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Turbidity and critical behavior of a colloid-polymer system

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The osmotic compressibility and correlation length of a colloid-polymer system, consisting of grafted silica particles in cyclohexane in the presence of the soluble polymer polydimethylsiloxane, are determined by turbidity measurements in the entire one-phase liquid region, with emphasis on the critical region. The renormalized critical exponents of the osmotic compressibility and the correlation length are found to be respectively $\gamma^* = 1.39 \pm 0.01$ and $\nu^* = 0.71 \pm 0.01$, while the amplitude of the correlation length is 16.0 ± 0.3 nm. Comparison is made with theoretical predictions.

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A necessary but not sufficient condition [1] for liquid-liquid phase separation in general, and in suspensions of colloidal particles in particular, is the presence of an attractive force. Addition of soluble and nonabsorbing polymer to colloidal dispersions under suitable conditions provides an attractive depletion force that induces liquid-liquid phase separation [2]. The appropriate thermodynamic potential to describe such colloid-polymer systems is the semigrand potential, which is grand canonical for the solvent and polymer molecules and canonical for the colloid particles [3]. Because increasing the polymer concentration in such colloid-polymer systems is equivalent to decreasing the temperature in ordinary fluids [3], criticality in colloid-polymer systems is approached by varying the concentration of added polymer rather than the temperature. Alternative elucidation on the effect of polymer in such systems on liquid-liquid phase separation could be made clear from the nature of the semigrand ensemble, where the volume fraction of polymer in the reservoir (or equivalently the polymer fugacity) is an appropriate variable. It is the latter that should be equivalent to T^{-1}, i.e., a field variable [3].

Recently, the liquid-liquid phase equilibrium of a colloid-polymer system was investigated in the critical region, and the order parameter and interfacial tension were determined [4]. In this Brief Report, we give details on turbidity measurements and the determination of the osmotic compressibility and of the correlation length of the same system.

Turbidity τ is defined as the attenuation of transmitted-light intensity per unit optical length L in the scattering medium, and can be expressed as $\tau = -\ln(I_\tau/I_0)/L$, where I_0 and I_τ are the intensities of incident and transmitted light, respectively. Using the Ornstein-Zernike theory [5], the turbidity τ near the critical region is obtained by integrating the scattering intensity over all angles [6],

$$\tau = A_0 T \chi f(\alpha), \tag{1}$$

where $A_0 = (\pi^3/\lambda_0^4)(\partial n^2/\partial \phi)^2_T k_B T$ can be treated as a constant, and χ, λ_0, n, ϕ, k_B, and T are, respectively, the osmotic compressibility, the wavelength of incident light in vacuum, the refractive index of the scattering medium, the order parameter, Boltzmann's constant, and the temperature. The correlation length ξ is related to the turbidity τ through the function $f(\alpha)$ [6],

$$f(\alpha) = \frac{2\alpha^2 + 2\alpha + 1}{\alpha^3} \ln(1 + 2\alpha) - \frac{2(1+\alpha)}{\alpha^2}, \tag{2}$$

where $\alpha = 2(k_0 \xi)^2$ and $k_0 = 2\pi n/\lambda_0$, with k_0 the wave vector of incident light in the scattering medium.

The osmotic compressibility χ and correlation length ξ diverge at the critical point according to

$$\chi = \chi_0 \varepsilon^{-\gamma^*}, \tag{3}$$

$$\xi = \xi_0 \varepsilon^{-\nu^*}. \tag{4}$$

where γ^* and ν^* are the renormalized critical exponents of χ and ξ, respectively; $\varepsilon = (x_c - x)/x_c$, where x is the polymer concentration and x_c is its value at the critical point.

