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SANS studies of fluid phase transitions in porous media

M.Y. LIN, S.K. SINHA, J.M. DRAKE, P. THIYAGARAJAN*, X.L. WU** and H.B. STANLEY***

Exxon Research and Engineering Company, Annandale, New Jersey 08801, U.S.A.

* *Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.*

** *University of Pittsburgh, Pittsburgh, Pennsylvania 15261, U.S.A.*

*** *University of Grenoble, France*

The study of binary fluid phase transitions in porous media has received a great deal of attention, both theoretically and experimentally, over the past few years. The preferential wettability of the internal surfaces by one of the fluids introduces a randomness that has led to consideration of Random Field Ising Models. However, in certain cases such as Vycor glass, the *confinement* in the pores plays a dominant role. A different limit is obtained in the case of aerogels which have internal mass fractal density correlations. We discuss the theory of scattering by binary fluid concentration fluctuations in both these types of porous solid and recent studies of the scattering from water/lutidine critical and near-critical mixtures in these systems.

Ever since P. G. deGennes, a decade ago, proposed that a binary fluid confined in a random microporous medium (such as a gel network) might behave analogously to an Ising ferromagnetic spin system acted on by a random magnetic field [1,2], there has been a considerable amount of experimental and theoretical effort in studying the phase behavior of such systems [3-9]. The analogue of the random field in this case is the preferential attraction of the internal surface of the random porous material for one component of the binary fluid mixture. SANS techniques can be used to study critical concentration fluctuations in a binary fluid mixture in the vicinity of its critical point, in cases where the correlation length varies between tens and hundreds of angstroms (see Figure 1). In principle, the case of a critical binary fluid mixture absorbed within a porous material can be studied as easily by the procedure of choosing the mixture so that its neutron scattering length density in the homogeneous phase matches that of the porous medium. In this contrast-matched situation, the SANS is again only sensitive to the critical concentration fluctuations of the binary mixture. The predictions of the Random Field Ising Model (RFIM) are that the scattering function $S(q)$ is given by the sum of a Lorentzian and a Lorentzian-squared term:

$$S(q) = \frac{A}{1 + q^2 \xi^2} + \frac{B}{(1 + q^2 \xi^2)^2} \quad (1)$$

and that the correlation length ξ diverges as $(T - T_c)^{-\nu}$, where T_c is a possibly shifted critical temperature and ν may differ from the conventional 3D Ising exponent [10]. In addition, the phase separation is predicted not to proceed to macroscopic phase separation in the two-phase region, but to be

hung up in microdomains with extremely long relaxation effects and irreversibility [3,4].

Vycor glass is a well-studied model porous glass whose pore space represents one of the phases separated out from a silica/boro-silicate mixture by quenching and subsequent spinodal decomposition [11]. The boron-rich phase is leached out, leaving the pore space in a silica matrix. The morphology of the pore space is random, but has a characteristic internal diameter of $\sim 80\text{\AA}$, and the porosity is typically 0.28. Dierker and Wiltzius used SANS to study the phase separation of a water/(2,6)-lutidine mixture in Vycor glass and obtained results which were stated to be consistent with the RFIM predictions [8]. However, in discussing experiments on such a system, there are certain diffi-

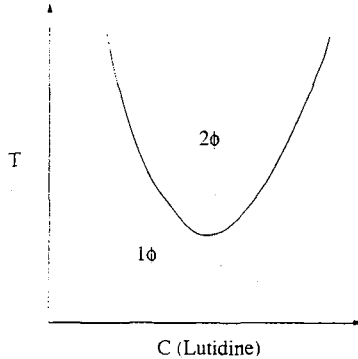


Figure 1. Schematic of phase diagram of water/2-6-Lutidine.

culties encountered with regard to applying the RFIM concepts. The first is that the ratio of water to lutidine changes considerably (relative to the reservoir) on loading into the Vycor (which preferentially absorbs lutidine), so that the mixture in the Vycor is not at the critical concentration, unless special precautions are taken. Secondly, the "random field" imposed by the Vycor is not really completely random. Finally, 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 data of Dierker and Wiltzius which was unexplained.

