Adsorption on Orderd and Disordered Duplex Layers of Porous Anodic Alumina

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ABSTRACT: We have carried out systematic experiments and numerical simulations of the adsorption on porous anodic aluminum oxide (AAO) duplex layers presenting either an ordered or a disordered interconnecting interface between the large (cavity) and small (constriction) sections of the structured pores. Selective blocking of the pore openings resulted in three different pore topologies: open structured pores, funnel pores, and ink-bottle pores. In the case of the structured pores having an ordered interface, the adsorption isotherms present a rich phenomenology characterized by the presence of two steps in the condensation branch and the opening of one (two) hysteresis loops during evaporation for the ink-bottle (open and funnel) pores. The isotherms can be obtained by summing the isotherms measured on uniform pores having the dimensions of the constrictions or of the cavities. The numerical analysis of the three different pore topologies indicates that the shape of the junction between the two pore sections is only important for the adsorption branch. In particular, a conic junction which resembles that of the AAO pores represents the experimental isotherms for the open and funnel pores better, but the shape of the junction in the ink bottle pores does not matter. The isotherms for the duplex layers with a disordered interface display the same general features found for the ordered duplex layers. In both cases, the adsorption branches coincide and have two steps which are shifted to lower relative pressures compared to those for the ordered duplex. Furthermore, the desorption branches comprise hysteresis loops much wider than those of the ordered duplex layers. Overall, this study highlights the important role played by morphologies where there are interconnections between large and small pores.

INTRODUCTION

Adsorption on mesoporous materials is typically characterized by hysteresis:1–5 liquid condenses in the small pores below the liquid–vapor bulk coexistence and evaporates at an even lower vapor pressure. Depending on the system parameters and geometry, the mechanism for emptying the pores is either by pore blocking6–9 (the adsorbate liquid remains trapped in the large pore sections until it is freed by desorption from the pore constrictions) or cavitation10–17 (the liquid trapped in the pores desorbs through the spontaneous nucleation of a gas bubble leaving adsorbate in narrower sections which empties at a lower pressure). Pore blocking has been invoked, for example, to explain the type H2 hysteresis loop, as designated by the IUPAC classification, which has a gradually increasing adsorption branch and a very steep desorption branch such as is typically displayed by disordered porous materials like Vycor.18,19 More generally, the influence of pore defects such as constrictions, wall roughness, and chemical inhomogeneities on hysteresis is the subject of intense studies.20–32 Only for very regular pores of large diameter with closed end and very smooth walls, no hysteresis is observed.33 Simulations suggest that even in closed pores hysteresis may occur when the diameter is smaller.34

To understand adsorption on pore constrictions better, tailored duplex layers formed by straight, cylindrical, non-interconnected pores of different diameter have been prepared. The two resulting geometries are “ink-bottle”,35 where a narrow pore (constriction) constricts a wider pore (cavity), and “funnel”, with the cavity above the constriction. Duplex layers with constrictions and cavities about 5–6 nm in diameter have been made by electrochemically etching a silicon wafer covered with an epilayer.36 Silicon duplex layers prepared on the same substrate by changing the etching conditions produced ink-bottle and funnel pores whose sections have different pore densities and diameters of 13 and 27 nm36 or a higher contrast in size, the small pores being below 10 nm and the large pores...
of diameter 54 ± 20 nm.\textsuperscript{37} In the latter two examples, the interface between the two layers is obviously highly disordered. Alumina double layers fabricated by controlling the electrolyte and anodization voltage form more uniform funnel pores and a better interface with characteristic diameters of 64 ± 10 and 15 ± 3 nm and ink-bottle pores with sections having size 14 ± 3 and 27 ± 3 nm.\textsuperscript{38} Adsorption on the ink-bottle pores shows cavitation in silicon double layers\textsuperscript{20,36} and pore blocking in alumina pores with similar diameters.\textsuperscript{38}

