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Study of molecular interactions in ternary non electrolyte solutions

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ABSTRACT

Excess volume (V^E_{123}) and speed of sound (u_{123}) data for three ternary mixtures were reported at 303.15 K. The mixtures include 1,1,1-trichloroethane and acetophenone as common components. The non-common components were chosen as 1-alkanols namely 1-propanol, 1-butanol and 1-pentanol. The experimental speed of sound and density data of ternary mixtures were used to compute isentropic compressibility (κ_{s123}) and the quantity $\Delta\kappa_{s123}$, the difference between measured value and that computed from the constituent binary data. Further, experimental ternary excess volume data were compared with predictive expressions in terms of Redlich–Kister, Kohler and Tsao–Smith equations. The experimental data were analyzed on the basis of intermolecular interactions between component molecules and also in terms of constituent binary data.

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1. Introduction

A thorough knowledge of the thermodynamic properties of multi-component liquid mixtures is essential in many industrial applications, such as design calculation, heat transfer, mass transfer, fluid flow and so forth [1]. Moreover thermodynamic properties of mixed solvents have been particularly served as main tool in elucidation of solute–solute and solute–solvent interactions that exist in the liquid mixtures. Investigation of thermodynamic properties of liquid and liquid mixtures are fascinating and of high fundamental practical importance for many industrial activities. In many industrial applications, liquid mixtures rather than single component liquid system are used in processing and product formulations [2]. The mixing of different compounds gives rise to properties such as volumes, enthalpies and entropies of mixing, which reflect the extent of the deviations from non-identity. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property in the system behaves ideally are useful in the study of molecular interactions and arrangements [3].

This work is a part of our ongoing program [4–6] to provide data for the characterization of molecular interactions between industrially important organic liquids and systematic study on thermodynamic properties of ternary liquid mixtures with molecules of significantly different sizes.

Though, a number of investigations were carried out, a systematic study pertaining to alkanol as one of the components in liquid mixtures is scarcely reported. Further, alkanols are highly polar and they can form azeotropes with one or other components in multi component liquid mixtures. It will be interesting to study the effect of increasing in chain length of 1-alkanol on their excess thermodynamic properties. Hence, a thorough study was carried out on the molecular interaction for three ternary mixtures containing 1,1,1-trichloroethane and acetophenone as common components and 1-propanol, 1-butanol and 1-pentanol as non-common components. The selected component liquids used in the present study have various industrial applications. 1,1,1-Trichloroethane is an excellent solvent for development of photo resist polymers used in printed circuit board manufacture and the other common uses include cleaning of electrical equipment, motors, electronic components and instruments. Acetophenone is used as base for bath soaps, chemical intermediate for resins, corrosion inhibitors and as a solvent for gums. 1-Alkanols are interesting simple examples of biologically and industrially important amphiphilic materials [7]. A survey of the literature has shown that ternary excess volume data containing 1,1,1-trichloroethane with n-hexane and n-heptane with 1-alkanols were reported earlier [8,9]. The measured data in the present investigation were compared with empirical equations to check the capability of predictive expressions [10].

2. Experimental details

2.1. Materials

All the chemicals used were of analytical reagent (AR) grade (procured from Sigma-Aldrich and S.D. Fine chemicals Ltd.,) and their

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purities were as follows: 1,1,1-trichloroethane (CAS 71-55-6) 99.5%, acetophenone (CAS 98-86-2) 99.5%, 1-propanol (CAS 71-23-8) 99.5%, 1-butanol (CAS 2346-54-1) 99.5% and 1-pentanol (CAS 71-41-0) 99.5%. Before the experimental measurements all the liquids were purified as described in the literature [11,12]. The purity of the chemical products was compared by measuring the densities and speed of sound which were in good agreement with literature values [13–15] and these were given in Table 1.

2.2. Measurements

Excess volume data for ternary mixtures were measured with the dilatometer described in the literature [16,17]. The mixing cell contained three bulbs of different capacities. Mercury was used to separate three components. One of the three bulbs was fitted with a capillary and the other two fitted with ground-glass stoppers. Each bulb of the dilatometer was fitted with a component whose mass was determined directly by weighing. The full dilatometer was placed in the thermostat that could be maintained to ±0.01 K. The densities of pure liquids were measured by using pycnometer. All the measurements were made at constant temperature employing a thermostat. The measured V^E values were accurate to ±0.003 $cm^3\ mol^{-1}$ [18].

The speed of sound of pure liquids and their mixtures were measured at 303.15 K by using a multifrequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) single-crystal variable-path by using a constant temperature water bath [19]. The speeds of sound were accurate to ±0.3%. The temperature stability was maintained to ±0.01 K by circulating thermostatic water bath around the cell with a circulating pump.

3. Results and discussion

3.1. Excess volume

The experimental ternary excess volume (V^E_{123}) data for the mixtures of 1,1,1-trichloroethane and acetophenone with 1-propanol, 1-butanol and 1-pentanol were given in Table 2 and graphically represented in Figs. 1–3.

