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Characterization of porous glass by adsorption of dibromomethane in conjunction with small-angle x-ray scattering

A. Ch. Mitropoulos,* J. M. Haynes, and R. M. Richardson
School of Chemistry, University of Bristol, Cantock's Close, BS8 1TS Bristol, United Kingdom

N. K. Kanellopoulos
National Centre for Scientific Research "Demokritos," Institute of Physical Chemistry, 153 10 Aghia Paraskevi Attikis, Greece

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Two porous glass samples of the Vycor type, one in a monolithic form and the other as a fine powder, were examined by the method of small-angle x-ray scattering (SAXS). Adsorption isotherms of dibromomethane (CH_2Br_2) were measured on the same samples, and analyzed according to the Kelvin equation. The SAXS measurements were repeated on samples that had been brought to equilibrium with known relative pressures (p/p_0) of CH_2Br_2, which has a similar electron density as Vycor. Analysis of the data, in terms of fractal geometry, was also accomplished. The fractal dimension for the dry samples was estimated to be 2.5 ± 0.1. Furthermore, as the adsorbate loading was increased defractalization was observed. Subsequently, the fractality in Vycor was estimated to have an upper cutoff limit equal to 15 Å. A correlation between the two methods was demonstrated, by reconstructing the adsorption isotherm from the SAXS data, in two ways: first, by plotting the scattering intensities against p/p_0 and second by plotting the Porod slopes against p/p_0.

I. INTRODUCTION

The wide application of porous solids in separation and catalysis technology requires, in many cases, a thorough determination of their pore structure. To this end, gas adsorption and mercury porosimetry techniques, used on a routine basis, should be supplemented by some other independent methods[1] such as radiation scattering, fluid flow, calorimetric determinations, etc. In this respect, the main objective of the present study was to interface two of these experimental methods, adsorption and small-angle x-ray scattering (SAXS), and to extract useful information concerning both the involved physical processes and the structural characteristics of the solid under investigation.

According to SAXS theory,[2] the intensity $I(Q)$ scattered by a two-phase system is related to the electron densities ρ_1 and ρ_2 of the phases in terms of the expression

$$I(Q)\propto(\rho_1-\rho_2)^2 . \tag{1}$$

Apparently, when $\rho_1=\rho_2$, the scattering intensity will be zero and contrast matching will be reached.

On the other hand, according to adsorption theory,[3] capillary condensation takes place when a class of pores fulfills the conditions required by the Kelvin equation

$$\ln(p/p_0)=-\frac{2\gamma V_L}{RTr_k} , \tag{2}$$

where γ and V_L are, respectively, the surface tension and molar volume of the liquid condensate, p/p_0 is the relative pressure, and r_k is the radius of the equivalent hemispherical meniscus (Kelvin radius). The condensed class of pores will cease to act as a scatterer, and only the remaining empty pores will produce a measurable intensity. In this way, an interface of the two methods can be achieved by selecting an adsorbate with electron density similar to that of the solid matrix. Then, by determining a number of scattering curves at various p/p_0, corresponding to both the adsorption and desorption branches, a correlation of the two methods could be possible. If the predictions of the Kelvin equation are in accordance with x-ray analysis, a reconstruction of the adsorption isotherm will be obtained from the SAXS data.

Vycor 7930 porous glass[4] was chosen as the solid matrix for the following two reasons. First, the material is characterized by practical homogeneity (i.e., the solid part is 96% SiO_2, the rest being 3% B_2O_3 and 0.4% Na_2O), and thus it may be considered as a two-phase system (silica and pores). Second, it possesses a mesopore[5] structure, ensuring the presence of the capillary condensation mechanism as adsorption progresses.

During Vycorization,[6] borosilicate glasses undergo a phase separation. Three mechanisms have been advanced to explain this process: namely, mass fractals,[7] spinodal decomposition,[8] and nucleation and growth.[9] The resulting two phases are topologically continuous, and the most soluble boron-oxide-rich phase may be leached out; a pore structure is obtained. In general, the adsorption isotherms of Vycor[10] are of type IV, after Brunouer-Deming-Deming-Teller (B.D.D.T.) classification,[3] with a hysteresis loop.

Wiltzius *et al.*[11] studied Vycor 7930 porous glass by using small-angle neutron scattering (SANS). They suggested that the long-wavelength behavior of the measured structure factor is in good agreement with Cahn's[8] prediction for a spinodal decomposition. The peak which corresponds to this process is found to be located at

$Q \simeq 0.023$ Å^{-1} (where Q is the scattering vector). In the same work, they also stated that it is difficult to make judgments as to whether or not Vycor has a fractal[12] surface.

Benham *et al.*[13] studied Vycor by using SANS and, in some cases, in conjunction with water adsorption. They concluded that the power-law exponent differs markedly between a dry and a water-saturated sample. For a dry sample,[13(a)] a surface fractal dimension D was calculated[14] equal to $\simeq 2.5$, whereas at various relative humidities Porod slopes[2] in the range of -4.2 to -4.5 were estimated. Moreover, they reported[13(b)] that when Vycor is partially saturated a feature appeared in the very-low-Q region having a fractal-like power law equal to $\simeq 1.75$.

Even *et al.*[7] examined Vycor by electronic energy transfer (EET). They arrived at a fractal dimension $D \simeq 1.74$, which corresponds to a three-dimensional cluster backbone. For the same material, they suggested a fractal dimension $D \simeq 2.6$ for a three-dimensional percolation cluster. A fractal pore structure was also suggested by Dozier *et al.*[15] They also reported that the pore size distribution for Vycor has a sharp maximum at 30 Å, with most of the features falling between 20 and 55 Å radius.