To further advance the study of adsorption on model pore constrictions, we have prepared well-controlled alumina membranes presenting duplex layers with pores of mean diameter 82 and 31 nm. Duplex layers with an ordered interface (i.e., the two layers have the same pore densities and each wide pore is connected to only one narrow pore) and a disordered interface (i.e., the two layers have different pore densities and a wide pore does not end in a narrow pore) have been used as substrates for argon adsorption at 85 K. By selectively blocking with glue one end of the pores,\textsuperscript{39} funnel and ink-bottle pores having exactly the same geometry can be realized. Porous anodized aluminum oxide (AAO) is characterized by a regular arrangement of the pores with a narrow pore size distribution and solid pore walls without micropores.\textsuperscript{40} Adsorption isotherms for closed end porous AAO\textsuperscript{39–41} show steep, symmetric hysteresis loops corresponding to type H1 in the IUPAC classification\textsuperscript{16,19} (i.e., a hysteresis loop with parallel adsorption and desorption branches), which is generally associated with capillary condensation and evaporation in ordered mesoporous materials with cylindrical pores. The experimental results are compared with Monte Carlo simulations in order to shed light on the microscopic mechanism of adsorption in structured pores.

\section*{METHODS}

\textbf{Preparation of Porous Duplex AAO Samples.} Porous anodic aluminum oxide (AAO) samples with different internal pore structures were prepared by anodization of aluminum. One side of a mirror finished aluminum disk (2 cm in diameter, Goodfellow, 99.999\%) was first anodized in 0.3 M H$_2$C$_2$O$_4$ (1 °C) at 40 V for 24 h. Then, the disordered porous oxide film formed on the aluminum substrate was removed using an aqueous mixture of 1.8 wt \% CrO$_3$ and 6 wt \% H$_3$PO$_4$. The surface of the resulting aluminum was textured with ordered arrays of almost hemispherical concave indents. Pores nucleate at the exact center of each concavity and grow normal to the aluminum substrate in the subsequent anodizing process.\textsuperscript{62} The second-step anodization was carried out for 6 h under the same conditions as the first anodizing step. Microscopic analysis of the resulting porous AAOs revealed that the nominal pore diameter ($D_p$), interpore distance ($D_{int}$), pore density ($\rho_p$), and thickness ($L_p$) are $D_p = 30$ nm, $D_{int} = 105$ nm, $\rho_p = 1.05 \times 10^{10}$ pores/cm$^2$, and $L_p = 30$ μm. After the second-step anodization, the pores in the AAOs were widened by performing wet-chemical etching of the pore wall oxide using a 5 wt \% H$_3$PO$_4$ solution (30 °C) for 50 min.\textsuperscript{43} This pore widening treatment increased the pore diameter ($D_p$) from 31 to ca. 83 nm. The resulting porous AAO samples with enlarged pores were kept in deionized water for subsequent use in the preparation of porous AAOs with duplexed pore structures, in which larger cylindrical pores are interconnected to smaller pores without losing their directional coherence. In order to investigate the effect of the details of the interconnecting interface on the adsorption behavior, we prepared (a) duplexed AAO pores with ordered interfaces and (b) duplexed AAO pores with disordered interfaces.

Figure 1 shows schematically the experimental procedure for the preparation of duplexed AAO pores with two different types of interconnecting interfaces. Duplexed AAO pores with an ordered interconnecting interface were prepared by further anodizing porous AAOs with $D_k = 83$ nm in 0.3 M H$_2$C$_2$O$_4$ (1 °C) at 40 V. The anodizing condition was chosen to be the same as that used for the second-step anodization in order to ensure uniform ordered growth of smaller pores. By monitoring the total amount of charge passed, the thickness of the newly grown AAO with smaller $D_p$ was controlled to be the same as that ($L_p = 30$ μm) of the existing AAO layer with larger $D_p$ (ca. 83 nm). For the preparation of duplex AAO pores with disordered interconnecting interface, on the other hand, porous AAOs with $D_k = 83$ nm were reanoled by using 0.3 M H$_2$SO$_4$ (1 °C) at 25 V. At the early stage of reanodization at 25 V, ordered large cylindrical pores branch into disordered smaller pores due to the potential mismatch between the second-step anodizing at 40 V and the third-step anodizing at 25 V. These initially disordered pores undergo gradual rearrangement to form a self-ordered porous AAO with reduced pore size ($D_p$) and interpore distance ($D_{int}$). From microscopic analysis of the self-ordered porous AAOs formed at 25 V, pore diameter ($D_p$), interpore distance ($D_{int}$), pore density ($\rho_p$), and thickness ($L_p$) were determined to be $D_p = 22$ nm, $D_{int} = 65$ nm, and $\rho_p = 2.73 \times 10^{10}$ pores/cm$^2$. The pore bottom of as-prepared porous AAOs with duplexed pore structure was closed by a thin barrier oxide layer in contact with the underlying aluminum substrate. AAO membranes with open-ended pores were prepared by selective removal of the
aluminum substrate with an acidified cupric chloride solution, followed by opening of the barrier layer by using a 5 wt % H₃PO₄ solution (30 °C). For duplex AAOs with disordered interconnecting interfaces, pores formed at 25 V were widened from 22 to 31 nm, so that the diameter of the smaller pores was comparable to that of duplex AAOs with ordered interconnecting interfaces. Figure 2 shows representative SEM images of the porous AAO membranes used in the present study.

