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Heat capacities and asymmetric criticality of the (liquid + liquid) coexistence curves for {dimethyl carbonate + *n*-undecane, or *n*-tridecane}

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ABSTRACT

The (liquid + liquid) coexistences and the critical behavior of isobaric heat capacity per unit volume for critical binary solutions {dimethyl carbonate + *n*-undecane, or *n*-tridecane} have been studied. The critical exponents β and α were deduced and found to be consistent with the 3D-Ising values. The critical amplitudes were determined and used to test the asymmetric criticality of coexistence curves. It was found that the heat capacity does play an important role in describing the asymmetric criticality of the coexistence curves.

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1. Introduction

Fluid mixtures can exhibit a variety of critical phase separation phenomena. As commonly accepted, the fluids and fluid mixtures belong to the 3D-Ising-like universality class [1,2]. In the immediate region of critical point, the difference of the general density variables of two coexisting phases $\Delta\rho$ (the width of the coexistence curve), such as refractive index or mole fraction or volume fraction, and the isobaric heat capacity per unit volume C_pV^{-1} show power-law dependences described as follows [1,2]:

$$\Delta\rho = |\rho^{\mathrm{U}} - \rho^{\mathrm{L}}| = B\tau^{\beta}, \quad (1)$$

$$C_pV^{-1} = (A^{\pm}/\alpha)|\tau|^{-\alpha}, \quad (2)$$

where τ is the reduced temperature ($\tau = |T - T_{\mathrm{c}}|/T_{\mathrm{c}}$, the subscript "c" denotes the critical value); ρ is the general density variable and the superscripts "U" and "L" denote upper and lower coexisting phases; β and α are the critical exponents relating to the width of the coexistence curve and the heat capacity; B and $A^{\pm}$ are the corresponding critical amplitudes with "+" or "−" denoting the one-phase or the two-phase region.

However, in a wide temperature range, corrections to simple power-law dependences should be taken and equations (1) and (2) may be rewritten as:

$$|\rho^{\mathrm{U}} - \rho^{\mathrm{L}}| = B\tau^{\beta} + B_1\tau^{\beta+\Delta} + \cdots, \quad (3)$$

$$C_pV^{-1} = C_{p0} + E\tau + (A^{\pm}/\alpha)|\tau|^{-\alpha}(1 + D^{\pm}|\tau|^{\Delta} + \cdots), \quad (4)$$

with Δ being a critical correction-to-scaling exponent relating to the first Wegner correction term; B_1 and $D^{\pm}$ are the amplitudes of the first term of correction-to-scaling [3]. The background term C_{p0} is the sum of B_{bg} and B_{cr}, where B_{bg} is a regular background heat capacity at the non-critical state of a binary solution, and B_{cr} is a critical-fluctuation induced contribution to the background heat capacity. The value of C_{p0} was thought to be the same in the one-phase and the two-phase region [3]. $E\tau$ is the non-critical linear term arising from the regular part of the free energy, which should be the same in both sides of the critical point. B, $A^{\pm}$, $D^{\pm}$, and B_{cr} are all system-dependent, however, some ratios of them were predicted to be universal [1–6]. For instance, A^{+} and A^{-} are depend on the microscopic characteristics of the system, but the value of the ratio A^{+}/A^{-} is a universal quantity and was predicted to be 0.530 ± 0.003 by high-temperature series expansion [7,8].

The asymmetric criticality has been paid more attention recently, driven by the original work of Fisher and co-workers [9–11]. The concept of "complete scaling" has been applied to explain the singularity of the diameter of the coexistence curves for one-component fluids [12] and incompressible [13–15] or weakly

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compressible binary fluid systems [16]. According to Pérez-Sánchez *et al.*, the width ΔZ_{cxc} and the diameter Z_{d} of a coexistence curve can be expressed by:

$$\Delta Z_{\text{cxc}} \equiv (Z^{\text{U}} - Z^{\text{L}})/2 \approx \pm \hat{B}_0^Z|\tau|^{\beta}(1 + \hat{B}_1^Z|\tau|^{\Delta} + \hat{B}_2^Z|\tau|^{2\beta}), \tag{5}$$

$$Z_{\text{d}} \equiv (Z^{\text{U}} + Z^{\text{L}})/2 \approx Z_{\text{c}} + \hat{D}_2^Z|\tau|^{2\beta} + \hat{D}_1^Z\left(\frac{\hat{A}^-}{1-\alpha}|\tau|^{1-\alpha} + \hat{B}_{\text{cr}}|\tau|\right), \tag{6}$$

where Z is the physical density, such as the mole fraction x_2 of the solute, the reduced density $\hat{\rho}$ ($\hat{\rho} = \rho/\rho_{\text{c}} = V_{\text{c}}/V$, ρ and V are the molar density and the molar volume of the binary solution, respectively; subscript "c" denotes the critical value), and the reduced partial molar density of the solute $\hat{\rho}x_2$ (the product of $\hat{\rho}$ and x_2); $\hat{B}_0^z$, $\hat{B}_1^z$, $\hat{B}_2^z$, $\hat{D}_2^z$, and $\hat{D}_1^z$ are the system dependent amplitudes; $\hat{B}_{\text{cr}} = B_{\text{cr}}V_{\text{c}}/R$ is a reduced variable with R being the gas constant; $\hat{A}^- = A^-V_{\text{c}}/\alpha R$ is a reduced critical amplitude of A^- for the isobaric heat capacity per unit volume in the two-phase region.

