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Sonu Dwivedi
Associate Professor,
Department of Chemistry D.
B. S. (P. G.) College,
Dehradun, Uttarakhand, India

Corresponding Author:
Sonu Dwivedi
Associate Professor,
Department of Chemistry D.
B. S. (P. G.) College,
Dehradun, Uttarakhand- India

Volumetric properties of binary liquid mixture of cyclopentyl methyl ether with 1-pentanol at 298.15 k temperature

Sonu Dwivedi

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Abstract
The densities (ρ) and ultrasonic speeds (u) of Cyclopentyl methyl ether, 1- Pentanol and their binary mixture with the whole composition range have been measured at 298.15 K. From the experimental data the excess molar volume (V^E), deviations in isentropic compressibility (Δks), deviations in ultrasonic speed (Δu), deviations in acoustic impedance (ΔZ) have been determined. The sign and magnitude of these parameters were found to be sensitive towards interactions prevailing in the studied system. Moreover, V^E values were theoretically predicted by using Flory's statistical theory. The variations of derived parameters mentioned above with composition offer a convenient method to study the nature and extent of interactions between the component molecules of the liquid mixture not easily obtained by other means.

Keywords: Density, isentropic compressibility, excess molar volume, ultrasonic speed

Introduction
Ultrasonic speeds are effectively used in the energetic environment of molecular interactions in pure liquids and liquid compounds. Ultrasonic technique shows the physical chemical behaviour of liquids as part of a pointer to comfort. The molecular coordination between liquid compounds components is based on analysis concentrations [1-3]. The properties of liquid mixtures basically depend on its local structure, expressed in terms of packing density, free volume or radial distribution function. However, this local structure depends on forces between molecules and their forms and volume of molecules. It changes with compositions [4-6]. Thermodynamic property is one which serves to describe a system. Fundamental variables of thermodynamic properties includes volume, temperature, energy and of course, the amount of substance. The nature and type of interactions in binary organic liquid mixtures have been studied in terms of mixing parameters such as excess molar volume [7-8]. The molecular interactions of binary non-aqueous liquid mixtures using thermodynamic and transport properties [9-10]. Here my study to the binary mixture containing 1-Pentanol and Cyclopentyl methyl ether at 298.15K over the whole composition range. The mixture studied are interesting from the experimental as well as from the theoretical point of view because Cyclopentyl methyl ether is mixed with 1- Pentanol. 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 [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]. Whereas 1- Pentanol is polar liquid, strongly self-associated by hydrogen bonding to the

extent of polymerization that may differ depending on temperature, chain length, and position of the –OH group. It would be interesting to examine the mixing of Cyclopentyl methyl ether with 1-Pentanol and also to observe the effect of the –OH group on the molecular interaction in this binary mixture.

This work reports the experimental densities (ρ) and ultrasonic speeds (u) of pure Cyclopentyl methyl ether, 1-Pentanol and their binary mixture over the entire composition range at 298.15 K. From the above experimental data of ρ, u, the excess molar volumes (V^E), deviationsin isentropic compressibility (Δk_s), deviations in ultrasonic speed (Δu), deviations in acoustic impedance (ΔZ) have been determined. Moreover, V^E values were theoretically evaluated by using Flory's statistical theory [13-14]. The variations of derived functions, namely, V^E , Δk_s, Δu, ΔZ, mixture with composition are discussed in order to gain insight into the type and magnitude of the molecular interactions in binary mixture of Cyclopentyl methyl ether with 1-Pentanol, and also the effect of the position of the –OH group on the molecular interactions has been discussed.

Table 1: Comparison of experimental densities ρ and ultrasonic speeds u of pure components of Cyclopentyl methyl ether and 1-Pentanol with literature values at 298.15K [15-17].