The theoretical description of phase transitions at critical points is generally provided by expressing the singular thermodynamic quantities in terms of field variables. Field variables, by definition, assume identical values in distinct coexisting phases. Those thermodynamic variables which, in contrast to field variables, assume different values in coexisting phases, are called density variables. The most convenient and commonly used field variable is the temperature, and critical exponents that describe the singular behavior of thermodynamic quantities at criticality are thus defined in terms of distance of the temperature from its critical value. However, when the critical point is approached at fixed temperature, upon variation of a density variable rather than a field variable, the critical exponents change and are said to be renormalized [7]. Here, the critical exponents assume their renormalized values rather than the ordinary, bare values, because a density (here, the polymer concentration) rather than a field variable (typically, the temperature) is used as the variable parameter to approach criticality [7]. In this study, the temperature is constant, equal to its room value (24 °C).

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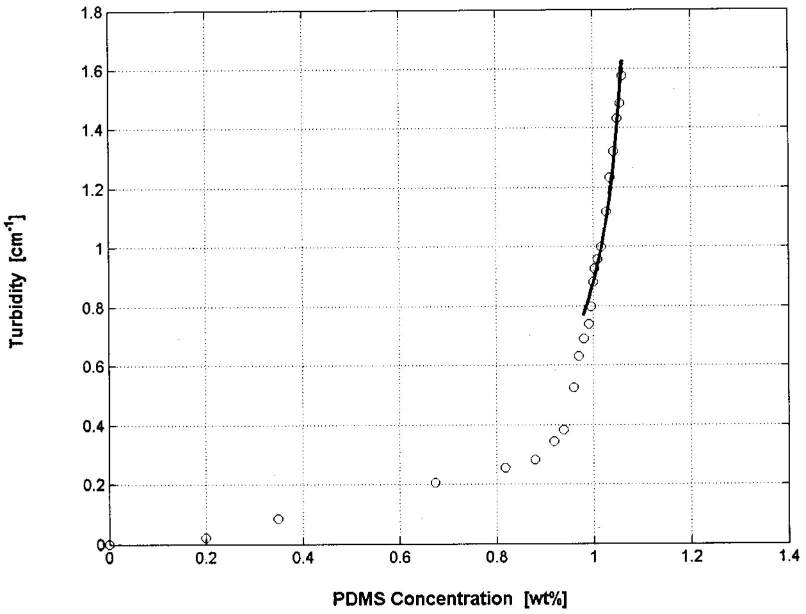

FIG. 1. Turbidity as a function of overall PDMS concentration.

Aqueous colloidal silica of Ludox® TMA, (34 wt %, DuPont), with particle sizes ranging from 15 to 20 nm, and polydimethylsiloxane 200® fluid with molecular weight of 92 000 Da (Dow Corning), were purchased from Aldrich Chemical. Stearyl alcohol (n-$C_{18}OH$) with a purity of 99% was obtained from TCI America, and cyclohexane from Fisher Chemicals. Neutral organophilic silica particles are prepared by grafting stearyl chains onto the silica surface according to the method described by Iler [8] and van Helden *et al.* [9]. Further details are given in our earlier report [4]. The critical composition is found to be 34.4 wt % grafted silica and 1.085 wt % polydimethylsiloxane (PDMS) in cyclohexane at 24 °C.

The turbidity τ is calculated from the absorbance A measured with incident light of wavelength of 600 nm by using a Bausch-Lomb ''SPECTRONIC® 1001'' spectrophotometer at 24 °C, along with square glass cuvets of optical-path length L of 10 mm. This spectrophotometer gives a photometric accuracy of 0.005 near $A = 1.0$, i.e., the intrinsic instrumental uncertainty is estimated to be 0.005 cm^{-1}. However, because there is obviously an absorbance A_0 of incident light through a sample without polymer, it is necessary to correct for the absorbance due to such background effects. The turbidity can then be written $\tau = (A - A_0)/L$ [10]. It should be noted that the turbidity measurements are performed at constant colloid concentration, the only variable being the PDMS concentration. The refractive indices are measured with a Bausch-Lomb Abbe-3L refractometer at 24 °C.