According to equations (5) and (6), test of the complete scaling theory requires both of coexistence curve data and heat capacity data for a series of binary solutions. In this work, we measure the coexistence curves and the heat capacities for critical binary solutions {dimethyl carbonate + *n*-undecane, or *n*-tridecane}. The experimental results are used to analyze the asymmetry of the coexistence curves and to evaluate the contribution of the heat capacity.

2. Experimental

2.1. Chemicals

Table 1 listed the purities and suppliers of the chemicals used in this work.

2.2. Apparatus and procedure

The (liquid + liquid) coexistences for {dimethyl carbonate + *n*-undecane, or *n*-tridecane} were obtained by measurements of refractive index, which have been described in details previously [17]. The critical composition was determined by the visual equal-volume method [18]. The temperature was controlled to within $T = 0.002$ K and measured with a platinum resistance thermometer and a Keithley 2700 digital multimeter in the experiment. The uncertainties in measurements were 0.0001 for the refractive index, $T = 0.02$ K for the temperature, and 0.003 K for the temperature difference ($T_{\text{c}} - T$).

The isobaric heat capacity per unit volume C_pV^{-1} was measured by using a Setaram Micro DSC III differential scanning calorimeter, which is based on the Tian–Calvet's principle. This calorimeter affords convenient operation over a wide temperature range with a small amount of sample (about 1 cm^3). Liquid heat capacity vessels were used in our measurements, which avoided the presence of the vapor phase over the liquid, thus no vapor phase correction was needed [19]. Background noise of Micro DSC III was less than ±0.2 μW, and the temperature stability was better than $T = \pm 0.002$ K. The scanning rate was selected to be (0.01 and 0.1) K · min^{-1} for the critical region and the temperature range away from the critical point, respectively.

In each measurement, the reference vessel was always filled with *n*-heptane, while the measuring vessel was filled with *n*-heptane, 1-butanol, and the sample to be investigated, respectively. All three measurements were performed in the down scanning model at the ambient pressure. The uncertainties in measurements of isobaric heat capacities per unit volume $C_{\text{p}}V^{-1}$ of the samples investigated were estimated to be less than 0.001 J · K^{-1} · cm^{-3} over the temperature range away from the critical point and ±0.01 J · K^{-1} · cm^{-3} near the critical point. An additional systematic uncertainty was introduced by the uncertainties of isobaric heat capacities per unit volume of the two reference samples *n*-heptane and 1-butanol, which was estimated to be about ±0.002 J · K^{-1} · cm^{-3}. More detailed description of the apparatus and the principle of the measurement could be found in our previously published article [20].

3. Results and discussions

3.1. Coexistence curves

The critical mole fraction $x_{2,\text{c}}$ and the critical temperature T_{c} of {$(1-x_2)$ dimethyl carbonate + x_2 *n*-undecane} and {$(1-x_2)$ dimethyl carbonate + x_2 *n*-tridecane} by visual method were determined and are shown in table 2, where x_2 are the mole fractions of the components with larger molar volume, *i.e.* the mole fractions of *n*-alkanes in this work.

The measured refractive indexes n for each coexisting phases at the wavelength $\lambda = 632.8$ nm are listed in columns 2 and 3 of table 3 for {$(1-x_2)$ dimethyl carbonate + x_2 *n*-undecane} and in columns 2 and 3 of table 4 for {$(1-x_2)$ dimethyl carbonate + x_2 *n*-tridecane}. They are also shown in figure 1a and figure 2a, as the plots of temperature against refractive index, and denoted as the (T,n) coexistence curves.

The temperature against mole fraction (T,x_2) can be obtained by conversion of the (T,n) coexistence curve, which requires the dependences of refractive index on the mole fraction x_2 and the temperature T. The refractive index n of binary mixtures may be

TABLE 2

Critical mole fractions, critical temperatures for {$(1-x_2)$ dimethyl carbonate + x_2 *n*-undecane, or *n*-tridecane}, respectively.

$x_{2,\text{c}}$ [a]	T_{c}/K [a]	$x_{2,\text{c}}$ [b]	T_{c}/K [c]
	{$(1-x_2)$ Dimethyl carbonate + x_2 n-undecane}		
0.284 ± 0.002	292.7 ± 0.1	0.284 ± 0.002	293.221
	{$(1-x_2)$ Dimethyl carbonate + x_2 n-tridecane}		
0.244 ± 0.002	303.0 ± 0.1	0.249 ± 0.003	303.427

[a] Visual method.

[b] Fitting by equation (23).

[c] Fitting by equation (4) within the range of $T = \pm 3$ K with $D^+ = D^- = 0$ using the data of the isobaric heat capacity per unit volume.

TABLE 1

Purities and suppliers of chemicals.

Chemical	Supplier	Purity, mass fraction	Dried and stored method
Dimethyl carbonate	Acros Organ	0.99	0.4 nm molecular sieves
n-Undecane	Aldrich	0.99	0.4 nm molecular sieves
n-Tridecane	Aldrich	0.99	0.4 nm molecular sieves
n-Heptane	Sinopharm Chemical Reagent Co., Ltd.	0.99	0.4 nm molecular sieves
1-Butanol	Sinopharm Chemical Reagent Co., Ltd.	0.99	0.4 nm molecular sieves

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