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Small-angle neutron-scattering studies of the fractal-like network formed during desorption and adsorption of water in porous materials

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Small-angle neutron scattering (SANS) has been used to study the adsorption and desorption behavior of a D_2O/H_2O water mixture in porous materials. When the porous solid is partially saturated, a feature appears in the scattering having a fractal-like power-law form Q^{-D} (where Q is the scattering wave vector) in the very-low-Q region, extending to below the limit of the instruments used and which covers a maximum range of about one and one-half orders of magnitude in Q. The gradient measured during desorption D, being 1.75 ± 0.1 for porous Vycor glass, 1.85 ± 0.1 for Ludox, and 2.0 ± 0.1 for a silica sol-gel, indicates that the percolation network forms a fractal-like geometry under these conditions. The gradient for adsorption is less than 1.0 for both Vycor and Ludox, and no power-law form of SANS is seen at all for the silica sol-gel. This implies that fractal-like percolation networks are not formed during the adsorption process.

The condensation of liquids in porous solids has long been a topic of considerable interest.[1] The process has traditionally been analyzed in terms of the hysteresis loop in the vapor adsorption/desorption isotherms.[2-4] The basic behavior is described by the Kelvin equation relating the partial pressure to the curvature of the liquid surface[5] combined with Brunauer-Emmett-Teller (BET) theory for multilayer adsorption.[6,7] The pore size distribution may be related to the hysteresis loop in a number of ways. For instance, Mason[8] has derived this function from an analysis of the "break-back" curves which are obtained when one changes from adsorption to desorption—or vice versa—at a point within the hysteresis loop. The local condensation process has also been modeled theoretically without resorting to the Kelvin equation.[9] These considerations have shown that a variety of microscopic models can "explain" the isotherm. There is, therefore, a clear need for a technique that can give unambiguous information at the microscopic level. In the present paper, we report on information about the correlation among the empty pores that can be obtained from small-angle neutron-scattering (SANS) measurements on porous solids in equilibrium with the matched water vapor at fixed points on the hysteresis loop of the isotherm. Using a range of porous solids, we demonstrate that desorption occurs through the establishment of very similar percolation networks of linked empty pores having fractal geometry in each of these systems. This appears to be the first unambiguous diffraction evidence for such a percolation system. In contrast, for adsorption, it is clear from the SANS data that there are no fractal features in any of these materials. Hence, as one would expect, the condensation process must first happen at a random distribution of points, at each of which the liquid phase is formed over a small region of pore space.

Small-angle scattering techniques have recently been applied to a range of porous solids with particular emphasis on determining whether these systems are fractal or not.[10-13] The results are somewhat controversial but it seems clear that for Vycor, the pores themselves are not distributed with fractal geometry although their interconnections may be,[14] but that when baked dry, the pore surfaces are apparently fractally rough.[15] In order to investigate the connectivity of the pores in more detail, we have exploited one of the advantages of the neutron method, namely, the fact that, by varying the H/D ratio, we can change the neutron-scattering density of water, ρ_W, from a negative value (pure H_2O) to one that is more positive than the value for the silica matrix (pure D_2O). We have therefore been able to use isotopically mixed water chosen to match the neutron-scattering density of the matrix of the porous solid (i.e., $\rho_{\text{water}}=\rho_{\text{solid}}$) with the objective of studying the local distribution of empty pores at different points on the isotherm. When a porous solid is fully saturated with its matched water mixture, the

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sample becomes transparent to neutrons (i.e., coherent scattering is zero). When the sample is partially saturated, the information about the network of the emptied pore can be highlighted because the coherent scattering is the Fourier transformation of the correlation function of the emptied pores combined with the contrast term $(\rho_{\text{water}}-\rho_{\text{solid}})^2$, i.e.,

$$I(Q)\propto(\rho_{\text{water}}-\rho_{\text{solid}})^2 P(Q)S(Q)\ , \tag{1}$$

where $P(Q)$ is the form factor of the pores which is determined by shapes of the individual pores and $S(Q)$ is determined by the correlation function of the pores. In the Porod region,[16] i.e., $Q>1/a$, where a is the averaged pore diameter (e.g., 30 Å for Vycor), $P(Q)\propto Q^{-d}$, where d is 4 for a system which has smooth internal surfaces[16] [for $Q<1/a$, $P(Q)=\text{const}$]. $S(Q)$ is the structure factor for the empty pores. For a fractal-like system, this term has been given by Sinha, Freltoft, and Landau[17] as

