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Volumetric and refractive index properties of isobutyric acid — water binary mixtures at temperatures ranging from 300.15 to 313.15 K

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Abstract

Refractive index deviations Δn, excess molar volumes V^E, and molar refractions R of isobutyric acid + water binary mixtures have been calculated from experimental data of refractive index and densities over the whole composition range at temperatures ranging from 300.15 K to 313.15 K under atmospheric pressure. The Δn and V^E results were correlated using the fourth-order Redlich–Kister polynomial equation with the maximum likelihood principle being applied for the determination of adjustable parameters. These quantities have been discussed in terms of intermolecular interactions between the components of the mixtures.

Keywords: Refractive index; Density; Excess molar volume; Isobutyric acid; Water; Binary mixture; Molecular interactions

1. Introduction

The physical properties and the thermodynamic behavior of binary mixtures have been studied for many reasons, one of the most important of which is that these properties may provide information about molecular interaction. Volumetric properties and refractive index of liquid mixtures represent together an important source of information for the characterization of the interaction between components.

This paper is a continuation of our earlier works that includes the study of the binary liquid mixture of isobutyric acid + water (I–W) [1–3]. We have reported the effect of (K^+, Cl^-) ions on the coexistence curves and on the Lorentz–Lorenz relation in the case of the near-critical binary fluid mixture (I–W). In our laboratory, we have investigated the excess molar V^E and the shear viscosity deviations $\Delta\eta$ for (I–W) system over the entire range of mole fractions at five different temperatures, both near and close to the critical temperature ($2.055\ \mathrm{K} \le T - T_C \le 13.055\ \mathrm{K}$) [4]. In our previous paper [2], we have investigated the coexistence curve of the binary mixture (I–W) which has an upper critical solution temperature T_c and critical composition x_c values respectively of about 26.945 °C and 0.3889 as mass fraction of isobutyric acid which corresponds to a critical mole fraction value 0.1114. These obtained results are in good agreement with the literature values (Seki et al. [5] reported $T_c = 27.05$ °C; Morrison and Knobler reported $T_c = 26.963$ °C and $x_c = 0.3830$ [6]; Beysens and Bourgou [7] $x_c = 0.3889$; Bouanz and Beysens [8] reported $T_c = 26.948$ °C and $x_c = 0.390$; Bouanz [9] reported $T_c = 26.948$ °C and $x_c = 0.3890$). The (I–W) solvent mixture is particularly attractive, and a great deal of work has been well explored by several researchers [10–20] with different detailed experimental studies, to understand the anomalous behavior in the vicinity of the critical point. To the best of our knowledge, there are no experimental refractive index data available in the literature for (I–W) over the full range of compositions under atmospheric pressure at various temperatures in the one-single homogeneous phase. This prompted us to carry out the experimental values of density

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and refractive index of (*I–W*) system over the entire range of composition from 300.15 (very near to $T_c=300.095$ K) to 313.15 K. From these data, excess molar volume, V^E, deviations in refractive index, Δn, and molar refraction, R, based on Lorentz–Lorenz relation have been computed. These results have been fitted to the Redlich–Kister polynomial equation [21] to derive binary coefficients and estimate the standard errors between experimental and calculated results. Calculated values are used to understand the nature of molecular interactions between the mixing components. We have also used several common mixing rules: Lorentz–Lorenz [22,23], Gladstone–Dale [24], Laplace [25], Eykman [26], Arago–Biot [27], and Oster [28] equations to predict refractive index of the mixtures from their respective experimental densities, refractive index, and densities of the pure component.

2. Experimental

The isobutyric acid was provided by Riedel de Haën. The purity was stated to be 99.99 mol%. Additional purification has not been considered necessary. The main impurity is probably water. The water, used in this study, was obtained from deionised and three times distilled operations, and has a specific conductivity of about 10^{-6} Ω^{-1} cm^{-1}.

