

## Wetting and Random-Field Transition of Binary Liquids in a Porous Medium

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(Received 13 October 1988)

Mixtures of lutidine and water imbibed in porous Vycor have been studied using Raman, elastic, and quasielastic light scattering. At low temperatures, adsorption of lutidine on the internal glass surface gives rise to local composition gradients. At higher temperatures, a transition from complete to partial wetting occurs. Composition fluctuations extend over several pores, and the local chemical and geometrical randomness sets the stage for a random-field transition. The critical exponent  $\beta$  associated with this latter transition is smaller than in the pure system.

PACS numbers: 64.60.Ht, 05.40.+j, 68.45.Gd

The behavior of liquids confined within porous host structures has recently enjoyed increased experimental and theoretical attention. The large surface-to-volume ratio gives rise to sharply restricted geometry and the loss of translational invariance on long length scales. Geometrical and chemical randomness in both pore size and pore volume are prone to alter a variety of properties of imbibed fluids. Of particular interest has been the phase-transition behavior of critical binary fluid mixtures in porous glasses and gels.<sup>1-3</sup> Depending on the magnitude of the correlation length  $\xi$  in the fluid mixture relative to the pore radius  $r_p$ , two different descriptions seem possible. In the case where  $r_p \gg \xi$ , wetting phenomena should dictate the structure in the liquid. If  $r_p \ll \xi$ , however, the chemical potential exerted by the internal glass surface is random on the relevant length scales in the fluid and should act as a random field. This would be the analog of magnets with random impurities, as suggested by de Gennes.<sup>4</sup> A random-field transition has indeed been observed in a fluid mixture imbibed in a porous glass.<sup>1</sup> The signature was strongly nonexponential dynamic correlation functions, as expected<sup>5-7</sup> from activated dynamic scaling at a random-field transition. The relaxation time  $\tau_A$  corresponding to activated processes was found to increase very rapidly. The wave-vector dependence showed that relaxations are more activated on short length scales, in agreement with recent theoretical predictions.<sup>7</sup>

For a two-component fluid mixture near its critical point which is in contact with a glass wall, Cahn has predicted<sup>8</sup> that one of the fluid phases completely wets the glass. It has thus been speculated that wetting phenomena must play an important role for binary fluids imbibed in porous glasses. However, it is theoretically and experimentally unexplored how random, sharply restricted geometries change the wetting behavior. In particular, the transition from the regime  $\xi \lesssim r_p$  to the above-mentioned random-field regime is not understood. In the present study we used Raman, elastic, and quasielastic light scattering to address this issue. Concentration measurements on lutidine-water mixtures imbibed in

porous Vycor show that the internal glass surface adsorbs lutidine. Measurements as a function of temperature reveal that the analog of transition from complete to partial wetting occurs. This allows domains to extend over several pores, a necessary precursor for the random-field transition. The temperature at which the latter transition happens is insensitive to the concentration, indicating a small value for the critical exponent  $\beta$ . This is the first experimental determination of  $\beta$  for a random-field transition and we find good agreement with predictions.<sup>6,9</sup>

Cleaned porous Vycor glass<sup>10</sup> was imbibed with mixtures of 2,6-lutidine and water of known global composition. The volume of the liquid was chosen to be twice the internal pore volume of the Vycor pieces. Even though the fluid mixture penetrated the glass samples (12 mm diameter, 45 mm length) in typically 24 h, equilibrium of the composition was reached only after ten days. The composition of the liquid was determined via measurement of the Raman intensity of lutidine.<sup>11</sup> Figure 1 shows the concentration shift of lutidine inside the porous glass as a function of the global concentration. Even at 22°C, well below the critical temperature  $T_c \cong 33^\circ\text{C}$  of the bulk mixture, as shown in the inset, we observe a strong concentration shift with a maximum around 27% lutidine, which is close to the critical composition. Except for an anomaly<sup>11</sup> around 90% lutidine, Vycor preferentially adsorbs lutidine. Wetting of Vycor glass (96% SiO<sub>2</sub>) by lutidine is in agreement with observations on aggregating silica spheres in lutidine-water mixtures by Beysens and Esteve.<sup>12</sup> Capillary-rise experiments<sup>13,14</sup> with the same mixture, however, indicate that water wets Pyrex glass. The detailed wetting behavior depends on the composition of the glass and the chemical treatment of the surface.<sup>15</sup> The solid line in Fig. 1 has been obtained with a simple model<sup>11</sup> using a Flory-Huggins-type free energy with parameters adjusted to approximate the coexistence curve. We added a term of the form  $h\phi$  to the free energy to describe the effect of a surface field. Here  $\phi$  is the lutidine volume fraction. A dimensionless field strength of  $h = 0.122$  was determined

