Phase Diagram of Isobutyric Acid and Water in Dilute Silica Gel

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Measurements of the isobutyric acid (IBA) concentration in a dilute silica gel, vs that in an IBA and water reservoir in equilibrium with the gel, show that first-order phase transitions occur at 15 and 19 °C, but not at 23 °C. The data show that the coexistence curve of this gel/mixture system is narrow, contained within that of the pure mixture, and lies below a broad region of apparent metastability. The existence of a metastable state above the critical temperature of the gel/mixture system is strikingly similar to the behavior observed for random-field magnets. [S0031-9007(96)01245-8]

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The effect of quenched, i.e., spatially fixed, impurities on phase transitions and critical phenomena has proved to be a challenging area. Research topics range from random-exchange and random-field effects in magnets [1] to the effect of gels (rigid or flexible networks) and porous glasses on the superfluid, gas-liquid, and liquid-liquid transitions. Some intriguing experimental results obtained to date include the following. The lambda line of ^{3}He-^{4}He mixtures becomes detached from the liquid-liquid coexistence curve when the mixture is in a dilute silica gel [2]. The exponent for the superfluid density of ^{4}He is apparently changed by such a gel [3,4]. The coexistence curves of single-component fluids in silica gel are drastically narrowed and lie below those of the pure (no gel) fluid [5,6]. Theoretical models capable of reproducing some of these results are now beginning to emerge [7–11].

The phase behavior of liquid mixtures confined in gels is not yet clear. Both flexible [12–14] and rigid [15–17] gels drastically alter the behavior of mixtures near their consolute points. Light scattering studies of mixtures in rigid dilute silica gel show that something resembling phase separation occurs [16] over a broad concentration range, in the vicinity of the pure (no gel) mixture's critical temperature, but no critical point has been located. In these studies [16], gel/mixture samples sufficiently rich in the species preferentially attracted by the silica [17] changed behavior markedly at a well defined, but somewhat sample specific, temperature T_S, when cooled at fixed overall composition. At and below this temperature, the intensity-intensity correlation function developed a very slow mode [16] which appeared when a sample was cooled and which then died away over a period of hours. Samples left below T_S for a day or so took up to days to return to equilibrium when restored to temperatures above T_S. This indicates mass transport over very long length scales, and neutron scattering [18] has confirmed the presence of domains many times larger than the gel correlation length for a different fluid mixture in similar gels. Although critical slowing down is clearly evident [16,17] at temperatures above T_S, the intervention of this dynamical process has masked even the location of the true critical point of the gel/mixture system.

The apparent difference between the behavior of gel/single-component-fluid samples and gel/mixture samples in rigid silica gels is puzzling. Single-component fluids and liquid mixtures belong to the same universality class, and in both cases it is very reasonable to model the gel strands as imposing a spatially localized field conjugate to the order parameter. (The silica attracts fluid, and for a mixture, preferentially attracts one species.) Since mixtures in gels have been studied almost exclusively by scattering, we have undertaken a preliminary thermodynamic exploration of a mixture, isobutyric acid (IBA) and water (W), in dilute (~2 vol %) rigid silica gel. Although very crude, the data serve to reconcile the mixture and single-component-fluid behavior to a considerable extent. They show that the gel/IBAW system exhibits true thermodynamic phase separation and that, like the gel/single-component-fluid system, the coexisting phases define a narrow coexistence curve lying below that of the pure system, and on the side of the phase rich in the species preferentially attracted by the silica.

To detect a first-order phase transition in the gel/IBAW system, it is sufficient to vary the chemical potential of either species, IBA or water, at fixed temperature while measuring the equilibrium concentration within the gel. During such a transition, the concentration must change discontinuously between the concentrations of the two coexisting phases (IBA-rich and IBA-poor) of the gel/IBAW system. This concentration change must take place with no change in the chemical potential of either IBA or water. Thus if a gel is placed in contact with a one-phase reservoir of the IBAW mixture, and IBA is progressively added to this system, it must behave as follows. While the gel/IBAW portion of the system is in its one-phase region, the added IBA will enrich both the reservoir and the gel/mixture portion. However, while the gel/mixture portion undergoes a first-order phase transition, any IBA added to the system must be entirely taken up by the gel/mixture portion, with no chemical potential change, and thus no concentration change, taking place in the reservoir.