**Adsorption Measurement.** The AAO samples were disks (D ~ 1 cm) cut out of aluminum foils or alumina membranes with a thickness of 400 or 100 μm, respectively. They were attached to the extremity of the tungsten rod of a torsional microbalance. When the sample is exposed to a vapor, the resonance frequency decreases because of an increase in the total moment of inertia. This is caused by a change in the mass of the adsorbed film and by a hydrodynamic contribution due to the mass of the dynamically displaced fluid. This latter contribution can be easily accounted for in the data analysis. From the vapor-corrected frequency shifts, it is then possible to derive the relative change of the oscillator moment of inertia which is proportional only to the mass of the adsorbed film.

**Figure 2.** SEM micrographs of duplexed AAO pores with (a–c) ordered and (d–f) disordered interconnecting interface: (a, d) top-surface views, (b, e) cross-sectional views at the interconnecting interfaces, and (c, f) bottom-surface views.

**Figure 3.** Pore models, dimensions, and shapes of ordered connected cylindrical pores studied in this work.
**Grand Canonical Monte Carlo Simulation.** In order to shed light on the experimental results, we used two models for connected cylindrical pores formed by joining a small pore to a larger pore as shown in Figure 3. The pore diameters were $D_1 = 6$ nm, $D_2 = 3.5$ nm, $L_1 = L_2 = 10$ nm, and $L_b = 2$ nm. We used the 12–6 Lennard-Jones (LJ) equation with the parameters $\sigma_f = 0.3405$ nm and $\epsilon_f/k = 119.8$ K to model the intermolecular interaction energy of argon. The LJ parameters of the oxygen atoms in alumina are $\sigma_c = 2.7$ Å and $\epsilon_c/k = 230$ K. The interaction energies between an adsorbate, a finite cylindrical pore (for models A and B), and a finite truncated cone (to model the junction between two cylinders in model B) have been given in previous work. To construct the funnel and ink-bottle model the junction between two cylinders in model B) have been given in previous work. To construct the funnel and ink-bottle models for connected cylindrical pores, we placed a flat aluminia surface modeled by the Bojan–Steele potential at the smaller or larger end of the pore.

The grand canonical Monte Carlo (GCMC) simulation was carried out at 85 K with 100,000 cycles in both the equilibration and the sampling stages. Each cycle has 1000 displacement, insertion, and deletion moves with equal probability, giving a total of $1 \times 10^6$ configurations in each stage. In the equilibration stage, the maximum initial displacement length was half of the largest dimension of the simulation box and was adjusted at the end of every cycle to give an acceptance ratio of 20%. The cutoff radius was half of the largest dimension of the simulation box. The pore mouths were exposed to a gas reservoir of 3 nm along the pore axis with the depth and height of 6 nm, which was the same dimension as the largest cylinder, to ensure that mechanical equilibrium was maintained between the pore and the gas surroundings. The simulated adsorption isotherms are presented as adsorbate density in the pore plotted against the relative pressure in the bulk phase. The vapor pressure of argon ($P_0$) at 85 K was calculated from the equation of Lotfi et al. as 64.3 kPa. The pore density is defined as the amount adsorbed in the pore per unit accessible volume. To obtain the mesoscopic density profile of the adsorbate in the pore, we divided the pore volume into two-dimensional bins in the radial and axial directions and ensemble-averaged the argon density in each bin during the sampling stage.