Conceptually, for critical binary fluid mixtures in a porous medium, there are two effects to be distinguished, namely (a) randomness and (b) confinement. For low-porosity solids (such as Vycor), the effects of confinement turn out to be more important, while for high-porosity solids (such as aerogels) the reverse may be true. In any case, it is intuitively obvious that for the RFIM concepts to apply, the correlation length ξ must be somehow able to become much larger than the typical "pore size", which can only be true if the fluid is not significantly confined. Liu and co-workers [12-14] have investigated how the components of a critical binary fluid mixture wet the walls of a finite tube. In the two-phase region, they find three possible phases: (1) where a uniform wetting layer of one phase coats the walls of the tube, (2) where "capsules" of one phase form inside the other phase, but do not contact the walls, and (3) where the system breaks up into "plugs" of each phase in contact with the walls (see Figure 7). We shall see that this phase diagram is probably relevant to the situation of water and lutidine in Vycor.

We now describe our experiments on the $\text{H}_2\text{O}/\text{D}_2\text{O}/(2,6)$ -lutidine/Vycor system. The experiments were done with the fluid imbibed into 10mm diameter x 1mm thick disks of Vycor, which were first cleaned by standard cleaning procedures and soaked overnight in reservoirs of the appropriate $\text{H}_2\text{O}/\text{D}_2\text{O}/$ lutidine mixtures. They were then isolated and sealed in a container for the SANS experiments so that the total imbibed fluid could not change with temperature. As stated above, the Vycor glass preferentially absorbs lutidine

from the reservoir. Thus, several samples were made from different trial reservoir concentrations, these concentrations being based on different guesses regarding how much lutidine is preferentially absorbed. The H_2O/D_2O /lutidine concentration in these trial reservoir concentrations were chosen such that if the guess was correct, the fluid in the Vycor would be at the critical concentration (corresponding to 31% lutidine by volume) and contrast matched (at least at the lowest temperature, i.e., well into the homogeneous phase). Thus, experimental observation of the contrast matching also ensured a mixture in the glass which was close to critical (to a reasonable approximation). SANS data were taken at both the SAD diffractometer on the IPNS pulsed neutron source at Argonne National Laboratory and at the LOQ diffractometer at the LANSCE pulsed neutron facility at Los Alamos National Laboratory.

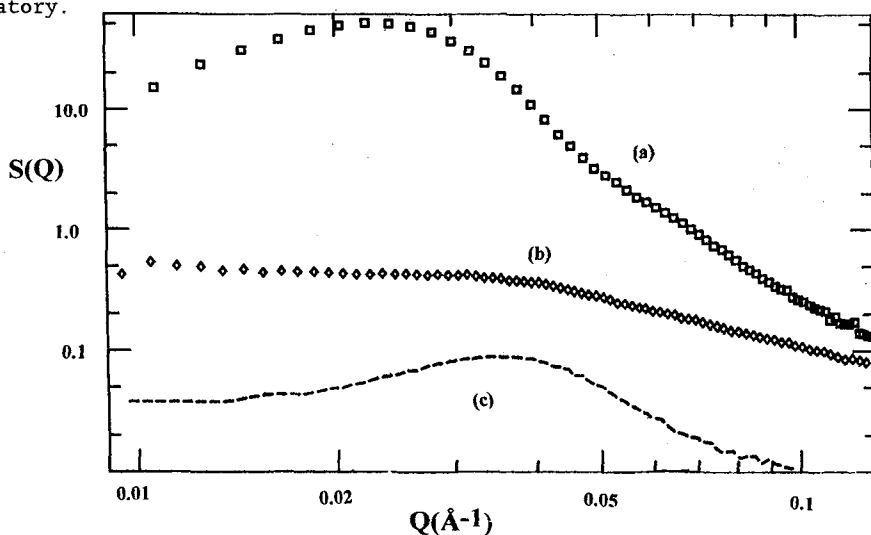


Figure 2. $S(q)$ (arbitrary units) for (a) dry Vycor glass, (b) Vycor + contrast-matching fluid at 25°C , and (c) Vycor derivatized with C8-alkylsiloxane surface layer and filled with contrast-matching hexane/d-hexane mixture.

