Acoustical and Excess Thermodynamical Studies of Molecular Interaction in Ternary Organic Liquid Mixture

S.BALAKRISHNAN[1] **& R.PALANI** [2]

[1]Department of Physics, Achariya college of Engineering Technology, Puducherry
[2] Department of Physics, DDE, Annamalai University, Annamalainagar, Tamil Nadu, India
e-mail: bala.phy@gmail.com

Abstract

Ultrasonic velocity (U), density (ρ) and viscosity (η) for the ternary liquid mixtures of tetrahydrofuran+octane+decane, have been measured as a function of the composition at 303, 308 and 313 K. The experimental data have been used to calculate some excess thermodynamical parameters such as viscosity (η^E), adiabatic compressibility (β^E), free length (L^E_f), free volume (V^E_f), internal pressure (π^E_i) and Gibb's free energy (ΔG^E). The results have been discussed and interpreted in terms of weak molecular interaction.

Keywords: Ultrasonic velocity, Excess adiabatic compressibility and Excess internal pressure.

Introduction

Ultrasonic velocity measurements find wide applications in characterizing the physico-chemical behavior of liquid mixtures [1]. Molecular interactions play an important role in understanding the structures and properties of liquids. The molecular interaction study from the variation of acoustical parameters and their excess values with composition gives insight in to the molecular process [2].The acoustics and thermodynamic study of ternary liquid mixtures of non-electrolytes have not received as much attention as that of binary liquid mixtures. It is therefore , interesting to estimate excess acoustical and thermodynamical deviation for system with more than two components.

The present work deals with the ultrasonic velocity and computation of related excess parameters in ternary system of tetrahydrofuran+octane+decane. The chemicals used in this work are chosen for their several applications in industries. 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[3]. Octane is an un-branched isomer, widely used as cheap, relatively safe and easily evaporated non-polar solvent. Decane is non-polar and does not dissolve in polar liquids. It is a component of automotive fuels and also used in gas chromatography as standard. A knowledge of thermophysical properties of mixtures of the organic liquids is of great importance in various field of petro-chemical industry and technology. In contrast to the mixtures of n-alkanes, which have been studied comprehensively, the mixtures of THF substituents are less well understood.

In the present study, the measurements on ultrasonic velocity, density and viscosity and their related excess thermodynamical and transport parameters for the system tetrahydrofuran +octane+decane at 303, 308 and 313 K have been undertaken. The dependence of excess parameters on composition has been used to explain the nature and extent of intermolecular interactions in the mixture.

Experimental Details

All the chemical used are of analytical reagent (AR) and spectroscopic reagent (SR) without further purification. The purities of the above chemicals were checked by density determination at 303, 308 and 313 $\pm$ 0.1 K, which showed an accuracy of $\pm 1\times10^{-4}$ gcm^{-3} with the earlier values[4,5]. The ternary liquid mixtures of different known compositions were 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 mixed solvent system in which THF was added to a binary mixtures of octane and decane. For this purpose binaries with fixed volume ratios $X_2/X_2 \cong 3:1$ were prepared. 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. Efflux time was determined using a digital chronometer within ± 0.01 s. An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of $\pm 0.1\%$ has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) 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 is ± 0.1 K.

Theory and Calculation

Various acoustical and thermodynamical parameters
calculated from the measured data are as follows:

Adiabatic compressibility

$$\beta = \frac{1}{U^2\rho} \qquad \text{…(1)}$$

Intermolecular free length

$$L_f = K\,\beta^{1/2} \qquad \text{… (2)}$$

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

Free volume

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

where M_{eff} is the effective molecular weight ($M_{eff}=\Sigma m_i x_i$, 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

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

where b is the cubic packing which is assumed to be 2 for all liquids and solutions. R is the universal gas constant.

Gibb's free energy

$$\Delta G = KT\ln\left(\frac{KT\tau}{h}\right) \qquad \text{… (5)}$$

where K is Boltzmann's constant (1.38×10^{-23} JK^{-1}), T is the absolute temperature, h the Planck's constant (6.626×10^{-34}Js) and τ is the relaxation time [$\tau=(4/3)\eta\beta$].

Excess values of the above parameters can be determined using:

$$A^E = A_{exp} - A_{id} \qquad \text{… (6)}$$

where $A_{id} = \Sigma A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid component.