$$S(Q)\propto\Gamma(D)\xi^{(D)}\frac{\sin[(D)\tan^{-1}(Q\xi)]}{Q[1+Q^2\xi^2]^{(D)/2}}+C\ , \tag{2}$$

where ξ is the upper fractal dimension (typically many times the pore separation distance, e.g., $\xi>1000$ Å for Vycor), D is the fractal dimension, and C is a constant. If $Q>1/\xi$, the term can be simplified as $S(Q)\propto Q^{-D}$ and $P(Q)\propto\text{const}$ while, if $Q<1/a$, the scattering intensity is

$$I(Q)\propto(\rho_{\text{water}}-\rho_{\text{solid}})^2 Q^{-D}\ . \tag{3}$$

If $Q>1/a$, $S(Q)=C$ and $P(Q)\propto Q^{-4}$, for smooth surface pores

$$I(Q)\propto(\rho_{\text{water}}-\rho_{\text{solid}})^2 Q^{-4}\ . \tag{4}$$

The SANS experiments were carried out for different Q ranges for Vycor glass, using the LOQ spectrometer at the ISIS pulsed neutron source at the Rutherford-Appleton Laboratory, UK, and the D11 spectrometer on the High Flux Reactor at the ILL, Grenoble, France. In the overlap region between the instruments, the data superimpose unambiguously so that, for simplicity, a single data set is presented here. In order to find the best matching ratio, a series of samples were prepared in which the proportion of D_2O was varied from 58 to 70 % in 3% steps and then finalized at 1% per step, thus extending the measurements reported earlier[13] through the matching range. The saturated samples were sealed in aluminum cans and pumped down to just less than 100% humidity. The 64% D_2O sample shows nearly perfect matching, i.e., the scattering intensity, $I(Q)$, is nearly flat through the position of the peak at $Q=0.025$ Å^{-1}, which is due to the spinodal decomposition process that takes place in Vycor as part of the manufacturing process. For this composition, the residual coherent scattering intensity is clearly less than the incoherent flat background that is present at all Q (see Fig. 1). Comparison with the sample having 8% D_2O (the ratio of isotopes that gives zero scattering density for water) shows that the peak is reduced by 3 orders of magnitude, representing excellent matching. 64% D_2O was therefore used for all subsequent measurements.

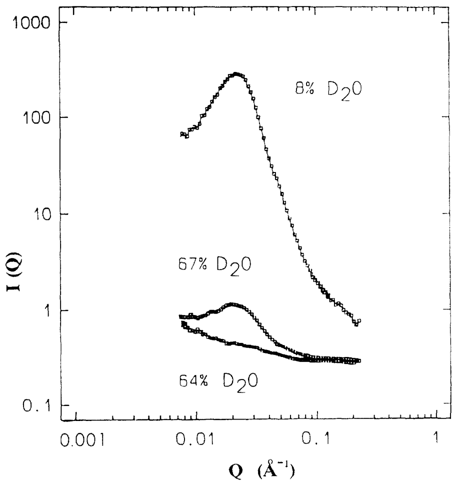

FIG. 1. Comparison of SANS from porous Vycor glass saturated with water as indicated in the figure. The sample saturated with 64% D_2O shows the best match with the Vycor matrix. The data for the 67% D_2O sample is also given to demonstrate the sensitivity of the peak intensity to the isotopic ratio.

The water content of the 64% sample was then reduced in stages using a vacuum pump and at each stage the SANS was measured. During the measurements, the partial pressure, p/p_0, was monitored with a Baratron gauge and hence the equilibrium values of p/p_0 were determined. To check on whether the corresponding water contents were, in fact, in equilibrium, the sample with $p/p_0=80\%$, having the strongest scattering from the percolation network, was remeasured after 4 h and after 24 h and the scattering was found to be unchanged to within 2%. Figure 2 shows plots of $I(Q)$ on a log-log

