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# Thermo Acoustical studies on Molecular Interaction in Ternary Liquid mixtures

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## Abstract

*Ultrasonic velocity (U), viscosity ($\eta$) and Density ($\rho$) were measured for three component liquid system of tetrahydrofuran (THF)+heptane+decane at 303, 308 and 313 K. The excess values of various acoustical parameters such as viscosity ($\eta^E$), adiabatic compressibility ($\beta^E$), free length ($L^E_f$), free volume ($V^E_f$), internal pressure ($\pi^E_i$) and Gibb's free energy ($\Delta G^E$) have been calculated from the experimental data and discussed in terms of weak molecular interaction present in the mixtures.*

**Keywords:** Ultrasonic velocity, excess adiabatic compressibility, excessfree length, excess free volume.

## Introduction

In recent years to understand the nature of molecular interactions existing between liquid mixtures, the ultrasonic velocity measurements are widely used. Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure liquids, binary and ternary mixtures[1]. Ultrasonic velocity measurements are useful when dealing with the problems of structure and molecular interactions in liquids because of their accuracy[2]. The studies on volumetric, ultrasonic and viscometric properties of liquid mixtures and their dependence on composition and temperature are of importance in many fields of applied research and find applications in many important chemical, industrial and biological processes[3].

The study of liquid mixtures containing polar and non-polar components find applications in industrial and technological processes, as such liquid mixtures provide a wide range of solutions with appropriate properties. As a part of investigations on intermolecular interaction between the components of non-aqueous ternary mixtures by ultrasonic speed[4], an attempt has been made to study the interaction of THF polar molecules with non-polar binary mixture of heptane and decane. The chemicals used in this work are chosen for their several applications in chemical industries. THF is a polar heterocyclic compound. It is a versatile solvent mainly used as a precursor to polymers. Heptane 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 standards.

In the investigation, we presented the values of ultrasonic velocity, density and viscosity and evaluated their related excess thermodynamical parameters for the ternary system THF+heptane+decane at 303, 308 and 313 K. The dependence of excess parameter on composition has been used to explain the nature and extent of intermolecular interactions in the studied mixture.

## Material and Methods

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[1,5]. 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 heptane 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 $\pm 0.01$ kgm$^{-3}$. The weight of the sample was measured using electronic digital balance with an accuracy of $\pm 0.1$ 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 $\pm 0.01$ 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 $\pm 0.1$ K. Various acoustical and thermodynamical parameters calculated from the measured data are as follows:

Adiabatic compressibility

$$\beta = \frac{1}{U^2 \rho} \quad (1)$$

Intermolecular free length

$$L_f = K \beta^{1/2} \quad (2)$$

Where $K$ is temperature dependent constant. Its value is $631\times10^{-6}$, $636\times10^{-6}$ and $642\times10^{-6}$, respectively at 303, 308 and 313 K.

Free volume

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

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 $4.28\times10^9$ for all liquids.

Internal pressure

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

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

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

Where $K$ is Boltzmann's constant ($1.38\times10^{-23}$ $JK^{-1}$), $T$ is the absolute temperature, $h$ the Planck's constant ($6.626\times10^{-34}$Js) and $\tau$ is the relaxation time [$\tau=(4/3)\eta\beta$].

Excess values of the above parameters can be determined using:

$$A^E = A_{exp} - A_{id} \quad (6)$$

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 ($\rho$), viscosity ($\eta$) and ultrasonic velocity ($U$) of pure liquids and liquid mixtures at 303, 308 and 313 K are given in table-1 and table-2. The values of excess viscosity ($\eta^E$), excess adiabatic compressibility ($\beta^E$), excess free length ($L_f^E$), excess free volume ($V_f^E$), excess internal pressure ($\pi_i^E$) and excess Gibb's free energy ($\Delta G^E$) 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].

According to Fort.*et.al*[7], the excess viscosity gives the strength of the molecular interaction between the interacting molecules. The excess viscosity are found to be negative where dispersion, induction and dipolar forces are acting, while they are positive values where there is existence of specific interactions like hydrogen bonding and charge transfer. The excess viscosity (table-3) is negative through the whole range of concentration at all temperatures. From the analysis and close observation it is found that they decrease with the increase of mole fraction ($X_1$) whereas it increases with the raising of temperature. This behavior shows the existence of molecular interactions takes place between the components of the mixtures.