S.No.	Component	ρ (kg m^{-3})		u (m s^{-1})	
		Expt.	Lit.	Expt.	Lit.
1.	1-Pentanol	812.7	812.4	1282.9	1282.6
2.	Cyclopentyl methyl ether	735.8	735.6	1369.0	1368.3

Experimental

Cyclopentyl methyl ether 99.7%, 1-Pentanol 99.5% (Sd fine chemicals India) were used as obtained but all the chemicals were stored over 0.4 nm molecular sieves to remove the traces of water, if any, and degassed just before use. The solutions were prepared by mass using a (Scaletec SAB 200E , India) electronic balance with a precision of 0.1 mg. The densities of pure liquids and their binary mixture were measured using a single-capillary pycnometer as described in the literature [8-10]. The ultrasonic speeds in liquid samples were measured by using a single crystal variable path interferometer (Mittal Enterprise, New Delhi, Model – M-82) at 2 MHz. The uncertainties in measured density and ultrasonic speed are 0.0001 g cm^{-3} and 0.15 m s^{-1}, respectively. The viscosities of pure liquids and their binary mixture were measured using Ubbelohde-type suspend level viscometer, calibrated with triple-distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostated water bath (Julabo, Model-MD) having a precision of 0.02 K in order to minimize thermal fluctuations. The uncertainty in viscosity measurement is ±0.003 mPa s. A minimum of three readings were taken for each sample and the average values were used in all the calculations. Reliability of the experimental data and the purity of the solvents were ascertained by comparing their densities, ultrasonic speeds and viscosities at different temperatures with the values reported in literature [18-23].

Results and Discussion

The experimental densities (ρ) and ultrasonic speeds (u) of pure Cyclopentyl methyl ether, 1-Pentanol, and their binary mixture over the entire composition range, expressed by the mole fraction x_1 of Cyclopentyl methyl ether at 298.15 K are presented in Table 2. Excess properties, which are the measure of the deviations from ideal behaviour are found to be influenced by the factors such as: (i) structure of the components i. e., different geometry of the unlike molecules, (ii) reorientation of the component molecules in the mixture (iii) intermolecular inter-actions [24-25]. Thus, excess molar volumes (V^E), deviations in isentropic compressibility's (Δk_s), ultrasonic speeds (Δu), acoustic impedance (ΔZ) were calculated with the help of the following standard relations:

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (1)$$

$$\Delta k_s = k_s - (\varphi_1 k_{s1} + \varphi_2 k_{s2}) \grave{} \quad (2)$$

Table 2: Values of experimental density ρ and ultrasonic speed u of binary liquid mixture of Cyclopentyl methyl ether and 1-Pentanol at 298.15K temperature.

x_1	ρ (kg · m^{-3})	u (m · s^{-1})
0.1047	806.4	1301.2
0.2032	802.5	1297.3
0.3017	798.1	1294.4
0.4010	794.8	1290.6
0.5043	790.7	1287.9
0.6102	787.8	1283.5
0.7076	784.0	1279.6
0.8145	781.3	1276.0
0.9043	778.9	1272.8

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \quad (3)$$

$$\Delta Z = Z - (x_1 Z_1 + x_2 Z_2) \quad (4)$$

where x and φ are the mole fraction and volume fraction respectively. Subscripts 1 and 2 stand for the pure components Cyclopentyl methyl ether and 1-Pentanol, respectively, k_s, V and Z are the isentropic compressibility, molar volume and acoustic impedance respectively and can be evaluated by the following reaction

$$k_s = 1/(u^2 \rho) \quad (5)$$

$$V = (x_1 M_1 + x_2 M_2)/\rho \quad (6)$$

$$Z = u\rho \quad (7)$$

where M is the molar mass of the pure components. The values of V^E, Δk_s Δu and ΔZ of the binary mixture were fitted to the Redlich and Kister type equation [26]:

$$Y^E = x_1 x_2 \sum_i^5 Ai\,(1 - 2 \cdot x_1)^{i-1} \quad (8)$$

where Y^E stands for V^E, Δk , Δu and ΔZ. The coefficients A_i of (8), evaluated using least-squares method, and the standard deviations σ (Y^E), calculated as

$$\sigma(Y^E) = [\Sigma\{(Y^E_{expt} - Y^E_{cal})\}^2 / (m - k)]^{1/2} \quad (9)$$

where m is the number of experimental data points and k is the number of A_i coefficients considered, have been listed in Table 3. The variations of V^E, Δk_s, Δu and ΔZ with mole fraction x_1 of Cyclopentyl methyl ether and 1-Pentanol at 298.15 K.

