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Excess molar volumes of (1-chlorobutane + heptane + 2-butanone or 2-pentanone) at (288.15, 303.15 and 313.15) K. Measurements and correlations

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ABSTRACT

Experimental densities for the ternary mixtures x_1 1-chlorobutane + x_2 n-heptane + $(1 - x_1 - x_2)$2-butanone or 2-pentanone and five corresponding binary systems have been measured at T = (288.15, 303.15 and 313.15) K and atmospheric pressure, using a DMA 5000 Anton Paar densimeter. Excess molar volumes have been calculated using the measured experimental densities of the pure liquids and mixtures. The V^E results were correlated and fitted by the Redlich–Kister equation for binary mixtures and by the Nagata and Tamura equation for ternary mixtures, as a function of mole fraction. Several predictive empirical relations were applied to predict the excess molar volumes of ternary mixtures from the binary mixing data. The excess molar volumes for the two ternaries are positive over the entire range of composition and at temperature between 288.15 K and 313.15 K.

1. Introduction

The thermodynamics of ternary mixtures of non-electrolytes has not received as much attention as the thermodynamics of binary mixtures. It is therefore interesting to estimate excess properties for systems with more than two components. As the number of components in the mixture increases, the determination of thermodynamic properties becomes more arduous. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved. In this work we present at T = (288.15, 303.15 and 313.15) K the excess molar volumes, V^E, of the ternary systems x_1 1-chlorobutane + x_2 n-heptane + $(1 - x_1 - x_2)$2-butanone or 2-pentanone and the binary systems x 1-chlorobutane + $(1 - x)$ (n-heptane, 2-butanone or 2-pentanone) and x n-heptane + $(1 - x)$ 2-butanone or 2-pentanone. The binary experimental data were fitted to Redlich–Kister equation [1]. The Nagata and Tamura equation [2] has been used in order to correlate adequately the experimental values of V^E of ternary mixtures. The experimental values were also used to test different symmetric [1,3,4] and asymmetric [5–7] empirical expressions. Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of the compounds in the mixture. In these cases, different geometric criteria are applied to match each point of ternary composition with the contributing binary compositions.

A survey of the literature indicates that volumetric properties of binary mixtures of 1-chlorobutane + 2-butanone or 2-pentanone have been studied by other authors [8,9] at (298.15, 308.15) K. Also excess molar volumes were performed for n-heptane + 1-chlorobutane [10] at (283.15, 298.15, 313.15) K and for n-heptane + 2-butanone [11] at 293.15 K. For the other systems presented in this work, the density data are not available in the literature.

2. Experimental

The liquids 1-chlorobutane, n-heptane, 2-pentanone and 2-butanone were obtained from Fluka AG. The purity of substances was not less than 99% in mole fraction and was checked by comparing the measured densities with those reported in the literature [12–18] and also by chromatographic analysis. The values are listed in Table 1.

Densities of pure components and mixtures were measured at T = (288.15, 303.15 and 313.15) K with Anton Paar vibrating-tube densimeter DMA 5000, with an estimating uncertainly of $\pm 5 \times 10^{-2}$ kg/m^3. The temperature inside the vibrating-tube cell was regulated to better than 0.01 K using a Haake G thermostat. Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double distilled freshly degassed water. The density data for water were taken from literature [9].

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Table 1
Comparison of experimental densities with literature values at different temperatures.

T/K	ρ exp ($\times 10^{-3}$ kg/m^3)	ρ lit. ($\times 10^{-3}$ kg/m^3)
Heptane		
288.15	0.688588	0.68766 [12]
303.15	0.675838	0.67547 [13]
		0.6753 [12]
313.15	0.665838	0.6666 [12]
2-Butanone		
288.15	0.810328	0.81030 [14]
		0.810217 [15]
303.15	0.794629	0.79467 [14]
313.15	0.784008	0.78412 [14]
		0.784326 [15]
1-Chlorobutane		
288.15	0.891747	0.8913 [16]
303.15	0.875099	0.8749 [16]
313.15	0.863833	0.86386 [17]
		0.8639 [16]
2-Pentanone		
288.15	0.811491	0.81107 [18]
303.15	0.796955	0.79660 [13]
313.15	0.787160	0.78683 [18]

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures. Mixtures were prepared by weight with a probable error in the mole fraction less 10^{-4}.