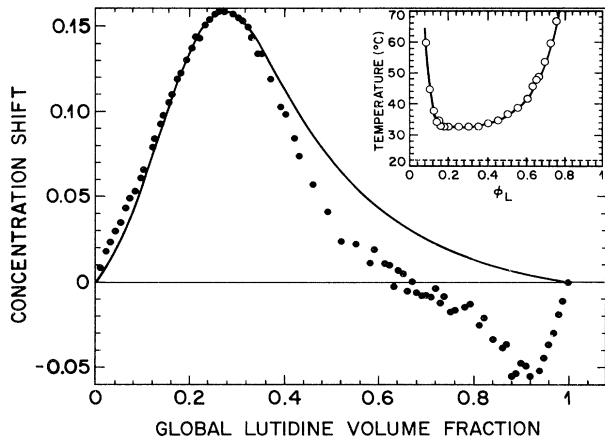


FIG. 1. The concentration shift of the mixture inside the porous Vycor glass as a function of the global concentration at 22°C, well in the one-phase region as indicated by the dashed line in the phase diagram in the inset. Note that the water-lutidine binary fluid mixture has an inverted coexistence curve. The solid line through the concentration-shift data has been obtained using a simple model (see text).

by fitting the calculated composition shifts to the data in Fig. 1. If we assume a surface area covered by a lutidine molecule of 0.3 nm<sup>2</sup>, the surface field at 22°C is  $h_s \cong 9.6$  meV/nm<sup>2</sup>. This is between  $h_s = 52.5$  meV/nm<sup>2</sup> found<sup>13</sup> for lutidine and water on Pyrex and  $h_s = 0.039$  meV/nm<sup>2</sup> for carbon disulfide-nitromethane of fused silica.<sup>15</sup>

Figure 2 shows static light scattering results for six samples with lutidine composition inside the Vycor,  $\phi_L$ , ranging between 8.3% and 69.4% by volume. The scattering angle was 90°, corresponding to a wave vector  $q = 2.0 \times 10^5$  cm<sup>-1</sup>, where length scales 50 times larger than the pore diameter are probed. The imbibed glass pieces were immersed in a high-molecular-weight polydimethylsiloxane ( $M_w = 100\,000$ ), which could not penetrate into the small pores (radius typically 30 Å). Thus the fluid inside was isolated and did not experience a chemical-potential difference from possibly phase-separated fluid that would otherwise have surrounded the glass. This guaranteed that the composition inside the porous glass was temporally stable, even at temperatures where the bulk fluid phase separated. The phase-separation temperatures  $T_s$  of the bulk fluid mixtures are indicated by filled symbols in Fig. 2. As the temperature was increased the samples scattered increasingly more light without any dramatic changes around  $T_s$ . This is in sharp contrast to the behavior in bulk liquid mixtures, for which the scattered intensity diverges at  $T_s$ . Only well above  $T_s$  did the Vycor samples get uniformly cloudy, accompanied by a pronounced increase in scattering. We never observed any macroscopic phase separation. Angular-dependence measurements showed that the scattering was only weakly  $q$  dependent and was

