VOLUME 72, NUMBER 14 PHYSICAL REVIEW LETTERS 4 APRIL 1994

Study of Phase Separation of a Binary Fluid Mixture in Confined Geometry

M. Y. Lin,* S. K. Sinha, and J. M. Drake
Exxon Research and Engineering Company, Annandale, New Jersey 08801

X.-l. Wu
University of Pittsburgh, Pittsburgh, Pennsylvania 15261

P. Thiyagarajan
Argonne National Laboratory, Argonne, Illinois 60439

H. B. Stanley†
University of Maryland, College Park, Maryland 20742

(Received 1 September 1993)

Small angle neutron scattering experiments were performed to measure the structure factor $S(q)$ for a binary fluid water/lutidine mixture imbibed inside porous Vycor glass at concentrations both near and away from critical. In both cases, the results can be interpreted as a combination of a lutidine-rich wetting layer coating the internal surfaces of Vycor and random single-phase domain growth with temperature. This result does not support the random field Ising model predictions for the phase separation behavior, but is in good agreement with theories based on pore confinement of the imbibed fluid mixture.

PACS numbers: 64.70.Ja, 61.12.Ex, 64.60.Cn, 68.45.Gd

The issue of how a binary liquid mixture phase separates inside a porous medium has attracted considerable theoretical and experimental attention [1-11]. In bulk, the phase separation of a binary liquid at the critical concentration is known to obey three-dimensional Ising-like behavior in the vicinity of the critical temperature and complete macroscopic phase separation occurs. In a porous medium, however, strong retardation of the kinetics is observed and macroscopic phase separation does not occur. Conventional critical fluctuations in the vicinity of the critical point are not observed [3-10]. It has been proposed [1,2] that the randomness of the pore structure gives rise to random field Ising model (RFIM) behavior, which predicts extremely long relaxation effects and irreversibility [2]. The RFIM may not always apply, however. Conceptually, there are two effects to be distinguished, namely, those of randomness and of confinement. For low-porosity solids (such as Vycor glass) the effects of confinement in the pore may be more important in determining the behavior of the phase separation than those of randomness, since the correlation length ξ may never be able to become larger than the pore size in order to sense the randomness of the pores. Liu and co-workers [11] have discussed the phase separation of a binary liquid mixture in a single cylindrical pore where one phase preferentially wets the pore surface. They have demonstrated that microphase separation into domains accompanied by slow kinetics should occur. Experimental confirmation that wetting layers form on the internal surfaces of microporous materials in the vicinity of the consolute point for a binary liquid mixture has been obtained earlier for water/lutidine in silica gels [9], and for ^{3}He and ^{4}He mixtures in aerogels [10].

The original motivation of this work was to determine whether critical fluctuations could be observed in a nominally critical mixture of water and 2,6-lutidine imbibed in Vycor glass, using small angle neutron scattering (SANS). This binary mixture system has an *inverted* phase diagram with the homogeneous phase existing at temperature *below* the bulk consolute point ($T_c \approx 33\,^\circ\mathrm{C}$). The predictions of the RFIM are that the scattering function $S(q)$ in the single phase region is given by the sum of a Lorentzian and a Lorentzian-squared term [8,12],

$$S(q)=\frac{A_1}{1+q^2\xi^2}+\frac{A_2}{(1+q^2\xi^2)^2}\,, \tag{1}$$

where ξ is the correlation length and the second term represents the scattering from frozen fluctuations induced by the random field.

Vycor glass is a well-studied model porous glass. The porosity is typically 28% and the characteristic internal diameter of the pores is 70 Å [13]. In principle, if one chooses instead of pure H_2O an H_2O/D_2O mixture of a certain ratio, it is possible to contrast match the homogeneous phase of the H_2O/D_2O/lutidine mixture with the silica, so that the scattering would be sensitive only to the concentration fluctuations in the mixture. Dierker and Wiltzius [8] used such a method to perform an earlier SANS study of this system. They observed an $S(q)$ which was more or less consistent with Eq. (1) and which they interpreted within the framework of the RFIM.

There are certain essential complications, however, which occur when one performs such experiments. The first is that the ratio of water to lutidine changes considerably (relative to the reservoir), as lutidine is preferentially absorbed by the porous Vycor, so that the mixture in the Vycor is not at the critical concentration [7], unless special precautions are taken. (If the sample is in continuous contact with a reservoir, the water/lutidine concentration ratio changes as a function of temperature.) The above fact is an indication that preferential wetting of the internal surfaces with a lutidine-rich phase occurs.

