

Research Article

Excess Thermodynamic Properties of Ternary Liquid Mixture of Para-xylene, Cyclopentyl methyl ether and 1-Pentanol at 293.15 K

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Abstract

Ultrasonic velocity (U), density (ρ) and viscosity (η) for the ternary liquid mixture of 1-Pentanol, Cyclopentyl methyl ether and Para-xylene equimolar have been measured as a function of the composition at 293.15 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_f^E), free volume (V_f^E) and Gibb's free energy (ΔG^E). The viscosity data have been correlated by Grunberg and Nissan correlation equation. The results have been used to discuss the nature and strength of heterogeneous H-bond interactions in the mixture.

Keywords: Adiabatic compressibility, Density, Interactions, Viscosity, Ultrasonic velocity

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Introduction

The study of excess thermodynamic properties are considerable interest in understanding the intermolecular interactions of liquid mixtures containing aromatic hydrocarbons and higher alkanol [1-2]. The practical importance of liquid mixtures rather than single component liquid systems has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physico-chemical behavior of such systems [3- 4]. The formation of molecular clusters and network structures due to strong intermolecular interactions through H-bonds in alcohols results in their complicated molecular structures in liquid state. The liquids were selected on the basis of their industrial use [5]. The characterization of heterogeneous interactions between associating polar liquids in binary mixtures over the entire concentration range using other studies have been the subject of several investigations [6-7]. Adiabatic compressibility, free volume, internal pressure and free length are strongly correlated with each other and support for strong interaction [8]. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures [9]. The present work is a part of systematic study on thermodynamic properties of ternary organic liquid mixtures containing molecules of significantly different sizes [10].

Para-xylene is a colorless, flammable, liquid hydrocarbon with a characteristic aromatic odor. It is commonly found in products such as varnish, ink, paint thinners, degreasers, and insecticides. Its like benzene and toluene are major components of gasoline and fuel oil. The primary uses of Para-xylene industrially is as solvent and synthetic intermediate. Commercial Para-xylene is often contaminated with other organic compounds such as ethyl benzene, toluene, benzene, trimethylbenzene, phenol, thiophene and pyridine [11]. 1-Pentanol is a colourless liquid with a distinctive aroma. 1-Pentanol, also known as 1-pentyl alcohol belongs to the class of organic compounds known as primary alcohols. Thus, 1-pentanol is considered to be a fatty alcohol. 1-Pentanol exists in all eukaryotes, ranging from yeast to plants to humans. 1-Pentanol is one of the promising "next generation" alcohol fuels with high energy density and low hygroscopicity. 1-Pentanol is used as a key starting material in the production of dichloro-acetic acid pentyl ester, 2-methyltetrahydrofuran, dinpenyl ether (DNPE), pentyl butyrate and amyl acetate. As a solvent, it is used for coating CDs and DVDs [12]. Cyclopentyl methyl ether is considered a key asymmetric ether in organic chemistry for its widespread use as an environmentally friendly solvent. This hydrophobic solvent has low solubility in water and good stability under acidic and basic conditions. However, CPME can only be a "green" and bio-based solvent if prepared from renewable raw materials. Nevertheless, biomass is a sustainable and renewable alternative to petroleum-derived specialty chemicals [13]. The H-bond has a considerable effect on the excess thermodynamical parameters of the ternary mixtures of the associating molecules. The evaluation of excess thermodynamical parameter properties over the entire concentration range provides information about the formation of heterogeneous molecular interaction and also about the molar ratio corresponding to the formation of the strongest H-bonded interactions between the mixture constituents. In the present work, density, viscosity and ultrasonic measurements on ternary mixture of Para-xylene, Cyclopentyl methyl ether and 1-Pentanol at 293.15K temperature was carried out, in order to get ideas about the formation of the H-bonded structure over the entire concentration variation of the mixture

constituents. This research is concerned to the systematic study of molecular interactions in the ternary mixtures, which are important in many fields of industrial and biological processes. Mixed solvents find practical applications as they provide wide range of mixtures with desired properties

Materials and Methods

Para-xylene, Cyclopentyl methyl ether and 1-Pentanol are used of analytical reagent (AR) and spectroscopic reagent (SR) without further purification. The purities of the above chemicals were checked by density determination at 293.15 K, which showed an accuracy of $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$. The ternary liquid mixture of different known compositions were prepared in stopper measuring flasks. The density, velocity and ultrasonic velocity were measured as a function of composition of the ternary liquid mixture at 293.15 K for mixed solvent systems in which 1- Pentanol, Para-xylene and Cyclopentyl methyl ether equimolar were added. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kg m}^{-3}$. The weight of the sample was measured using electronic digital balance with an accuracy of $\pm 0.1 \text{ mg}$ (Model: SHIMADZU AX-200). An Ostwald's viscometer (10ml) was used for the time flow measurement. Efflux time was determined using a digital chronometer within $\pm 0.01 \text{ s}$. An ultrasonic interferometer having the fixed frequency of 3MHz (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 $\pm 0.1 \text{ K}$.