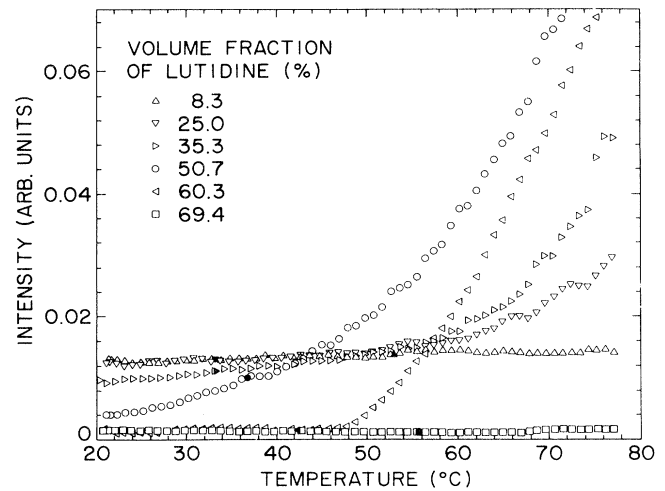


FIG. 2. The scattered intensity for various compositions of the fluid mixture inside the porous glass. The filled symbols denote the phase-separation temperatures of these mixtures in bulk. The scattering angle is 90°, corresponding to a wave vector  $q = 2.0 \times 10^5$  cm<sup>-1</sup>.

determined by short-length-scale features ( $< 200$  Å). An important contribution to the scattered light originates from the refractive index mismatch between the liquid and the glass. We confirmed this by imbibing simple fluids with known index of refraction into Vycor. Measurements with water, ethanol, carbon tetrachloride, cyclohexane, toluene, and lutidine showed that the scattered intensity is described by

$$I = I_0 \left( n_{\text{Vycor}} - n_{\text{liquid}} \right)^2 + I_B, \quad (1)$$

where  $n_{\text{Vycor}} = 1.433$  and  $1.333 \lesssim n_{\text{liquid}} \lesssim 1.5$  are the known indices of refraction of Vycor and the liquids, respectively.  $I_0$  is a constant amplitude equal to 0.777, and the small background  $I_B = 0.0012$  is probably due to imperfections in the glass and spurious stray light.

In order to understand the temperature and composition dependence exhibited by the data in Fig. 2, we measured the temperature dependence of the index of refraction  $n_{\text{liquid}}(T, \phi_L)$  of bulk mixtures as a function of  $\phi_L$ . In Fig. 3 we plot  $\langle \delta n^2 \rangle \equiv \Delta I / I_0$  for various temperatures as a function of  $\phi_L$ . Here  $\Delta I$  is the difference between the measured intensity and the intensity calculated using Eq. (1). As expected, this difference tends to zero for pure water and pure lutidine. At low temperatures, as can be seen in the inset,  $\langle \delta n^2 \rangle$  has a maximum around  $\phi_L \approx 0.3$ . As the temperature is increased,  $\langle \delta n^2 \rangle$  is constant for  $\phi_L \lesssim 0.2$ , but grows for  $\phi_L \gtrsim 0.2$  and develops a very strong maximum centered around  $\phi_L \approx 0.5$  for temperatures of 60°C and higher.

The origin of  $\langle \delta n^2 \rangle$  must come from a spatially nonuniform composition in the fluid mixture, giving rise to lo-

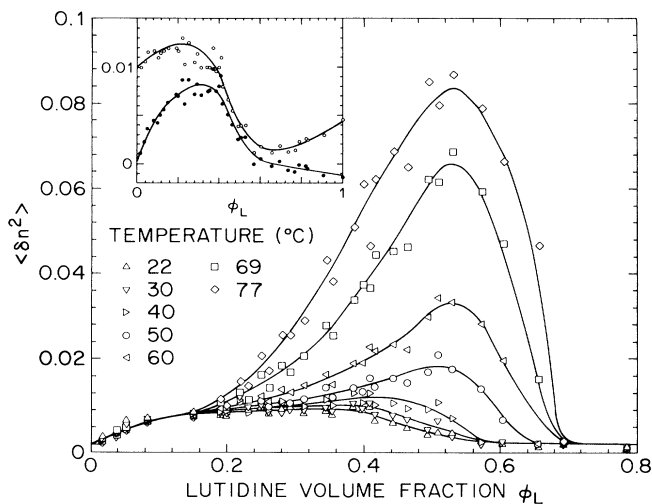


FIG. 3. The difference  $\langle \delta n^2 \rangle$ , between measured intensity and the intensity calculated for a spatially homogeneous fluid with known index of refraction  $n_{\text{liquid}}(T, \phi_L)$  as a function of lutidine volume fraction  $\phi_L$ . Inset: the measured intensity (open circles), and  $\langle \delta n^2 \rangle$  (filled circles) at 22°C. The lines are guides to the eye.

