

## Effect of Dilute Silica Gel on Phase Separation of a Binary Mixture

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We report the results of an experimental study of the effect of a dilute silica network on critical phenomena in a binary mixture of 2,6-lutidine and water. Light-scattering measurements of this system show that its structure does not differ significantly from that of the gel, but that the scattered intensity increases dramatically as the two-phase region is approached. We interpret these results in terms of a layer of lutidine-rich fluid adsorbed on the silica surface and the resulting changes in concentration of the nonadsorbed fluid.

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The effect of “quenched disorder” or random fields on phase transitions has attracted considerable experimental and theoretical attention in recent years.<sup>1</sup> Random-field systems have been realized by applying magnetic fields to doped antiferromagnetic samples. This system has been well studied and is known to have long-range order in three dimensions. With increasing field, the behavior crosses over from random exchange to random field. It also exhibits metastability and very slow dynamics, related to the existence of energy barriers. It has been argued that the same ideas may apply to fluids or fluid mixtures confined within porous media or in contact with a gel network.<sup>2</sup> Here the order parameter is conserved, while in the magnetic case it is not. Theoretical treatments indicate that metastability and activated dynamics are also to be expected for the conserved-order-parameter case.<sup>3</sup> In fact, light-scattering data for lutidine-water mixtures in Vycor (a porous glass having pore diameters of  $\sim 70$  Å) have revealed activated dynamics and metastability, but only well into what would be the two-phase region for the bulk system.<sup>4</sup>

Rather than confining a fluid within pores, a gel network can be imbedded within the fluid, and such networks may occupy only a small fraction of the sample volume. Experiments involving agarose, polyacrylamide, and gellan gum gels in liquid mixtures have been reported.<sup>5</sup> These studies revealed strong light scattering, no critical fluctuations, and cloud points near the bulk coexistence curves. Their interpretation has remained problematic because such gels are either flexible or not covalently cross-linked and might participate in the phase-separation process. Furthermore, the structure of these gels is not well understood at present. The effects of Vycor, aerogel, and xerogel on the superfluid transition have also been studied.<sup>6</sup> The superfluid density exhibited power-law behavior in all three media, but for the gels the exponents differed from each other and from that for bulk  $^4\text{He}$ . Aerogels are silica networks formed by hypercritically drying gels created by polymerization of a molecular precursor, while xerogels result from drying similar gels by evaporation, which destroys much of the

delicate structure. Finally, a recent study of the effect of aerogel on phase separation in  $^4\text{He}$  revealed a drastically narrowed coexistence curve standing under the bulk coexistence curve.<sup>7</sup>

Motivated by this work, we have studied the effect of silica networks on critical phenomena in the binary mixture, 2,6-lutidine and water. The networks were formed by polymerization of a silica precursor in water and were never dried.<sup>8</sup> Light-scattering studies<sup>9</sup> show that they have a fractal structure, with fractal dimension  $D_f \cong 2.2$ , at length scales smaller than a crossover length  $\xi_x$  and scatter as a random collection of fractal objects for length scales  $\gtrsim \xi_x$ . We find that  $\xi_x$  can be varied from  $\sim 100$  Å to  $\gtrsim 2$  μm. This structure is similar to that of colloidal silica gels<sup>10</sup> and of aerogels.<sup>11</sup>

We have studied samples made with gels of 1-, 2-, and 4-wt% silica, having volume fractions of 0.0046, 0.0092, and 0.019, respectively. The gels were grown in 4.7-mm-i.d. glass tubes and were about 10 mm in length. After aging, they were exposed, at room temperature, to lutidine-water mixtures in the one-phase region. After equilibration, mixture above the gels was removed to fix the concentration. The lutidine concentration in the gels was measured by gas-phase chromatography after making light-scattering studies.

For each sample, the intensity and angular distribution of scattered light ( $\lambda = 6328$  Å) were measured as functions of temperature in the one-phase region. The apparatus and techniques have been described previously.<sup>10,12</sup> Similar behavior was observed for all samples. The dependence of the scattered intensity  $S(q)$  upon the scattering wave vector  $q$  was nearly identical to that of the pure gel-water system for all temperatures and gel and mixture concentrations, while the overall scattered intensity increased strongly as the temperature was increased toward  $T_c$ . Figure 1 shows results for 1-, 2-, and 4-wt% gels which contained mixtures of 17-, 28-, and 39-wt% lutidine and were characterized by crossover lengths of 1600, 1200, and 250 Å, respectively. The values of  $S(q)$  are relative to those of toluene. As these samples scatter strongly, the data have been corrected