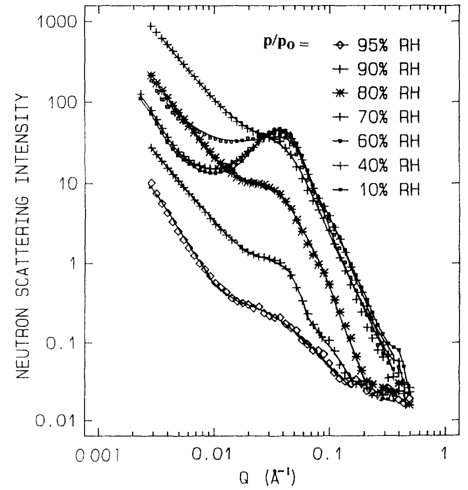

FIG. 2. A log-log plot of SANS data for Vycor containing water having 64% D_2O and various p/p_0, measured for the desorption process at room temperature. The lowest curve is for the sample at $p/p_0=95\%$. For decreasing p/p_0, the intensity at the peak (0.025 Å^{-1}) increases monotonically. The fractal component at very low Q (<0.01 Å^{-1}) also initially increases but then starts to decrease when the p/p_0 goes below 70%.

scale for the p/p_0 values measured. In addition to the familiar peak at 0.025 Å^{-1} due to the spinodal decomposition, the data show a new linear component—with no sign of a change in gradient at the lowest Q's measured. This very-low-Q scattering component has a fractal-like power-law form which results from the percolation network formed by the pores as they empty as described above. This is the first diffraction evidence for the interpore scale "percolation network" with fractal geometry. We can fit this data using Eq. (2) for the fractal component and a function that provides a good fit to the peak as observed for dried Vycor.[18] Figure 3 illustrates the fitting of the measured scattering intensity, $I(Q)$, for sample at 70% RH (relative humidity). As one can see, the fitted profiles (smoothed curves in Fig. 3) agree well with experimental data. The fractal component covers a range of Q from 0.001 to 0.05 Å^{-1}, giving one and a half orders of magnitude of Q range. This suggests that the empty pores are connected to the surface in a manner reminiscent of silica aerogels[19] or branching polymers, both systems showing fractal geometry. The correlation length, ξ', for the percolation clusters cannot be defined here, simply because of the limitation of the Q range. From the lowest Q data measured, the conclusion we draw is that the correlation length is larger than 1000 Å for the higher humidity samples, a distance equivalent to about five times the average pore separation distance.

As can be seen from Fig. 3, the bend in the fractal shape gives an accentuated hump on the composite curve where there is a rapid change in gradient to -4 at about 0.05 Å^{-1}. This hump and the associated gradient change, which are much less prominent in the saturated samples, are rather similar to features seen in the $I(Q)$ obtained for aerogel by Schaefer and Keefer.[19] The gradient at low Q corresponds to a fractal with $D \approx 1.75 \pm 0.1$, giving a Q range of one and one-half orders of magnitude if one accepts the fitted power-law range of the fractal component. This value of the fractal dimension has also been suggested by Even *et al.*[15] based on the EET measurements for porous Vycor glass. As p/p_0 is reduced, the intensity of this low-Q feature shows a characteristic behavior, first increasing to well above the spinodal peak and then decreasing, while, simultaneously, the spinodal peak is seen to rise—at first slowly and then more quickly—towards its maximum value as the humidity is progressively reduced. This behavior parallels that of a binary alloy, where the intensity of the diffuse scattering varies as $c(1-c)$, c being the proportion of one of the components, such as empty pore concentration, and where, if one component has zero scattering length, the intensity of the Bragg peaks vary as c^2. Thus, the low-Q feature clearly corresponds to the diffuse scattering from some distribution of empty pores, and, by analogy, the spinodal peak corresponds to the Bragg scattering. Figure 4 shows that this process of change in the scattering is associated with the gently sloping portion of the upper isotherm, being due to well-separated pores—perhaps those that acted as channels interconnecting to surfaces. Further reduction of p/p_0, corresponding to the steep part of the isotherm, i.e., a removal of adsorbed water in every pore, the power-law form of scattering disappears. On reducing the p/p_0 further, the data show little change in shape, apart from a relatively small shift of the peak towards high Q.