Figure 1 displays the results of the turbidity measure-

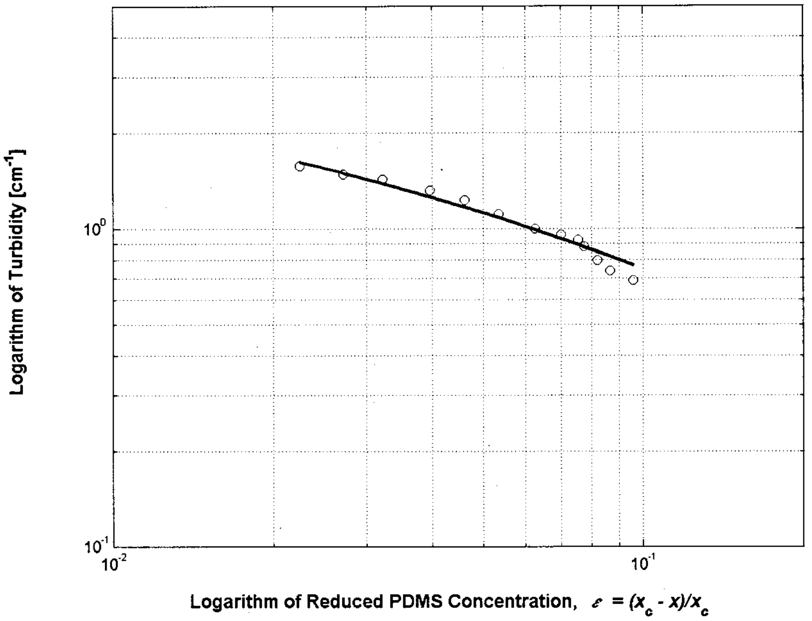

FIG. 2. Log-log plot of turbidity as a function of reduced concentration of PDMS.

ments in the entire one-phase region, as a function of PDMS concentration. Circles denote experimental data and the solid line is the fitting curve as described in the following paragraph. The data points lying within 0.1 wt % of PDMS concentration from the critical point are used, via a nonlinear least-squares method, to determine the optimal values of the parameters, γ^*, ν^*, $A_0\chi_0$, and ξ_0. Estimates of the corresponding uncertainties are based on the bootstrap [11] statistical method, valid for small sample size [12].

Figure 2 shows a double-logarithmic plot of turbidity as a function of the reduced concentration of PDMS, $\varepsilon=(x_c-x)/x_c$, where x is the overall PDMS concentration and x_c its critical value. These data, fitted with the nonlinear least-squares method, yield $\gamma^*=1.39\pm0.01$, $\nu^*=0.71\pm0.01$, $A_0\chi_0=(1.11\pm0.04)\times10^{-4}\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$, and $\xi_0=(16.0\pm0.3)\,\mathrm{nm}$. The uncertainties correspond to a 95% confidence-level interval. The accuracy of the fit is checked with the F statistics tests for the entire fit, which gives $F=17.3$ greater than the critical value $F_{0.05}(4,8)=3.84$ for a 95% confidence-level interval. A larger F value, at least greater than its critical value, corresponds to a good fit [13].

It is expected on theoretical grounds that the critical behavior of the colloid-polymer system is identical to that of the three-dimensional Ising (lattice-gas) model with short-ranged forces. This is because the attraction responsible for the liquid-liquid phase separation is due to the depletion force, which is of finite range. The critical exponents are, however, expected to be renormalized, as explained above.

These experimental values of the critical exponents γ^* and ν^* are in good agreement with the theoretical predictions for the fully renormalized critical exponents of the three-dimensional Ising model [7a], for which $\gamma^*=\gamma/(1-\alpha)=1.393$ and $\nu^*=\nu/(1-\alpha)=0.708$, using the accepted values $\alpha\approx0.11$, $\gamma=1.24$ and $\nu=0.63$ [14].

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