0031-9007/94/72(14)/2207(4)$06.00

Second, the scattering from even a nominally contrast-matched mixture turns out to be more complicated than that described above. In particular, an extra peak appeared in the $S(q)$ as shown in the measurements by Dierker and Wiltzius [8]. The origin of this peak was not identified in the work. We show below that this peak is a signature of the lutidine-rich wetting layers.

The present experiments were carried out using disks of Vycor glass 15 mm in diameter and 1 mm thick. These were first cleaned by boiling in 30% hydrogen peroxide, then baked at 130 °C in a vacuum oven for more than 24 h, to remove any contamination from the internal pore surfaces. After cleaning, they were soaked overnight in solutions of H_2O/D_2O/lutidine. The Vycor disks were then isolated and sealed at room temperature (in the homogeneous phase) in a container for the SANS experiment so that the total volume of imbibed fluid could not change with temperature. The best contrast-matched sample was obtained from a supernatant solution with volume fractions of 14% lutidine, 18.4% H_2O, and 67.6% D_2O. Taking the neutron scattering density of Vycor glass to be $3.64\times10^{10}/\mathrm{cm}^2$ as for pure silica [14], we calculate that at contrast matching the global concentration of the mixture imbibed into the Vycor consisted of 34% lutidine, 14.1% H_2O, and 51.9% D_2O. Allowing for experimental uncertainties this is close to the critical concentration of 31.2% of lutidine in the mixture. This sample was then used to measure $S(q)$ as a function of temperature up to 85 °C. The measurements were made at the Small Angle Diffractometer of the Intense Pulsed Neutron Source (IPNS) facility at Argonne National Laboratory. A subsequent set of similar measurements on another set of samples were made at the LQD (low-Q diffractometer) of the LANSCE facility at Los Alamos National Laboratory. In the LANSCE experiment, we did not limit the concentrations to being both critical and contrast matching. We chose a best contrast-matched sample which had a reservoir composition of 31.2% lutidine and 68.8% D_2O. By similar arguments, we estimate that the volume fractions inside the Vycor were 52.8% lutidine and 47.2% D_2O, and it is thus quite far from critical. This sample was also used to perform temperature dependent SANS experiments. Both the IPNS and LANSCE results are similar, suggesting that the present measurements are not sensitive to any possible critical behavior in the system, a point we shall return to later.

In each case, a contrast-matching condition at room temperature (23–24 °C, well inside the "homogeneous" phase) was observed as an overall decrease in the scattering intensity of more than 2 orders of magnitude, and as the disappearance of the "Vycor peak" at about $q_0 = 0.023$ Å^{-1}. This peak is characteristic of the quasiperiodic pore-solid structure of Vycor. Figure 1(a) shows the scattering from dry Vycor glass and Fig. 1(c) that from the contrast-matched sample taken at 23 °C. It is seen that the Vycor peak has disappeared, but there is a weak peak at 0.03 Å^{-1}, which is similar to that seen in the earlier SANS work [8]. We interpret this peak in terms of the internal Vycor surfaces being coated with a lutidine-rich phase having a slightly different contrast from the rest of the medium. A simple physical picture can be envisioned in terms of these skin layers effectively creating a new quasiperiodic structure in an otherwise contrast-matched medium. Such a structure would have a period d' about half of that of the original solid-pore structure. However, such a model is too crude to be used in an actual fit since it assumes an infinitely thin skin and takes no account of distortions at corners, narrow necks, etc. It was thus decided to experimentally measure such surface layer scattering by derivatizing the internal surface of Vycor glass with alkylsiloxanes of various carbon-chain lengths, and running a subsidiary set of SANS experiments with a contrast-matched *simple* fluid (mixture of hexane/deuterated hexane) inside the pores. Figure 1(b) shows the scattering curve obtained for a C_{18}-alkylsiloxane on Vycor at room temperature. The broad peak at 0.03 Å^{-1} is reproduced, confirming its origin as the adsorbed layer structure on the Vycor internal surfaces. The peak is more pronounced than that in Fig. 1(c), due to larger contrast mismatch between the C_n chains and the rest of the medium. Measurements were made from various chain lengths of alkylsiloxanes (C_8, C_{12}, and C_{18}), all with similar results. The peak position depended slightly on the carbon-chain length (i.e., the thickness of the adsorbed layer) and thus these data were stored as a series of canonical "skin-scattering" functions $S_{\mathrm{sk}}(q)$ to be used to analyze the water/lutidine SANS data.