To study the phase behavior of IBAW in silica gel we used a 10 mm × 10 mm square cross-section glass

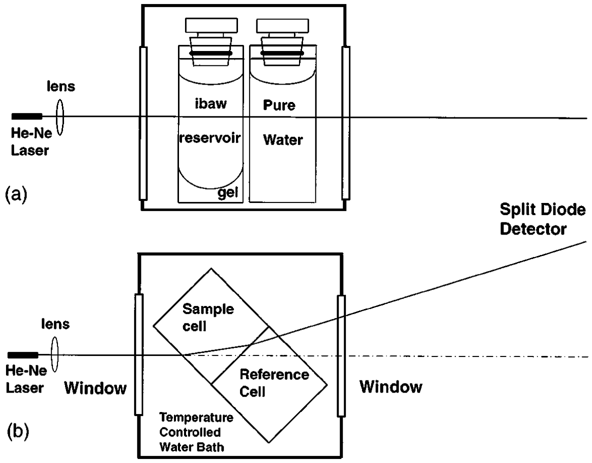

FIG. 1. Schematic diagram of the gel and reservoir in the differential refractometer arrangement. (a) Side view and (b) a view from above. The cells and temperature controlling bath were moved up or down to measure the gel or reservoir, respectively.

cell in the bottom of which a 4.0 wt% silica gel about 2 mm high was grown, as indicated in Fig. 1(a). A portion of the space above the gel was occupied by the IBAW reservoir, which contacted the gel over its entire upper surface. The gel was made by polymerization of tetramethylorthosilicate in water. Samples from the same batch were characterized by static light scattering [19] and found to have a correlation length [20] of 326 Å. The gel was aged and then washed by exposing it to 3 ml of purified water for 10 days, with the water being replaced twice daily. The water was then replaced by an IBAW mixture to form the reservoir.

To measure IBA concentration, the cell containing the sample was incorporated in a differential refractometer, as shown in Fig. 1. The two cells could be rotated as a unit about a vertical axis midway between them. They were usually oriented at 45° with respect to the He-Ne laser beam and functioned as prisms. In traversing the cells the beam was angularly deflected by an amount roughly proportional to the difference in refractive index between the contents of the sample cell and those of the reference cell. The beam displacement was measured about 1 m from the exit window. The beam waist was about 0.4 mm in diameter in the sample. Both cells were completely immersed in flowing temperature controlled (± 1 mK) water. The water bath and sample cells could be translated vertically. This allowed measurement of the refractive index, and thus IBA concentration, of either the IBAW reservoir or the gel/mixture sample.

Because of the difficulty of directly calibrating refractive index vs IBA concentration in a gel, we used a two step procedure to estimate this relationship. We measured the refractive index n, of pure mixtures of IBA and water having accurately known (± 0.01 wt%) concentrations, for the temperatures 21, 25, 30, 35, and 40 °C, over the full concentration range from pure water to pure IBA. The data were fitted by a modified [21] Lorentz-Lorenz equation,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{K_{\mathrm{IBA}}\phi_{\mathrm{IBA}} + K_{\mathrm{W}}\phi_{\mathrm{W}}}{[1 - F_{\mathrm{IBA}}]}, \qquad (1)$$

to determine the small correction F_{IBA}, as a function of ϕ_{IBA} and temperature. Here $\epsilon = n^2$ is the dielectric constant, $K = \frac{\epsilon - 1}{\epsilon + 2}$, and ϕ is the volume fraction. We also measured the gel in pure water, and used Eq. (1) to obtain $F_{si} = 0.0037$, independent of temperature. For IBAW mixtures in the gel, we used the three component version of Eq. (1) to relate the measured index n to ϕ_{IBA}, approximating F by $F_{\mathrm{IBA}} + F_{si}$. Since $F \leq 0.03$, any errors should be minor. The results for ϕ_{IBA} were then used to deduce the weight fraction of IBA in the *fluid* portion of the gel/mixture system. In converting to weight fraction, the small effect of volume change on mixing was neglected.

Because silica gels preferentially attract water, the measurements were begun with a reservoir concentration equal to that of the IBA-rich phase of the pure mixture at the temperature being studied. The reservoir concentration was gradually increased by the addition of pure IBA. After each addition it took about 4 days to reach equilibrium. During this time the reservoir was mixed twice a day by tilting and rocking the entire apparatus by hand. While working at 23 °C we verified that the same state was reached whether the concentration was increased or decreased.

