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Density and refractive index measurements of critical mixture 1,4-dioxane + water + saturated KCl in homogenous phase region

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ABSTRACT

The ternary critical mixture of 1,4-dioxane (1) + water (2) + saturated KCl (3) has a lower critical point. The density ρ and refractive index n of this system have been measured as function of temperature for nine critical mixtures along the coexistence curve below the temperature of phase-transition. The water mole fraction in free basis x_2 in the mixtures extends from (0.550 to 0.880) and the molality m of KCl from 0.47 to 2.039 mol kg^{-1}. With increase of temperature, water mole fraction and KCl molality, the obtained density decreased, while the refractive index decreases with increase in temperature, water mole fraction and molality of salt. Both represented anomalies near the critical temperature T_c. The molar fraction of critical mixture, increase less than 1%, with temperature and decrease by 10%, with water mass fraction and molality of salt. The critical density and the critical refractive index vary linearly with water mass fraction w_2 with molality m of KCl as a third degree polynomial.

The temperature of separation of phase T_t varies with critical composition in water and molality of KCl.

1. Introduction

Studies about the physical properties of the liquid–liquid mixtures are important for the understanding of the thermodynamic of such system and for their use in the chemical engineering industry. One of the most important of which is that these properties provide information about intermolecular, ion–ion and ion–molecular interactions, also for association, pair-formation and clustering phenomenon. We have been investigating and reporting data of the critical properties of isobutyric acid + water mixture for many years: transport phenomena [2], ionic structures [3], solvation phenomena in the binary fluid [4], the effect of ions on mixture [5] and phase equilibrium properties occurring in the presence of added ions [6–8]. The electrical conductivity of isobutyric acid + water mixtures have also been studied [9–13]. In the previous paper [1], we investigated conductivity κ and refractive index n along with the coexistence curve of the system 1,4-dioxane (1) + water (2) + saturated KCl (3) and in the homogenous phase region near and far away from the critical temperature. We have reported that the electrical conductivity κ constitute an order parameter as well as the refractive index n [1]. Moreover, the density ρ constitute an order parameter as shown in the work of Gutkowski et al. [23,24].

We note that 1,4-dioxane and water are miscible in all proportions at all temperatures. The addition of salt to a homogeneous 1,4-dioxane + water mixture causes to some compositions, a phase separation [15–22].

We report in this paper the density ρ, refractive index n and the molar refraction R of the system 1,4-dioxane (1) + water (2) + saturated KCl (3) along with the coexistence curve below of the temperature of phase-transition for nine compositions in that such as water mole fraction in free basis x'_2 extends from 0.550 to 0.880 and the molality m of KCl extends from 0.7 to 2.039 mol kg^{-1}.

2. Experimental procedure

2.1. Sample preparation

The 1,4-dioxane was provided by Merck. The purity was stated to be 99.99%. The water was obtained from deionised and three times distilled water, and has a specific conductivity of about $10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ or less.

The guaranteed purity of the potassium chloride (Merck product) is better than 99.5%. All mixtures were prepared by masses, with uncertainty $\pm 10^{-3}$ g. Some care was taken to avoid moisture and dust in the final sample, by baking the syringes and the cells

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overnight under vacuum and preparing the mixtures in a dust-free area. The solution was maintained at equilibrium temperature, with stirring in order to dissolve completely the excess salt. Additional purification had not been considered necessary. The main impurity in the salt and 1,4-dioxane was probably water. Later, the sample was kept to reach the equilibrium state which bring fourth two distinct phases.

2.2. Transition temperature

The temperature was measured using a quartz thermometer (HP 2804 A), giving a resolution of $\pm 2 \times 10^{-4}$ K. The densities and the refractive indices data are measured in the one-phase region at each temperature T below the temperature of phase-transition T_t. In order to determine the temperature of phase-transition T_t, i.e. the temperature where the meniscus becomes visible, we proceeded as follows.

For all studied compositions of 1,4-dioxane (1) + water (2) + saturated KCl (3), the samples prepared are rigorously shaken and introduced into a thermostat bath at temperature T_1 until all the quantity of salt dissolved and the meniscus becomes visible, then $T_1 > T_t$, the temperature of the bath was decreased to T_2, and the same operation was repeated. If the meniscus was not visible, the bath temperature has changed to T_3, while shaking the sample. This method allows T_t to be determined by $T^+ > T_t$ and $T^- < T_t$, when $(T^+ - T^-) \cong 2 \times 10^{-3}$ K, we stopped the operation and verified that after having heated and vigorously shaken the sample out-side the bath, the meniscus was again visible at T^+ and not visible at T^-.