Mason[8] has described a porous network as a system of cavities with interconnecting "windows," or constrictions. He points out that, during desorption, the condensed liquid within a pore cannot evaporate unless the pore is connected to the vapor phase, even if the external vapor pressure is sufficiently low for evaporation to occur. This means that only those pores connected to the vapor phase are able to desorb. If the distribution of pore neck diameters is entirely random, the system will respond in just the same way as in the conventional percolation model[20] except that we limit consideration to percolating clusters linked to the surface. In the conven-

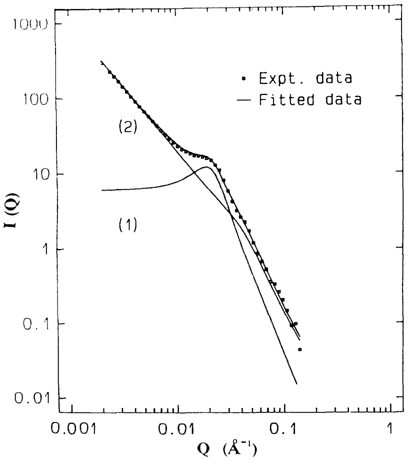

FIG. 3. A log-log plot of $I(Q)$ vs Q for Vycor containing a water mixture with ratio of H_2O/D_2O 36:64 at relative humidity of 70% during desorption process. The smooth curve is fitted with the $S(Q)$ in Eq. (2) and a model for Vycor (Ref. 18). Curve (1) is the fractal component from the $S(Q)$ and curve (2) is for dry Vycor.

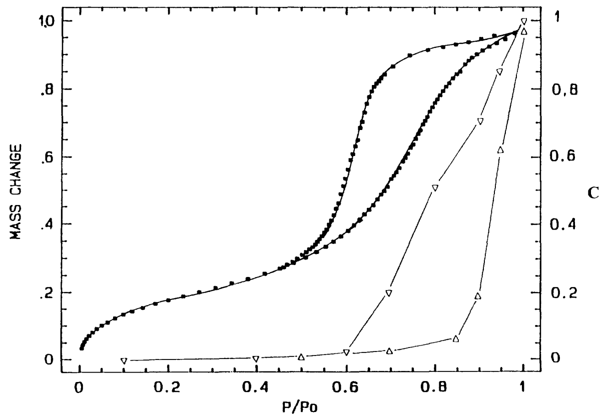

FIG. 4. Desorption-adsorption isotherm for water in porous Vycor (i.e., mass vs p/p_0), measured with an automated microbalance and the corresponding values of the fraction of the empty pores C (right-hand scale) for measured humidities on desorption (∇) and adsorption (△), respectively.

tional models,[20–25] small clusters of pores (linked to the surface) will be the first to be emptied. The average size of these chains of empty pores will increase and will eventually diverge at the percolation threshold.[20] For an infinite system, desorption would start discontinuously at this point and would rapidly extend through the system. The percolation limit should therefore correspond to the end of the plateau on the desorption isotherm. On the adsorption branch, condensation can initiate itself in any neck, even if the neck has become isolated from the surface by other filled necks because the vapor pressure on either side of a filled neck will eventually equilibrate and so there are no threshold effects. It should be noted here that we are considering a system from which air or other gas been removed. The presence of air should not have any effect on desorption but would be expected to have a major effect on this adsorption model.

To illustrate this model for the desorption process, a Monte Carlo calculation was carried out. Figure 5 demonstrates the desorption process using a square 100×100 lattice with pore neck sizes distributed at random according to a given size distribution with the imposed constraint that only those pores connected to the vapor phase by sufficiently large neck channels may desorb. In this case, the percolation cluster of empty pores is clearly visible at a relative humidity of 95% as shown in Fig. 2. When the p/p_0 is lowered, the large-scale fractal structures penetrate deep into the bulk material as shown in Fig. 5. This is precisely the behavior observed with the very-small-angle-scattering (VSAS) component. The fractal dimensions of these systems have been much studied by theoreticians in the past two decades.[20–25] These studies often suggest that D should be 1.89 for a two-dimensional cluster and 2.4 for a three-dimensional (3D) system and with little dependence on connectivity if every pore has more than three connects. However, our measurement shows that $D=1.75$ which is significantly less than 2.4 for a 3D system, suggesting that the real system is somewhat more complicated than the basic model. The real difference may be due to the fact that Vycor is produced by spinodal decomposition followed by an etching process, which means that it has a spaghetti-like structure with very low connectivity.

To confirm this picture, we have chosen some other porous systems produced by coagulation of particles of silica, having large porosity and better connectivity, such as Ludox and silica sol-gels to extend our measurements. We chose these systems not only because they have higher connectivities than Vycor, but also because they are composed of silica glass only (>98% SiO_2), have a uniform density, and their structure is known.