**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) | $\rho$/(kg m$^{-3}$) | | $\eta$/(x10$^{-3}$ Nsm$^{-2}$) | | $U$/(ms$^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | Expt. | Lit | Expt. | Lit | Expt. | Lit |
| tetrahydrofuran | 303 | 875.0 | 875.2[1] | 0.6450 | 0.6455[1] | 1242.2 | 1240.1[1] |
| | 308 | 869.6 | 870.1[1] | 0.6116 | 0.6120[1] | 1218.0 | 1222.1[1] |
| | 313 | 864.3 | 864.5[1] | 0.5609 | 0.5600[1] | 1190.6 | 1186.4[1] |
| heptane | 303 | 673.1 | 674.5[5] | 0.3712 | 0.3750[5] | 1112.6 | 1116.0[5] |
| | 308 | 670.2 | 670.3[5] | 0.3551 | 0.3500[5] | 1091.3 | 1092.0[5] |
| | 313 | 666.6 | 667.2[5] | 0.3257 | 0.3250[5] | 1070.5 | 1072.0[5] |
| decane | 303 | 719.0 | - | 0.8562 | - | 1194.0 | - |
| | 308 | 710.1 | - | 0.8339 | - | 1156.2 | - |
| | 313 | 701.9 | - | 0.8174 | - | 1109.2 | - |

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

| Mole fraction ($X_1$) | P (kg $m^{-3}$) | H ($\times10^{-3}$Nsm$^{-2}$) | U ($ms^{-1}$) |
|---|---|---|---|
| 303 K | | | |
| 0.0 | 689.0 | 0.5154 | 1157.0 |
| 0.1 | 697.7 | 0.4366 | 1189.0 |
| 0.2 | 703.6 | 0.4374 | 1171.1 |
| 0.3 | 719.2 | 0.4417 | 1146.0 |
| 0.4 | 723.0 | 0.4457 | 1142.2 |
| 0.5 | 735.4 | 0.4496 | 1130.0 |
| 308 K | | | |
| 0.0 | 688.7 | 0.4357 | 1103.0 |
| 0.1 | 693.6 | 0.4230 | 1143.7 |
| 0.2 | 702.6 | 0.4256 | 1134.1 |
| 0.3 | 714.9 | 0.4316 | 1123.8 |
| 0.4 | 720.9 | 0.4337 | 1116.2 |
| 0.5 | 731.2 | 0.4384 | 1106.7 |
| 313 K | | | |
| 0.0 | 683.8 | 0.4098 | 1048.0 |
| 0.1 | 692.2 | 0.3979 | 1079.6 |
| 0.2 | 701.5 | 0.4010 | 1068.0 |
| 0.3 | 709.5 | 0.4034 | 1062.5 |
| 0.4 | 715.2 | 0.4052 | 1055.2 |
| 0.5 | 727.8 | 0.4109 | 1045.5 |

The values of excess adiabatic compressibility ($\beta^E$) and excess free length ($L_f^E$) depends upon several physical and/or chemical contributions. The physical contribution consists of dispersion forces or weak dipole-dipole interaction that leads to positive values of $\beta^E$ and $L_f^E$. Chemical contributions include breaking up of the associates present in pure liquids, resulting in positive $\beta^E$ and $L_f^E$. As the values of $\beta^E$ and $L_f^E$ (table-3) are negative at lower molefractions of THF whereas positive at higher molefractions indicates the weakening of interaction between the component molecules[8]. The same trend is observed for the system at all the temperatures.

From the table-3, it is observed that the excess free volume $V_f^E$ and excess internal pressure $\pi_i^E$ are negative at all the temperature for the entire range of molefractions. According to Fort. *et. al*[7], the negative excess values of $V_f^E$ and $\pi_i^E$ is an indicative of weak interaction between the component molecules. Similar effect was observed by Das *et.al.,*[9]

The values of $\Delta G^E$ (table-3) is found to increase with the molefraction of THF content, but decreases with raising of temperature. According to Reed *et al*.[10], the positive $\Delta G^E$ may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative values may be ascribed to the dominance of dispersion forces[11]. From the observed behavior of $\Delta G^E$, weak molecular interactions may be existing between the components of the molecules.

