Sorption Hysteresis of Benzene in Charcoal Particles

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Charcoal is found in water, soil, and sediment where it may act as a sorbent of organic pollutants. The sorption of organic compounds to natural solids often shows hysteresis. The purpose of this study was to determine the source of pronounced hysteresis that we found in the sorption of a hydrophobic compound (benzene) in water to a maple-wood charcoal prepared by oxygen-limited pyrolysis at 673 K. Gas adsorption (N₂, Ar, CO₂), ¹³C NMR, and FTIR show the charcoal to be a microporous solid composed primarily of elemental (aromatic) C and secondarily of carboxyl and phenolic C. Nonlocal density functional theory (N₂, Ar) and Monte Carlo (CO₂) calculations reveal a porosity of 0.15 cm³/g, specific surface area of 400 m²/g, and appreciable porosity in ultramicropores <10 Å. Benzene sorption—desorption conditions were chosen to eliminate artificial causes of hysteresis (rate-limiting diffusion, degradation, colloids effect). Charcoal sorbed up to its own weight of benzene at ~69% of benzene water solubility. Sorption was highly irreversible over most of the range tested (10⁻⁶–10⁻¹ µg/mL). A dimensionless irreversibility index (Ii) (0 ≤ Ii ≤ 1) based on local slopes of adsorption and desorption branches was evaluated at numerous places along the isotherm. Ii decreases as C increases, from 0.9–1 at low concentration to ~0 (~fully reversible) at the highest concentrations. Using sedimentation and volumetric displacement measurements, benzene is observed to cause pronounced swelling (up to >2-fold) of the charcoal particles. It is proposed that hysteresis is due to pore deformation by the solute, which results in the pathway of sorption being different than the pathway of desorption and which leads to entrapment of some adsorbate as the polyaromatic scaffold collapses during desorption. It is suggested that intra-charcoal mass transport may be influenced by structural rearrangement of the solid, in addition to molecular diffusion.

Introduction

Black carbon (BC) refers to incompletely combusted residues of biomass and fossil fuel materials and includes charcoal and soot (1). BCs have been detected (or postulated to exist) in atmospheric aerosols (2), estuarine and deep-sea sediments (3, 4), and soils (5), where their influence on transport and bioavailability of organic contaminants is thought to be of importance (2, 6–10). The sorption of organic compounds to natural solids often shows hysteresis or irreversibility of the sorption–desorption cycle (11–21). Such compounds include pesticides (e.g., atrazine, lindane), chlorinated benzenes, and polycyclic aromatic hydrocarbons (PAHs) among others. Typically, the affinity of adsorbate for solid appears to be greater along the desorption branch than along the adsorption branch; in extreme cases, complete desorption cannot be achieved without vigorous intervention such as organic solvent extraction.

Two types of hysteresis are distinguished (22): permanent or true hysteresis caused by spontaneous mechanisms associated with pore filling and emptying and artificial hysteresis caused by an insufficient time allowed for diffusion equilibrium or some auxiliary process. The latter depends on conditions and can be eliminated, while the former is reproducible in repeated sorption–desorption cycles. Pollutant transport and bioavailability models generally rest on the assumption of sorption reversibility. Sorption coefficients used in such models are normally based on forward-constructed (adsorption) isotherms. If sorption is irreversible, then these models will incorrectly predict the movement or biological fate of the chemical; contaminated materials may be less hazardous than expected; contaminant plumes in an aquifer may tail more extensively and require longer times to be flushed out; contaminated materials may prove resistant to biological, physical, or chemical treatment.

BCs have demonstrated high and nonlinear sorption of organic compounds (6, 10). However, studies dealing with hysteresis in BCs are scant. Irreversible sorption implies that the microscopic pathways for adsorption and desorption are different. Hysteresis in mesoporous reference solids, which gives rise to a closed “hysteresis loop” at concentrations typically greater than 40% of the saturated vapor pressure, has been attributed to the attainment of metastable states associated with capillary liquid condensation (23). Hysteresis in microporous solids, on the other hand, is generally absent unless the pores are deformable by the adsorbate (23). Irreversible pore deformation is the assigned mechanism for hysteresis in the adsorption of alcohol vapors in the interlayers of dry clays (24, 25) and in the adsorption of gases or hydrocarbon vapors in the nanovoids of glassy polymers (26, 27).