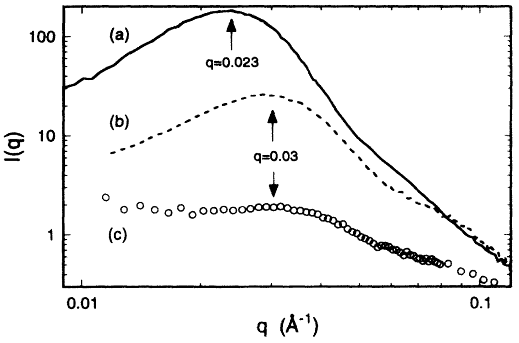

FIG. 1. Scattering intensity $S(q)$ (arbitrary units) for (a) dry Vycor glass, (b) Vycor derivatized with C_{18}-alkylsiloxane surface layer and filled with contrast-matching hexane/d-hexane mixture, and (c) Vycor with contrast-matching binary lutidine/water mixture at 23 °C.

Figure 2 shows a series of data from the "contrast-matched" Vycor/water/lutidine sample as the temperature is raised through the bulk consolute point ($T_c \approx 33$ °C). The SANS data shown were taken at IPNS, although the LANSCE data are in quantitative agreement. Both sets of data were fitted by a function of $S(q)$ given by

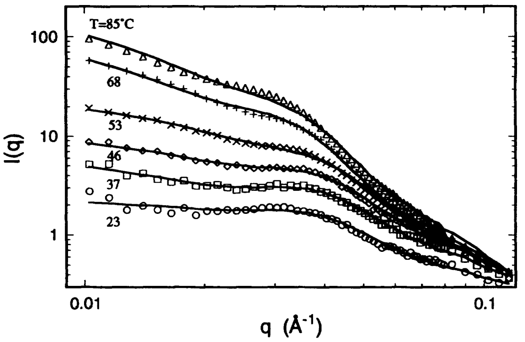

FIG. 2. Scattering intensity measured at IPNS facility for Vycor+binary fluid sample shown in Fig. 1(c) at various temperatures. The solid lines are fits using Eq. (2).

$$I(q)=\frac{A_1}{1+q^2\xi_1^2}+\frac{A_2}{(1+q^2\xi_2^2)^2}+A_3S_{\mathrm{sk}}(q)+B\,. \qquad (2)$$

The first term represents the genuine critical fluctuation scattering. The amplitude of this term always came out to be relatively small and ξ_1 never appeared to be greater than 20 Å for the measurements below T_c. For most of the data above T_c, this term is zero. Thus, even for the IPNS sample (where the concentration inside the Vycor was believed to be close to critical), we did not observe true critical behavior. This may be due to the fact that the concentration of the free fluid inside the pores moves away from its value at room temperature due to the formation of the skin layer having more and more lutidine (see discussion of A_3 below).

The second term is not to be interpreted as the Lorentzian-squared term of the RFIM in the single-phase region [Eq. (1)] (note that $\xi_1 \neq \xi_2$), but rather as a general form of scattering from a series of random domains of characteristic size ξ_2 in the spirit of the treatment of Debye, Anderson, and Brumberger [15]. The first two terms are actually consistent with the RFIM model in the *two-phase region.* In fact, some years ago, Wong, Cable, and Dimon [16] discussed the form of the scattering in this region, where the microseparated domains are kinetically hung up and give rise to Lorentzian-squared Debye-Anderson-Brumberger (domain) scattering. They found in fact that $S(q)$ in this region should be given by the first two terms of Eq. (2) (with $\xi_1 \neq \xi_2$). Thus it is the third term that provides the crucial difference from the RFIM predictions. The third term represents the scattering from the adsorbed lutidine-rich layer and its form $S_{\mathrm{sk}}(q)$ was chosen from the scattering from the C_n chain derivatized Vycor sample whose peak closely matches the position of the observed peak at that temperature. The last term in Eq. (2) represents a q-independent incoherent background from the hydrogen nuclei in the sample. Using this form, we were able to get excellent fits to the data as shown in Fig. 2. Figure 3(a) shows the parameter ξ_2 as a function of temperature T for both sets of data. It may be seen that the "domain size" never gets larger than the Vycor pore size even well above T_c. This fact and the existence of the wetting layer lead us to believe that the RFIM picture is inapplicable to the present system. By considering the $q \to 0$ limit of the second term, and equating it to the scattering from a binary system of N domains with contrast $\Delta\rho_d$ and average domain size ξ_2, we obtain