## RESULTS AND DISCUSSION

Figure 4 summarizes the main results of our adsorption study on ordered duplex layers. They consist of experimental adsorption isotherms for argon representing the relative change of the oscillator moment of inertia, $\Delta I/I_0$, as a function of relative pressure, $P/P_0$, where $P_0 = 65$ kPa is the Ar bulk saturated vapor pressure at 85 K. To facilitate the comparison between the closed and open ended pores, the inset displays the same data on a much enlarged scale (between relative pressures of 0.86 and 1.0), close to saturation. In the inset, the amount adsorbed has been normalized to the value observed at the plateau before the bulk vapor condenses at $P/P_0 = 1.0$. The isotherms have a complex shape which is quite different from the single hysteresis loop, with parallel adsorption and desorption branches (type H1 in the IUPAC classification), which is typically found in AAO straight pores. However, they can be qualitatively understood in terms of the Cohan or Kelvin equations, which relate the value of $\ln(P/P_0)$, at which liquid fills a cylindrical pore, to the curvature $C$ of the meniscus:

$$\ln \frac{P}{P_0} = -\frac{\gamma}{n_{\text{liq}} K_B T} C$$

where $\gamma = 13.1$ erg/cm$^2$ is the liquid argon surface tension and $n_{\text{liq}} = 2.1 \times 10^{22}$ atoms/cm$^3$ is the liquid argon number density both evaluated at the temperature $T = 85$ K, $K_B = 1.38 \times 10^{-23}$ erg/K being the Boltzmann constant. For an ideal cylindrical pore closed at one end, the meniscus, according to this classical thermodynamic approach, is expected to have the same hemispherical shape during condensation and evaporation, so that $C = 4/D_p$, where $D_p$ is the pore diameter. In an open-ended cylindrical pore, the meniscus has a cylindrical shape during adsorption with a curvature $C = 2/D_p$ (the Cohan equation).

The isotherm on open-ended duplex pores is characterized by two pronounced hysteresis loops formed during gas addition (adsorption) and removal (desorption) from the sample cell. At $P/P_0 > 0.9$ a step occurs in the adsorption branch (midpoint position $P_{\text{midpoint}}/P_0 = 0.950$), indicating capillary condensation in the constricted region of the pores, followed by a plateau, a second steeper and higher step ($P_{\text{midpoint}}/P_0 = 0.974$) corresponding to capillary condensation in the pore cavities, and a new rise, very close to saturation, due to condensation of a thick film on the two faces of the AAO disk. Pumping gas out of the cell yields a narrow hysteresis loop at higher pressure and a wider one at lower $P/P_0$. The presence of two steps in the adsorption branch confirms the existence of pores of two different sizes. Similar isotherms have been observed on closed bottom duplex layers of porous silicon and of porous AAO. The graph also compares the isotherms taken on AAO duplex layers formed by funnel and ink-bottle pores. The ink-bottle pores were obtained by blocking with glue the large open ends of the same sample used for the open duplex isotherm, and the funnel pores were made by blocking the small open ends of a different sample, nominally equivalent to the open duplex one. The isotherm for the funnel pores looks quite similar to that for the open-ended duplex, apart from a slight variation in the location of the first adsorption step. By contrast, the isotherm for the ink-bottle pores has a very wide hysteresis loop with only a single desorption branch, while the adsorption branch almost coincides with that of the open pores when it is taken into account that the length of the cavities is slightly different between these two samples because of the glue. The observed behavior contrasts with that reported on porous silicon and AAO. Actually, on the duplex silicon structures, the entire adsorption branch of the funnel geometry is shifted to higher $P/P_0$ with respect to that of the ink-bottle geometry.
The inset in Figure 4 compares the final portion of the normalized isotherm for the open duplex with that of the funnel and ink-bottle pores. It clearly shows that the narrow hysteresis loops at high $P/P_0$ coincide, except for a small difference in their height which is probably due to small differences in pore length due to the glue. In the inset the vertical scale for the funnel and open pores has been rescaled by a factor 1.29. The resulting desorption branch coincides with that of the open duplex while the adsorption step occurs at slightly lower $P/P_0$. Apart from this, the full isotherm for the open-ended duplex resembles very closely that of the funnel sample. This is consistent with the observation that condensation and evaporation in any pore section of a complex structure are independent of boundary conditions if there is direct access to the gas reservoir. However, the isotherm for the funnel pores disagrees with that reported in a previous study of adsorption of hexane on funnel AAO pores having pore sizes comparable to ours. The hexane isotherm has two capillary condensation steps, but that at the higher pressure shows no hysteresis, while there is a standard hysteresis loop associated with the step at lower $P/P_0$. We do not know how to explain this difference. In our work on porous AAO we have always found hysteresis regardless of the pores closure and inner morphology. The only isotherms we have measured that do not show any hysteresis were for adsorption in very ordered silicon matrices made by nanolithography where the pores have smooth vertical walls. Given the narrowness of the higher pressure loop in Figure 5, we wonder whether the limited temperature control which can be achieved working with organic solvents like hexane at room temperature may be responsible for the lack of any observed hysteresis.