Schaefer *et al.*[16] criticized the idea that Vycor possesses a fractal surface. Their work, based on SAXS and SANS measurements, supported a smooth surface ($D = 2$). Even *et al.*[17] replied to these criticisms, claiming that the SANS data of Schaefer *et al.* are not enough and that the SAXS data may be erroneous if good care is not taken in order to eliminate moisture. Höhr *et al.*[18] studied Vycor by SAXS and SANS too. They interpreted the characteristic peak to be due to interconnected clusters with an average diameter of 350 Å and a surface fractal dimension of $D \simeq 2.4$.

Levitz *et al.*[19] probed the microstructure of Vycor by electron microscopy, direct energy transfer, small-angle scattering, and molecular adsorption. They concluded that the pore interface exhibits a roughness, which has an upper cutoff of less than 20 Å. Additionally, they reported a persistence length of the interface of 45 Å.

Recently, Hua *et al.*[20] demonstrated the use of the contrast matching method with SAXS. In some cases, they also reported a decrease in the Porod slope, less than -4, as the vapor loading increases.

II. EXPERIMENTAL DETAILS

Two samples of Vycor 7930 were used in the present study. One was in a powder form (mean particle size $\simeq 325$ mesh), and the other was cut from a rod of diameter $\simeq 6$ mm and ground to $\simeq 0.8$ mm. The samples were cleaned by immersion in 30% hydrogen peroxide and exposed to oxygen at 350 °C for 24 h.

The adsorption isotherms were obtained gravimetrically and dibromomethane (CH_2Br_2), which has a similar electron density as Vycor, was used as an adsorbate. The gravimetric arrangement[21] consisted of an electronic beam microbalance and a pressure sensor. When the isothermal temperature was established (17.2 °C), an oil bath with a thermostat ensured an error of not more than ±0.1 °C.

The small-angle scattering experiments were carried out in a Q range of $0.005 < Q < 0.15$ Å^{-1}. The x rays were produced using a copper-anode x-ray tube, and the most intense of the characteristic lines was selected as the experimental wavelength ($\lambda = 1.54$ Å). Monochromatization and collimation of the beam were also held. The main feature of the apparatus was a two-dimensional x-ray imaging[22] system (XIS) connected on line with a minicomputer frame.

In order to achieve SAXS in conjunction with adsorption, a special cell, shown in Fig. 1, was designed. The cell is made from stainless steel and consists of two parts. When parts A and B are attached, there is a path difference of the required thickness ($\simeq 0.8$ mm). The four apertures, two for each part, are about 0.5 cm in diameter, but the exterior of part B is larger with a conic shape in order to eliminate any parasitic scattering. The cell windows are covered with Mylar sheets. Part A has an internal flow system connected to a temperature-controlled bath; when the isothermal temperature is established, a continuous flow ensures an error of not more than ±0.2 °C.

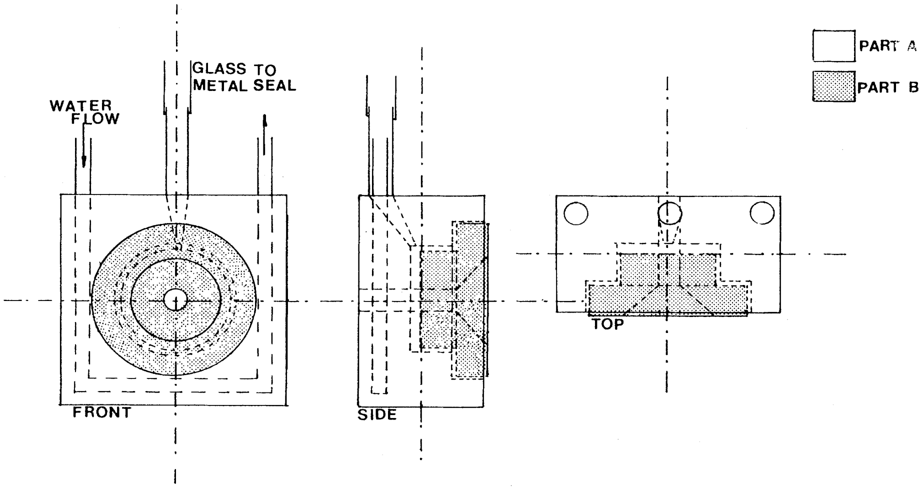

FIG. 1. Schematic representation of the sample cell. Part A has an internal flow system which allows temperature control. When part A is attached to part B, a path difference equal to $\simeq 0.8$ mm is formed.

III. RESULTS AND DISCUSSION

A. Adsorption and SAXS

Figure 2(a) shows the Vycor/CH_2Br_2 isotherm. The Gurvitsh[3] volume was estimated to be $\simeq 0.2$ cm^3/g (liquid volume), and the surface area was found to be $\simeq 80$ m^2/g. Unfortunately, a well-established cross-sectional area was not found in the literature[23] for CH_2Br_2, and the value used, 26 Å^2, was calculated from its density.

The Kelvin pore size distribution (fit for cylinders) determined from the adsorption branch shows a broad allocation with a maximum at about 50 Å, while that determined from the desorption branch shows a sharp maximum at about 40 Å. Such a broad distribution, after application of the Kelvin equation to the adsorption branch of the isotherm, is also reported in the literature,[24] although sharp peaks due to desorption are more common.

