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The measurements of coexistence curves and light scattering for $\{x\mathrm{C_6H_5CN} + (1 - x)\mathrm{CH_3(CH_2)_{10}CH_3}\}$ in the critical region

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Abstract

The coexistence curves and light scattering data for a critical solution of (benzonitrile + dodecane) have been reported. The critical exponents relating to the difference in density variables of two coexisting phases β, the correlation length v, and the osmotic compressibility γ have been determined. The experimental results of the coexistence curves have also been analyzed to examine the Wegner correction terms and the behavior of the diameter of the coexistence curves. The data analysis shows that the 3D-Ising behavior is valid in a temperature range close to the critical point. However, in a wide temperature range the exponential values of v and γ change with the temperature significantly, clearly exhibiting the critical crossover from the 3D-Ising universality class to the classical one.

Keywords: Critical phenomena; Coexistence curve; Light scattering; Correlation length; Osmotic compressibility; Benzonitrile; Dodecane; Crossover phenomena

1. Introduction

The character of critical behavior in physical systems depends on the range of interactions. In the limit of infinite range of the interactions, the critical behavior a system does not affected by fluctuations of the order parameter and exhibits classical mean-field critical behavior. If the interaction range is finite, the critical behavior asymptotically close to the critical point is determined by fluctuations and the actual critical behavior depends on the particular universality class [1–3]. A variety of systems, including anisotropic ferromagnets, binary alloys, simple fluids, fluid mixtures, and polymer blends, belong to the 3D-Ising universality class [4–7]. At intermediate temperatures, a continuous crossover occurs from one universality class to the other. The critical crossover has attracted much attention.

Near the critical solution point, the difference $\Delta\rho$ of a general density variable, such as refractive indices, mole fraction and volume fractions, between two coexistence phase, the correlation length ξ, and the osmotic compressibility χ exhibit universal power-law dependences on the reduced temperature $t\{t = |T - T_c|/T_c\}$:

$$\Delta\rho = \rho_2 - \rho_1 = B\, t^{\beta}, \tag{1}$$

$$\xi \propto t^{-v} = \xi_0\, t^{-v}, \tag{2}$$

$$\chi \propto t^{-\gamma} = \chi_0\, t^{-\gamma}, \tag{3}$$

where T_c is critical temperature; B, ξ_0, and χ_0 are the critical amplitudes. The values of β, v, and γ are 0.327, 0.63, and 1.24 [8,9] for the 3D-Ising universality class; while they are 0.5, 0.5, and 1 from the classical mean-field theories.

In this paper, we report the experimental results of the coexistence curves and the light scattering for the system

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of (benzonitrile + dodecane). The results are analyzed to obtain the critical exponents and critical amplitudes corresponding to $(\rho_2 - \rho_1)$, ξ, and χ. The diameters ρ_d of the coexistence curves are examined to discuss the goodness of the general density variables used to construct the order parameters. Furthermore, values of v and γ obtained from different temperature ranges are compared, which shows the crossover behavior from 3D-Ising values to the classical mean-field values as the temperature departs away from the critical point.

2. Experimental

The benzonitrile, mass fraction 0.99, obtained from the Shanghai Kaiming Chemical Factory was distilled slowly under reduced pressure. The middle part of the distillate was collected and stored over a 0.4 nm molecular sieve. The dodecane, mass fraction 0.99, supplied by Fluka Co., was dried and stored over a 0.4 nm molecular sieve.

The coexistence curves were determined by measurements of the refractive indices n of two coexisting phases using a technique of “minimum deviations”. The apparatus and the experimental procedure for measurements of refractive index, and the techniques for determination of the critical concentration and the critical temperature have been described previously [10]. During measurements, the temperature was constant at ±0.001 K. The accuracy and the precision of the temperature measurements were ±0.01 K and ±0.001 K, respectively. The accuracy of measurement 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.