BCs are composed of single and stacked polyaromatic sheets that are arranged in a highly disordered fashion (1, 28–30). The sheets vary in size from a few to several tens of fused rings and may be functionalized along the edges. Chars may contain curved, fullerene-like structures that contribute to the disorder and prevent transformation to graphite at high temperature (30, 31). The pore structure of BC is not well known but has often been compared to that of activated carbons (32–34 and references therein), which historically have been regarded as fixed-pore adsorbents (35). Deformation of activated carbon micro pores is said to require breakage of covalent bonds (36).

The research herein investigated sorption–desorption hysteresis of benzene in a charcoal synthesized by pyrolysis of wood chips under oxygen-deficient conditions at 673 K. While this sample does not represent all charcoals in the environment, it does represent some. Adsorption–desorption isotherms were constructed spanning 7 orders of magnitude in concentration under conditions that rule out artificial
causes of hysteresis. An index is proposed to quantify irreversibility. We find that this charcoal swells under the influence of benzene and propose a mechanism involving pore deformation to explain the high degree of sorption irreversibility.

**Experimental Section**

**Materials.** Charcoal was prepared by atmospheric pyrolysis according to a modification of the method of Glaser et al. (37). Maple-wood shavings were placed in a 15-cm watch-glass-covered crucible and heated at 673 K for 2 h. The yield of charcoal from four portions (14.5, 29.7, 31.1, and 34.9 g) was 24.7 ± 0.6%. The four batches were combined, pulverized gently in a mortar to pass through a sieve no. 100 (0.150 mm), and stored in a glass vial at room temperature. Elemental analysis (Galbraith Laboratories, Knoxville, TN) gave 71.97% C, 2.83% H, 0.51% N, and 2.03% ash.

**Spectroscopic Analyses.** The 13C NMR spectrum of the charcoal was obtained by using CPMAS-TOSS techniques (cross-polarization magic-angle spinning with total sideband suppression). This method has proved valid for a wide range of organic samples from highly aromatic (coal humic acids) to highly aliphatic plant materials (38, 39). The sample (~700 mg) was packed in a 7-mm-diameter zirconia rotor with a Kel-F cap and run at 75 MHz (13C) in a Bruker DSX 300 MHz instrument. The spinning speed was 4.5 kHz. A 90° pulse was followed by a contact time (t_c) of 1 ms, and then a TOSS sequence was used to remove sidebands (38, 39). Contact time is sample-specific; preliminary tests determined 1 ms as optimal, as opposed to 0.5 ms used in our previous work (38). Line broadening of 30 Hz was used. The 90° pulse length was 3.4 μs; the 180° pulse was 6.4 μs. The recycle delay was 1 s with the number of scans about 4096. There was no signal observed for the rotor and Kel-F cap (38), thus no background correction was necessary.

The diffuse reflectance FTIR spectrum (32 scans at 4 cm−1 resolution) was obtained on a Mattson Infinity Gold spectrophotometer using a SpectraTech Collector sampling cell. The charcoal concentration was 1.4% in KBr.

**Pore Structure Characterization.** Carbon dioxide (273 K), nitrogen (77 K), and argon (77 K) adsorption—desorption isotherms were measured volumetrically using an Autosorb-1C (Quantachrome Corp.) equipped with a Baratron 1 Torr pressure transducer. Temperature was controlled using a liquid nitrogen bath (N2, Ar) or a homemade electric thermostat with an estimated accuracy of ±0.2 K (CO2). Low-pressure adsorption data were corrected on the thermal transpiration effect according to standard procedures (Autosorb User Manual). For Ar at 77 K, the saturation pressure of the supercritical liquid Ar was used (P_s = 230 Torr) (40). The saturation pressure of CO2 at 273 K was taken to be 2.614 × 10^6 Torr. Separate experiments were done with samples vacuum-outgassed at 298, 373, and 573 K.

Pore size distribution, pore volume, and surface area were calculated from nonlocal density functional theory (NLDFT) and Monte Carlo (MC) molecular models, assuming slit-shaped pores with graphitic walls, as given in detail elsewhere (41, 42). In this approach, the experimental isotherm is modeled as a collection of individual isotherms in pores of different sizes. N2 and Ar were modeled as Lennard-Jones (LJ) fluids using NLDFT. CO2 was modeled as a three-center LJ fluid with an quadrupole moment using the grand canonical MC simulations. Pore size distributions (PSD) were calculated by solving the generalized adsorption isotherm equation using regularization methods.