Results and Discussion

The values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids and liquid mixtures at 303, 308 and 313 K are given in Tables 1 and 2. The values of excess viscosity (η^E), excess adiabatic compressibility (β^E), excess free length ($L^E{}_f$), excess free volume ($V^E{}_f$), excess internal pressure ($\pi^E{}_i$) and excess Gibb's free energy (ΔG^E) have been calculated and presented in Table 3.

The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of the liquid mixtures. The sign and magnitude of deviation of excess properties depend on the strength of the interaction between unlike molecules. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions[6].

Table 1. Comparison of experimental values of density(ρ), viscosity(η) and ultrasonic velocity(U) of pure liquids at 303, 308 and 313 K with literature values

Organic liquids	T (K)	ρ/(kg m^{-3})		η/(x10^{-3} Nsm^{-2})		U/(ms^{-1})	
		Expt.	Lit	Expt.	Lit	Expt.	Lit
tetrahydrofuran	303	875.9.0	875.2[4]	0.6450	0.6455[4]	1242.2	1240.1[4]
	308	869.6	870.1[4]	0.6116	0.6120[4]	1218.0	1222.1[4]
	313	864.3	864.5[4]	0.5609	0.5600[4]	1190.6	1186.4[4]
octane	303	693.4	693.9[5]	0.4961	0.4910[5]	1146.2	1148.0[5]
	308	690.0	690.4[5]	0.4509	0.4500[5]	1129.0	1132.0[5]
	313	686.8	687.0[5]	0.4170	0.4150[5]	118.4	1120.0[5]
decane	303	719.0	-	0.8562	-	1194.0	-
	308	710.1	-	0.8339	-	1156.2	-
	313	701.9	-	0.8174	-	1109.2	-

A perusal of Table 3 shows that the excess viscosity is negative throughout the whole range of concentration. The excess viscosity increases with increase in mole fraction of THF at all temperatures. The negative values of excess viscosity can be attributed to the presence of dispersion, induction and dipolar forces between the components[7].

Table 3 shows that the excess values of adiabatic compressibilities are positive and these value varies non-linearly with increasing the molefraction of THF at all temperatures. Fort et.al.,[8]found that the negative values of excess compressibilities indicates greater interaction between the components of the mixtures. Positive values in excess properties corresponds mainly due to the existence of dispersive forces. The negative values of β^E is associated with a structure forming tendency while a positive value is taken to indicate a structure breaking tendency due to the hetero-molecular interaction between the component molecules of mixtures. In the present investigation the positive deviation in β^E

have been attributed to dispersive forces that From table 3 it is observed that the variation of excess free length are positive and varies non-linearly with increasing concentration of THF at all temperatures. According to Ramamoorthy et. Al.,[9], negative values of excess intermolecular free length indicates that sound waves cover longer distances due to decrease in intermolecular free length ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Fort et.al.,[8] indicated that the positive values of excess free length can be attributed to the dispersive forces and negative values due to charge transfer, dipole-induced dipole and dipole-dipole interactions. Thus the positive excess values indicates that weak molecular interaction is present in the mixture. shows weak interaction between unlike molecules.

Table 2—Values of density (ρ), viscosity (η) and ultrasonic velocity (U) for tetrahydrofuran (X_1) +octane (X_2)+decane (X_3) [(X_2)/(X_3)]=3:1 at 303, 308 and 313 K .

Mole fraction (X_1)	ρ (kg m^{-3})	η ($\times10^{-3}Nsm^{-2}$)	U (ms^{-1})
303 K			
0.0	697.1	0.5546	1178.0
0.1	706.7	0.5247	1199.0
0.2	710.1	0.5254	1193.5
0.3	716.2	0.5266	1185.5
0.4	728.0	0.5289	1175.5
0.5	735.8	0.5311	1163.1
308 K			
0.0	696.5	0.5356	1137.6
0.1	702.3	0.5059	1175.7
0.2	709.2	0.5064	1169.4
0.3	714.8	0.5077	1161.2
0.4	723.4	0.5122	1153.4
0.5	731.1	0.5133	1145.9
313 K			
0.0	696.1	0.4969	1069.0
0.1	700.2	0.4812	1141.8
0.2	704.7	0.4829	1137.2
0.3	712.0	0.4864	1130.6
0.4	722.3	0.4875	1120.9
0.5	728.5	0.4934	1112.1

Table 3 gives a qualitative picture of the excess free volume for the three ternary liquid systems. This indicates the extent of deviation from ideal with the mole fraction of the mixtures. The excess values for the system was found to be positive. These values decreases with increasing the mole fraction of X_1 as well as with the rising of temperature. These changes in free volume can be explained in terms of molecular interaction, structural effect and interstitial accommodation. The sign of $V^E{}_f$ depends upon the relative strength between the contractive forces and expansive forces.

