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Topological studies of molecular interactions of formamide with propanol and butanol at 298.15 K

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ABSTRACT

Molar excess volumes have been measured at 298.15 K for formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures. For an equimolar mixture, molar excess volumes follow the sequence: 1-butanol > 1-propanol > 2-methyl-1-propanol > 2-methyl-2-propanol > 2-propanol. The excess molar volume (V_m^E) values have been fitted to Redlich–Kister polynomial equation and other volumetric properties like apparent molar volume, partial molar volume, excess partial molar volume were calculated. The excess volume data have also been rationalized by graph-theoretical arguments. It has been observed that V_m^E calculated by this approach agree well with the corresponding experimental values. This analysis has further yielded information about the state of aggregation of pure components that is consistent with the existing views on their nature of association. The infrared spectral studies lend further credence to the graph theoretical arguments.

1. Introduction

The thermo-physical properties of mixtures would be of great importance in processing engineering designs and also helpful in getting information about molecular structure and intermolecular forces in liquid mixture, which can be very helpful in making the choice of solvent in various applications. Alcohols are self associated organic compound through hydrogen bonding of their hydroxyl groups. These are biologically and industrially important amphiphilic materials. Branching of alkyl group attached to the hydroxyl group results in abnormal behaviour of alcohols [1]. Amides are known as an important class of bio-organic solvents and are convenient model systems for investigating peptide and protein–solvent interactions. The H-bond formation ability of these solvents with other H-bonded self-associating solvents is useful in understanding the peptide linkage in complex bio-systems [2]. Formamide is selected for this study, as it is the simplest amide that contains a peptide linkage, the fundamental building block of proteins. Formamide molecules are highly polar [3] and are strongly self-associated through extensive three-dimensional network of hydrogen bonds, through its three hydrogen bond donors (3 H-atoms) and three acceptors (two lone pairs of electrons at oxygen and one on nitrogen atom). Since the components of these binary mixtures have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules is expected [4]. Further in view of the two well known resonance structures [5] of the amide group, the lower amides in pure state may exist like alkanols [6,7], dimers and higher r-mers, though Davies [8] favors dimeric state for them in solution. Although such a situation can be handled by the ideal association model approach [9,10] yet the result would be strongly dependent on the particular type of model assumed for formamide and alkanols. This calls for an entirely different approach. Since binary mixture is formed by the replacement of like contacts in the pure state by unlike contact in the mixture and as the formations of molecular entities in the present mixtures may be visualized [11] due to the changes in the topology of formamide brought on by alkanol, it appears that a recent graph theoretical approach [12,13] should provide valuable information about the state of formamide and alkanol in an binary mixture. This prompted us to perform molar excess volume studies at 298.15 K on formamide + 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures. The Redlich–Kister equation was used to correlate the experimental data and to obtain the partial molar volumes at 298.15 K and at atmospheric pressure [14]. The excess volume data have also been rationalized by graph-theoretical arguments. It has been observed that V_m^E calculated by this approach agree well with the corresponding experimental values.

2. Experimental

Formamide, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol mixtures (Merck or Sigma) were

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purified by standard procedures [15,16]. The purities of the purified samples were checked by measuring their densities and refractive indices at 298.15 K. The densities were measured with a precision of $\pm 5 \times 10^{-5}$ g cm^{-3} by a specially designed densimeter, consisting of a bulb of approximate volume 35 cm^3 attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissenberger [17]. Air buoyancy correction was also applied to achieve a greater accuracy. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of ±0.0001. Our experimental values for the density, and refractive index of the pure compounds compared well with the literature values as shown in Table 1. Molar excess volumes, V_m^E, for the binary mixtures have been measured by V-shaped dilatometer at 298.15 K in the manner described elsewhere [18]. The temperature of water thermostat was controlled to ±0.01 K by a mercury-in-toluene regulator. The change in the position of the liquid level in the capillary was noted with a cathetometer (OSAW, Ambala) that could read to ±0.001 cm. The performance of dilatometer was checked by measuring the molar excess volume of the benzene + cyclohexane mixture at 298.15 K and these agreed to within the experimental limits with corresponding literature. The uncertainty in the measured V_m^E values was ±1%.

3. Results

The excess molar volume is defined by

$$V_m^E = V_m - x_1 V_1^o - x_2 V_2^o \quad (1)$$

where V_m represents the volume of a mixture containing one mole of (formamide + alkanol), x_1 and x_2 are the mole fraction of formamide and alkanol, respectively and V_1^o and V_2^o are the molar volume of pure components.