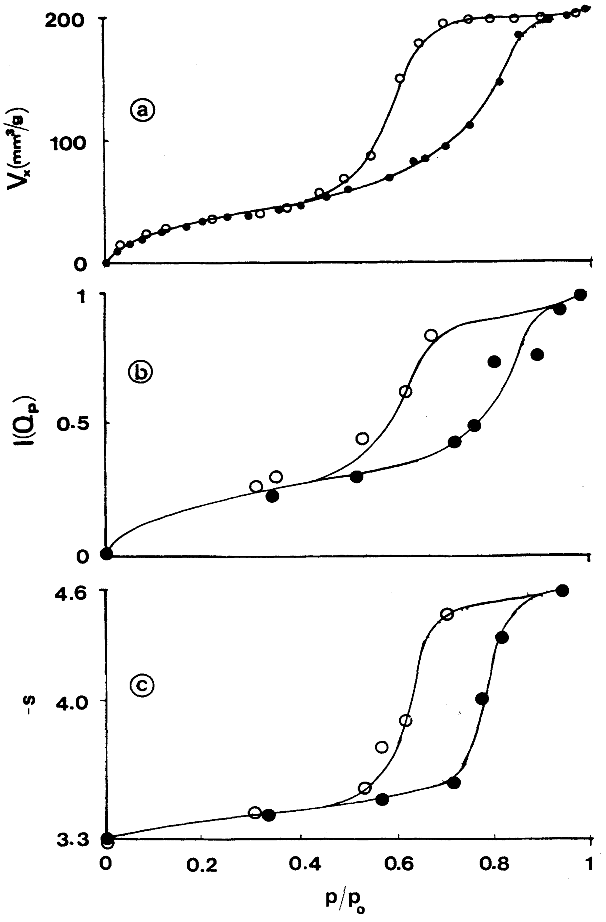

FIG. 2. Various adsorption type and isothermal profiles for Vycor. Solid symbols denote adsorption and unfilled desorption. In all cases, the abscissa represents relative pressures p/p_0, while the ordinate represents different functional parameters as described next. (a) The adsorption isotherm of dibromomethane on Vycor; the amount adsorbed, V_x, is in liquid volume. (b) A reconstruction of the adsorption isotherm from the scattering intensity values $I(Q_p)$ according to Eq. (6). (c) A reconstruction of the adsorption isotherm from the Porod slopes $-s$ (i.e., in positive terms).

In general, for an isotropic scatterer the spherically averaged intensity $I(Q)$ may be represented[25] by the integral

$$I(Q)=4\pi\rho^2 V\int_0^\infty r^2\gamma(r)\frac{\sin(Qr)}{Qr}dr\ , \tag{3}$$

where V is the volume of the sample, ρ is the electron density, $\gamma(r)$ is the correlation function at point r, and Q is the scattering vector $Q=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength. Again, at high Q values, if the inequality $Ql \gg 1$ holds[26] (where l is the smallest dimension affecting the scattering), the scattering intensity $I(Q)$ may be approximated by the Porod formula[2]

$$I(Q)=\frac{2\pi\rho^2 A}{Q^4}\ , \tag{4}$$

where A is the surface area. Thus, on a logarithmic scale (Porod plots), the scattering intensity will decay following a power law. However, deviations greater than a -4 slope were observed and they may be explained in terms of a fractal dimensionality according to the Bale-Schmidt[14] formula

$$I(Q)\propto Q^{D-6}\ , \tag{5}$$

where D is the surface fractal[12] dimension. From this slope, the roughness of an internal surface boundary may be extracted. When the slope is equal to -4, a smooth surface is exhibited, and $D=2$; i.e., it is Euclidean. When $2<D<3$, a fractal surface is defined.

Figure 3 illustrates the scattering curves of both Vycor samples, powder and monolithic particle, at $p/p_0\simeq 0$, and Fig. 4 illustrates the scattering curves of Vycor (particle) at various p/p_0. The dry (unloaded) samples, Fig. 3, have a main peak at $Q_1\simeq 0.025$ Å^{-1}. Another minor, second hump appears at $Q_2\simeq 0.06$ Å^{-1}, and after that the scattering intensity decays following a noninteger

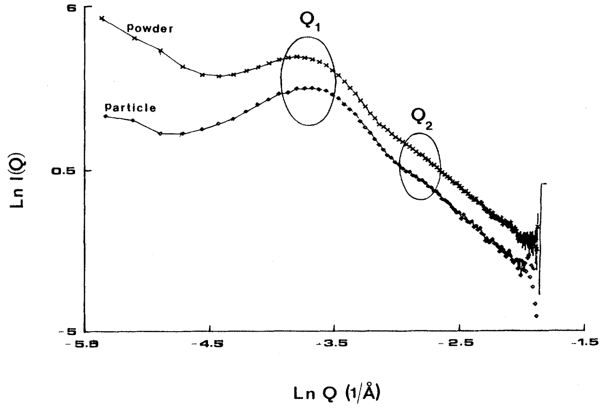

FIG. 3. Porod plots for two dry Vycor samples. The upper curve corresponds to a powder form and the lower to a monolithic particle. In the case of powder, the innermost part (low Q) shows a rise of the intensity. The oval areas Q_1 and Q_2 indicate, respectively, where the main peak and hump are located.

