Critical behaviour of binary mixture of {$xC_6H_5CN + (1 - x)CH_3(CH_2)_7CH_3$}: Measurements of coexistence curves, light scattering, and heat capacity

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ABSTRACT

Liquid + liquid coexistence, light scattering, and isobaric heat capacity per unit volume for the critical solutions of (benzonitrile + n-nonane) have been measured. The critical exponents relating to the coexistence curve β, the osmotic compressibility γ, the correlation length v, and the heat capacity α have been deduced and the values are consistent with the 3D-Ising values in the range close to the critical point. The experimental results of the liquid + liquid coexistence were analyzed to examine the Wegner correction terms and the behaviour of the diameter of the coexistence curves. The light scattering data were well described by the crossover model proposed by Anisimov and Sengers, and showed a tendency of monotonic crossover of the critical exponents γ and v from the 3D-Ising values to the mean-field values as the temperature departures from the critical point. From calorimetric measurements, the amplitude $A^{\pm}$ and the critical background B_{cr} of the heat capacity in the critical region have been deduced and some universal ratios are tested.

1. Introduction

The most fascinating feature of critical phenomena is universality since it implies that systems of different physical natures exhibit similar behaviour near the critical point. Close to the critical point of a particular system, large local fluctuations in the density or concentration effectively mask the identity of the system and produce universal phenomena. Therefore, seemingly very different systems can be grouped into a small number of universal classes depending on the spatial dimensionalities and the symmetry of the ordered phase. The fluids and fluid mixtures belong to the universality class of the 3D-Ising model, of which various thermodynamics properties, such as the difference $\Delta\rho$ of a general density variable of two coexisting phases, the correlation length ξ, the osmotic compressibility χ, and the isobaric heat capacity per unit volume C_pV^{-1} at the critical composition exhibit universal power-law dependences upon the reduced temperature t {$t = (T - T_c)/T_c$, where T_c is the critical temperature} near the critical point. These dependences may be described by the following forms:

$$\Delta\rho = \rho_2 - \rho_1 = Bt^{\beta}, \quad (1)$$
$$\chi = \chi_0 t^{-\gamma}, \quad (2)$$

$$\xi = \xi_0 t^{-v}, \quad (3)$$
$$C_p V^{-1} \propto (A^{\pm}/\alpha)|t|^{-\alpha}, \quad (4)$$

where ρ is the general density variable, ρ_1 and ρ_2 are the values of the density variables in the upper and lower coexistence phases; B, χ_0, ξ_0, and $A^{\pm}$ are the critical amplitudes. The amplitudes of one-phase and two-phase are denoted by the superscripts of + and −, respectively. The values of the critical exponents β, γ, v, and α are 0.326, 1.24, 0.630, and 0.110 [1,2], respectively, for the 3D-Ising universality class; while they are 0.5, 1, 0.5, and 0 from the classical mean-field theory. As distance from the critical point increases, a crossover from the 3D-Ising universality to the classical mean-field one should be expected.

Although the critical amplitudes are system-dependent, some ratios among the critical amplitudes corresponding to the correlation length, the susceptibility, the heat capacity, and the coexistence curves were predicted to be universal in a given university class. However, theoretical calculations and experimental tests of these universalities gave inconsistent results; therefore the validity of the universality needs further verification.

As a part of the continuous investigations on the critical behaviour of the binary mixtures of (benzonitrile + n-alkanes) [3–6], in this paper, we report the measurements of the liquid + liquid coexistence, light scattering, and isobaric heat capacity per unit volume for the binary solutions of (benzonitrile + n-nonane). The results are analyzed to obtain the critical exponents and the critical

amplitudes corresponding to $(\rho_2 - \rho_1)$, χ, ξ, and C_pV^{-1}, and to examine the Wegner correction terms and the behaviour of the diameters ρ_d of the coexistence curves. The crossover from the 3D-Ising class to the mean-field one is investigated and the universality of the critical amplitude ratios are tested and discussed.

2. Experimental

2.1. Chemicals

The benzonitrile (C_6H_5CN) and *n*-nonane ($CH_3(CH_2)_7CH_3$) used in measurements of coexistence curves and light scattering were supplied by Shanghai Kaiming Chemical Factory and Fluka Co., while those used in measurement of isobaric heat capacity per unit volume were purchased from Alfa Aesar Co. and Sinopharm Chemical Reagent Co., Ltd., respectively. All the chemicals had the mass fraction purity of 0.99, and were dried and stored over 0.4 nm molecular sieves.

2.2. Apparatus and procedure

2.2.1. Coexistence curves

The apparatus and the experiment procedure for measurements of refractive index, and the techniques for determinations of the critical composition and the critical temperature have been described previously [7]. The accuracy and the precision of the temperature measurement were ±0.01 K and ±0.001 K, respectively. The accuracy of the measurements was ±0.003 K for the temperature difference $(T - T_c)$, ±0.0001 for the refractive index in each coexisting phase, and ±0.001 for the critical mole fraction x_c.