cal gradients in the index of refraction. At low temperatures, this is likely to be due to an enhanced lutidine concentration near the internal glass surface. This effect is in agreement with the Raman measurements showing that Vycor is indeed wetted by lutidine. The energy of mixing of water and lutidine molecules is temperature dependent, being negative below  $T_s$  and positive above  $T_s$  in bulk mixtures. Competition between it and the adsorption energy of lutidine and Vycor determines the composition shift. Thus we expect that adsorption is favored over mixing in the proximity of the coexistence curve. This explains the maximum of  $\langle \delta n^2 \rangle$  around the critical composition  $\phi_L \approx 0.3$  at low temperatures.

It is known from capillary-rise experiments<sup>13,14</sup> that the system of water and lutidine in contact with Pyrex undergoes a transition from complete to partial wetting at a temperature of about 48°C, well in the two-phase region. This is due to the different temperature dependences of the three interface energies and has been predicted by Cahn.<sup>8</sup> Even though it is inappropriate to envision macroscopically thick wetting layers in the small pores of Vycor, it is very plausible that lutidine-water interfaces and gradients are energetically unfavorable at high temperatures. In analogy with the transition from complete to partial wetting, the system can minimize its energy by removing the lutidine gradients from the glass surface and having water- and lutidine-rich microdomains fill the pore space. The intensity scattered by such a configuration is

$$I \propto (n_{VL}^* - n_{VW}^*)^2 \phi_{VL} \phi_{VW}, \quad (2)$$

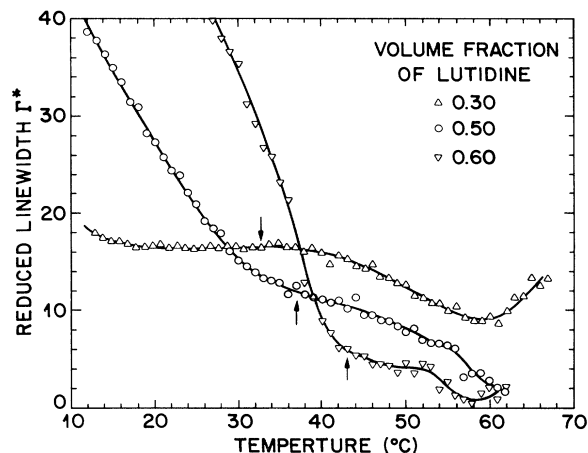


FIG. 4. The temperature dependence of the nonactivated relaxation rate at three different lutidine volume fractions. The bulk mixture's  $T_s$  is indicated by arrows. The random-field transition is characterized by autocorrelation functions that are *not* single exponentials. The lines are guides to the eye.

where  $n_{VL}^*$  and  $n_{VW}^*$  are the effective indices of refraction of the lutidine- and water-rich domains in the glass, and  $\phi_{VL}$  and  $\phi_{VW}$  are the respective volume fractions. With  $\phi_{VW} = 1 - \phi_{VL}$ , one can show at once that Eq. (2) has a maximum at  $\phi_{VL} = \phi_{VW} = 0.5$ , where the internal volume occupied by water-rich domains is equal to the internal volume occupied by lutidine-rich domains. This explains the maximum in intensity at  $\phi_L \approx 0.5$  for temperatures of 60°C and higher.

In order to test further the concept that the finite-size analog of the transition from complete to partial wetting occurs in the porous network, we performed quasielastic light scattering measurements similar to those reported earlier.<sup>1</sup> These measurements probe the hydrodynamic behavior of composition fluctuations in the fluid mixture, which have an autocorrelation function of the form  $e^{-\Gamma t}$ . Figure 4 shows the reduced decay rate of order-parameter fluctuations,

$$\Gamma^* \equiv 6\pi\eta\Gamma/k_B Tq^3, \quad (3)$$

for lutidine volume fractions of 0.30, 0.50, and 0.60 as a function of temperature. Here  $\eta$  is the shear viscosity.  $\Gamma^*$  is inversely proportional to the correlation length in the long-wavelength limit. The qualitative behavior at all three compositions in Fig. 4 is similar and has four distinct regimes. At low temperatures, far away from  $T_s$ ,  $\Gamma^*$  decreases, as it would in a bulk mixture—phenomenon described as critical slowing down. Viscous damping due to the porous medium reduces the value of  $\Gamma^*$  compared to the value measured in bulk. A plateau regime followed by a further decrease of  $\Gamma^*$  characterizes the intermediate temperatures. The saturation of  $\Gamma^*$  can be interpreted as a finite-size effect, where the

correlation length in the mixture becomes comparable to the pore size. This saturation happens in all three cases below  $T_s$  of the bulk mixtures indicated by arrows in Fig. 4.

