

Excess molar volumes and partial molar volumes for (propionitrile + an alkanol) at $T = 298.15$ K and $p = 0.1$ MPa

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Abstract

The excess molar volumes and the partial molar volumes for (propionitrile + an alkanol) at $T = 298.15$ K and at atmospheric pressure are reported. The hydrogen bonding between the OH...NC groups are discussed in terms of the chain length of the alkanol. The alkanols studied are (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 1-pentanol).

The excess molar volume data was fitted to the Redlich–Kister equation. The partial molar volumes were calculated from the Redlich–Kister coefficients.

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1. Introduction

The excess molar volumes, V_m^E , were determined over the entire composition range for (propionitrile + an alkanol) at $T = 298.15$ K and at atmospheric pressure. Alkanol molecules are protic and strongly self-associated through hydrogen-bonds in their pure state, with degrees of association depending on the chain length, position of the OH group, temperature, and dilution by other substances [1–3]. The results obtained for the V_m^E data were used to discuss the hydrogen bonding between the OH...NC groups in terms of the chain length of the alkanol. There are no data in the literature on the systems studied in this work. The results are also compared to the V_m^E values for (acetonitrile + an alkanol) in the literature.

The Redlich–Kister equation was used to correlate the experimental data and to obtain the partial molar volumes at $T = 298.15$ K and at atmospheric pressure [4].

2. Experimental

The chemicals, suppliers, purity, the literature and experimental densities, ρ , and refractive indices, n_D , are given in table 1. Densities and refractive indices of pure liquids and the mixtures were obtained at atmospheric pressure and at $T = 298.15$ K by means of a vibrating U-tube densimeter and a refractometer, respectively.

Propionitrile (C_2H_5CN) (>0.99 mass fraction) was used without any further purification. The alkanols were dried by distillation shortly before each set of experiments. Methanol and ethanol were first refluxed over Grignard reagent ($Mg + I_2$) for 6 h, with protection from the atmosphere and then distilled at atmospheric pressure [5,6]. The solvents 1-propanol, 2-propanol, and 1-butanol were dried with aluminum amalgam and then distilled [5,6]. 1-Pentanol was first dried with anhydrous calcium sulphate followed by distillation [5,6]. All distillations were done in a fumehood with minimum exposure to the atmosphere. The dried solvents were stored in sealed quick-fit conical flasks over 0.4 nm molecular sieves.

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TABLE 1

Pure component specifications: suppliers (A = Aldrich, B = DBH Chemicals, M = Merck), purity, the literature and experimental densities and refractive indices at $T = 298.15$ K

| Component | Supplier | Mole fraction | $\rho/(\text{g} \cdot \text{cm}^3)$ | | n_D | |
|---------------|----------|---------------|-------------------------------------|----------------------|--------|----------------------|
| | | | Exp. | Lit. | Exp. | Lit. |
| Propionitrile | A | >0.99 | 0.7768 | 0.77682 ^a | 1.3633 | 1.3636 ^a |
| Methanol | B | >0.99 | 0.7866 | 0.78664 ^a | 1.3265 | 1.32652 ^a |
| Ethanol | B | >0.99 | 0.7851 | 0.78509 ^a | 1.3593 | 1.35941 ^a |
| 1-Propanol | M | >0.99 | 0.7996 | 0.79960 ^a | 1.3834 | 1.38370 ^a |
| 2-Propqanol | B | >0.99 | 0.7809 | 0.78126 ^a | 1.3748 | 1.37520 ^a |
| 1-Butanol | B | >0.99 | 0.8058 | 0.80575 ^a | 1.3970 | 1.39741 ^a |
| 1-Pentanol | M | >0.98 | 0.8108 | 0.81080 ^a | 1.4078 | 1.40800 ^a |

^a Reference [21].

The densities were obtained using a Mettler Toledo KEM DA-300M vibrating tube densimeter. The temperature around the U-tube was controlled at a temperature of 298.15 ± 0.005 K. The temperature control system consists of three components: the temperature sensor, the Peltier element and the temperature controller. The densimeter had a built-in temperature display screen capable of displaying temperature to three decimal places.

The densimeter was calibrated with dry air and distilled water every day before any experimental work commenced. The literature value of the density of dry air and water at $T = 298.15$ K is $1.2 \cdot 10^{-3} \text{ g} \cdot \text{cm}^3$ and $0.9970 \text{ g} \cdot \text{cm}^3$, respectively. The excess molar volumes were determined for the test system {benzene(x_1) + toluene(x_2)} [7]. This was done to validate the technique used for the determination of the excess molar volumes of mixing. The V_m^E value ($x = 0.50$) from the literature was $0.0855 \text{ cm}^3 \cdot \text{mol}^{-1}$ and the experimental V_m^E value ($x = 0.50$) was $0.0863 \text{ cm}^3 \cdot \text{mol}^{-1}$. The V_m^E results from our measurements and that of the literature values were better than $0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$. The maximum error in V_m^E is estimated to be better than $0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$. A comparison between the experimental and the literature densities and refractive indices for the pure chemicals are given in table 1. There is good agreement between the literature and experimental values, with $\rho \leq 0.003$ and $n_D \leq 0.0004$.

3. Results

The excess molar volumes, V_m^E , for the binary mixtures were calculated from the following equation:

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}, \quad (1)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 molecular masses, ρ_1 and ρ_2 densities of the pure components 1 and 2, and ρ the density of the mixture.

The excess molar volumes for {propionitrile + an alkanol} is given in table 2. The plot obtained for the excess

molar volumes are given in figure 1. The Redlich–Kister smoothing function (equation (2)) was fitted to each set of the experimental values

$$V_m^E/(\text{cm}^3 \cdot \text{mol}^{-1}) = x(1-x) \sum_{i=0}^N A_i (2x-1). \quad (2)$$

The parameters A_i obtained by the method of least squares are given in table 3 together with the standard deviation, σ .

4. Discussion

Of the six binary mixtures studied, four of them had positive V_m^E over the entire mole fraction range, the exceptions were (propionitrile + methanol or ethanol). The magnitude of V_m^E is the result of physical, chemical, or structural contributions [8,9]. The minimum, and/or maximum, and equimolar values of the excess molar volumes are given in table 4.

The excess molar volumes, V_m^E , for (propionitrile + methanol) are negative over the entire composition range. The curve is skewed towards high mole fractions of the alkanol due to (1) greater differences in the molar volumes of propionitrile and methanol and to (2) strong free-volume effects [10]. The V_m^E curve for (propionitrile + ethanol) is sigmodal; at low ethanol concentrations ($0.000 < x_2 < 0.693$) the excess molar volumes are positive and at mole fractions of ethanol > 0.710 it is negative. The negative V_m^E values for (propionitrile + methanol or ethanol) are due to the association between the nitrile (CN) and hydroxyl (OH) groups [11]. This effect is greater than any self-dissociation effects arising from the propionitrile or alkanol molecules [11]. The excess molar volumes for (propionitrile + 1-propanol or 2-propanol or 1-butanol or 1-pentanol) are positive over the entire composition range and increases with an increase in the concentration of the alkanol. The V_m^E curves for these mixtures are asymmetrical, with their maxima displaced towards low mole fractions of the alkanol (table 4 and figure 1).

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