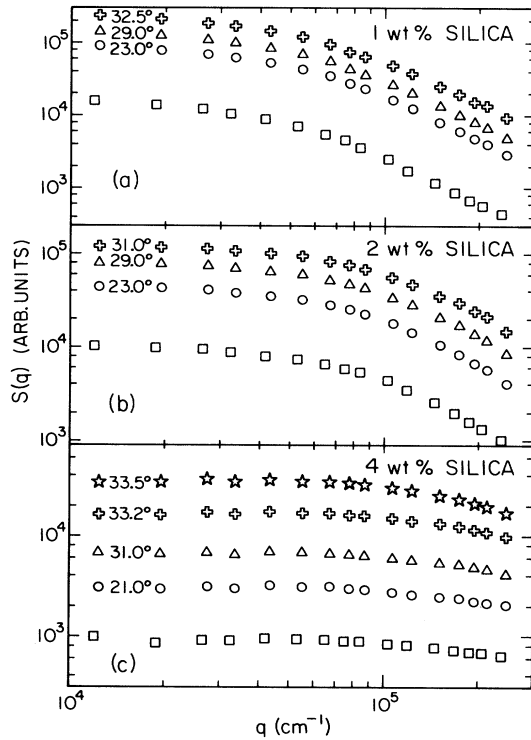


FIG. 1. Structure factor vs the scattering wave vector for silica gels in water at 23°C ( $\square$ ) and in lutidine-water mixtures at various temperatures as indicated. The lutidine concentrations were (a) 16.9, (b) 27.5, and (c) 38.9 wt%.

for double scattering.<sup>13</sup> To minimize double scattering, we have focused on 4-wt% gels, as higher concentration gels scatter less strongly.

The dependence of intensity on temperature for different lutidine concentrations, in 4-wt% gels, is shown in Fig. 2. In every case the intensity increased with increasing temperature, and the data were reproducible to within 1% whether increasing or decreasing the temperature. The solid horizontal line shows the intensity scattered by a gel immersed in water at 23°C, and the solid inverted triangles are data for  $S(q=0)$  for a bulk mixture at the critical concentration.

In addition to making intensity measurements, we searched for the fluctuations normally present near a critical point. Using a 4-wt%-gel-containing mixture of 29-wt% lutidine, we detected no fluctuations in the one-phase region. Our sensitivity was adequate to detect fluctuations at 15% of the level displayed by the bulk system within 0.5°C of  $T_c$ .

We interpret our data as follows.  $S(q)$  is the spatial Fourier transform of the correlation function  $\langle \delta\epsilon(\mathbf{R}) \times \delta\epsilon(\mathbf{0}) \rangle$  for the fluctuations of the local dielectric constant  $\epsilon(\mathbf{r})$ . Neglecting any volume change upon mixing,  $\epsilon(\mathbf{r})$  is given by

$$\frac{\epsilon(\mathbf{r}) - 1}{\epsilon(\mathbf{r}) + 2} = K_s \phi_s(\mathbf{r}) + K_l \phi_l(\mathbf{r}) + K_w \phi_w(\mathbf{r}), \quad (1)$$

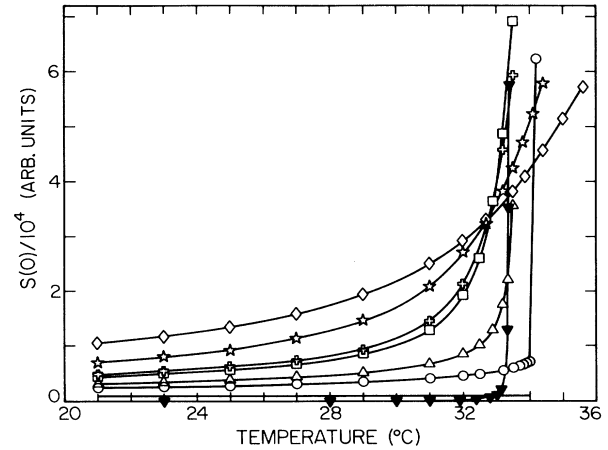


FIG. 2. Temperature dependence of the scattered intensity  $S(0)$  for the bulk lutidine water system ( $\blacktriangledown$ ), gel immersed in water at 23°C (—), and various gel-mixture samples. The lutidine concentrations were 22.2 ( $\diamond$ ), 27.1 ( $\star$ ), 32.5 ( $+$ ), 35.2 ( $\square$ ), 38.9 ( $\triangle$ ), and 42.6 ( $\circ$ ) wt%. The lines through symbols are shown as guides to the eye.