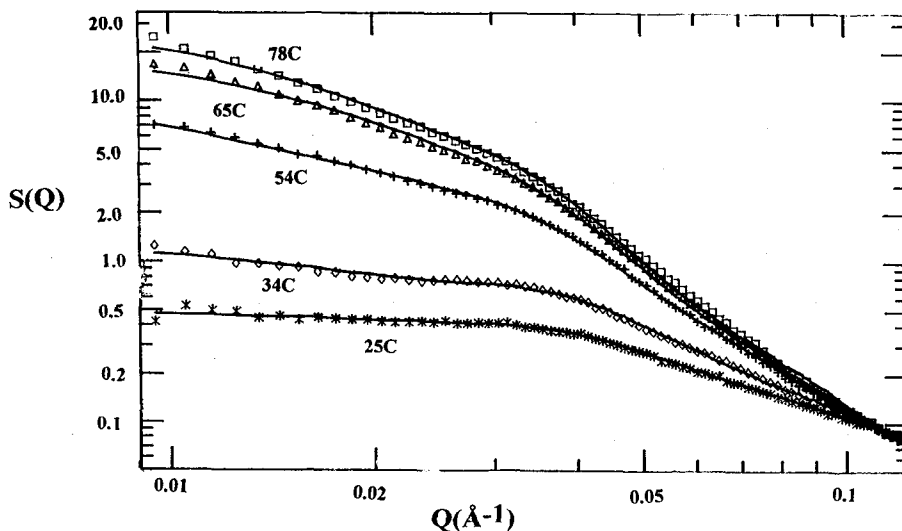


Figure 3. $S(q)$ (arbitrary units) measured on LANSCE facility for Vycor + binary fluid at various temperatures.

Figure 2(a) shows the scattering from a sample of clean, dry Vycor glass. The most obvious feature is the well-known peak at 0.022\AA^{-1} , reflecting the pore-structure which arises from spinodal decomposition during the manufacture of the glass. Also shown (Figure 2(b)) is $S(Q)$ from the "best" contrast-matched sample (as described above) where the main peak has essentially disappeared. A very slight peak is visible at a Q of 0.035\AA^{-1} . This is an indication of a lutidine-rich wetting layer on the internal surface, and corresponds to the extra peak seen by Dierker and Wiltzius. A simple chord distribution model for the solid and pore space obtained from electron micrographs of Vycor glass [11] can be used to account for the $S(q)$ for dry Vycor, and with the appropriate modification for the $S(q)$ of contrast-matched Vycor decorated with a wetting layer on its internal surface, yielding a very similar shifted peak in $S(q)$ [15]. SANS data from the contrast-matched sample as the temperature is raised through the bulk consolute point ($T_b = 30^\circ\text{C}$) is shown in Figure 3. For reasons of space, only the data taken at LANSCE are shown here. (The IPNS data are in quantitative agreement with these results.) It is obvious that the scattering increases dramatically into the two-phase regions, as does the intensity of the peak at 0.035\AA^{-1} . In order to account for this peak, instead of relying on the chord distribution model, we carried out subsidiary experiments on clean Vycor glass derivatized with an alkyl-siloxane layer anchored to the internal surface and filled with contrast-matching hexane/d-hexane, to simulate the wetting layer. The alkyl chain lengths ranged from C_8 to C_{18} and did indeed produce a peak at $Q \approx 0.035\text{\AA}^{-1}$, whose exact position depended slightly on chain length. An example of the scattering from the C_8 -derivatized layer is shown in Figure 2(c). The data in Figure 3 was then fitted with the form