3. Results and discussion

The excess molar volumes V^E for the five binary systems and the corresponding ternary system were evaluated using the following equation:

$$V^E = V - \sum_{i=1}^{n} \left(\frac{x_i M_i}{\rho_i} \right) \tag{1}$$

$$V = \sum_{i=1}^{n} \frac{x_i M_i}{\rho} \tag{2}$$

where x_i, M_i and ρ_i are the mole fraction, molar mass and the density of component i respectively, ρ the measured density of the solution.

The uncertainty in the V^E calculation is less than $\pm 10^{-8}\ \mathrm{m^3\,mol^{-1}}$. V^E for the binary systems were fitted by the least squares method to the Redlich–Kister [1] equation:

$$V^E = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \tag{3}$$

Excess molar volumes, V^E, for the binary mixtures, are listed in Table 2 and plotted in Fig. 1. The fitting parameters A_i of Eq. (3) and the standard deviations σ are presented in Table 3.

Excess molar volumes for the ternary mixtures were correlated using the following equation:

$$V^E_{123} = V^E_{12} + V^E_{13} + V^E_{23} + x_1 x_2 x_3 \Delta_{123} \tag{4}$$

where V^E_{ij} is the binary contribution for each ij binary mixture, $x_1 x_2 x_3 \Delta_{123}$ is the ternary contribution which was correlated using the Nagata and Tamura equation [2].

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 \tag{5}$$

The parameters, B_i used in Eq. (4) are adjustable parameters.

Standard deviations, σ, presented in Tables 3 and 5 were determined by the following equation:

$$\sigma = \left[\frac{\sum_{i=1}^{N} (V^E_{(\mathrm{exp})} - V^E_{(\mathrm{cal})})}{N-p} \right]^{\frac{1}{2}} \tag{6}$$

where p is the number of parameters and N is the number of experimental data.

Table 4 presents the experimental values of densities, ρ, and excess molar volumes, V^E, for the ternary mixtures. Experimental data for V^E for ternary systems are shown in Fig. 2 which also present ternary fitting curve for the Nagata–Tamura equation. Although prediction of the physical properties of multicomponent mixtures from those of their pure components is generally unreliable because of mixing effects, numerous schemes have been put forward for predictions based on the properties of the binary systems formed by pairs of components of the multicomponent systems. In this work, several empirical methods have been proposed to estimate ternary excess properties from available experimental results of binaries. These methods are asymmetric when the numerical predictions depend on the arbitrary designation of component numbering and symmetric on the contrary case. The equation of Redlich–Kister [1], Kohler [3] and Colinet [4] are symmetrical whereas those of Tsao and Smith [5], Toop [6] and Scatchard et al. [7] are asymmetrical (Table 6).

For the asymmetric methods, we must indicate the order of components in the ternary mixtures

Redlich–Kister [1] model

$$V^E_{ijk} = \sum_{j \succ i} V^E_{ij}(x'_i, x'_j), \quad x'_i = x_i, x'_j = x_j \tag{7}$$

Kohler [3] model

$$V^E_{ijk} = \sum_{j \succ i} (x_i + x_j)^2 \cdot V^E_{ij}(x'_i, x'_j), \quad x'_i = \frac{x_i}{x_i + x_j}, x'_j = 1 - x'_i \tag{8}$$

Colinet [4] model

$$V^E_{ijk} = \frac{1}{2}\sum_{i \prec j} \left[\frac{x_j}{(1-x_i)} V^E_{ij}(x'_i, x'_j) + \frac{x_i}{(1-x_j)} V^E_{ij}(x''_i, x''_j) \right],$$

$$x'_i = x_i = 1 - x'_j, x'_j = x_j = 1 - x''_i \tag{9}$$

Tsao and Smith [5] model

$$V^E_{123} = \frac{1}{1-x_1}[x_2 V^E_{12}(x'_1, x'_2) + x_3 V^E_{13}(x'_1, x'_3)] + (1-x_1) V^E_{23}(x''_2, x''_3) \tag{10}$$

Component 1 asymmetric $x'_i = x_1 = 1 - x'_j$ for system 1.2 and 1.3 $x'_i = 1 - x'_j = x_i/(x_i + x_j)$ for system 2.3.

Toop [6] model