Ideally one would measure the chemical potential of water in the reservoir $\mu_{\mathrm{W}}^{\mathrm{res}}$ and the weight fraction of IBA in the fluid portion of the gel/mixture system $W_{\mathrm{IBA}}^{\mathrm{gel}}$ [22]. Since we could not measure $\mu_{\mathrm{W}}^{\mathrm{res}}$, we determined the weight fraction of water in the reservoir $W_{\mathrm{W}}^{\mathrm{res}} = 1 - W_{\mathrm{IBA}}^{\mathrm{res}}$ instead. Because $\mu_{\mathrm{W}}^{\mathrm{res}}$ is a monotonically increasing function of $W_{\mathrm{W}}^{\mathrm{res}}$, plots of $W_{\mathrm{W}}^{\mathrm{res}}$ vs $W_{\mathrm{IBA}}^{\mathrm{gel}}$, at fixed temperature, are similar to pressure vs volume isotherms for a single-component fluid, as shown in Fig. 2.

Both the 15 and 19 °C isotherms contain flat portions where $W_{\mathrm{IBA}}^{\mathrm{gel}}$ changes discontinuously, with no measurable change in $W_{\mathrm{W}}^{\mathrm{res}}$, indicating a first-order phase transition. The portions we judged to be flat are indicated by the horizontal bars. The 23 °C isotherm contains no such flat portion, and thus the gel/mixture system is thermodynamically one phase at this temperature, with the critical point presumably lying between 19 and 23 °C.

To relate these results to the phase diagram of pure IBAW, we measured the concentrations of the two coexisting phases for a pure mixture containing 37.70 wt% IBA. The results are shown in Fig. 3 as open circles. The crosses show data taken with a mixture in equilibrium with the gel, indicating no detectable impurity problems. The data for the pure mixture are well fit by a leading singularity and a single Wegner term of the form

$$\Delta W / W_c = B t^{\beta} (1 + b_1 t^{\frac{1}{2}} + \cdots),$$

where ΔW is the difference in concentration between the coexisting phases, and $t \equiv (T_c - T)/T_c$. The results

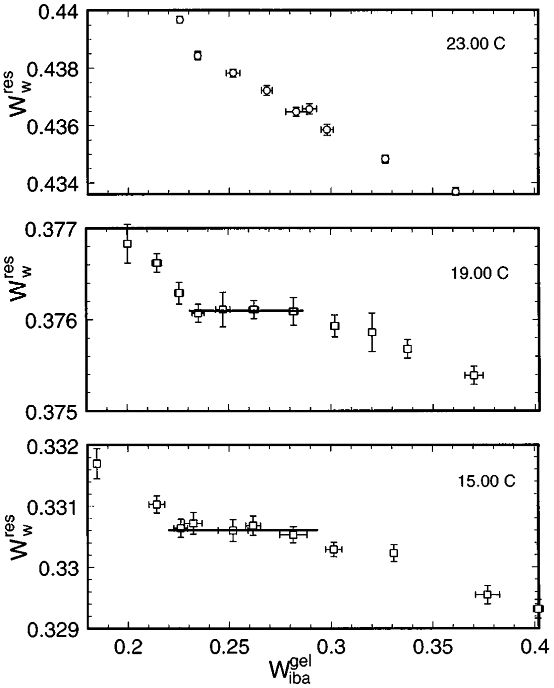

FIG. 2. Plots of the weight fraction of water in the reservoir vs the weight fraction of IBA in the gel/mixture portion of the sample at equilibrium for three different temperatures.

are $\beta = 0.334$, $T_c = 25.722$ °C, $W_c = 0.391$, and $b_1 = -0.15$. This fit is shown by the solid line in the figure.

Figure 3 also shows, as open diamonds, the concentrations of the two coexisting phases for the gel/IBAW system estimated from the flat portions of the 15 and 19 °C isotherms. The region between these concentrations is a two-phase region for the gel/IBAW system with a 4.0 wt% gel. Presumably this two-phase region shrinks continuously in extent with increasing temperature and, somewhere below 23 °C, ends in the critical point of this system. Within its two-phase region the sample appeared cloudy, consistent with coexisting phases in the form of domains, while outside that region it was clear. When cooled in the one-phase region the sample immediately became cloudy or opaque, but returned to its clear equilibrium state within a few days.