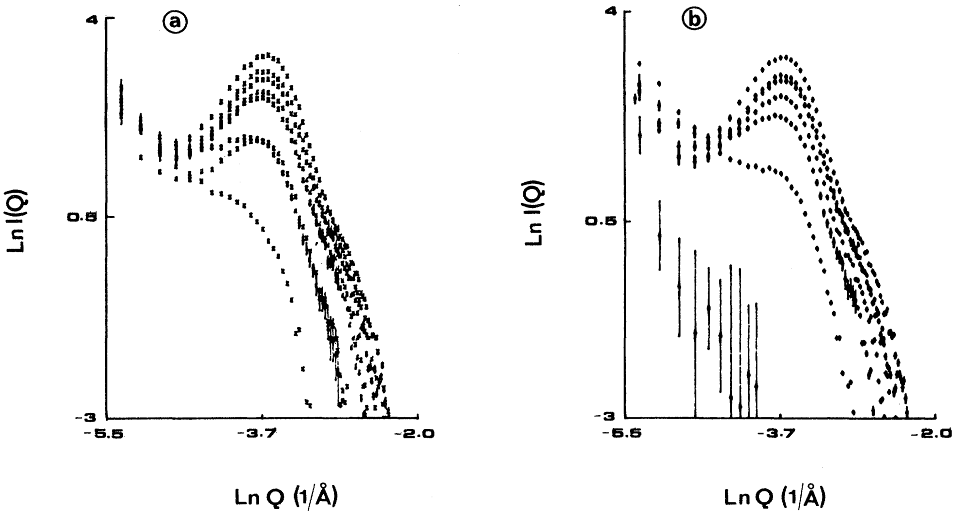

FIG. 4. Porod plots for Vycor samples loaded with dibromomethane at various relative pressures p/p_0. (a) Adsorption at p/p_0 (from top to bottom): 0, 0.34, 0.51, 0.72, 0.76, 0.80, 0.90, and 0.95. (b) Desorption at p/p_0 (from top to bottom): 0, 0.31, 0.35, 0.51, 0.62, 0.67, and 1 (saturated).

power law greater than -4. As the relative pressure increases (loaded samples), Fig. 4, the scattering intensity and power law decrease, whereas the peak shifts slightly to the left (i.e., to lower Q).

The main peak may be attributed to a spinodal decomposition process as other investigators[11,13] have already proposed. The second hump corresponds to $\simeq 100$ Å, which is about half the value of the main peak in terms of Bragg spacing.[2] The noninteger power law (>-4) indicates scattering from a fractal surface. As the relative pressure increases, the scattering intensity decreases, because a number of scatterers is eliminated (eventually due to adsorption). The main peak shifts to the left, because large pores influence the form of the spectrum; i.e., in a range of pore sizes, the small pores condensed first, as predicted by the Kelvin equation. The power law decreases, because defractalization[27] takes place.

However, the nucleation and growth mechanism[9] may also explain the features of Vycor spectra. As an example, we discuss the shift of the main peak to the left as p/p_0 increases [Fig. 4(a)]. Assuming a hard-sphere "liquid" model for Vycor, the peak may be attributed to massive entities (of diameter $\simeq 250$ Å). On adsorption, the radius of these entities will increase by a thickness t equal to that of the adsorbed film, and thus a displacement of the peak to lower Q is expected to occur. A careful examination of Fig. 4(a) could support such a conclusion. At early stages of the adsorption process, this displacement is extremely small; at higher p/p_0, as the film thickens, it becomes more evident. For instance, at $p/p_0 \simeq 0.76$, t will be $\simeq 15$ Å or the size of the massive entities will be $\simeq 280$ Å, implying that the peak will be located around 0.022 Å^{-1}. This is a reasonable case for our results.

The innermost part (low Q) of the scattering curves, Fig. 3, is different between the powder and particle; with the rise of intensity, it was observed only in the former case. Therefore, this rise was attributed to the scattering from the interparticle voids and/or the grains of the powdered material.

Near the saturation point (i.e., as $p/p_0 \rightarrow 1$), the scattering intensity undergoes a considerable decrease. In the case of the particle, the intensity takes on an almost zero value [bottom curve in Fig. 4(b)], whereas, in the case of the powder, it is low but not zero. Some other investigators[20] have also reported a low, but not zero, scattering intensity at this point. They suggested either an incomplete contrast matching or an incomplete pore filling during the allocated equilibration time. Our result favors the latter explanation. If there is some scattering intensity, near the saturation point, this will mainly be caused by the unfilled interparticle voids of the powdered material.

B. SAXS in conjunction with adsorption

In relation to adsorption theory, two mechanisms may result in a decrease in the scattering intensity [Fig. 4(a)]. One is the deposition of an adsorbed film on the surface of the solid, and the other is the condensation in an entire class of pores. Again, during adsorption, the drop in the scattering intensity is expected to be small as a result of the first mechanism and large as a result of the second one. A convenient way to quantify these cases is to consider the scattering intensity $I(Q_p)$ at the Q point where the peak is located.

For a large interval of p/p_0, from 0 to 0.76, there is a rather small and gradual drop of $I(Q_p)$, whence the prime mechanism has to be the formation of a monolayer and later of a multilayer film. However, at the early stages of this region, some microporous filling[19] may also occur as is discussed in the following section.