The Ludox we used is the Ludox colloidal silica HS-40, having particle size 13.5±0.5 mu and 40.1% of porosity with surface area 220±10 m^2/g. The second material is a homemade silica sol-gel sinterated at 500 °C which has a large range of particle size and higher porosity than Lu-

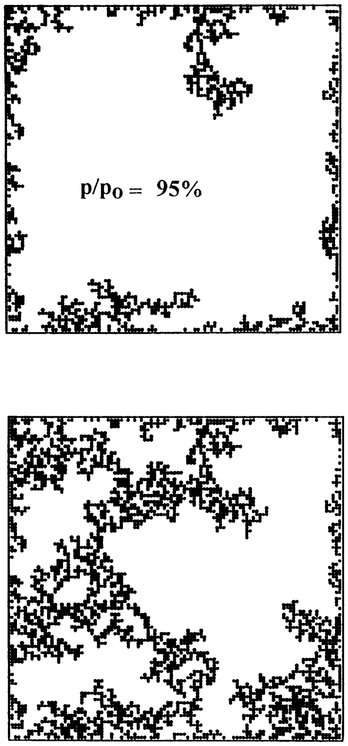

FIG. 5. Monte Carlo simulations for desorption as a percolation process. The sample is shown as a two-dimensional 100×100 square lattice. The pores are situated on the lattice sites, with the empty pores represented as disks at $p/p_0=95\%$ (upper figure) and $=75\%$ (lower figure).

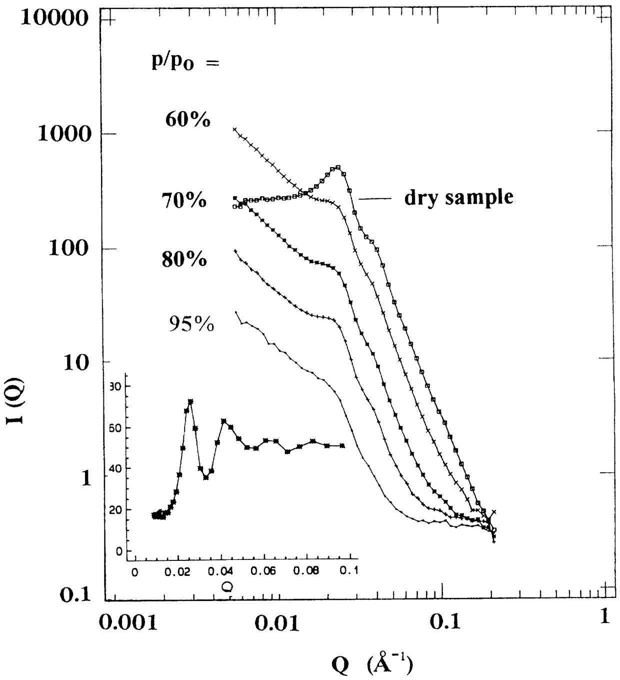

FIG. 6. Plot of SANS from porous Ludox HS-40 at different point of p/p_0 as indicated in the figure. The sample saturated with 62% D_2O shows the best match with the solid matrix. The data in the bottom left corner is a plot of $S(Q)=I(Q)Q^{-4}$ for the dry sample, showing that the structure factor is rather like an amorphous system. The lowest curve is for the sample at $p/p_0=95\%$. The others are at $p/p_0=80\%$, 70%, 60 % and dry from the same sample, as indicated.

dox. When matched, D_2O/H_2O water mixtures were used, we were able to reduce the scattering from the contrast between the silica matrix of the Ludox (or the silica sol-gel) and the water mixtures (62% D_2O for Ludox and 58% D_2O for the sol-gel). As one can see from Fig. 6, the dry sample of Ludox has strong scattering intensity, similar to porous Vycor glass. However, if plotted as $I(Q)^*Q^4$ as shown in the bottom left corner, the scattering pattern is rather like an amorphous material, i.e., made by packing spheres. The scattering intensity for the matched sample reduces to an almost flat background. A similar situation occurs for the sol-gel (see Fig. 7), where the saturated sample is very flat. However, in this case, the dry sample has no sharp peaks; instead, it has a broad hump at larger Q with relative low intensity. This indicates that this material does not have any strong correlation amongst the pore separations as is seen in the Vycor and Ludox cases.