Adsorption in the ink bottle pores is quite different as shown in Figure 6, which compares the final portion of the normalized isotherm for the open-ended duplex with that of the ink-bottle pores. Their adsorption branches coincide after rescaling: the (pink) dashed line represents the data points for the ink-bottle pores after dividing the vertical scale by a factor 1.18. The resulting height of the second step is smaller than that of the open duplex, indicating that some glue has entered the open ends of the cavities. The narrow hysteresis loops at higher $P/P_0$ are also quite similar to the loop measured in straight, closed bottom AAO pores having the same size ($83 \text{ nm}$) as the cavities in the funnel pores. Again, the vertical scale is diverse because the pore lengths are not the same. Instead, the desorption branch of the ink-bottle pores is quite different and occurs in a single step. It is very close to that measured on the closed end AAO pores having the same nominal size ($31 \text{ nm}$) as the constrictions of the funnel pores. This confirms that the observed behavior is due to the classical pore blocking effect as found in porous AAO and porous silicon using solid Ar.

Figure 6. Final portion of normalized adsorption isotherms of Ar at $T = 85 \text{ K}$ on ordered AAO duplex layers open at both ends and with the cavity end blocked. The curves are compared with previously published adsorption isotherms on straight closed end alumina pores having the same nominal size as the cavities and constrictions in the duplex layer samples.

Adsorption on the disordered duplex layers, as shown in Figure 7, presents a complex phenomenology significantly different from that of the ordered duplex layers. Figure 7 compares the normalized adsorption isotherms for the three possible geometries and for the ordered duplex. To better appreciate the differences, the isotherms have been normalized to the plateau corresponding to the filling of the constrictions of the disordered open duplex sample. The resulting adsorption branches on the second step of the isotherm coincide and they are very close to the desorption branch of the ordered open duplex. The three disordered duplex geometries show distinct desorption paths. The branches corresponding to desorption from the cavities of the disordered funnels and open duplex (the second step in the isotherm) are also quite similar. However, the desorption branch on the first step of the isotherm, due to the constricted part of the funnels, has moved to a lower $P/P_0$ with respect to that of the open pores. As before, desorption from the ink-bottle pores occurs as a single event with a midpoint pressure $P_{\text{midpoint}}/P_0 = 0.874$ slightly lower than that of the desorption branch for the constrictions in the open pores, $P_{\text{midpoint}}/P_0 = 0.887$, and very close to that of the constrictions of the funnel pores, $P_{\text{midpoint}}/P_0 = 0.872$.