All mixtures were prepared from weighed amounts of the pure components. The weight is obtained with a resolution of 10^{-3} g. Some care was taken to avoid moisture and dust in the final sample, namely, baking the syringes and the cells overnight under vacuum and preparing the mixtures in a dust-free area. The cell, in which the isobutyric acid and water were mixed together, was immersed in a thermally stabilized water bath with thermal regulation in the order of 10^{-3} K over hours. The temperature was measured by using a quartz thermometer (HP 2804 A) giving a resolution of 10^{-3} K, and which was calibrated on an absolute scale within 0.01 K.

Excess volumes V^E have been determined from densities measured with an Anton Paar digital precision densimeter (model DMA46) which was modified in our laboratory. The density ρ (g cm^{-3}) of a solution was calculated from the electronically measured frequency of a mechanical oscillator filled with the fluid. The filling was operated by means of a medical syringe. The oscillator was a U-shaped glass tubing (volume of 0.7 cm^3) placed in a metal block. This apparatus needs to be carefully calibrated with two liquids of different densities; we choose as standards water, with density data from Ref. [29]; and methanol, with density data from Ref. [30]. The response time of the apparatus to temperature changes is much higher than the time needed to reach a stable signal. In order to avoid systematic errors when measuring densities of pure liquids at different temperatures, each temperature change was followed by a waiting time of 2 h. The precision of density measurements was $\pm 10^{-4}$ g cm^{-3} and the accuracy for V^E is lower than 2×10^{-3} cm^3 mol^{-1}.

Refractive index of the pure liquids and solutions were measured to an accuracy of $\pm10^{-4}$ in the temperature interval of 300.15–313.15 K by using a thermostatic digital Abbe refractometer (Atago, 3T, Tokyo, Japan) at the wavelength of the D-line of sodium, 589.3 nm and atmospheric pressure. Temperature was controlled by circulating water into the refractometer through a thermostatically controlled bath with the digital temperature control unit in order to maintain the desired temperature within ±0.01 K. A check of the calibration was performed by comparing the refractive index of isobutyric acid with the existing data [29] which were extrapolated at the same temperature and wavelength. The remaining discrepancies amounted to a few 10^{-4} and were of the order of the scatter of the data as reported by different authors. The sample was injected into the prism assembly by means of an airtight syringe. Refractive index values were measured to an accuracy of ±0.0001 after the sample mixture was thermostatically at equilibrium. In order to obtain consistent values, we held the temperature constant throughout each set of measurements and repeated every experiment three times under the same conditions.

3. Results and discussion

3.1. Excess molar volume and refractive index deviation

From refractive index and densities measurements, refractive index deviations, Δn, defined on a volume fraction basis [31,32] and excess volumes, V^E, have been calculated as:

$$\Delta n = n - \phi_1 n_1 - \phi_2 n_2 \tag{1}$$

$$V^E = x_1 M_1\left(\frac{1}{\rho}-\frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho}-\frac{1}{\rho_2}\right) \tag{2}$$

where n is the refractive index of the mixture, ϕ_i and n_i are the volume fraction associated to the unmixed state and the refractive index of component i, respectively, ρ is the density of the mixture, x_i, M_i, and ρ_i are the mole fraction, the molar mass, and the density of component i, respectively.

The experimental densities, ρ, refractive index, n, as well as calculated refractive index deviations Δn, and excess volume V^E for the mixture isobutyric acid+water (*I–W*), including those of pure components, over the entire composition range, expressed by isobutyric acid molar fraction are presented in Table 1 at different temperatures near and far away from the critical temperature: $T-T_c=0.055$ K, $T-T_c=3.055$ K, $T-T_c=8.055$ K, $T-T_c=13.055$ K where $T_c=300.095$ K. V^E and Δn are shown graphically in Figs. 1 and 2. Each set of the experimental results for all systems were fitted by the method of least squares with all points weighed equally to the Redlich–Kister polynomial equation [21]:

$$Y = y_1(1-y_1)\sum_{i=0}^{j} A_1(2y_1-1)^i \tag{3}$$

where Y is matching to Δn or V^E, y_1 denotes the isobutyric acid volume fraction for Δn or the corresponding mole fraction for V^E, A_i is the polynomial coefficients, j is the polynomial degree, respectively. The solid lines in Figs. 1 and 2 represent the values calculated from the smoothing Eq. (3). For none of