	697.8	694.5	685.4	0.4152	0.4071	0.3871	1159.1	1120.0	1063.8
0.3	700.6	695.6	693.3	0.4155	0.4077	0.3879	1154.8	1118.7	1057.2
0.4	712.2	710.9	700.0	0.4209	0.4093	0.3882	1143.2	1105.4	1051.8
0.5	721.4	719.5	710.7	0.4250	0.4119	0.3929	1130.0	1098.6	1039.2
System-II : tetrahydrofuran (x_1) + heptane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	689.0	688.7	683.8	0.5154	0.4357	0.4098	1157.0	1103.0	1048.0
0.1	697.7	693.6	692.2	0.4366	0.4230	0.3979	1189.0	1143.7	1079.6
0.2	703.6	702.6	701.5	0.4374	0.4256	0.4010	1171.1	1 134.1	1068.0
0.3	719.2	714.9	709.5	0.4417	0.4316	0.4034	1146.0	1123.8	1062.5
0.4	723.0	720.9	715.2	0.4457	0.4337	0.4052	1142.2	1116.2	1055.2
0.5	735.4	731.2	727.8	0.4496	0.4384	0.4109	1130.0	1106.7	1045.5
System-III : tetrahydrofuran (x_1) + octane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	697.1	696.5	696.1	0.5546	0.5356	0.4969	1178.0	1137.6	1069.0
0.1	706.7	702.3	700.2	0.5247	0.5059	0.4812	1199.0	1175.7	1141.8
0.2	710.1	709.2	704.7	0.5254	0.5064	0.4829	1193.5	1169.4	1137.2
0.3	716.2	714.8	712.0	0.5266	0.5077	0.4864	1185.5	1 161.2	1130.6
0.4	728.0	723.4	722.3	0.5289	0.5122	0.4875	1175.5	1153.4	1120.9
0.5	735.8	731.1	728.5	0.5311	0.5133	0.4934	1163.1	1145.9	1112.1

Table 2.Values of adiabatic compressibility (β), freelength (L_f), and specific acoustic impedance(Z) at 303, 308 and 313K.

Mole fraction	*β/(×10^{-10} m^2 N^{-1})*			*L_f/(×10^{-10} m)*			*Z/(×10^4 Kgsm^{-2})*		
x_1	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System-I : tetrahydrofuran (x_1) + hexane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	11.50	12.33	13.66	214.00	223.28	237.30	7.65	7.38	6.99
0.1	10.66	11.46	12.79	205.98	215.30	229.56	7.98	7.68	7.27
0.2	10.67	11.48	12.89	206.08	215.49	230.52	8.08	7.77	7.29
0.3	10.70	11.49	12.90	206.45	215.54	230.64	8.09	7.78	7.33
0.4	10.74	11.51	12.91	206.84	215.80	230.70	8.14	7.85	7.36
0.5	10.86	11.52	13.03	207.92	215.84	231.74	8.15	7.90	7.38
System-II : tetrahydrofuran (x_1) + heptane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	10.84	11.93	13.32	207.77	217.72	234.27	7.97	7.60	7.17
0.1	10.13	11.02	12.39	200.92	211.15	226.03	8.29	7.93	7.47
0.2	10.36	11.07	12.49	203.14	211.58	226.97	8.23	7.97	7.49
0.3	10.59	11.08	12.50	205.32	211.66	226.98	8.24	8.03	7.54
0.4	10.60	11.13	12.55	205.47	212.23	227.51	8.25	8.05	7.55
0.5	10.65	11.17	12.57	205.92	212.53	227.62	8.31	8.09	7.60
System-III : tetrahydrofuran (x_1) + octane (x_2) + decane (x_3) [x_2/ x_3 = 3:1]									
0.0	10.34	11.09	12.57	202.88	211.82	227.59	8.21	7.92	7.44
0.1	9.84	9.90	9.93	197.97	200.16	202.35	8.47	8.26	7.99
0.2	9.89	10.31	10.97	198.45	204.24	212.68	8.48	8.29	8.01
0.3	9.93	10.38	10.99	198.89	204.87	212.82	8.49	8.30	8.05
0.4	9.94	10.39	11.01	198.96	205.03	213.11	8.55	8.34	8.09
0.5	10.04	10.42	11.11	200.01	205.28	214.00	8.56	8.38	8.10

Table 3. Values of free volume (V_f) , internal pressure (π_i), viscous relaxation time (τ) and Gibb's free energy (ΔG) at 303, 308 & 313 K

Mole fraction	$V_f/(\times 10^{-7} m^3\ mol^{-1})$			$\pi_i/(\times 10^8\ Nm^{-2})$			$\tau/(\times 10^{-10}\ s)$			$\Delta G/(\times 10^{-20}\ KJ\ mol^{-1})$		
x_1	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	318 K
System-I : tetrahydrofuran (x_1) + hexane (x_2) + decane (x_3) [x_2/x_3 = 3:1]												
0.0	4.30	4.46	4.62	2.39	2.45	2.48	6.504	6.907	7.250	3.059	3.133	3.215
0.1	4.78	4.86	5.06	2.41	2.46	2.49	5.709	6.139	6.563	3.011	3.094	3.176
0.2	4.54	4.56	4.65	2.53	2.56	2.58	5.905	6.230	6.654	3.023	3.099	3.181
0.3	4.34	4.39	4.47	2.58	2.64	2.68	5.930	6.244	6.667	3.025	3.100	3.182
0.4	4.17	4.18	4.21	2.70	2.75	2.76	6.029	6.283	6.683	3.031	3.103	3.183
0.5	4.00	4.05	4.08	2.77	2.81	2.84	6.152	6.324	6.825	3.039	3.105	3.191
System-II : tetrahydrofuran (x_1) + heptane (x_2) + decane (x_3) [x_2/x_3 = 3:1]												
0.0	4.27	5.12	5.20	2.14	2.19	2.21	6.852	6.933	7.275	3.078	3.140	3.216
0.1	5.39	5.42	5.45	2.20	2.21	2.26	5.902	6.217	6.576	3.023	3.099	3.177
0.2	5.04	5.05	5.09	2.28	2.33	2.36	6.044	6.280	6.682	3.032	3.103	3.183
0.3	4.67	4.70	4.78	2.43	2.46	2.47	6.235	6.374	6.715	3.043	3.108	3.185
0.4	4.42	4.45	4.52	2.52	2.56	2.57	6.301	6.439	6.784	3.047	3.112	3.189
0.5	4.15	4.18	4.23	2.65	2.67	2.70	6.384	6.528	6.887	3.052	3.117	3.194
System-III : tetrahydrofuran (x_1) + octane (x_2) + decane (x_3) [x_2/x_3 = 3:1]												
0.0	4.60	4.60	4.69	2.11	2.14	2.16	7.644	7.923	8.329	3.119	3.191	3.268
0.1	4.85	4.97	5.13	2.14	2.15	2.17	6.886	6.948	7.029	3.080	3.141	3.200
0.2	4.56	4.67	4.81	2.25	2.26	2.28	6.926	6.963	7.066	3.083	3.142	3.205
0.3	4.28	4.38	4.49	2.36	2.38	2.39	6.976	7.020	7.126	3.085	3.145	3.208
0.4	4.01	4.09	4.22	2.49	2.50	2.51	7.011	7.097	7.163	3.087	3.149	3.209
0.5	3.76	3.87	3.92	2.61	2.62	2.64	7.114	7.130	7.302	3.093	3.154	3.210

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