The experimental results have clearly shown that the various topologies of connected pores behave differently. Now we turn to discuss the mechanisms of adsorption underlying the

Figure 5. Final portions of normalized adsorption isotherms for argon at $85 \text{ K}$ on ordered AAO duplex layers open at both ends and having one end of the constrictions closed. Inset shows the enlargement of their final part close to saturation. The open squares represent the data for the funnel pores after multiplication of the vertical scale by a factor 1.29.
Experimental results with the aid of Monte Carlo simulations. Simulation of mesopores with diameters as large as those studied experimentally is outside any acceptable range for current supercomputers; here we have chosen mesopore diameters of $D_1 = 6$ nm and $D_2 = 3.5$ nm such that simulations can capture the essential behavior observed experimentally. We studied two connected pores topologies in order to investigate the effects of locating a junction between the two sections of the pore: uniform connected cylindrical pores (model A) and a truncated cone joining the two cylinders (model B), as illustrated in Figure 3. We have also modeled different junction topologies designated C, D, and E as shown in Figure 13; these gave isotherms very similar to that for model B. Detailed studies of the effect of pore dimensions and temperature for simple pore connectivity on adsorption behavior have been reported in earlier work.6,49,59,60 The simulated adsorption isotherms for the two pore models are shown in Figure 8, and the following general observations can be made: (1) The main features of the experimental data are reproduced qualitatively: a single hysteresis loop with two-step adsorption, and one-step desorption, branches for ink-bottle pores and two distinct hysteresis loops for the funnel and open pores. (2) The isotherms for the funnel pores for each model are similar to those of open duplex pores, as found in the experiments, except that the first hysteresis loop for the funnel pores is smaller than that for the open pores. (3) The topology of model B closely resembles the SEM micrographs of the ordered samples shown in Figure 2; the second hysteresis loop for the funnel pore in this model is smaller than that for model A and therefore agrees better with experimental data. The same is also true for the open pores and highlights the importance of the junctions between the two sections of the pore. (4) For the ink-bottle pores, models A and B give similar adsorption and desorption isotherms, suggesting that the structure of the junction is not important for evaporation from the pore cavities by the pore blocking mechanism.

To shed further light on the part played by the junctions, we examined snapshots, taken at specific points on the adsorption–desorption isotherms, of a configuration across the diameter of a cylindrical section. Figures 9a and 9b show adsorption–desorption isotherms and snapshots for models A and B, respectively, of adsorbate on the open duplex pore and (in the bottom panels) in uniform open pores whose size is the same as that of the constrictions and of the cavities and in a closed-end pore whose size is the same as that of the cavities. The adsorption branch of isotherms for the open duplex pores proceeds by a two-step condensation: the first step (whose end points are labeled A1 and B1) corresponds to condensation in the constriction, which occurs at the same pressure as the corresponding open pore of 3.5 nm diameter, and the second step (points A2–A3 and B2–B3) corresponds to condensation in the cavity. This second step is very sensitive to the junction morphology. In model A, the condensation in the cavity of the duplex pore (A2) is identical to the condensation in a uniform open pore (a first-order transition) of diameter 6 nm. This is because the contribution to the potential energy field from the junction in model A is very weak compared to that from the pore walls, and adsorption occurs in layers along the pore walls of the larger section. On the other hand, in model B the junction has a much higher affinity, and consequently, once the small section has been filled, the larger section behaves like a closed-end pore, and the second condensation in this model is exactly the same as in the closed end pore of 6 nm diameter (see Figure 9b). On desorption from a completely filled pore, two menisci are formed one at each end of the duplex pore, and the one at the large end recedes more than the one at the small end (points A3–A5 and B3–B5). Therefore, desorption from both models A and B are identical; i.e., the evaporation of

Figure 7. Final portion of normalized adsorption isotherms of Ar at $T = 85$ K on disordered AAO duplex layers open at both ends or with one end closed. For comparison, the isotherm for the ordered open ended duplex layer is also shown. The data are normalized to the value of the plateau corresponding to the filling of the constrictions of the disordered open duplex sample.

Figure 8. Adsorption isotherms for argon at 85 K in ink-bottle, funnel, and open duplex pores: model A (left panel) and model B (right panel).
Figure 9. Adsorption isotherms and configuration snapshots for composite (top panels) and single pore models (bottom panels) for argon at 85 K in open duplex pores: (a) model A; (b) model B. The red solid arrows show the direction of condensation in the larger section.