Next, within a very short interval of p/p_0, from 0.76 to 0.8, there is a sharp drop of $I(Q_p)$. Clearly, a major class of pores has ceased to act as scatterer. In this case, the prime mechanism has to be that of capillary condensation. The Kelvin radii for the major class of pores are estimated to range between 40 and 55 Å. This result is in good agreement with the average pore size obtained from adsorption data.

At $p/p_0 \simeq 0.9$ the main peak is converted to a shoulder, while at the same time a significant drop in the scattering intensity is not detected. This conversion probably reflects a flattening of the menisci caused by the new equilibrium conditions (i.e., from $p/p_0 \simeq 0.8$ to 0.9). After that, a second sharp drop of $I(Q_p)$, at $p/p_0 \simeq 0.95$, occurs. Three different contributory factors may be identified to be responsible for this drop: the completion of the contrast matching, a further filling of the menisci, and a last condensation within some large pores (> 100 Å). At this point it is worth recalling that Amberg and McIntosh,[10(a)] in their pioneering work on adsorption hysteresis, have also observed a turnover for the Vycor/water adsorption isotherm for $p/p_0 > 0.87$. They have concluded that some large pores or wide channels must exist within the glass matrix.

During desorption, the scattering intensity increases as the relative pressure decreases. From Fig. 4(b), it can be seen that for the majority of pores evaporation takes place according to the predictions of the Kelvin equation. At $p/p_0 \geq 0.67$ some large pores empty first, and then, between 0.67 and 0.62, a major class of smaller pores (same sizes as in the adsorption process) follows. However, it is also possible that network effects exist, in some limited extent, within the solid matrix; i.e., smaller pores control the entrances of some larger ones. Thus the scattering curve at $(p/p_0)_{\mathrm{des}} \simeq 0.67$ is in at a level lower than that for $(p/p_0)_{\mathrm{ads}} \simeq 0.9$.

Following the above description, a relation between $I(Q_p)$ and p/p_0 may be given as

$$I(Q_p,0) - I(Q_p, p/p_0) = f(p/p_0) \; . \tag{6}$$

Figure 2(b) demonstrates the reconstruction of the adsorption isotherm from SAXS data, when the scattering intensities $I(Q_p)$ were used to solve[28] Eq. (6). A comparison with the actual isotherm of Fig. 2(a) is now possible, and the agreement is good if one takes into account the experimental errors, the sample differences, and the fact that many fewer points contribute to the reconstruction than the real isotherm.

C. Porod slopes

Using Eq. (4) [or (5)], the slope values s, at various p/p_0, were calculated. Table I summarizes these results, only, for the case of powder. We chose to present the slope values for powder because the residual error of the recorded data points, especially at higher relative pressures, was found to be much less than that for the particle. This is probably due to the lower transmission we were able to achieve in the latter case. However, the particle also gives similar results, but the computation of s becomes extremely uncertain for all $p/p_0 > 0.8$.

For the dry sample of Vycor, the slope was found equal to -3.4, which according to the Bale-Schmidt formula corresponds to a fractal dimension of 2.6. Similar results have also been reported in previous studies.[7,13,18] However, as the relative pressure increases, the slope decreases and in some cases it decreases even below -4. Moreover, if these slope values (in positive terms, i.e., $-s$) are plotted against the corresponding relative pressures, a curve possessing a general form strongly reminiscent of the adsorption isotherm is obtained. Figure 2(c) demonstrates this correlation.

TABLE I. Vycor 7930: Porod slopes at various relative pressures.

Relative pressure	Porod slope
Adsorption	
0.00	−3.4
0.34	−3.5
0.56	−3.5
0.72	−3.6
0.76	−4.1
0.81	−4.3
0.95	−4.6
Desorption	
0.69	−4.5
0.60	−3.9
0.55	−3.8
0.53	−3.6
0.31	−3.5
0.00	−3.3

As was mentioned previously, at an early stage of the adsorption process, the adsorption effect is expected to be the dominant mechanism. Thus an adsorbed film will be deposited on the surface of the solid, resulting in a smothering of some small geometrical details. Consequently, the fractal dimension and slope will decrease. From Table I it can be seen that between relative pressures 0 and 0.34 the slope from -3.4 decreases to -3.5 or the surface fractal dimension from 2.6 diminishes to 2.5. However, the fractal dimension is not equal to 2 at $p/p_0 \simeq 0.34$. We also arrived at the same conclusion by examining the other Vycor sample. Although, for the particle, at $p/p_0 \simeq 0$, the fractal dimension was estimated to $\simeq 2.3$, i.e., lower than the powder, at $p/p_0 \simeq 0.34$ it was estimated to $\simeq 2.2$, i.e., higher than 2. Both results provide evidence that the fractality in Vycor may not be exclusively related to microporosity as all pores less than $\simeq 30$ Å in width are expected to be filled[29] at $p/p_0 < 0.3$. Then it might be possible that the microstructure of Vycor is a mixture of cavities and perturbing bumps, as the following example demonstrates.

During the leaching process,[30] a deposition of a soft hydrogel layer on the pore walls may take place. Following drying, this soft hydrogel layer may be converted to an asymmetric xerogel layer that will include some cavities, some bridges, and some bumps. The bridges will be formed through neighboring —OH groups. Bumps will be formed as a result of the ordered accumulation of decreasing size silica clusters on the surface and also as part of the general pattern evolving during the acidic dissolution. Cavities will be formed as a result of faster accumulation and condensation of various silica clusters and, possibly, as a result of connections between smaller bumps.