$\Gamma^*$  resumes its decrease some  $8^\circ\text{C}$  above  $T_s$ . This is similar to the temperature at which the static light scattering results begin to evolve from their low-temperature behavior to their high-temperature behavior. Both observations are consistent with the view that they are due to the finite-size analog of the transition from complete to partial wetting. When it becomes energetically favorable to remove the lutidine gradients from the glass wall, the composition gradients can extend over several pores, allowing the correlation length to grow. These larger blocks will experience locally varying energy barriers due to the chemical and geometrical randomness, which is a precondition for the random-field transition.<sup>1</sup>

At a temperature  $T \approx 59^\circ\text{C}$  the autocorrelation functions change their character dramatically from being single exponential, as expected from dynamic scaling theory, to strongly non-single-exponential. This effect can be attributed to the crossover to activated relaxation of the fluctuations.<sup>1,7</sup> In Fig. 4 only the nonactivated relaxation rate is plotted. It is proportional to  $q^2$  as expected for diffusive processes. Interestingly, the activated relaxation rate is also proportional to  $q^2$ ,<sup>1</sup> in disagreement with findings on binary-liquid gels.<sup>16</sup> The activated time  $\tau_A$  diverges as  $T$  approaches  $63 \pm 1^\circ\text{C}$ , independent of composition. In bulk mixtures of critical binary fluid mixtures, the coexistence curve, and hence the phase-separation temperatures in the vicinity of the critical composition, is known to be described by

$$|\phi_A - \phi_B| = B |T - T_c|^\beta. \quad (4)$$

Here  $\phi_A$  and  $\phi_B$  are the compositions of the coexisting phases,  $T_c$  is the critical temperature,  $B$  is an amplitude, and  $\beta$  is the magnetization exponent, which for Ising systems has the value 0.33. If we attribute the temperature at which  $\tau_A$  diverges to the critical temperature of the random-field transition, and if we assume that  $B$  is of similar size as for regular Ising systems, our measurements give an upper bound for  $\beta$  of 0.21. This is in agreement with theoretical predictions,<sup>5,6</sup> results from computer simulations,<sup>9</sup> and observations on binary-liquid gels.<sup>17</sup>

We note that the quasielastic evidence for the occurrence of a random-field transition at  $\sim 63^\circ\text{C}$  to a frozen domain state is also consistent with the static light scattering results. Above this temperature, we observe domains, which do not grow significantly in size ( $< 200$

$\text{\AA}$ ). Their dynamic fluctuations are rapidly quenched and their domain walls rapidly sharpen with increasing temperature above  $\sim 59^\circ\text{C}$ .

In summary, we have presented results on the temperature and composition dependence of the behavior of binary fluids in porous Vycor. Wetting phenomena play a very important role. Complete wetting opposes the growth of the correlation length due to finite-size effects. The particular system studied, lutidine and water, shows a finite-size analog of a transition from complete to partial wetting. This transition diminishes the role of finite-size effects and allows composition fluctuations to span several pores. The geometrical and chemical randomness of the porous network then exerts a random field on the fluid. The random-field transition to a frozen domain state, characterized by activated dynamics with strongly non-single-exponential autocorrelation functions, occurs at a temperature  $30^\circ\text{C}$  above the bulk critical temperature. The transition temperature is independent of composition (between 30% and 60%) giving an upper bound of 0.21 for  $\beta$ . This is in agreement with recent theoretical<sup>5,6</sup> and numerical<sup>9</sup> predictions. It would be interesting to know whether in other fluid systems, which do not have a transition to partial wetting, the random-field transition is prevented from occurring.

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