Further, the ternary excess volume data predicted from binary data using Redlich–Kister, Kohler and Tsao–Smith equations were also included in Table 2. The methods of calculation were explained as follows:

Redlich–Kister equation [10] expressed as:

$$V^E_{123} = \sum_{i<j} V^E_{ij}(x_i, x_j) \tag{1}$$

where $V^E_{ij} = x_i x_j \sum_{s=0}^{n} (A_s)_{ij}(x_i - x_j)^s$ and x_i,x_j are the mole fractions of the components in a ternary mixture.

Kohler expression [10]:

$$V^E_{123} = (x_1 + x_2)^2 V^E_{12} + (x_1 + x_3)^2 V^E_{13} + (x_2 + x_3)^2 V^E_{23} \tag{2}$$

where $V^E_{ij} = x_i' x_j' \sum_{s=0}^{n} (A_s)_{ij}(x_i' - x_j')^s$

Table 1
Density (ρ) and speed of sound (u) data of pure components at 303.15 K.

Compound	Density(ρ) g·cm^{-3}		Speed of sound (u) m s^{-1}	
	Experiment	Literature	Experiment	Literature
1,1,1-Trichloroethane	1.32097	1.32099 [11]	944	942 [13]
Acetophenone	1.01944	1.01941 [12]	1455	1457 [12]
1-Propanol	0.79590	0.79592 [12]	1192	1190 [12]
1-Butanol	0.80196	0.80195 [12]	1226	1225 [12]
1-Pentanol	0.80756	0.80758 [12]	1255	1257 [12]

at composition (x_i', x_j'), such that

$$x_i' = 1 - x_j' = \frac{x_i}{x_i + x_j}$$

where x_i and x_j are the ternary mole fractions.

Tsao–Smith expression [10] is of the form:

$$V^E_{123} = x_2(1 + x_1)^{-1} V^E_{12} + x_3(1 - x_1)^{-1} V^E_{13} + (1 - x_1) V^E_{23} \tag{3}$$

where $V_{12}{}^E$, V^E_{13} and V^E_{23} are the binary excess volumes at composition (x_i', x_j'), such that $x_i' = x_1$ for 1,2 and 1,3 binary systems and $x_2' = \frac{x_2}{x_2 + x_3}$ for 2,3 binary system.

The quantity ΔV^E_{123}, difference between measured ternary data and computed from the constituent binary data through the Redlich–Kister relation were given Table 2.

The binary V^E parameters required to compute ternary V^E_{123} data in terms of constituents binaries for the systems of 1,1,1-trichloroethane with acetophenone [13], 1,1,1-trichloroethane with 1-alkanols [20] and acetophenone with 1-alkanols [14] were taken from the literature and were given in the form of least-square parameters in Table 3.

A perusal of data in Table 2 reveal that density increases with increase in mole fraction of acetophenone. The increase in density indicates the presence of solvent–solvent interactions in the ternary mixture [21]. The results in Table 2 also suggest that the ternary excess volume data in all the three mixtures were negative over the entire composition range.

The sign and magnitude of excess volumes can be interpreted as composed from three contributions, namely of physical, chemical and structural effects.

i. The physical effects involve dispersion forces and nonspecific interactions in the mixture, adding positive contributions to V^E.
ii. The chemical and specific interactions result in decrease in volume, which includes charge transfer type forces and other complex forming interactions between the two species, thereby these chemical effects contribute negative values to VE.
iii. The structural effects that arise from the geometrical fitting of one component into the other are due to the different molar volumes and free volumes of pure components, and add negative contributions to V^E.

The experimental results in the present investigation indicate that the factors which are responsible for contraction in volume are dominant over entire composition range in all the three ternary mixtures of 1,1,1-trichloroethane and acetophenone with 1-alkanols. In most of the thermodynamic properties of binary systems with ketones negative deviations in excess functions have been reported [22,23].

Alcohols, which exist in a highly associated form in the pure state [23,24] when mixed with polar solvents like ketones the monomerization occurs and new specific interactions appear in the solution. Dipole–dipole interactions too affect the properties of 1-alkanols [25]. The experimental results show that negative excess volume decrease with increase in chain length of 1-alkanols. Further, the strength of association in alkanol decreases [26] as the chain length of alkanol molecule increases from 1-propanol to 1-pentanol due to steric factors. Thus, it is expected that mixing of 1,1,1-trichloroethane and acetophenone with 1-alkanols would cause dissociation of hydrogen bonded structures in the alkanols, releasing several dipoles of alkanol molecules, the protons of the –OH group of these dipoles are likely to interact with π-electrons of aromatic ring forming new hydrogen bonds. The degree of association in alkanols decreases as the carbon chain length in the alkanol increases because the higher alkanols possess less proton donating capacity than lower one and hence hetero association effect decrease in the mixtures with an increase in chain length of 1-alkanols.

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