The measured V_m^E data at 298.15 K are recorded in Table 2 and are fitted to the following Redlick and Kister equation

$$V_m^E\,(\mathrm{cm^3\ mol^{-1}}) = x_1(1-x_1)\left[\sum_{j=0}^{n} A_j(2x_1-1)^j\right] \quad (2)$$

where A_j are the adjustable parameters, and x_1 is the mole fraction of formamide in formamide + alkanol mixture. These parameters were evaluated by fitting V_m^E data to Eq. (2) by the least squares method and recorded in Table 3 with the standard deviations of V_m^E, $(\sigma(V_m^E))$.

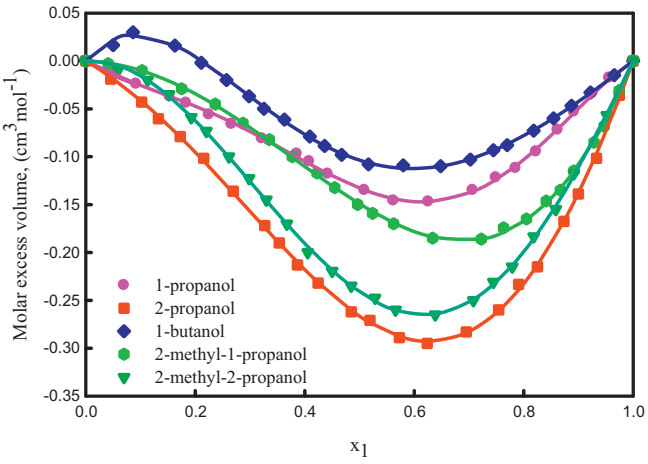

Fig. 1. Molar excess volume (V_m^E) of formamide (1) + alkanol (2) mixtures as a function of mole fraction of formamide (x_1) at 298.15 K; symbols represent experimental value and lines represent value calculated from Eq. (2).

$$\sigma(V_m^E)\,(\mathrm{cm^3\ mol^{-1}}) = \left\{\frac{\left[\sum\left(V^E_{\mathrm{expt.}} - V^E_{\mathrm{cal.(Eq.\,(2))}}\right)^2\right]}{m-n}\right\}^{1/2} \quad (3)$$

where m is the number of experimental values, and n is the number of adjustable parameters in Eq. (2). The choice of n to have 0–3 values was dictated by the consideration that the maximum deviation $\sigma_m(V^E)$ of V_m^E (as calculated from Eq. (2) from the corresponding experimental V_m^E values satisfied the relation $\sigma(V_m^E) \le 2\sigma(V_m^E)$.

Comparison of V_m^E experimental for the studied system together with smoothing curves using Eq. (2) is shown in Fig. 1.

We have also calculated the excess partial molar volumes, $\bar{V}_1^E = (\bar{V}_1 - \bar{V}_1^o)$ and $\bar{V}_2^E = (\bar{V}_2 - \bar{V}_2^o)$, from V_m^E. The excess molar volumes, $\bar{V}_1^E$ and $\bar{V}_2^E$, were evaluated using following equations:

$$\bar{V}_1 = \bar{V}_m^E + \bar{V}_1^o + (1-x_1)\left(\frac{\partial \bar{V}_m^E}{\partial x_1}\right)_{p,T} \quad (4)$$

Table 1
Measured densities (ρ) and refractive indices (n_D) of the pure components at 298.15 K.

Compound	Temperature (K)	ρ (kg m^{-3})		n_D	
		This work	Literature	This work	Literature
Formamide	298.15	1129.02	1129.01 [25] 1129.1 [26]	1.4461	1.44597 [26]
1-Propanol	298.15	799.77	799.75 [27] 799.79 [29] 799.48 [30]	1.914	1.915 [28]
2-Propanol	298.15	781.2	781.28 [29] 781.01 [30] 781.06 [32]	2.0650	2.0652 [31]
1-Butanol	298.15	805.85	805.565 [33] 805.98 [29] 805.83 [30]	1.3972	1.39741 [16]
2-Methyl-1-propanol	298.15	797.6	797.37 [33] 797.8 [34] 798.52 [35]	1.3937	1.3939 [34]
2-Methyl-2-propanol	298.15	780.8	780.59 [33] 781.2 [34]	1.3854	1.3852 [34]