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Critical phenomena of {1-butanol + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide} binary solution

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ABSTRACT

The liquid-liquid equilibrium data and the specific heat capacities for the binary room temperature ionic solution {1-butanol + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide} have been reported. The corresponding critical exponents β and α were obtained and found to be well coincided with the 3D-Ising criticality. The critical complete scaling theory was applied to successfully describe the asymmetric behavior of the diameter of the coexistence curve with the consideration of the heat capacity related term. The large values of the reduced critical density, the reduced critical temperature and the critical amplitude related to the heat capacity were deduced, which indicated a solvophobic criticality of the studied system.

1. Introduction

In recent decades, the room temperature ionic liquids (RTILs) and the binary solutions containing RTILs have been applied in many chemical engineering fields to replace the traditional solvents [1–6]. These applications require the knowledge of various physical-chemical properties of RTIL systems, among which liquid-liquid equilibria and heat capacities of binary solutions containing RTILs particularly received much attention, because they are not only important to industrial applications but also to fundamental research of the universal critical phenomena of binary solutions [7–15]. It is expected that the 3D-Ising universality criticality may be challenged as the long distance coulombic interaction is dominated in the RTIL solutions, which requires more precise experimental data to be explored. In addition, the combination of the liquid-liquid equilibrium data and heat capacities of binary RTIL solutions are demanded for study of the asymmetric behavior of the coexistence curves based on the newly developed "complete scaling theory" [16,17].

In this paper, liquid-liquid equilibrium data and heat capacities of a binary solution {1-butanol + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide} are reported. These experimental results are used to obtain the corresponding critical exponents, which confirms the critical universality. Furthermore, we analyze the asymmetric behavior of the coexistence curve to test the validity of the complete scaling theory and discuss the solvophobic or coulombic character in the studied RTIL solutions.

2. Experimental

2.1. Chemicals

In this work we used 1-butanol and ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) to construct a binary solution for study, whose purities, suppliers, purification methods and water contents are listed in Table 1. After these chemicals were dried, the water remaining in them were analyzed by the coulometric Karl-Fischer titration.

2.2. Measurement of coexistence curve

A home-built instrument [18,19] was used for measurement of the coexistence curve. The critical mole fraction was searched through the judgment of "equal volume" of two coexisting phases near the phase separation temperature by visual observation [18,20], which can be determined with a precision of ±0.001.

A binary solution with the known critical composition was prepared by weighing in a rectangular fluorescence cell. After the cell was sealed, it was installed in a water bath, where the temperature stability was ±0.002 K. The temperature in the water bath was measured by a platinum resistance thermometer and a Keithley 2700 digital multimeter with standard uncertainty and reproducibility being 0.02 K and 0.002 K, respectively. It was found that although the standard uncertainty in measurement of critical temperature T_c was as large as 0.05 K, the reproducibility in measurements of the phase separation temperature T and the critical temperature T_c was only about ±0.002 K. Thus the standard uncertainty in measurement of $|T_c - T|$ was ±0.003 K.

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Table 1
Purities, suppliers, purification methods, and water contents of chemicals.

Chemical	Purity, mass fraction	Supplier	Dried and store method	Water content
$[C_2mim][NTf_2]$	0.99	ChengJie Chemical Co. LTD	Dried under vacuum at 328 K for 48 h and then stored in a desiccator over P_2O_5	400 ppm
1-Butanol	0.999	Aladdin	0.4 nm molecular sieves	200 ppm

The liquid-liquid coexistence curve of {1-butanol + $[C_2mim][NTf_2]$} was determined by refractive index measurement by the "minimum deviations angle technique" with a He-Ne laser as a light source having a wavelength of 632.8 nm [18]. The standard uncertainty in measurement of the refractive index was estimated to be about 0.0001. The measurements were taken at the vapor pressure of the solution prepared in the sealed rectangular cell, which depended on the temperature. However, the influence of the vapor pressure variation on the liquid-liquid equilibrium in the cell was negligible; thus the measurements were assumed carried at a constant ambient pressure.

2.3. Measurement of specific heat capacity

The specific heat capacities for the critical binary solution of {1-butanol + $[C_2mim][NTf_2]$}at various temperatures were measured by a differential scanning calorimeter, Micro DSC III (Setaram, France). The instrument provided 2 standard batch vessels, the reference and the sample. The determination of heat capacities of {$(1 - x_c)$1-butanol + $x_c[C_2mim][NTf_2]$} was conducted by three heat flow measurements. The reference vessel was always filled with aluminium oxide (Al_2O_3), while the sample vessel was filled with heptane, 1-butanol and the sample to be investigated in sequence. The corresponding heat flows of these three steps are HF_h, HF_b, and HF_x, respectively. After the binary solution with the critical composition was prepared in the sample vessel by weighing, it was placed in an air bath with the temperature sufficiently higher than its critical one, followed by violently shaking to ensure uniform mixing of the solution in the sample vessel. The background noise of Micro DSC III was less than ±5 μW and ± 10 μW for the first two steps and the last one, respectively. The temperature stability was better than ±0.002 K. The specific heat capacity $c_{p,x}$ of the investigated sample was calculated by