$$S(q) = \frac{A_1}{1 + q^2 \xi_1^2} + \frac{A_2}{(1 + q^2 \xi_2^2)^2} + A_3 S_s(q) + B \quad (2)$$

where the first term represents the genuine critical fluctuations, the second term, random domains of characteristic size ξ_2 , as given by Debye, Anderson, and Brumberger [16], the third term, the appropriate derivatized and contrast-matched Vycor sample ("skin" term), chosen so that its peak closely matched the position of the observed peak at that temperature, and the last term represents an incoherent background. The first term is rather weak and is negligible above T_b . Figure 4 shows the temperature dependence of the amplitude of the second term, and Figure 5 shows that of the domain size ξ_2 , and Figure 6, the amplitude of the "skin" (wetting layer) term as a function of temperature. The Argonne IPNS results, when fitted, yielded almost identical parameters and temperature dependence. From these results, we conclude that (a) there is always a lutidine-rich wetting layer on the internal surface. If $\Delta\rho$ is its contrast with the average scattering length density and t is its thickness, then the amplitude A_3 is proportional to $(\Delta\rho t)^2$, and Figure 6 shows that this increases rapidly into the two-phase region; and (b) in addition to the wetting layer, capsules of lutidine-rich phase fluid form above T_b , and their size saturates when they reach approximately the pore diameter. Thus, we conclude that the behavior of the system is governed more by "wetting in a confined geometry" than by RFIM behavior, and follows the behavior predicted by Liu et al. [12-14]. Figure 7 shows a possible path of the present system on their predicted phase diagram.

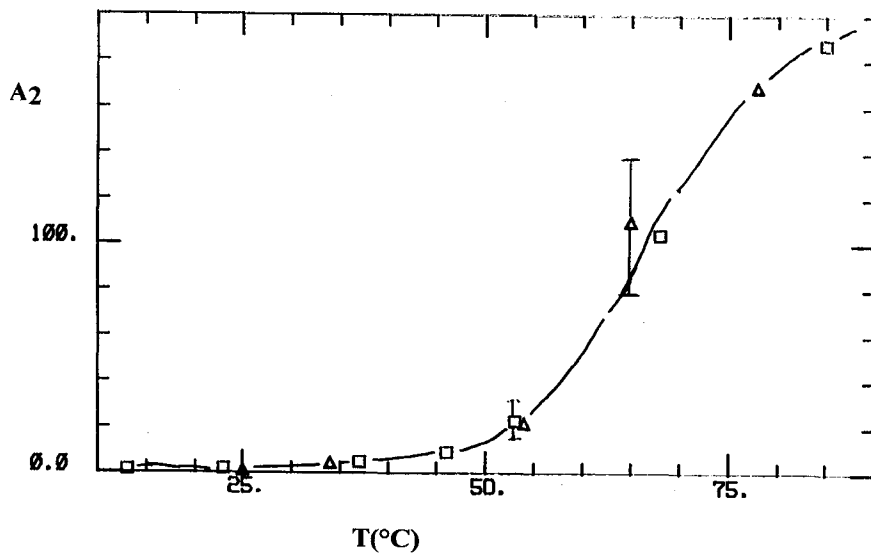


Figure 4. Amplitude of Lorentzian-squared term vs. temperature. Squares are from fits to data taken at IPNS facility and triangles from fits to data taken at LANSCE facility.