When the water vapor pressure is progressively reduced around the saturated Ludox sample using our pressure control system, we were able to observe a very strong SANS component in the low-Q region as already observed in Vycor. This component (see Fig. 6) gives a straight line on a log-log plot (in a limited Q range because of the limitation of LOQ at low Q) having a gradient about -1.85 ± 0.1. As the p/p_0 is reduced, the intensity of the straight line first increases and then decreases with little change in gradient ($\delta D = \pm 0.1$) as was seen in the Vycor case, while the peak at $Q = 0.025$ Å^{-1} increases in intensity during the whole desorption process. Although the Q range for the very low-Q component is very limited (from 0.005 to 0.02 Å^{-1}) because of the limitation of the instrument used, these lines probably extend much further towards lower Q as observed for Vycor. The case for the sol-gel is similar as shown in Fig. 7. The fractal component from 0.005 to 0.02 Å^{-1} increases and then decreases as p/p_0 is reduced. Eventually it disappears, leaving the hump centered at 0.08 Å^{-1} just as in the dry sample. The fractal dimension for the sol-gel is 2.0 ± 0.1. This value is still much less than the theoretical value for percolation systems.

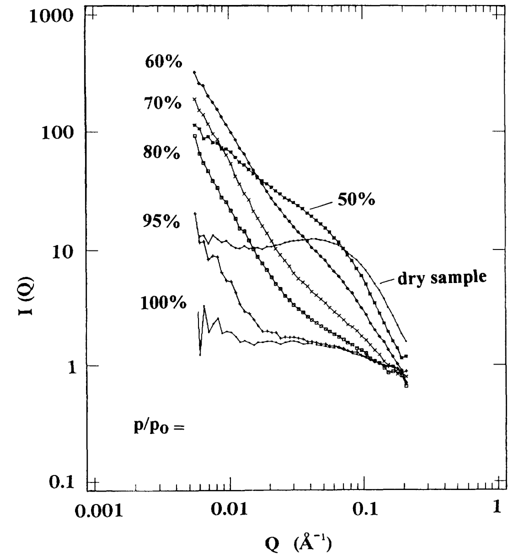

FIG. 7. A log-log plot of SANS data for the sol-gel containing water having 58% D_2O and at various humidities, measured for the desorption process at room temperature. The lowest curve is for the sample at $p/p_0 = 100\%$. The others are $p/p_0 = 95$, 80, 70, 60, 50%, and dry from the same sample.

Recently Ray and Klein[26] have employed both simulations and scaling arguments to investigate the mean-field regime of long-range bond percolation on a Bethe lattice at $p < p_c$ and have demonstrated a percolation system with fractal dimension $D = 2d/3$, where d is the geometric dimension, i.e., for two-dimensional system, $d = 2$, and the fractal dimension D is 4/3, and for three-dimensional system ($d = 3$), $D = 2.0$. This value agrees well with our observed value for the sol-gel, but is still slightly larger than the values for Ludox and Vycor. Although the conclusion from the theoretical analysis is that D is independent of the connectivity of the network used, in reality, we believe that connectivity, diameter of the channels, viscosity, and the surface tension of the liquid used all contribute to determining the final geometry of the fractal network, i.e., the fractal dimension D. These physical parameters (apart from the connectivity) are not often introduced in theories of percolation. Imagining that a porous system has pores connected with channels of equal diameter, surface tension tends to block the channels which are not open yet. If the diameter of the channels are different, thinner channels are less likely to give up water. Both effects will tend to drive the system towards having a lower fractal dimension. If we compare the three porous solids used, we can see a clear tend. Thus, porous Vycor has the lowest connectivity and thinner channels compared with Ludox and sol-gel. Hence it has the lowest D values.

To confirm that this fractal property is only associated with the desorption process in these materials, we also measured the adsorption process for Vycor and the sol-gel carefully. The corresponding results for the adsorption process for Vycor are shown in Fig. 8. These again include data from both D11 and LOQ. The experimental runs were started from dry in an evacuated container. Water vapor with the matching composition was then admitted and the p/p_0 value was monitored as before. When the adsorption was complete, i.e., the sample was fully saturated with the same ratio of D_2O and H_2O water mixture (64:36), we found the sample was again complete matched out, showing flat background small-angle scattering only. This implies that there is no observable isotopic separation in either the desorption or the adsorption process. During adsorption, we observe a decrease in the spinodal scattering and a new diffuse feature again begins to appear as the humidity rises. There are, however, two important differences from the desorption case. First, as expected from the isotherm (Fig. 4), the SANS only starts to change at a rather higher humidity than was necessary to complete the changes on the desorption series and, second, the diffuse part of $I(Q)$ varies as $Q^{-0.4}$ to $Q^{-0.6}$ which is too flat to be explained on a fractal model. If, however, one assumes that the water first condenses in a random distribution of isolated pores or tubular sections, one would expect to see a diffuse com-