2.3. Density measurement

The density data in the homogeneous phase was measured with a commercial digital densitometer (Anton Paar, Model DMA 46, Austria), that was modified in our laboratory. The density of mixture was calculated from the electronically measured frequency of a mechanical oscillator filled with the fluid. The filling was accomplished by means of a medical syringe to prevent preferential evaporation and to reduce the possible errors. The densitometer needs to be carefully calibrated periodically with triple-distilled water [24] and methanol [25] at 298.15 K. The uncertainties of the measured values of density were $\pm 10^{-4}$ g cm^{-3}, a thermal regulation of the sample, to within, 3×10^{-3} K was needed. This was obtained by circulating water from a thermostat.

2.4. Refractive index measurement

Refractive index n of the studied solutions were measured in the temperature interval of 303.315–325.476 K by using a thermostatic digital Abbe refractometer at the wavelength of the D-line of sodium, 589.3 nm and atmospheric pressure. The precision of the measure is estimated to $\pm 10^{-4}$. 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 required temperature within ±0.01 K. A check of the calibration was performed by comparing the refractive index of 1,4-dioxane 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 uncertainty of $\pm 10^{-4}$ 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 under the same conditions three times.

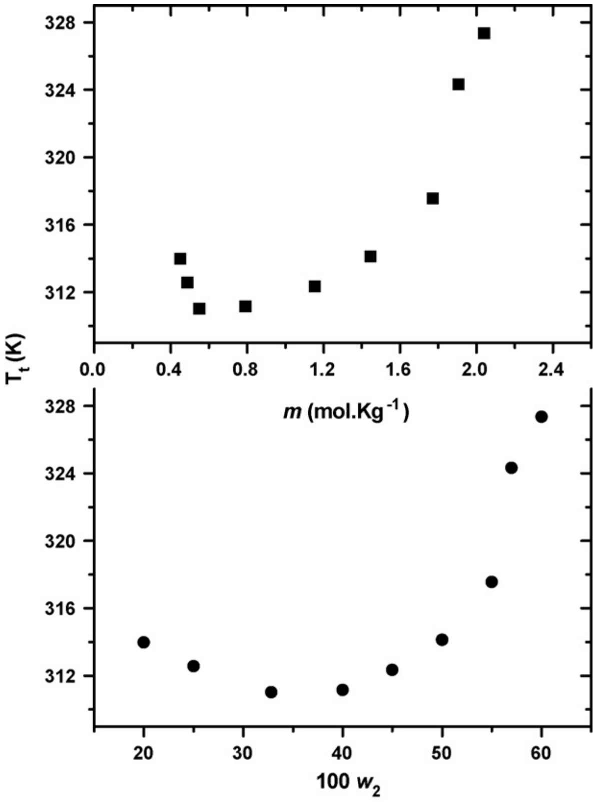

Fig. 1. Variation of the temperature of phase separation T_t as function of water mass fraction and the KCl molality.

3. Results and discussion

3.1. Transition temperature

Fig. 1 displays respectively the experimental variation of the temperature of phase separation as a function of molality m of potassium chloride and of the water mass fraction w_2. We note that T_t has a minimum for the two cases equal to 311.032 K.

3.2. Density

The density results as function of the temperature of 1,4-dioxane (1) + water (2) + saturated KCl (3) at different water mass fraction w_2 and chloride potassium molality m are reported in Table 1 and plotted in Fig. 2. The representation shows that the density decreases with, increase in temperature and increase with increasing water mole fraction and molality of KCl. The density ρ values can be correlated as a function of temperature T, according to the following equation:

$$\rho\ (\mathrm{kg\,m^{-3}}) = A^{\mathrm{I}} + B^{\mathrm{I}} T\,(\mathrm{K}) \qquad (1)$$

The A^{I} and B^{I} coefficients for Eq. (1) are given in Table 2. Analyzing these coefficients, we obtained that A^{I} decreases linearly with increase in water mole fraction and decreases with increase in the concentration of salt, while B^{I} increases linearly with increase in water mole fraction and increases with increase in the concentration of salt.

Fig. 3 shows the reduced temperature $t = |T/T_c - 1|$ dependence of the densities, where T_c is the critical temperature of 1,4-dioxane (1) + water (2) + saturated KCl (3). The densities represented a noticeable critical anomaly near the critical temperature, which can be related to the singularity in the heat capacity at constant pressure and concentration, which has a power-low with the