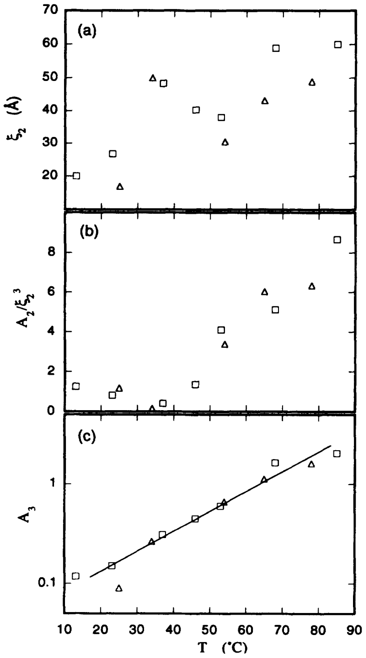

FIG. 3. Fitted parameters ξ_2, A_2/ξ_2^3, and A_3 in Eq. (2) as functions of temperature T derived from the data shown in Fig. 2 (IPNS, squares) and from LANSCE data (triangles). The solid line is a guide to the eye.

$$A_2 \propto N(\Delta\rho_d)^2\xi_2^6\,. \qquad (3)$$

The second term in Eq. (2) is then consistent with Porod's law at large values of q, being proportional to Σ/q^4 (Σ being the total interface area between the domains). $N\xi_2^3$ is proportional to the total system volume. Thus A_2/ξ_2^3 should be proportional to the square of the "order parameter" $\Delta\rho_d$ in the two-phase region, and its behavior is plotted in Fig. 3(b). This form is also consistent with the behavior of the Lorentzian term given by Wong and co-workers [16,17]. Figure 3(c) shows the behavior of the amplitude A_3 which should be proportional to $(\Delta\rho_{\mathrm{sk}})^2\Delta t^2$ where $\Delta\rho_{\mathrm{sk}}$ is the contrast of the material in the adsorbed layer ("skin") relative to the average and Δt is the thickness of the absorbed layer. The IPNS and LANSCE data are in good *quantitative* agreement with regard to the derived parameters. We believe that as the phase separation develops the skin becomes more lutidine rich, therefore resulting in a bigger contrast $\Delta\rho_{\mathrm{sk}}$. The skin thickness Δt, in the single pore model, is predicted to decrease with increasing T. However, the movement of the peak position q_s corresponds to a layer thickening

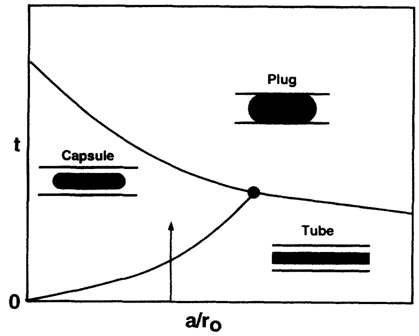

FIG. 4. Phase diagram of the single-pore model by Liu *et al.* (Ref. [11]) for phase separation inside a confined pore geometry. The arrow indicates the observed behavior of the water/lutidine system in Vycor deduced from the present experiment. Here t is the reduced temperature, r_0 is the tube radius, and a is a molecular length.

with T, when compared with the C_n-derivatized Vycor data. While we cannot quantitatively determine the precise thickness of the layers, the following argument may explain the apparent disagreement. When a C_n layer forms on the surface of a pore, it may fill the pore entirely if the pore is very small or narrow. Thus the smaller pores contribute less to the skin scattering term. Since these pores correspond to smaller skin separations, the net effect is to shift the peak position q_s to smaller q and a thicker layer would correspond to a smaller q_s. In the binary fluid experiments, the shift of q_s toward low q may not necessarily be due to thickening skin; it could be caused by increasing single-phase domains occupying small pores, hence also eliminating their contribution towards the skin scattering and shifting q_s to smaller values in a similar fashion.