$$c_{p,x} = \frac{1}{m_x}\left[(m_b c_{p,b} - m_h c_{p,h})\frac{(HF_x - HF_h)}{(HF_b - HF_h)} + m_h c_{p,h}\right] \quad (1)$$

where m_h, m_b, and m_x are the masses of heptane, 1-butanol, and the sample, respectively; $c_{p,h}$ and $c_{p,b}$ are the specific heat capacities of heptane and 1-butanol, which can be calculated by their molar heat capacities $C_{p,mi}$ though $c_p = C_{p,mi}/M_i$ with M_i being the molar mass of heptane or 1-butanol. The molar heat capacities $C_{p,mi}$ for heptane or 1-butanol were taken from the literature [21,22]. The measurements were carried out in the down scanning model with the scanning rate being selected as 0.1 $K \cdot min^{-1}$. In fact, the experiments were performed at the vapor pressure in the sealed batch vessel, which depended on the temperature. However, the influence of the vapor pressure variation on the heat capacity in the cell was negligible, thus the measured heat capacities were approximately taken as the isobaric ones at a constant ambient pressure and denoted by C_p throughout this paper.

The heat capacity per unit volume of the sample was calculated by

$$C_p V^{-1} = c_{p,x}\frac{M_c}{V_c} \quad (2)$$

where M_c and V_c are the molar mass and molar volume of the binary solution with the critical composition, respectively, which was calculated by

$$M_c = x_{1,c}M_1 + x_{2,c}M_2 \quad (3)$$

$$V_c = x_{1,c}V_1^0 + x_{2,c}V_2^0 \quad (4)$$

where $x_{i,c}$, M_i and $V_i^0$are the critical mole fraction, molar mass and molar volume of the ith component, respectively. Subscripts 1 and 2 in Eqs. (3) and (4) refer to 1-butanol and $[C_2mim][NTf_2]$, respectively. The molar volume V_i^0 was calculated by M_i and the density of the ith component. The densities of 1-butanol and $[C_2mim][NTf_2]$ at various temperatures were measured by the Anton Paar DMA 5000 M density meter, which were listed in Table 1 of the supplementary data. Linear fitting of the density data of 1-butanol and $[C_2mim][NTf_2]$ gave $\rho_1/(g{\cdot}cm^{-3})$ and $\rho_2/(g{\cdot}cm^{-3})$ as:

$$\rho_1/(g \cdot cm^{-3}) = -8.08882 \times 10^{-4}(T/K) + 1.05305 \quad (5)$$

$$\rho_2/(g \cdot cm^{-3}) = -9.94113 \times 10^{-4}(T/K) + 1.81493 \quad (6)$$

The standard uncertainty in determination of the specific heat capacity including the propagated ones from the uncertainties of two reference samples reported in the literature [21,22] were estimated to be 0.030 $J \cdot g^{-1} \cdot K^{-1}$ and 0.011 $J \cdot g^{-1} \cdot K^{-1}$ in the critical and non-critical regions, respectively. The standard uncertainty of the heat capacity per unit volume were estimated to be 0.031 $J \cdot cm^{-3} \cdot K^{-1}$ and 0.013 $J \cdot cm^{-3} \cdot K^{-1}$ in the critical and non-critical regions, respectively.

3. Results and discussions

3.1. Coexistence curves

By using the "equal volume" technique described in Section 2.2 we determined the critical mole fraction x_c of $[C_2mim][NTf_2]$ and the critical temperature T_c, which were $x_c = 0.145 \pm 0.001$, $T_c = 321.622$ K respectively for the studied binary solution. The former is in well agreement with those determined by the other research groups, i.e. 0.146 ± 0.001 [23] and 0.141 ± 0.004 [24]. We measured refractive indexes n in two coexisting phases at various temperatures, which are listed in columns 2 and 3 of Table 2.

It has been commonly accepted that the critical anomaly in refractive index n may be neglected [18,25]; which allow us to describe n as a linear dependence of temperature or composition for any of pure liquids or their mixtures in a certain range of temperature [18]:

$$n(T,x) = n\left(T^0,x\right) + R(x)\left(T - T^0\right) \quad (7)$$

$$R(x) = (1-x)R_1 + xR_2 \quad (8)$$

where $R(x)$ is the derivative of n with respect to T for a particular mole fraction x, and R_1 and R_2 are the values of $R(x)$ for $x = 0$ and $x = 1$, respectively. The refractive indexes of pure components at different temperatures and of mixtures with different compositions in one-phase region at $T = 321.780$ K were respectively measured. The measured results are listed in Table 3.

Fitting of the temperature dependent refractive index data for the two pure components with Eq. (8) gave $R_1 = -0.000416\ K^{-1}$ for 1-butanol, $R_2 = -0.000287\ K^{-1}$ for $[C_2mim][NTf_2]$ and a standard deviation of the fitting being about 0.0001. With the values of R_1 and R_2 and the experimental indexes of {$(1 - x)$ 1-butanol + x $[C_2mim][NTf_2]$} at $T = 321.780$ K listed in Table 3, we calculated the index values for