Measurements of the liquid–liquid phase equilibria of binary solutions of 1-methyl-3-octylimidazolium tetrafluoroborate with 1-heptanol or 2-pentanol

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ABSTRACT

Liquid–liquid phase equilibria of binary solutions of the room temperature ionic liquid (RTIL) 1-methyl-3-octylimidazolium tetrafluoroborate ([C_8mim][BF_4]) with 1-heptanol or 2-pentanol were measured. The critical exponents β obtained from the liquid–liquid equilibrium data in the critical region were consistent with the 3D-Ising value, which confirmed the 3D-Ising criticality of the investigated binary ionic solutions. The asymmetry of the diameters of the coexistence curves was analyzed by the complete scaling theory, indicating a significant contribution of the heat capacity related term. The RPM (restricted primitive model)-rescaled critical parameters were calculated, which showed dual characters of both solvophobic and coulombic criticalities of the studied binary ionic solutions.

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1. Introduction

Room temperature ionic liquids (RTILs) are ambient temperature molten salts with low vapor pressures, high conductivity, large heat capacity and good dissolving ability, etc. [1–4]. RTILs as one kind of green solvents have the perspective of replacing traditional solvents in many chemical engineering applications [5–7]. Specially, the mixed RTILs/organic solvents have been used as the chemical reaction media to facilitate the separation of the products, the solvent, and the catalyst by varying the temperature or composition in the media. Moreover, the critical behaviors of the ionic solutions have drawn much attention in the field of fundamental research [8–12]. It was proposed that the liquid–liquid phase transitions of binary ionic solutions near the critical points are driven by the coulombic interaction or the solvophobic mechanism or both, depending on the permittivity of the organic solvents [9,13–15]. Therefore, more extensive and precise measurements on liquid–liquid phase equilibria of binary solutions containing RTIL are highly desired to gain further understanding about the phase behavior and the critical phenomena of RTIL solutions.

In recent years, Anisimov and co-workers extended the concept of complete scaling [16] to incompressible or weakly compressible binary liquid mixtures which suggested [17,18] that the scaling fields may be expressed by the linear combinations of all physical fields: the chemical potential of the solvent μ_1, the difference of the chemical potentials between the solvent and the solute $\Delta\mu$, the temperature T and the pressure p, which has been shown to well describe the asymmetric criticality of binary molecular solutions and ionic liquid solutions [18–22]. Although some investigations involving the application of the complete scaling theory to describe the asymmetric criticality of ionic solutions have been reported [12–15,22,23], only a few articles reported high quality coexistence curves in the critical region for binary solutions containing RTIL and detailed analysis of the asymmetric behavior of the diameters of coexistence curves.

As a continuum of the investigations on the phase equilibrium of binary solutions containing RTIL, in this paper, we report the liquid–liquid coexistence curves for binary solutions of {x 1-methyl-3-octylimidazolium tetrafluoroborate ([C_8mim][BF_4]) + (1 − x) 1-heptanol} and {x [C_8mim][BF_4] + (1 − x) 2-pentanol}. The experimental results are used to determine the critical exponent β relating to the coexistence curves, and to discuss the asymmetric behavior of the diameters of the coexistence curves through the complete scaling theory. Furthermore, the dual characters of both solvophobic and coulombic criticality for the studied binary solutions are detected and discussed.

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2. Experimental

2.1. Chemicals

The purities, the suppliers, and the dried and stored methods of the ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate ($[C_8mim][BF_4]$), 1-heptanol and 2-pentanol used in this work are listed in Table 1. The mass fraction of water remaining in the $[C_8mim][BF_4]$ after drying was analyzed by the coulometric Karl–Fischer titration and found to be 158 ppm.

2.2. Apparatus and procedure

The sample was prepared in an Ace glass tube with an Ace-thread connector by weighting proper amounts of pure components using a Mettler-Toledo analytical balance with a precision of 0.1 mg. The tube was then sealed by a Teflon cap. The critical composition of the binary mixture was determined by the criterion of "equal volume" of the two phases near the phase-separation point [24]. The critical mole fraction x_c was able to be determined within ±0.001 by this method using the visual observation. Thereafter, a sample with the critical composition was prepared in a rectangular fluorescence cell also with an Ace-thread connector and sealed by a Teflon cap. The cell was set on a sample hold in a water bath. The temperature in the bath was controlled within ±0.002 K. A platinum resistance thermometer connected with a Keithley 2700 digital multimeter was used to measure the temperature T, which was calibrated against a standard platinum resistance thermometer and believed to have an accuracy of ±0.02 K in measurement of T. The precision in measurement of T or T_c is about ±0.002 K, thus the accuracy of $(T_c - T)$ was estimated to be about ±0.003 K. The refractive indexes were measured by the method of "minimum deviation" [25]. A He–Ne laser with wavelength λ being 632.8 nm was used as a light source. The uncertainty in measurement of refractive index in each coexisting phase was estimated to be ±0.0001.