Table 3—Excess values of viscosity (η^E), adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E) and Gibb's free energy (ΔG^E) for tetrahydrofuran (X_1) +octane (X_2)+decane (X_3) $[(X_2)/(X_3)]$=3:1 at 303, 308 and 313 K .

Mole fraction (X_1)	**$-\eta^E$ ($\times10^{-4}$ N sm^{-2})**	**β^E ($\times10^{-10}$m^{2}N^{-1})**	**L_f^E ($\times10^{-10}$m)**	**V_f^E ($\times10^{-7}$m^{3}mol^{-1})**	**$-\pi_i^E$ ($\times10^{8}$Nm^{-2})**	**$-\Delta G^E$ ($\times10^{-21}$ KJ mol^{-1})**
303 K						
0.0	0.2402	0.2028	1.9453	0.0174	0.0114	3.5792
0.1	0.4996	0.3685	3.3100	0.4813	0.1991	3.4435
0.2	0.4530	0.0157	0.7152	0.4053	0.3068	3.2657
0.3	0.4013	0.3900	4.7005	0.3393	0.4144	3.0890
0.4	0.3387	0.7342	8.3157	0.2832	0.5021	2.9123
0.5	0.2771	1.1686	12.9111	0.2472	0.5998	2.7316
308 K						
0.0	0.1855	0.5353	5.0269	0.0316	0.0133	3.9060
0.1	0.3772	1.3498	12.8420	0.5000	0.1705	3.7162
0.2	0.2670	0.5642	4.9164	0.3616	0.2544	3.4754
0.3	0.1487	0.1187	0.4412	0.2333	0.3283	3.2325
0.4	-0.0015	0.2668	3.5640	0.1050	0.4022	2.9887
0.5	-0.1177	0.6723	7.6593	0.0466	0.4762	2.7439
313 K						
0.0	0.3520	0.0738	0.5791	0.0317	0.0255	4.1790
0.1	0.4209	2.3054	21.7871	0.5918	0.1692	4.0185
0.2	0.3158	0.8570	7.4246	0.4555	0.2640	3.7850
0.3	0.1927	0.4286	3.2523	0.3192	0.3588	3.5535
0.4	0.0936	0.0002	1.0700	0.2329	0.4436	3.3240
0.5	-0.0535	0.5080	5.9923	0.1166	0.5184	3.0946

The factors responsible for volume contraction are: (a) specific interaction between component molecules; (b) interstitial accommodation of molecules of one component in to the vacant spaces of molecules of the other components. This occurs preferentially when the size difference between the components molecules is large, or when large gaps are available in the structural network of molecules and (c) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vander waal's forces. The factors that cause expansion in volume are dispersion force, steric hindrance of component molecules, unfavourable geometric fitting and electrostatic repulsion.

The positive values of V^E_f (Table 3) for the system asserts that the combined effect of the factors responsible for volume contraction outweigh the combined effect of the factors causing volume expansion and vice-versa[10]. Adgaonkar et.al., [11], showed positive value of V^E_f, indicating the existence of weak molecular interaction in the liquid mixtures. However, in the present paper the observed behaviour of V^E_f shows the presence of weak molecular interaction between unlike molecules.

The variation of internal pressure may give some information regarding the nature and strength of the forces existing between the molecules. The excess internal pressure (Table 3) is negative and it decreases with the increase in molefraction of THF at all temperatures. The negative values of internal pressure indicates that only dispersion and dipolar forces are operating with complete absence of specific interaction.

The values of ΔG^E (Table 3) is negative and increases with increasing the molefraction of THF at all temperatures , but it is found to decrease with rising of temperature. According to Reed et al [12], the positive ΔG^E may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative values may be ascribed to the dominance of dispersion forces[13]. In the present study the observed behaviour of ΔG^E shows the existence of weak molecular interactions between the components of unlike molecules.

5.Conclusions

Ultrasonic method is a powerful tool for characterizing the physico-chemical properties and existence of molecular interaction in the mixture. The results of excess acoustical and thermodynamical property reveals the existence of weak molecular interaction between the components in the mixture, which may be due to the dominance of dispersion forces and dipolar interaction between the unlike molecules.

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