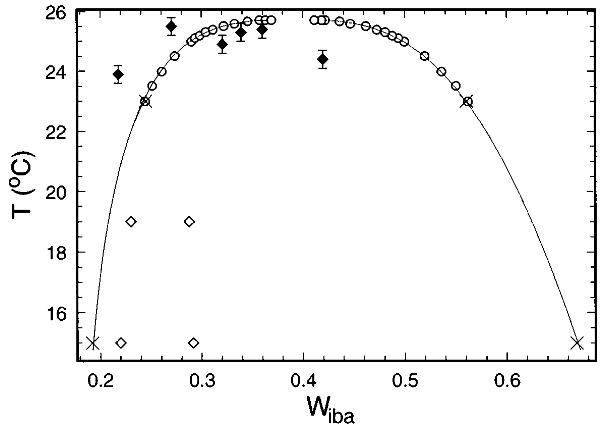

FIG. 3. Phase diagram showing the relationship between the coexistence curve of the pure mixture (open circles, crosses), the narrow two-phase region of the gel/mixture system, which lies between the open diamonds, and the slow mode onset temperature (solid diamonds).

As mentioned previously, there is a slow mode onset temperature, below which gel/IBAW samples sufficiently rich in water and held at fixed composition show evidence of a phase-separation-like process [16]. On cooling, such samples show marked overshoots in scattered intensity [17] at a small scattering wave vector, consistent with the formation and collapse of a ring of scattered light, such as is observed in samples undergoing nucleation or spinodal decomposition. To relate the onset temperature for this behavior to the phase diagram, we prepared seven additional gels from the same batch from which the sample used to measure gel/IBAW isotherms was made. These gels were formed in 10 mm inner diameter cylindrical scattering cells and were ~2 mm thick. They were aged and precleaned by exposure to pure water changed twice daily for a week. They were then exposed to IBAW mixtures at 40 °C, with the mixtures replaced twice daily for at least 3 days. Removing the mixtures fixed these samples in overall concentration, and they were then studied by means of light scattering. The IBA concentration of their fluid portions ranged from ~21 to ~47 wt% IBA, based on previous experience.

Upon cooling, the six lowest concentration samples developed the additional very slow transient mode and intensity overshoots mentioned above. Consistent with previous work [17], the highest concentration sample, lying well above the critical concentration for the pure mixture, did not. The measured slow mode onset temperatures are shown as solid diamonds in Fig. 3. Below T_S, the samples began to scatter very strongly and became opaque upon further cooling. This is consistent with the formation of domains of IBA-rich and IBA-poor fluid. It is interesting to note that our samples developed slow modes only for temperatures somewhat below the critical temperature of the pure mixture, T_c^p. Previously [16,17] this had been observed to occur about 0.5 °C *above* T_c^p. We attribute the difference to the extensive precleaning procedure we followed, which was not done in previous work.

In light of the present results, the process signaled by the slow mode onset cannot correspond to thermodynamic phase separation. The critical temperature of the gel/IBAW system is below 23 °C, based on the measured isotherms, while the slow mode onset occurs above 24 °C. Furthermore, the coexistence curve of the gel/IBAW system is so narrow that only samples within a very limited concentration range would actually enter a true two-phase region upon being cooled. Instead of signaling phase separation, the slow mode onset and overshoots seem to indicate that the system is entering a metastable state. It is not clear that this state is truly metastable in the sense of involving energy barriers or is just very slow to reach equilibrium. Samples enter this state despite the fact that their concentration and temperature history maintains them in what is clearly a one-phase region for the gel/IBAW system at all times. In the one-phase region of the gel/IBAW system the equilibrium state is generally transparent, but the "metastable" state is opaque, or nearly so, making them easy to distinguish. Thus the critical point of the gel/IBAW system is located below a broad region of metastable behavior. The existence of this region explains why previous experiments did not observe complete critical slowing down; the samples entered the metastable state instead. Because our observations are limited, it is logically possible that the opaque state is actually stable, although apparently not thermodynamically two phase, in some limited region of the phase diagram, but we have seen no evidence of this.

Although samples at fixed composition enter the metastable state when cooled, samples in contact with a reservoir of IBA and water reach equilibrium instead. In fact, a sample held for weeks in the metastable state cleared within hours when accidentally exposed to a thin layer of water. The fluid layer apparently offered a mechanism to nucleate the equilibrium state at the surface, and this state displaced the metastable state. We interpret this as evidence that the transparent state has a lower free energy than does the opaque metastable state. The existence of this metastable state for the gel/mixture system is reminiscent of the fact that many random-field magnets fall out of equilibrium [23] when cooled with the random field applied, and thus its study may help unify understanding.

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