3. Results and discussion

The critical mole fractions of $[C_8mim][BF_4]$ and the critical temperatures were determined to be $x_c = (0.131 \pm 0.001)$, $T_c = (307.538 \pm 0.02)$ K for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{1-heptanol}\}$ and $x_c = (0.101 \pm 0.001)$, $T_c = (294.937 \pm 0.02)$ K for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{2-pentanol}\}$, respectively.

The refractive indexes n measured for each coexisting phase at various temperatures are listed in columns 2 and 3 for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{1-heptanol}\}$ in Table 2 and for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{2-pentanol}\}$ in Table 3, which are also shown in Fig. 1(a) and Fig. 2(a) as (T, n) coexistence curves. In order to obtain the values of mole fractions x in each of the coexisting phases at various temperatures, a series of refractive indexes n as a function of temperature in one-phase region for binary mixtures of $\{x\ [C_8mim][BF_4] + (1-x)\ \text{1-heptanol}\}$ and $\{x\ [C_8mim][BF_4] + (1-x)\ \text{2-penta-nol}\}$ with various known mole fractions were measured, which are listed in Table 4. Since the critical anomaly in the refractive index is negligible, the refractive index n of a mixture may be expressed as a linear function of temperature in a certain temperature range [25,26]:

$$n(T, x) = n\left(T^0, x\right) + R(x)\left(T - T^0\right) \tag{1}$$

$$R(x) = (1 - x)R_1 + xR_2 \tag{2}$$

where $R(x)$ is the derivative of n with respect to T for a solution with the particular composition x; R_1 and R_2 are the values for pure alkanol and $[C_8mim][BF_4]$, respectively. The refractive indexes of pure $[C_8mim][BF_4]$, 1-heptanol and 2-pentanol at different temperatures were fitted to Eq. (1), which gave $R_1 = -3.94 \times 10^{-4}\,K^{-1}$ for 1-heptanol, $R_1 = -4.31 \times 10^{-4}\,K^{-1}$ for 2-pentanol, and $R_2 = -2.69 \times 10^{-4}\,K^{-1}$ for $[C_8mim][BF_4]$. Therefore, the data listed in Table 4 were fitted with Eqs. (1) and (2) to obtain the values of $n(T^0, x)$ with T^0 being the middle temperature of the coexistence curve, namely, $T^0 = 303.202$ K for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{1-heptanol}\}$ or $T^0 = 289.762$ K for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{2-pentanol}\}$, which were further fitted to a polynomial form:

$$n(T^0 = 303.202K, x) = 1.4194 + 0.0198x - 0.0238x^2 \\ + 0.0368x^3 - 0.0355x^4 + 0.0138x^5 \tag{3}$$

for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{1-heptanol}\}$ or

$$n(T^0 = 289.762K, x) = 1.4068 + 0.0607x - 0.0636x^2 \\ + 0.0408x^3 - 0.00843x^4 + 0.00220x^5 \tag{4}$$

for $\{x\ [C_8mim][BF_4] + (1-x)\ \text{2-pentanol}\}$ with the standard deviations of 0.0001. The values of mole fractions in the coexisting phases at various temperatures were then obtained from (T, n) data by simultaneously solving Eqs. (1)–(4) using the Newton iteration method.

The values of the volume fraction ϕ in the two coexisting phases at various temperatures were calculated from the mole fractions x through:

$$\frac{1}{\phi} = (1 - K) + \frac{K}{x} \tag{5}$$

$$K = \frac{d_2 M_1}{d_1 M_2} \tag{6}$$

where d is mass density taken from Refs. [27–29]; M is the molar mass and subscripts 1 and 2 refer to alkanol and $[C_8mim][BF_4]$, respectively. The values of x and ϕ of the coexisting phases at various temperatures are listed in columns 4–7 in Tables 2 and 3, and shown as plots of the temperature against the mole fraction (T, x) and the temperature against the volume fraction (T, ϕ) in Fig. 1(b), (c), and Fig. 2(b), (c), respectively.

Taking the assumption of ideal mixing, the molar volumes V in the solutions of the coexisting phases can be calculated by:

$$V^{U(L)} = \left(1 - x^{U(L)}\right)\frac{M_1}{d_1} + x^{U(L)}\frac{M_2}{d_2} \tag{7}$$

and their critical values V_c can be obtained through:

$$V_c = (1 - x_c)\frac{M_1}{d_{1,c}} + x_c\frac{M_2}{d_{2,c}} \tag{8}$$

where the superscripts "U" and "L" refer to the upper and the lower phase, respectively. The values of d_i at each phase separation temperature and $d_{i,c}$ at the critical point were

Table 1
Purities, suppliers, and dried and stored methods of chemicals.

Chemical name	Supplier	Purity, mass fraction	Dried and stored method
$[C_8mim][BF_4]$	Cheng Jie Chemical Co. Ltd.	0.99	Dried under vacuum at 330 K for 2 weeks and then stored in a desiccator over P_2O_5
1-Heptanol	Aladdin	0.99	0.4 nm molecular sieves
2-Pentanol	Alfa Aesar	0.99	0.4 nm molecular sieves