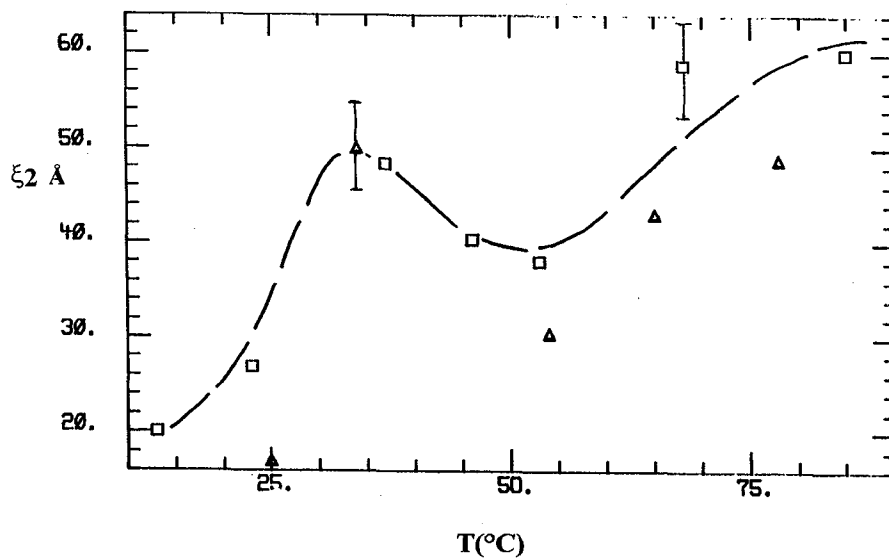


Figure 5. Domain size ξ vs. temperature. Squares and triangles have same meanings as in Figure 4.

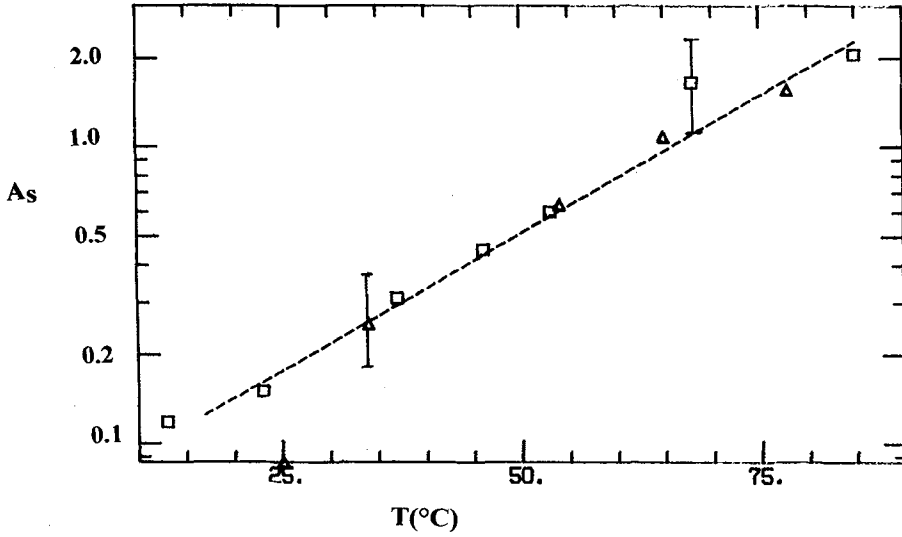


Figure 6. Semilogarithmic plot of amplitude of wetting layer term $S_s(q)$ vs. temperature. Squares and triangles have same meanings as in Figure 4.

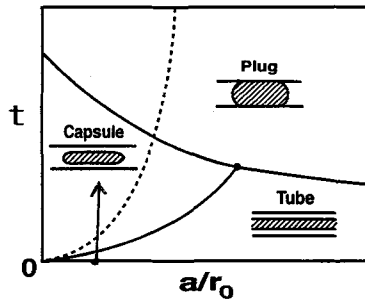


Figure 7. Phase diagram of Liu et al. (Ref. [14]) for phase separation inside a confined tube geometry. The arrow indicates the observed behavior of the water/lutidine system in Vycor deduced from the current experiment. t is the reduced temperature, and r_0 is the tube radius.

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