Next, between relative pressures 0.34 and 0.76, a further decrease of the slope and consequently a further decrease of the fractal dimension occur. Finally, at

$p/p_0 \simeq 0.76$ a Euclidean surface is obtained. In this direction, Cheng *et al.*[27(a)] have outlined a detailed analysis concerning the small-angle x-ray scattering from films adsorbed on fractal surfaces. They suggested that for length scales greater than the thickness t of the film, the film-vapor interface (although smoother than the substrate) will possess a fractal character. On the other hand, for length scales $\ll t$, the interface can be seen to be locally flat. They concluded that for $Qt \rightarrow 0$, $I(Q) \propto Q^{D-6}$, for $Qt \rightarrow \infty$, $I(Q) \propto Q^{-4}$, and for $Qt \simeq 1$ defractalization of the film takes place.

In relation to the Porod formula, two parameters may change as the adsorption progresses: the surface area A and the electron density ρ. When the film thickness is small, the surface area A may be described[27(a)] as power law of t, $A \propto t^{2-D}$. In terms of physical adsorption, this means that before defractalization takes place the prime mechanism of the adsorption process is the adsorption effect. However, as the film approaches its defractalization, the influence of this effect will tend to diminish. Clearly, there is a consistent relationship between t and $-s$ (or $-D$), and in particular, as t increases, s (or D) decreases. Then, for this region, it is possible that a plot of $-s$ vs p/p_0 would follow a similar path along the adsorption isotherm[31] or on a t curve.

In particular, our SAXS data show that defractalization occurs at $p/p_0 \simeq 0.76$, which according to the adsorption data, corresponds to a statistical film thickness[32] $V_x/A_0 \simeq 15$ Å [where V_x is the liquid volume of the adsorbed amount at $p/p_0 = x$, i.e., at $\simeq 0.76$, and A_0 is the Brunauer-Emmett-Teller (B.E.T.) area]. This result is in good agreement with the conclusions of Levitz *et al.*[19] for an upper cutoff length scale, of the interface roughness in Vycor, smaller than 20 Å. However, adsorption theory predicts such an upper cutoff limit, as it is expected to see the effect of the surface structure to largely smooth out after the formation of about two to three molecular layers (cross-sectional area of $CH_2Br_2 \simeq 26$ Å^2). Unfortunately, the SAXS-Vycor system does not contrast match[33] with a smaller molecule (e.g., water) and thus no further conclusions can be derived on whether a fractal surface would prolong the influence of the adsorption effect.

Beyond this region, the partial molar entropy of the adsorbed film may be assumed as equal to that of the liquid adsorbate. Then the prime mechanism will shift from the adsorption to the Kelvin effect. According to Everett and Haynes,[34] during this transition the system passes from a single solid/fluid interfacial region, to one in which a duplex-film description (involving two interfacial regions solid/film and film/vapor) is more appropriate. In terms of SAXS, such a complication may strongly influence the electron density distribution. In fact, from the results of Table I, it is obvious that there are negative deviations from the Porod law (i.e., slopes less than -4).

Although Cheng *et al.*[27(a)] have argued that above the defractalization point the slope should assume a constant -4 value, this is not the case for our results. Similar observations have been reported by other investigators[13,20] too. However, Cheng *et al.*[27(a)] have also stated that it is difficult to determine what effect the difference between the film and substrate will make. It appears possible that the Kelvin effect is related to a diffuse surface. Ruland[35] first and Koberstein *et al.*[36] later examined the effect of such a surface. They suggested that the density transition scattering intensity in the Porod region may be given by

$$I(Q) = \frac{2\pi\rho^2 A}{Q^4} H^2(Q) , \tag{7}$$

where $H(Q)$ is a smoothing function, the form of which is dependent on the geometrical model for the interphase gradient. Assuming, for the sake of argument, that the smoothing function is Gaussian, then the corresponding Porod law relation becomes

$$I(Q) = \frac{2\pi\rho^2 A}{Q^4} e^{-\sigma^2 Q^2} , \tag{8}$$

where σ is the standard deviation of the Gaussian smoothing function and is a measure of the transition layer width. Taking a sequence of Gaussian functions with different σ for a range of relative pressures, it can be shown that the slope s has a consistent relation with σ of the type

$$(s+4) \propto -\sigma^2 . \tag{9}$$

During adsorption and above defractalization, the thickness of the adsorbed film increases and, possibly, the system passes through an unduloid configuration before condensation occurs. In this course of events, σ^2 can be considered as a parameter consistent with the thickness t of the adsorbed film, and thus a plot of $-s$ vs p/p_0 practically will have the shape of a t curve. As soon as capillary condensation takes place within a large fraction of pores (i.e., at $p/p_0 > 0.9$), the system will reach an equilibrium stage[37] and no further change of σ (and hence no further change of $-s$) can be observed. During evaporation, the emptying process is driven by a meniscus penetration within a given range of pores. In this case, a lens configuration is more probable. Since the configuration of the interphase is different between adsorption and desorption, the smoothing function $H(Q)$, and consequently σ, will be different too. As a result, hysteresis is observed in the $-s$ vs p/p_0 plot until the effect of the diffuse surface becomes weak.[38] After that, the system follows a reverse course of events as described previously.

IV. CONCLUSIONS

The use of two different methods (adsorption and SAXS) was examined for the characterization of the structure of the same material (Vycor 7930). The results obtained from adsorption were compared with those obtained from SAXS, and a reconstruction of the adsorption isotherm from SAXS data was demonstrated in two ways: first, by plotting $I(Q_p)$ vs p/p_0 and, second, by plotting the Porod slopes $-s$ vs p/p_0. A description for these reconstructions was given in terms of adsorption and Kelvin effects. Additionally, the correlated SAXS and adsorption parameters were discussed.