Table 3. Values of Ai parameters along with standard error, σ (YE) of binary liquid mixtures at 298.15 K temperature.

Property	A_1	A_2	A_3	A_4	A_5	$\sigma (Y^E)$
$V^E . 10^7$ ($m^3 . mol^{-1}$)	14.2541	−1.7854	7.2548	1.8687	6.9878	0.0417
$\Delta k_s . 10^{11}$ ($m^2.N^{-1}$)	20.5489	2.7854	9.5845	5.3458	2.6587	0.0468
Δu (m. s^{-1})	−7.5879	−1.0215	−2.8024	−2.5436	2.0854	0.0407
$\Delta Z . 10^{-3}$ (kg · mol^{-1})	−21.6327	−2.2036	−11.0024	−2.8790	−5.2547	0.0286

Only, to avoid overcrowding of data points at remaining temperature The observed V^E values exhibit positive deviations over the entire mole fraction range for the binary liquid system. The positive deviations in excess molar volumes can be explained by considering the fact that mixing of Cyclopentyl methyl ether with 1-Pentanol leads to (i) the loss of dipolar association between the a molecules which tends to make V^E positive, (ii) dipole-induced-interactions between free Cyclopentyl methyl ether and 1-Pentanol molecules (iii) geometrical fitting of smaller molecules of 1-Pentanol molecules into the voids created by the bigger Cyclopentyl methyl ether. Thus, the observed positive V^E values suggest that the effect due to (i) dominates over that of (ii) and (iii) effects. Like V^E the behaviour of Δk_s with x_1 shows positive deviations in the binary system investigated. It should be noted that the extent of positive deviation in Δk_s is more pronounced than in V^E. This is due to the fact that the compressibility is a more powerful thermodynamic parameter in sensing the presence of intermolecular interaction than does V^E [27]. The observed positive values of Δk_s in the mixture over the entire composition range indicate the presence of weak interactions between the component molecules. This is in accordance with the views suggested by Fort and Moore [28]. The behaviour of Δu is similar to that of ΔZ and show negative deviation in the mixture. Negative deviations in Δu and ΔZ indicate weak interaction between the component molecules in the mixture [29]. The observed negative deviation in ΔZ, where Z = uρ, and an opposite trend in Δk_s, where $k = 1/u^2\rho$, over the whole composition range support my view regarding the structural order and, hence, intermolecular interactions in this mixture [30]. In the present paper, the excess molar volume V^E has also been evaluated by using Flory's statistical theory [13-14] V_F^E. According to Flory's equation of state [13-14] V_F^E is given as:

$$V_F^E = [\sum_{i=1}^{2} Xi . Vi^*] [\tilde{V}^{0\,7/3} / \{(4/3) - (\tilde{V}^0)^{1/3}\}] \quad (10)$$

The terms and notations used in (10) are the same as given in the literature [13-14]. Flory's statistical theory, though unable to predict excess molar volume quantitatively, seems to be satisfactory in predicting it qualitatively for the present systems studied.

Conclusion

The observed positive V^E values, over the entire composition range in the binary systems of Cyclopentyl methyl ether and 1-Pentanol at 298.15K temperature indicate that disruption of associated structures of 1-Pentanol by Cyclopentyl methyl ether molecules in the mixture dominates over that of the combined effect due to dipole-induced interactions and fitting of smaller molecules of 1-Pentanol into the voids created by bigger Cyclopentyl methyl ether molecules. Also, the positive values of Δk_s for the system under study support the behaviour of V^E. Further, the positive deviations in Δk_s are more pronounced than in V^E for the system studied, thereby, suggesting that compressibility is a more powerful thermodynamic parameter than V^E in sensing the presence of molecular interaction in a mixture. The observed negative values of Δu, ΔZ in the binary mixture clearly reinforce the behaviours of V^E and Δk_s.. In the binary mixture clearly suggest the presence of weak interactions between the component molecules. A comparison between the experimental V^E and the theoretically predicted V^E, using Flory's statistical theory, suggests that, though, Flory's theory is unable to predict excess molar volume quantitatively is satisfactory in predicting it qualitatively for the systems investigated.

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