## Conclusion

The ultrasonic method was found to be a powerful tool in characterizing the physico-chemical behavior of liquid mixtures. In the ternary liquid system, molecular interaction exists between the component molecules is suggested by the excess function calculated from the ultrasonic velocity, density and viscosity data. The values of $\eta^E$, $V_f^E$, $\pi_i^E$ and $\Delta G^E$ are found to be negative which shows the presence weak dipolar and dispersive interaction among the component molecules of the mixture.

**Table-3**
**Excess values of viscosity ($\eta^E$), adiabatic compressibility ($\beta^E$), free length ($L_f^E$), free volume ($V_f^E$), internal pressure ($\pi_i^E$) and Gibb's free energy ($\Delta G^E$) for tetrahydrofuran ($X_1$) +heptane ($X_2$)+decane ($X_3$) [($X_2$)/($X_3$)]=3:1 at 303, 308 and 313 K**

| Mole fraction ($X_1$) | $-\eta^E$ ($x10^{-4}$ N $sm^{-2}$) | $\beta^E$ ($x10^{-10}m^2N^{-1}$) | $L_f^E$ ($x10^{-10}$m) | $V_f^E$ ($x10^{-7}m^3mol^{-1}$) | $-\pi_i^E$ ($x10^8Nm^{-2}$) | $-\Delta G^E$ ($x10^{-21}$ KJ $mol^{-1}$) |
|---|---|---|---|---|---|---|
| 303 K | | | | | | |
| 0.0 | 0.2295 | -0.8250 | -7.6814 | 0.8684 | 0.0084 | 3.1889 |
| 0.1 | 0.6050 | -1 .1088 | -9.9236 | 0.5211 | 0.1634 | 3.1123 |
| 0.2 | 0.6436 | -0.4122 | -3.0957 | 0.4406 | 0.2984 | 2.9717 |
| 0.3 | 0.6472 | 0.2645 | 3.6922 | 0.3402 | 0.3633 | 2.8291 |
| 0.4 | 0.6537 | 0.7214 | 8.4501 | 0.3597 | 0.4883 | 2.6935 |
| 0.5 | 0.6612 | 1.2175 | 0.1351 | 0.3593 | 0.5732 | 2.5570 |
| 308 K | | | | | | |
| 0.0 | 0.4660 | -0.9703 | -0.1060 | 0.1864 | 0.0033 | 3.6424 |
| 0.1 | 0.5596 | -1.3771 | -0.1218 | 0.6783 | 0.1706 | 3.4750 |
| 0.2 | 0.5002 | -0.8240 | -6.7593 | 0.5001 | 0.2378 | 3.2627 |
| 0.3 | 0.4068 | -0.3115 | -1.6862 | 0.3420 | 0.2950 | 3.0493 |
| 0.4 | 0.3524 | 0.2420 | 3.8769 | 0.2838 | 0.3823 | 2.8370 |
| 0.5 | 0.2720 | 0.7850 | 9.1700 | 0.2057 | 0.4595 | 2.6236 |
| 313 K | | | | | | |
| 0.0 | 0.6433 | -0.8301 | -6.8717 | 0.4421 | .03009 | 4.0674 |
| 0.1 | 0.7321 | -1.2013 | -9.7822 | 0.8794 | 0.1743 | 3.8943 |
| 0.2 | 0.6710 | -0.5426 | -3.5126 | 0.7067 | 0.2685 | 3.6762 |
| 0.3 | 0.6169 | 0.0271 | 1.8269 | 0.5840 | 0.3528 | 3.4620 |
| 0.4 | 0.5688 | 0.6362 | 7.6865 | 0.5113 | 0.4470 | 3.2459 |
| 0.5 | 0.4816 | 1.2150 | 0.1312 | 0.4086 | 0.5113 | 3.0288 |

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