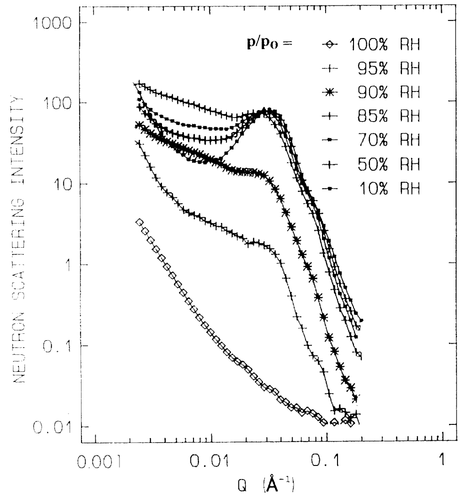

FIG. 8. A log-log plot of SANS data for Vycor containing water having 64% D_2O and various humidities, measured for the adsorption process at room temperature. The lowest curve is for the sample at $p/p_0=95\%$. The data show an extra component, Q^{-D}, $D=0.5\pm0.1$.

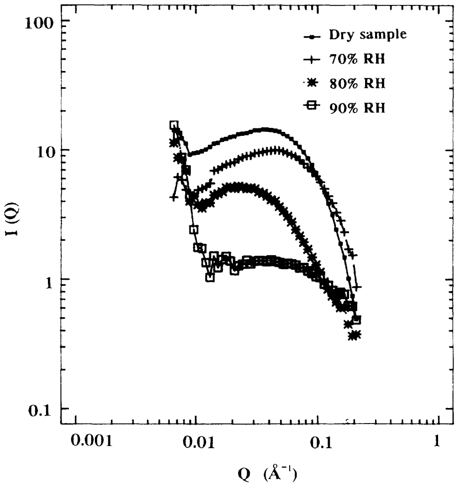

FIG. 9. A log-log plot of SANS data for the sol-gel containing water having 58% D_2O and various humidities, measured for the adsorption process at room temperature. The lowest curve is for the sample at $p/p_0=90\%$. The others are $p/p_0=80\%$, 70 %, and dry from the same sample and the data show no sign of the extra fractal component as seen in the desorption case.

ponent corresponding simply to the form factor of the shapes in question. The decrease with Q can thus be ascribed to the form factor of tubular sections or of localized clusters of pores that become filled once condensation is initiated at a point. For the sol-gel, there is no tendency to form power-law scattering, Q^{-D}, as is shown in Fig. 9. This indicates that because of the large cavities of the solid, water has condensed on the surfaces of pores uniformly throughout the adsorption process.

Since the fractal concept was developed by Mandelbrot,[27] small-angle-scattering techniques have become a very useful tool for investigating this type of behavior for these materials on microscopic scales. The data presented here constitute unambiguous diffraction evidence for such a percolation type of fractal system which was first predicted a decade ago.[20] The fractal dimension from the percolation network lies in the range of 1.7–2.0 from three very different porous solids and it only occurs in the desorption process for $p>p_c$ rather than at the point, p_c, as predicted theoretically. Although these observed values of the fractal dimension are still somewhat smaller than most theories predict, we would expect that when more physical parameters are taken into account in the theories, the value of D should be reduced in line with the observed values. It should be noted that the process involved must be similar to "capillary fingering" as discussed by Lemormand, Touboul, and Zarcone,[28] a phenomenon seen in the low viscosity limit when a nonwetting liquid is pushed into a porous medium already saturated with a second, immiscible, liquid. Computer simulations of fluid configurations in partially saturated porous solids[29] have also paralleled our conclusions. Our observation of the characteristic diffraction pattern of a percolation network is, however, strong evidence for this behavior and the results presented here shed much light on the process of liquid condensation-evaporation in porous solids. They demonstrate that the desorption process provides a remarkably close representation of a percolation system, and, in the process, settle the controversy as to whether a model for the loop in the isotherm has to involve a geometric description of the pore network or merely the geometry of a single pore. Our results thus open up a broad field for SANS in investigations of local pore geometries in porous solids.

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