A high precision goniometer and a water bath [11] with a temperature stability better than ±0.003 K were incorporated in a BI-200SM Static and Dynamic laser light scattering system to measure the angular dependence of the scattered-light intensity of the critical mixture. The apparatus was equipped with an argon ion laser operating on 488 nm line. A sample cell with a diameter of 10 mm was purchased from Ace-glass Co. and used as a scattering cell, in which the sample with critical composition was prepared. The cell was sealed by a Teflon cap and was set in a sample holder, which was adjusted in multiple dimensions of translation and rotation to ensure the cell being located at the center of the goniometer and normal to the incident light. An attenuator was used to adjust the intensity of incident light. The scattered light was recorded by a photomultiplier operated in the photon counting mode. Measurements were made in the angular range of $35° < \theta < 150°$. The total uncertainties in measurements of scattering light intensity and temperature difference $(T - T_c)$ were about ±2%, and ±0.005 K, respectively. The intensities of incident light and transmitted light also were measured by a light-power meter (Model 1825-C) purchased from Newport Co. 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 the attenuation. All measurements were carried in the one phase region above the critical point. After each change of the temperature, we waited at least 1 h for the system to establish a new equilibrium before the new data were taken. The new equilibrium may be indicated by the unchanged readout on the power meter. It was found that when the temperature was close to the critical point, the time for the equilibrium was longer than 4 h.

3. Results and discussion

3.1. Coexistence curves

The critical mole fraction and the critical temperature of $\{xC_6H_5CN + (1 - x)CH_3(CH_2)_{10}CH_3\}$ were determined to be $x_c = (0.586 \pm 0.001)$ and $T_c = (293.0 \pm 0.3)$ K, respectively. 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 [12]:

TABLE 1
Coexistence curves of (T,n), (T,x), and (T,ϕ) for $\{xC_6H_5CN + (1 - x)\text{-}CH_3(CH_2)_{10}CH_3\}$

$(T_c - T)$/K	n_1	n_2	x_1	x_2	ϕ_1	ϕ_2
0.002	1.4623	1.4589	0.598	0.566	0.402	0.371
0.003	1.4626	1.4588	0.602	0.566	0.405	0.370
0.004	1.4633	1.4583	0.607	0.560	0.411	0.365
0.014	1.4642	1.4575	0.616	0.552	0.419	0.357
0.032	1.4650	1.4567	0.623	0.544	0.427	0.350
0.054	1.4658	1.4560	0.630	0.537	0.434	0.343
0.084	1.4665	1.4553	0.636	0.529	0.441	0.336
0.118	1.4672	1.4546	0.642	0.522	0.447	0.330
0.185	1.4683	1.4537	0.651	0.512	0.457	0.321
0.280	1.4694	1.4526	0.660	0.500	0.467	0.311
0.383	1.4704	1.4518	0.668	0.490	0.476	0.303
0.521	1.4715	1.4509	0.676	0.479	0.485	0.293
0.693	1.4725	1.4502	0.684	0.470	0.494	0.286
0.914	1.4737	1.4493	0.693	0.459	0.504	0.277
0.938	1.4742	1.4490	0.696	0.455	0.508	0.274
1.219	1.4751	1.4480	0.703	0.442	0.516	0.263
1.554	1.4766	1.4472	0.713	0.430	0.528	0.254
1.973	1.4782	1.4462	0.724	0.416	0.542	0.243
2.417	1.4796	1.4455	0.733	0.405	0.553	0.235
2.920	1.4811	1.4446	0.742	0.390	0.564	0.224
3.536	1.4828	1.4437	0.752	0.375	0.577	0.213
4.307	1.4845	1.4428	0.762	0.359	0.590	0.202
5.239	1.4867	1.4421	0.774	0.343	0.606	0.190
6.190	1.4885	1.4413	0.783	0.326	0.619	0.179
7.323	1.4907	1.4408	0.794	0.312	0.635	0.170
8.648	1.4930	1.4401	0.805	0.292	0.650	0.157
10.843	1.4963	1.4394	0.820	0.266	0.672	0.141

Refractive indices n were measured at wavelength $\lambda = 632.8$ nm, and $T_c = 293.028$ K. Volume fraction is denoted by ϕ. Subscripts 1and 2 relate to upper and lower phases, respectively.