2.2.2. Light scattering

The apparatus for measurement of static light scattering has been reported previously [3,5]. The temperature stability of the thermostat was better than ±0.003 K. The apparatus was equipped with an argon ion laser operating on 488 nm line. An attenuator was used to adjust the intensity of incident. The scattered light was recorded by a photomultiplier operated in the photon counting mode. Measurements were made in the angular range of $30° \leqslant \theta \leqslant 150°$. The intensities of the incident light and the transmitted light were measured by a light-power meter (Newport Model 1825-c). The intensity of incident light was used to normalize the scattering intensity for reduction of the uncertainties from the laser power fluctuation. The transmitted light intensity was used to calculate the turbidity in the sample for the correction of attenuation. The total uncertainties in measurements of the scattering light intensity and the temperature difference $(T - T_c)$ were about ±2% and ±0.005 K, respectively. All measurements were carried in one-phase region above the critical point.

2.2.3. Isobaric heat capacity per unit volume

The isobaric heat capacity per unit volume of the critical mixture was measured by means of a high sensitivity differential scanning calorimeter, Micro DSCIII (Setaram, France) based on the Tian–Calvet principle. Thermal effects in the calorimeter were measured by two flux meters (one on the measurement vessel side and the other on the reference vessel side), each of which measured the thermal power exchanged constantly between the experimental vessel and the calorimetric unit. The Tian–Calvet type flux metric probe enveloped the sample and was therefore capable of measuring almost all the energy exchanges between the experimental vessel and the calorimetric unit. The assembly was set in an inert atmosphere of dry nitrogen. An additional external water circulation circuit was used to provide or remove heat from

the thermoelectric elements. Background noise was less than ±0.2 μW, and temperature stability was better than ±0.002 K.

The special heat capacity vessels supplied by Setaram were used in measurement of isobaric heat capacity per unit volume of liquid, which avoided the presence of the vapour phase over the liquid, thus no vapour phase correction was needed [8].

According to the principle of the Calvet calorimeter, the heat flow rate *HF* is related to the total heat capacity *C* and the scanning rate *R* by:

$$HF \propto C \cdot R. \tag{5}$$

The isobaric heat capacity per unit volume of the liquid sample was determined by three steps of *HF* measurements at various temperatures, which was termed "continuous with reference". In each of the three measurements, the reference vessel was always filled with *n*-heptane, while the sample vessel was filled with *n*-heptane, 1-butanol, and the liquid sample to be investigated separately. The *n*-heptane and 1-butanol were calibration liquids, whose molar heat capacities C_p and densities ρ were taken from the literatures [9–11] and converted into isobaric heat capacity per unit volume through $C_pV^{-1} = C_p \cdot \rho/M$ with *M* being the molar mass. The isobaric heat capacity per unit volume $(C_pV^{-1})_s$ of the sample was calculated by:

$$(C_pV^{-1})_s = (C_pV^{-1})_0 + ((C_pV^{-1})_r -$$
$$(C_pV^{-1})_0) \cdot ((HF_s - HF_0)/(HF_r - HF_0)), \tag{6}$$

where $(C_pV^{-1})_0$ and $(C_pV^{-1})_r$ are the isobaric heat capacity per unit volumes of *n*-heptane and 1-butanol, and HF_0, HF_r, and HF_s are the heat flow rates of *n*-heptane, 1-butanol, and the liquid sample, respectively. This method of "continuous with reference" allowed a large temperature range to be covered in one run, which gave a continuous curve of heat capacity versus temperature.

The measurements were carried out in the down scanning model. Because the choice of proper scanning rates is practically important, we carefully examined the effects of scanning rate on the uncertainty of measurements, and balanced the time consumption and thermal delay, and finally selected 0.1 K · min^{-1} over the range $T = (289.9$ to $314.1)$ K and 0.01 K · min^{-1} over the range $T = (278.5$ to $289.9)$ K. The corresponding uncertainties were estimated to be less than 0.0005 J · K^{-1} · cm^{-3} within the range $T = (289.9$ to $314.1)$ K, 0.004 J · K^{-1} · cm^{-3} with the range $T = (284.3$ to $289.9)$ K, and 0.007 J · K^{-1} · cm^{-3} over the range $T = (278.5$ to $284.3)$ K, respectively, except for the region where the temperature was very close to the critical point, because in this region the heat capacity is very sensitive to the temperature change.

3. Results and discussion

3.1. Coexistence curves

The critical mole fraction and the critical temperature of $\{xC_6H_5CN + (1 - x)CH_3(CH_2)_7CH_3\}$ were determined to be $x_c = (0.497 \pm 0.001)$ and $T_c = (284.6 \pm 0.2)$ K, respectively, where *x* is the mole fraction of benzonitrile, the subscript c denotes the critical value. The refractive indices *n* were measured for each coexisting phase at various temperatures. The results are listed in columns 2 and 3 of table 1 and are shown in figure 1a.

The refractive index *n* of a pure liquid or a mixture may be well expressed as a linear function of temperature in a certain temperature range [7]:

$$n(T, x) = n(T^0, x) + R(x)(T - T^0), \tag{7}$$
$$R(x) = xR_A + (1 - x)R_B, \tag{8}$$

where $R(x)$ is the derivative of *n* with respect to *T* for a particular composition *x*, and R_A and R_B are the values of $R(x)$ for $x = 1$ and $x = 0$, respectively. Eqs. (7) and (8) allowed us to obtain $n(T, x)$ as a function of *T* and *x* simply by measurements of $R(x)$ for two pure components at various temperatures, and of the refractive indices for mixtures with various known compositions at a fixed temperature. The refractive indices of pure *n*-nonane and benzonitrile at various temperatures were measured and are listed in table 2. Fitting Eq. (7) to the data listed in table 2 gave