where  $K \equiv (\epsilon - 1)/(\epsilon + 2)$ ,  $\phi(\mathbf{r})$  is a local volume fraction, and the subscripts  $s$ ,  $l$ , and  $w$ , refer to silica, lutidine, and water, respectively. If lutidine, e.g., is attracted to the silica, we may model this for long enough length scales by writing

$$\delta\phi_l(\mathbf{r}) = \alpha(T) \delta\phi_s(\mathbf{r}), \quad (2)$$

where  $\delta\phi(\mathbf{r})$  is the deviation from the average and  $\alpha(T)$  is independent of position. Thus, we find the ratio of the scattering for the gel-mixture system to that of the gel-water system to be

$$\frac{S_{gm}(q)}{S_{gw}(q)} = \frac{(\epsilon_{gm} + 2)^4}{(\epsilon_{gw} + 2)^4} \left[ \frac{(K_s - K_w) + \alpha(T)(K_l - K_w)}{K_s - K_w} \right]^2, \quad (3)$$

which is  $q$  independent, as observed.

Using Eq. (3), we obtained  $\alpha(T)$  for each mixture. The results for the samples containing mixtures of 35.2- and 38.9-wt% lutidine are shown in Figs. 3(a) and 3(b), respectively. Well below the bulk  $T_c$ , the data exhibit power-law behavior, as may be seen by the accompanying deviation plots which refer to fits of the form  $\alpha(T) = \alpha_0(T_c^* - T)^{-\gamma^*}$  carried out over the data shown as solid symbols. At higher temperatures the deviations are systematic, but opposite for the two samples. All samples containing mixtures of at least 38.9-wt% lutidine deviated above the fit, while those with concentration  $\leq 35.2$  wt% deviated below. The values of  $\gamma^*$  obtained for the various samples were 0.75, 0.84, 0.64, 0.60, 0.69, and 0.84, and those for  $T_c^*$  were 39.1, 37.1, 34.1, 33.8, 35.6, and 38.9°C, in order of increasing concentration. Because of the complicated structure of the silica and the possibly strong nonlinear interaction be-

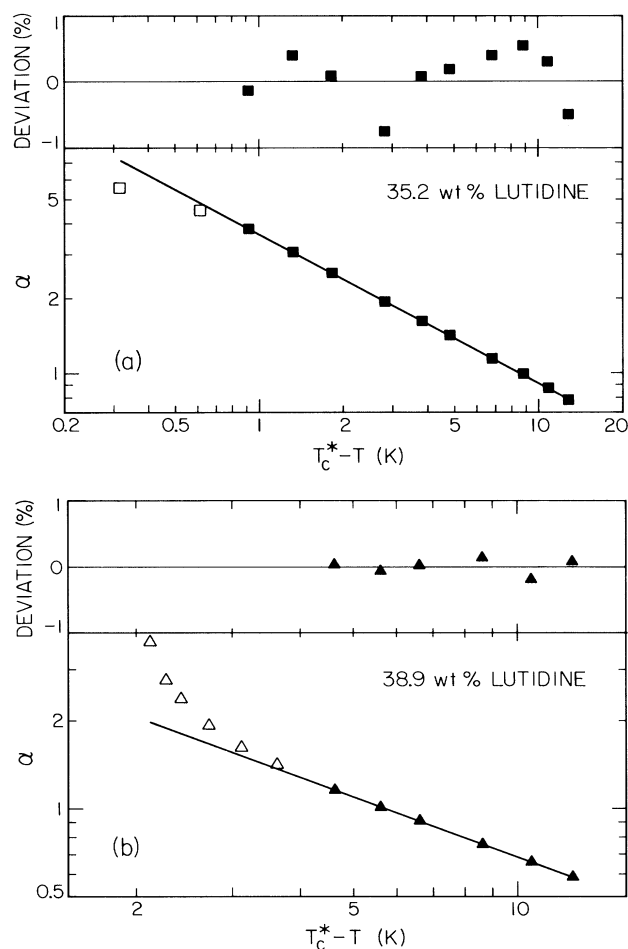


FIG. 3. Dependence of the parameter  $\alpha$  (see text) on temperature for two different samples. The solid line is the result of fitting the data shown as solid symbols by a simple power law with an adjustable critical temperature. The deviations from the fit are shown in the upper portion of the figures.

tween lutidine and silica, we do not know how to interpret  $\gamma^*$ .

Since  $\alpha(T)$  is positive, it is the lutidine which is attracted to the silica. Because the scattered intensity does not fluctuate, this lutidine is present in a quasistatic configuration and does not participate in critical fluctuations. This has an important consequence for a system with a conserved order parameter (here concentration); namely, the concentration in the portion of the system which is not immobilized by its interaction with silica differs from the mean and changes with temperature. Physically we might imagine a layer of lutidine-rich fluid coating the silica and growing in thickness as the temperature is raised. This growing layer depletes the rest of the fluid of lutidine and reduces the volume available for phase separation and/or critical fluctuations.