Figure 10. Adsorption isotherms and configuration snapshots for composite (top panels) and single pore models (bottom panels) for argon at 85 K in funnel pores (narrow end closed): (a) model A; (b) model B. The red solid arrows show the direction of condensation in the larger section.
adsorbate from the cavity of the duplex pore is the same as evaporation from a closed end pore and evaporation from the constriction is the same as from an open end pore.

Argon adsorption–desorption isotherms and configuration snapshots, at various points along the isotherms, are shown for models A and B of funnel pores in Figures 10a and 10b, respectively. For comparison, the figure also shows the isotherms for uniform closed end pores of diameter 3.5 and 6 nm and for an open end pore of diameter 6 nm. Condensation in the cavity and evaporation from the cavity are the same for both models as discussed earlier for open duplex pores. The only difference is that the first hysteresis loop for both models A and B for (closed end) funnel pores is smaller than for the open end duplex pores because the narrow section of the funnel pore now behaves like a closed end pore of 3.5 nm diameter.

Finally, Figure 11 shows the adsorption–desorption isotherms and the snapshots at various points along the isotherms for models A and B for the ink-bottle pores. As before, the bottom graphs display the isotherms for uniform sized pores of diameter 3.5 nm, open at both ends, and open and closed end pores of diameter 6. The adsorption isotherms are almost the same for both models; the first condensation in the constriction is similar to that in an open pore of diameter 3.5 nm and is followed by condensation in the cavity similar to that in a closed end pore of diameter 6 nm for model A and as in a closed end pore of diameter 6 nm for model B. The second condensation in model B occurs at the same pressure as model
A, corresponding to the condensation pressure of a closed pore, but higher pore density just before condensation because of the advance of two menisci, one from the closed end and the other from the junction, while the second condensation in model A results from the advance of only one meniscus from the closed end. Upon desorption from the completely filled pore, a meniscus is formed at the pore mouth and recedes through the smaller section (points A3–A4 and B3–B4), resulting in a knee on the desorption branch for both models. Once it reaches the junction between the small and large sections, evaporation of the condensate in the large section occurs (points A4 and B4–B5) via the well-known pore-blocking mechanism.59

To investigate the adsorption behavior of the disordered interconnecting interface, we modeled an ink-bottle with constriction at the junction to simulate the disordered structure by means of increasing the solid–fluid interaction. This is done by adding a truncated cylindrical pore of 2 nm in diameter joining the cavity and the neck as shown in Figure 12a. The isotherm of this pore model for argon adsorption at 85 K is shown in Figure 12b, and as a comparison, we also plotted the isotherm for the pore model with an ordered junction (Figure 3). It is seen that the new model with disordered junction by means of constriction is able to describe the experimental data qualitatively.

## CONCLUSION

The main goal of this study was to investigate the role played by the morphology of the interconnecting interface between large (cavity) and small (constriction) pores on the adsorption in structured pores. We have carried out systematic experiments and numerical simulations of porous AAO duplex layers which, by selective blocking of the pore openings, could be constructed in three different pore topologies: open structured pores, funnel pores (closed at the narrow end), and ink-bottle pores (closed at the wide end). Adsorption isotherms present a rich phenomenology characterized by the presence of two steps in the condensation branch and the opening of one (two) hysteresis loops during evaporation for the ink-bottle (open and funnel) pores. When the structured pores have an ordered interface, the isotherms can be reproduced by summing the isotherms for uniform pores having the dimensions as the constrictions or of the cavities. The numerical analysis of the three different pore topologies indicates that the shape of the junction between the two pore sections is only important for the adsorption branch. In particular, a conic junction (designated model B) that resembles that of the experimental AAO pores better describes the experimental isotherms for open and funnel pores, while in the ink-bottle pores the junction shape does not matter. The isotherms for duplex layers with a disordered interface present the same general features found for the ordered duplex layers. The adsorption branches all coincide and have two steps which are shifted to lower relative pressures than those for the ordered duplex. Furthermore, the desorption branches comprise hysteresis loops much wider than those of the ordered duplex. We conclude by pointing out that this rich phenomenology is only the result of the morphology of the interface between the two porous layers. More generally, it confirms the fundamental importance of morphological disorder on adsorption in real straight pores.

## REFERENCES


Figure 13. The three pore models of disordered connected cylindrical pores.


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