A detailed study of the scattering curves at various p/p_0 has led to the conclusion that within the Vycor structure there are three kinds of pores: viz., a major class of pores (mean r_k around 40–55 Å), some micropores ($r_k < 15$ Å), and few large pores ($r_k > 100$ Å). Thus the material can be considered to exhibit an almost monomodal pore size distribution. Network effects have also been detected, but their influence was not found to be large.

A fractal dimension D equal to 2.5 ± 0.1 (averaged) for the dry Vycor was estimated. Furthermore, as adsorption progressed, defractalization was observed. At the crossover point, the thickness of the adsorbed film was estimated to be $\simeq 15$ Å, introducing a new upper cutoff limit for the fractality of the solid.

Finally, a general description of the nature of the fractal surface of Vycor was given. It was suggested that this may not be exclusively based on the microporosity of Vycor structure, but possibly results from a mixture of cavities and perturbing bumps present on the surface of the solid.

This work is extended[39] to the study of well-defined mesoporous alumina pellets, formed by uniaxial compaction.[40] At the same time, the adsorption and SANS methods are supplemented by dynamic permeability techniques.

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[*] Author for correspondence. Present address: NCSR Demokritos, Institute of Physical Chemistry, 153 10 Aghia Paraskevi Attikis, Greece.

[1] J. Rouquerol *et al.*, Pure Appl. Chem. **66**, 1739 (1994).

[2] (a) A. Guinier and G. Fournet, *Small Angle X-ray Scattering* (Wiley, New York, 1955); (b) O. Glatter and O. Kratky, *SAXS* (Academic, New York, 1982).

[3] S. J. Gregg and K. S. W. Sing, *Adsorption Surface Area and Porosity,* 2nd ed. (Academic, London, 1982).

[4] Vycor Brand Porous Thirsty glass No. 7930, Corning Glass Works, P. O. Box 5000, Corning, NY 14830.

[5] According to IUPAC classification, the average width of mesopores lies between 20 and 500 Å. See also Ref. 3, p. 25, and Pure Appl. Chem. **31**, 578 (1972).

[6] H. P. Hood and M. E. Nordberg, US Patent No. 2, 106,744 (1 Feb 1938).

[7] U. Even *et al.*, Phys. Rev. Lett. **52**, 2164 (1984).

[8] (a) J. W. Cahn, J. Chem. Phys. **42**, 93 (1965); (b) J. W. Cahn and R. J. Charles, Phys. Chem. Glasses **6**, 181 (1965); (c) N. F. Berk, Phys. Rev. Lett. **58**, 2718 (1987).

[9] W. Haller, J. Chem. Phys. **42**, 686 (1965).

[10] (a) C. H. Amberg and R. McIntosh, Can. J. Chem. **30**, 1012 (1952); (b) P. H. Emmett and T. W. DeWitt, J. Am. Chem. Soc. **65**, 1253 (1943); (c) G. Mason, Proc. R. Soc. London A **415**, 453 (1988).

[11] P. Wiltzius *et al.*, Phys. Rev. A **36**, 2991 (1987).

[12] (a) B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982); (b) P. Pfeifer and D. Avnir, J. Chem. Phys. **79**, 3558 (1983).

[13] (a) M. J. Benham *et al.*, Phys. Rev. B **39**, 633 (1989); (b) J-C. Li *et al.*, *ibid.* **49**, 5911 (1994).

[14] (a) H. D. Bale and P. W. Schmidt, Phys. Rev. Lett. **53**, 596 (1984); (b) P. Pfeifer and P. W. Schmidt, *ibid.* **60**, 1345 (1988); (c) P. Wong and A. J. Bray, *ibid.* **60**, 1344 (1988); (d) A. J. Hurd *et al.*, Phys. Rev. B **39**, 9742 (1989); (e) D. F. R. Milder and P. L. Hall, J. Phys. D **19**, 1535 (1986); (f) J. E. Martin and A. Hurd, J. Appl. Crystallogr. **20**, 61 (1987).

[15] W. D. Dozier *et al.*, Phys. Rev. Lett. **56**, 197 (1986).

[16] D. W. Schaefer *et al.*, Phys. Rev. Lett. **58**, 284 (1987).

[17] U. Even *et al.*, Phys. Rev. Lett. **58**, 285 (1987).

[18] A. Höhr *et al.*, Phys. Rev. B **38**, 1462 (1988).

[19] P. Levitz *et al.*, J. Chem. Phys. **95**, 6151 (1991).

[20] D. W. Hua *et al.*, in *Studies in Surface Science and Catalysis, Characterization of Porous Solids III,* edited by J. Rouquerol, F. Rodriguez-Reinoso, K. S. W. Sing, and K. K. Unger (Elsevier, New York, 1994), Vol. 87.

[21] L. Cahn and H. R. Schutz, Vac. Microbalance Technol. **3**, 29 (1962).

[22] J. E. Bateman *et al.*, Nucl. Instrum. Methods Phys. Res. A **259**, 506 (1987).

[23] A. L. McClellan and H. F. Harnsberger, J. Coll. Interface Sci. **23**, 577 (1967).