We may use our results for  $\alpha(T)$  to estimate the effect of adsorption on the concentration of lutidine in the free

fluid by considering the sample to be made up of two regions: one of free fluid and the other of silica and immobilized fluid. The concentration of lutidine in either region is given by  $\phi_l = \bar{\phi}_l + \delta\phi_l$ , where the overbar denotes a sample average. But we can relate the amplitude of the lutidine fluctuations to those of silica through Eq. (2). In the free volume,  $\delta\phi_s = -\bar{\phi}_s$ , resulting in

$$\phi_f = \bar{\phi}_l - \alpha(T)\bar{\phi}_s. \quad (4)$$

Rather surprisingly,  $\phi_f$  is determined solely by  $\alpha(T)$ , regardless of the volume occupied by the immobilized fluid or its concentration.

Figure 4 shows the estimated weight fraction  $x_f$  of lutidine in the free fluid for each sample at the various temperatures studied. The arrows show  $x$  for each mixture, as measured by gas-phase chromatography. Had no adsorption occurred, the samples would have followed vertical paths from the arrows up to the coexistence curve. Instead, there is both an initial shift at 21 °C and a temperature-dependent swing to lower lutidine concentrations, which is stronger for samples containing mixtures near  $x_c = 0.29$ . The solid curve shows the coexistence curve as measured by Cox and Herington<sup>14</sup> but shifted downward to agree with the bulk critical temperature we measure (33.4 °C) with no gel present. Data from a sample with a path which curves toward the critical concentration should deviate above a power-law fit at higher temperatures and vice versa, as observed.

For all the data shown in Fig. 4, the scattered intensity relaxed monotonically towards equilibrium following a temperature change. Except within a few tenths of a degree of the bulk coexistence curve, the intensity equilibrated within a few minutes. There was, however, a remarkable difference in the behavior of the different sam-

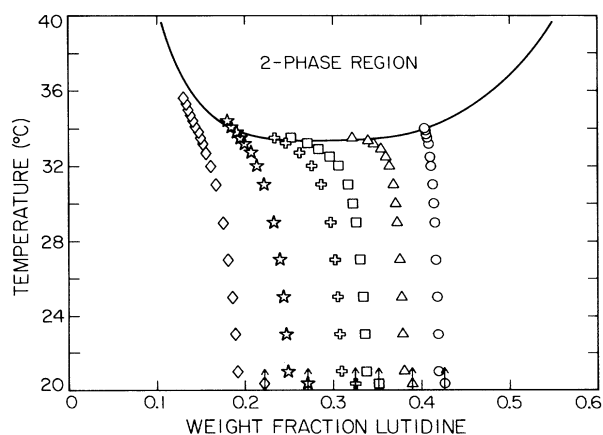


FIG. 4. Estimated values of the lutidine concentration in the nonadsorbed fluid for various samples and temperatures. The overall composition of each sample is shown by the arrows, and the solid line is the coexistence curve of the bulk mixture. Samples of 22.2 ( $\diamond$ ), 27.1 ( $\star$ ), 32.5 ( $+$ ), 35.2 ( $\square$ ), 38.9 ( $\triangle$ ), and 42.6 ( $\circ$ ) wt % are shown.

ples. For the samples represented by squares, triangles, and circles, a step beyond the highest-temperature point shown resulted in a large ( $> 2\times$ ) and rapid ( $\leq 10$  s) increase in scattering which decayed over hours (triangles and circles) or minutes (squares) to a new equilibrium value. These overshoots were largest in the case of the sample represented by triangles. Studies of this sample showed that further small temperature increases resulted in further overshoots, while temperature decreases did not. The equilibrium values reached appeared to be continuous with lower-temperature values except for the sample represented by circles where a further step resulted in a large discontinuity as shown in Fig. 2. For the samples represented by stars, plusses, and diamonds, we observed no overshoots in the scattered intensity.

There may be a simple explanation for this behavior.<sup>15</sup> If a sample enters the two-phase region with  $x_f$  below the critical value  $x_c$ , the nucleating phase will be lutidine rich and it should nucleate heterogeneously on the lutidine-rich fluid adsorbed on the silica. This should occur with a monotonic increase in the scattered intensity. On the other hand, if  $x_f > x_c$ , phase separation should occur by homogeneous nucleation of the water-rich phase in the free volume. The rapid increase and subsequent decay in the intensity scattered from the higher-concentration samples could thus be associated with nucleation and coarsening of the water-rich phase. The data shown in Figs. 3(a) and 4 together with the fit values of  $T_c^*$  indicate that the sample represented by squares hits the coexistence curve with  $x_f \sim x_c$  so that the overshoots observed here may possibly be associated with spinodal decomposition.

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