Theory

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

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

where K_j is temperature dependent constant. Its value is 631×10^{-6} at 293.15 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 ($M_{eff} = \sum_i M_i X_i$) in which M_i molecular weight and X_i the mole fraction of the individual constituents respectively. k is a temperature independent constant which is equal to 4.28×10^9 .

Gibb's free energy

$$\Delta G = K_B T \ln \left(\frac{K_B T \tau}{h} \right) \quad (4)$$

where K_B is Boltzmann's constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), h the Planck's constant ($6.626 \times 10^{-34} \text{ Js}$) and τ is the relaxation time ($\tau = \left(\frac{4}{3}\right) \eta \beta$).

Excess values of the above parameter can be determined using

$$A^E = A_{exp} - A_{id} \quad (5)$$

where $A_{id} = \sum_i A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid component. Grunberg and Nissan [14] formulated the following relation between the viscosity of a binary liquid mixture and pure components.

$$\ln \eta_{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d \quad (6)$$

on applying to a ternary liquid mixture, this equation takes up the form

$$\ln \eta_{\text{mix}} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_3 \ln \eta_3 + X_1 X_2 X_3 d \quad (7)$$

where d is an interaction parameter regarded as a measure of the strength of molecular interactions between the mixing components.

Results and Discussion

The values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids and liquid mixture at 293.15 K are given in **Tables 1-2**.

The values of excess viscosity (η^E), excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) excess Gibb's free energy (ΔG^E) and Grunberg's interaction parameter (d) have been calculated and presented in **Tables 3 - 4**.

Table 1 Comparison of experimental and literature values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids at 293.15 K [15-17]

S. No	Compounds	$\rho / (\text{kg m}^{-3})$		$\eta / (\times 10^{-3} \text{ Nsm}^{-2})$		$U / (\text{m.s}^{-1})$	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1.	1-Pentanol	813.9	814.6	4.0471	4.0462	1255.0	1256.0
2.	Para-xylene	864.2	861.0	0.6469	0.6475	1319.0	1324.0
3.	Cyclopentyl methyl ether	863.2	863.0	0.5537	0.5532	1286.0	1287.0

Table 2 Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 293.15 K for Ternary liquid mixture of Para-xylene, Cyclopentyl methyl ether and 1-Pentanol

S. No.	Mole fraction (X_3)	$\rho / (\text{kg m}^{-3})$	$\eta / (\times 10^{-3} \text{ Nsm}^{-2})$	$U / (\text{m.s}^{-1})$
1.	0.0000	847.2	7.8542	1295.5
2.	0.2000	843.8	7.4525	1289.6
3.	0.4000	878.5	7.1202	1284.3
4.	0.6000	874.6	6.8801	1280.4
5.	0.8000	870.1	6.5432	1276.8
6.	1.0000	867.4	6.2306	1271.1

Table 3 Excess values of viscosity (η^E), adiabatic compressibility (β^E), free length (L_f^E) and free volume (V_f^E) at 293.15 K for Ternary liquid mixture of Para-xylene, Cyclopentyl methyl ether and 1-Pentanol

S. No.	Mole fraction (X_3)	$-\eta^E / (\times 10^{-3} \text{ Nsm}^{-2})$	$-\beta^E / (\times 10^{-12} \text{ m}^2 \text{ N}^{-1})$	$-L_f^E / (\times 10^{-10} \text{ m})$	$-V_f^E / (\times 10^{-9} \text{ m}^3 \text{ mol}^{-1})$
1.	0.0000	36.2145	6.2145	1.0245	0.2145
2.	0.2000	34.2145	10.2545	1.8547	0.4215
3.	0.4000	31.0214	14.5249	2.4554	0.7458
4.	0.6000	29.8798	17.2140	2.9658	0.9801
5.	0.8000	27.0214	19.2771	3.4251	1.2004
6.	1.0000	24.8547	23.2148	3.9854	1.5462

Table 4 Excess values of Gibb's free energy (ΔG^E) and Grunberg's interaction parameter (d) at 293.15 K for Ternary liquid mixture of 1 Para-xylene, Cyclopentyl methyl ether and 1-Pentanol

S. No.	Mole fraction (X_3)	$\Delta G^E / (\times 10^{-21} \text{ KJ mol}^{-1})$	d
1.	0.0000	2.3541	1.5424
2.	0.2000	2.0213	9.4522
3.	0.4000	1.8721	7.3365
4.	0.6000	1.6325	5.5480
5.	0.8000	1.2879	3.6588
6.	1.0000	1.0421	2.3654