In discussing the present model for the scattering, it is natural to ask why the Vycor peak does not reappear as the absorbed fluids preferentially separate into the adsorbed layer and the domains. In fact, it can be shown in similar fashion to the original derivation for scattering from a porous medium that if the total material trapped in the pores is globally contrast matched (true in this case) and if there is no spatial correlation between the positions of the domains of the water-rich phase relative to the surface of the Vycor, then the Vycor peak will remain absent and, further, no interference effects will arise between the "skin" and "domain" scattering.

Thus the present results provide strong experimental evidence for binary fluid phase separation in Vycor glass to be in the category of fluid phase separation in confined geometries with preferential wetting effects, as calculated by Liu and co-workers. In fact, as a function of the reduced temperature $t=(T-T_c)/T_c$ above zero, our system seems to follow the path on their phase diagram shown in Fig. 4, going from a "tube" phase with a wetting layer to a "capsule" phase (tube+phase separated water-rich "bubbles" inside). Since the adsorbed layer is always observed, we never appear to reach the "plug" phase. This may be due to the nonuniformity of the pore space from the idealized case of simple cylinders, resulting in a large differential capillary pressure in the plugs which would tend to move them into more "open" regions [17].

We acknowledge helpful conversations with A. Liu, G. Grest, C. Glinka, M. Chan, and P.-z. Wong. This work has benefited from the use of the various neutron scattering facilities: the IPNS at ANL, funded by the U.S. DOE under Contract No. W31-109-ENG.38; the LANSCE at LANL, funded by the U.S. DOE under Contract No. W7405-ENG.36; and the CNRF at NIST.

---

*Present address: National Institute of Standards and Technology, React E151, Gaithersburg, MD 20899.
†Present address: Université Joseph Fourier, B.P. 87-38402, St. Martin D'Heres, France.

[1] P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984).
[2] D. Andelman and J. F. Joanny, in *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985), p. 183.
[3] J. V. Maher, W. I. Goldburg, D. W. Pohl, and M. Lanz, Phys. Rev. Lett. **53**, 60 (1984).
[4] J. S. Huang, S. K. Sinha, W. I. Goldburg, J. V. Maher, and S. K. Satija, Physica (Amsterdam) **136B**, 291 (1986).
[5] M. C. Goh, W. I. Goldburg, and C. M. Knobler, Phys. Rev. Lett. **58**, 1008 (1987).
[6] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **58**, 1865 (1987).
[7] P. Wiltzius, S. B. Dierker, and B. S. Dennis, Phys. Rev. Lett. **62**, 804 (1989).
[8] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **66**, 1185 (1991).
[9] B. J. Frisken, F. Ferri, and D. S. Cannell, Phys. Rev. Lett. **66**, 2754 (1991); B. J. Frisken and D. S. Cannell, Phys. Rev. Lett. **69**, 632 (1992).
[10] A. Maritan, M. R. Swift, M. Cieplak, M. H. W. Chan, M. W. Cole, and J. R. Banavar, Phys. Rev. Lett. **67**, 1821 (1991); S. B. Kim, J. Ma, and M. H. W. Chan, Phys. Rev. Lett. **71**, 2268 (1993).
[11] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. **65**, 1897 (1990); A. J. Liu and G. Grest, Phys. Rev. A **44**, R7894 (1991); L. Monette, A. J. Liu, and G. Grest, Phys. Rev. A **46**, 7664 (1992).
[12] E. Pytte, Y. Imry, and D. Mukamel, Phys. Rev. Lett. **46**, 1173 (1981); D. Mukamel and E. Pytte, Phys. Rev. B **25**, 4779 (1982).
[13] P. Levitz, G. Ehret, S. K. Sinha, and J. M. Drake, J. Chem. Phys. **95**, 6151 (1991).
[14] M. Y. Lin *et al.*, in *Neutron Scattering for Materials Science*, edited by S. M. Shapiro, S. C. Moss, and J. D. Jorgensen, MRS Symposia Proceedings No. 166 (Materials Research Society, Pittsburgh, 1990), p. 449.
[15] P. Debye, H. R. Anderson, and H. Brumberger, J. Appl. Phys. **28**, 679 (1957).
[16] P.-z. Wong, J. W. Cable, and P. Dimon, J. Appl. Phys. **55**, 2377 (1984).
[17] P.-z. Wong (private communication).