[24] (a) J. M. Haynes and F. G. McCaffery, J. Coll. Interface Sci. **59**, 24 (1977); (b) P. H. Doe and J. M. Haynes, in *Characterization of Porous Solids,* edited by S. J. Gregg, K. S. W. Sing, and H. F. Stoeckli (The Society of Chemical Industry, London, 1979), p. 253; (c) D. H. Everett Proc. Colston Res. Soc. **10**, 95 (1958).

[25] P. Debye *et al.*, J. Appl. Phys. **28**, 679 (1957).

[26] M. Kalliat *et al.*, *Title,* ACS Symp. Series No. 169 (ACS, Washington, D.C., 1983), p. 3.

[27] (a) E. Cheng *et al.*, Phys. Rev. B **39**, 12 962 (1989); (b) P. Pfeifer *et al.*, Phys. Rev. Lett. **62**, 1997 (1989).

[28] In general, it is difficult to quantify Eq. (6). However, as a first approach, one may consider the normalization relation [see Ref. 2(a), p. 81] $\int Q^2 I(Q)dQ = 2\pi^2\rho^2 c(1-c)V$, where V is the volume of the sample, ρ is the electron density, and c is the fraction of the volume occupied by matter. The first term in this equation is, essentially, equal to the area under the curve of a plot of $Q^2 I(Q)$ vs Q. During the adsorption process, a film is deposited on the pore walls. The volume of this film is proportional to the amount adsorbed, V_x, at $p/p_0 = x$. When the electron density of the adsorbate fluid is similar to that of the solid matrix, then the solid volume fraction will increase by V_x/V and the pore volume fraction will decrease accordingly. Thus $\int Q^2 I(Q,x)dQ / \int Q^2 I(Q,0)dQ = 1 - v + Cv - Cv^2$, where $C = (1-c)/c$, $v = V_x/V_p$, and V_p is the pore volume.

[29] According to the Kelvin equation, pore radii corresponding to $p/p_0 < 0.3$ would be smaller than 15 Å; see S. Lowell and J. E. Shields, *Powder Surface Area and Porosity,* 3rd ed. (Chapman and Hall, London, 1991). See also Ref. 3.

[30] K. Beltsios (private communication).

[31] Since there is a consistent relationship between t and $-s$,

there must be a similar relation between the amount adsorbed, V_x, and $-s$ too. From a V_x vs t plot, it can be seen that t increases as V_x increases. In fact, this relation is linear up to the point where condensation commences and above this point deviates upward from linearity. In the case of Vycor, defractalization is observed before capillary condensation, in the major class of pores ($40 < r_k < 55$ Å), takes place; thus a plot of $-s$ vs p/p_0 may follow a path similar to the adsorption isotherm or to a t curve (i.e., t vs p/p_0).

[32] The assumption here is that the adsorbed film depth in a pore is the same as that on a plane surface for any value of $p/p_0 < 0.76$. If, however, this assumption is not true and microporous filling or capillary condensation has taken place before 0.76, then V_x is overestimated. On the other hand, CH_2Br_2 gives a B.E.T. area for Vycor lower than that of N_2 ($\simeq 103$ m^2/g see Ref. 19); i.e., A_0 is underestimated. In all cases, the value of $t \simeq 15$ Å is overestimated and thus the upper cutoff limit may be taken as a safe one.

[33] In this direction SANS experiments are more useful.

[34] D. H. Everett and J. M. Haynes, J. Coll. Interface Sci. **38**, 125 (1972).

[35] W. Ruland, J. Appl. Crystallogr. **4**, 70 (1971).

[36] J. T. Koberstein *et al.*, J. Appl. Crystallogr. **13**, 34 (1980).

[37] At $p/p_0 > 0.9$, the scattering intensity will be produced from the menisci of the filled pores, from a few large pores which remain empty and mainly (in the case of powder) from the interparticle voids. Thus s would be expected to be equal to -4. However, at $p/p_0 > 0.9$, s approaches a constant value less than -4. Two explanations are that, first, Eq. (4) [or (7)] may undergo a general failure at this point. In fact, the last point in Fig. 2(c) is very uncertain. Second, composition gradients within the glass may result in a diffuse surface. For the latter explanation, see Ref. 11 and also B. A. Blajeni *et al.*, J. Phys. Chem. **91**, 600 (1987).

[38] Another point which supports the idea that the system passes through different configurations is the fact that during adsorption the slope decreases progressively below -4, whereas during desorption a sharp increment of the slope (from -4.5 at $p/p_0 \simeq 0.69$ to -3.9 at $p/p_0 \simeq 0.6$) is observed. Assuming an assembly of cylindrical pores, in the first case, the effect of a diffuse surface increases with t. At the same time, the condensed pores have reached a curvature at least equal to half of that corresponding to a hemispherical meniscus and therefore will contribute very little to the spectrum. In the second case, at certain p/p_0, some of the menisci will approach a "back-to-back" position, and in some others the film between them will burst, irreversibly leaving a thin film on the pore walls of about two to three molecular layers. The surface of this film cannot be considered highly diffuse, and therefore the experimental indication of a diffuse surface may be attributed to the menisci of the filled pore. Since the intensity due to empty pores is greater than the intensity due to menisci, the contribution of the diffuse surface soon becomes weak. However, for the time being, this contribution, although weak, is not zero, and thus hysteresis is observed too.

[39] A. Ch. Mitropoulos and N. K. Kanellopoulos (unpublished).

[40] J. Petropoulos *et al.*, Chem. Eng. Sci. **44**, 2967 (1982).