The excess thermodynamic properties of mixture which correspond to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements in the ternary liquid mixture. In particular, they reflect the interactions that take place between solute - co-solute and solute- solvent species. The effects which are expected to operate between the component molecules under study are, (i) structural effect which is due to the differences in shape and size of the component molecules (ii)

re-orientational effect between component molecules and (iii) energetic effect, i.e., molecular interaction that can be weakened or destroyed or established during the mixing process [18]. The excess viscosity (Table 3) is negative through the whole range of concentration in the system. From the analysis and close observation it is found that they increase with increase in mole fraction of X_3 . This observed behaviour shows that the existence of molecular interaction between the components of mixture for the system studied. The β^E (Table 3) values are negative and these values are decreasing with increase in mole fraction of X_3 in the system studied. The observed β^E values depend upon several contributions, which are of physical and chemical nature [19-20]. The physical contributions comprise of dispersion forces and non specific physical (weak) interactions that lead to positive β^E values; physical contribution is also due to geometrical effect allowing the fitting of molecules of different size into each other's structure resulting in negative β^E values. Chemical contributions involve breaking up of the hydrogen-bonded structure (s), specific interactions such as the formation of hydrogen bonds and formation of charge transfer complex resulting in negative β^E values. Mixing of 1-Pentanol with binary mixture of Para-xylene, Cyclopentyl methyl ether would induce mutual dissociation of the hydrogen-bonded structures present in pure liquids with subsequent formation of (new) H-bonds between 1-Pentanol and Para-xylene, Cyclopentyl methyl ether molecules in the mixture [21-22], resulting to decrease in the compressibility of the mixture and hence negative β^E values. From the variation of excess free length (Table 3) it was observed that the L_r^E values are negative over the entire mole fraction range. The L_r^E value are decreases with increasing of the mole concentration. The negative value of L_r^E 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 [23]. The negative excess values should be due to charge transfer and hydrogen bond formation. In the present study, it is found that the negative contribution of L_r^E in the system prevails with the existance of H-bond interaction. The V_f^E values for the system are found to be negative. These values are decreases with increasing the mole fractions of X_3 in the system studied. These results can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with changes in free volume. The sign V_f^E depends upon the relative strength between the contractive forces and expansive forces. The factors that cause expansion in volume are following: dispersion force, steric hindrance of component molecules, unfavorable geometric fitting, electrostatic repulsion, etc.

The negative value of V_f^E of 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 [24]. The positive value of V_f^E , indicating the existence of weak molecular interaction in the liquid mixtures [25]. The negative excess free volume tends to decrease as the strength of the interaction between unlike molecules increases although they are not parallel with the excess compressibilities. However, in the present study the observed behavior of V_f^E shows that the strength of molecular interaction increases. The values of excess Gibb's free energy (Table 4) are found to be positive and these values are decreases with increasing the mole fraction of X_3 in the system studied. The negative values of ΔG^E may be ascribed to the dominance to dispersion forces [26]. In the present study the observed behavior of ΔG^E shows that the formation of H-bond heterogeneous interactions between the components of unlike molecules. Para-xylene, Cyclopentyl methyl ether and 1-Pentanol molecules exist in self-associated structures through H-bonds with parallel (same direction) dipole alignment in their pure liquid state [27]. Self-association depends not only on the steric arrangement of the respective groups, but is also sensitive to the size and shape of the polar molecules. The ethyl alcohol molecule has one -OH group but forms higher order self-associated structures, which results the linear polymeric structures with a switch-over type of molecular reorientation throughout their homogeneous structures [28-29]. To indicate various types of interaction [30] as follows: Large and positive d-value indicated strong specific interaction; small positive value indicated weak specific interaction and large negative value indicated no specific interaction. It is evident from Table 4 that d-values are positive in the system studied. It is seen that the values of 'd' fluctuate with the increasing of mole fraction of X_3 . Further the behavior of d-values exhibits fluctuation the strength of molecular interaction between the unlike molecules.

Conclusion

A systematic study of ternary mixture of 1-Pentanol, Para-xylene and Cyclopentyl methyl ether equimolar have been carried out at 293.15K temperature using ultrasonic measurements. The ultrasonic velocity data and other acoustical parameters give valuable information to understand the solute-solvent interactions in the mixture. The investigated mixture was chosen in order to obtain information about the molecular interactions between their components. The variations in excess acoustical parameters with composition indicate the specific H-bond heterogeneous interactions in this mixture. The strength of interactions tends to be weaker due to the presence of weak intermolecular forces, Weak molecular interaction are responsible to weak types forces. Further, it is observed that the order of interactions in this mixture depends upon the hydroxyl group because when an alcohol molecule is mixed with other organic liquids, part of the alcohol molecules will tend to dissociate from the polymeric aggregates through the hydrogen

bond to form other kinds of hydrogen bonds with different kinds of molecules. From the magnitude of $'L_r^E'$ and $'d'$ it can be concluded that the strength of interactions.

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