**Benzene Adsorption—Desorption.** A known mass of charcoal (23 mg, oven-dry basis) was added to each of several 13-mL glass screw-cap tubes. Each tube was then filled to capacity with “simulant water,” consisting of distilled—deionized water with 0.01 M CaCl2 to simulate environmental water and 200 mg/L NaN3 to inhibit degradation by incidental bacteria. The tubes were sealed with aluminum foil topped with a PTFE-lined cap and shaken for 17 days to allow the charcoal to hydrate. Duplicate tubes were then amended with 9.5 × 10^6 Ci 14C-labeled benzene and unlabeled benzene in methanol. The mole fraction of methanol in the simulant water in all tubes was 0.002 and therefore not expected to affect benzene sorption. The tubes were rotated end-over-end 15 times per min for 32 days in the dark at 21 ± 1°C. Shorter times were used in kinetic experiments. After centrifugation (750g for 30 min), 1 mL of the supernatant was assayed for radioactivity by liquid scintillation counting in 15 mL of Opti-Fluor (Packard Instrument Co.).

For desorption, 5.0 or 9.0 mL of supernatant was removed and immediately replaced. To ensure continuity of the liquid phase, the replacement fluid was benzene-free simulant water previously equilibrated at the same charcoal:solution ratio for 32 days. Volatilization losses during replacement were minimized by performing the operation quickly (~2 min per vial), inserting the syringe needle through the foil, and minimally disturbing the liquid. The tubes were ressealed and mixed for an additional 32 days (fewer in kinetic runs). Sorbed benzene was calculated by the difference between mass added and mass in solution, subject to correction for bottle losses of benzene. Bottle losses were evaluated in tubes without charcoal and assumed linear with the equilibrium solute concentration. They varied between 1.8 and 8% of total benzene added—negligible as compared to the observed percentages of benzene remaining with the solid because of hysteresis.

**Addressing Artifacts.** Hysteresis can be due to experimental artifacts such as degradation, sorption to nonsettling colloids, or failure to reach equilibrium because of diffusion limitations. These artifacts have confounded many previous studies of hysteresis. We verified that none of these artifacts could explain the hysteresis here. Thus, we deal with a permanent or true hysteresis.

After the desorption step, some tubes were checked for benzene mass balance. The charcoal was extracted with acetonitrile at 70°C (4 h). The benzene was then phase-transferred to dichloromethane (DCM) after dilution with water (acetonitrile:water:DCM, 10:20:5). DCM extracts with naphthalene as internal standard were analyzed by GC/FID (DB624 column; J&W Scientific, Folsom, CA). Benzene recovery based on GC quantitation was 99 ± 8%, indicating that biotic and abiotic transformations were negligible.

Sorption to colloids can lead to overestimation of the truly dissolved concentration. Artificial hysteresis can be observed if some colloids are removed when the supernatant is replaced in desorption steps. Although the replacement fluid here was simulant water that had previously been equilibrated at the same charcoal:solution ratio (thus any colloids removed would have been replenished), we nevertheless sought to rule out any interference because of possibly different colloid concentrations during adsorption and desorption steps. The colloid effect was evaluated by the solubility enhancement method. Open tubes of simulant water or supernatant of a centrifuged charcoal suspension were placed in a sealed Erlenmeyer flask containing benzene. After 7 days equilibration with the headspace at 21°C, the tubes were sampled, extracted with DCM, and analyzed for benzene by GC. The solubility of benzene in the supernatant of a centrifuged charcoal suspension in simulant water (1678 ± 150 µg/mL; standard deviation of triplicates) was not statistically different (p = 0.05) from that in simulant water alone (1626 ± 92 µg/mL), showing that the colloid effect can be neglected.
benzene solubility in pure water is reported to be 1780 µg/mL at 25 °C (43).

Finally, rate studies at two widely spaced initial concentrations indicated no significant changes in dissolved benzene concentration after ~100 h in both uptake and release experiments (Figure 1). This compares with an experimental equilibration period of 768 h for both adsorption and desorption processes. The variation in irreversibility of natural solids has been offered (13, 18–21). However, those models are unsatisfactory here for a variety of reasons, particularly because they are not suitable for evaluating variation in hysteresis over the isotherm. Irreversibility cannot be defined thermodynamically, as has been done by Neimark (46, 47), unless the hysteresis loop is closed.

Hysteresis is related to the tendency to desorb in response to dilution as compared with the hypothetical fully reversible and fully irreversible (zero desorption) cases. The tendency to desorb is given by the local rate of change (slope) of the adsorption and desorption branches, respectively, at C. Implicit in the denominator of eq 1 is the first derivative of the functions describing the adsorption and desorption branches, respectively, at C. Implicit in the denominator of eq 1 is the first derivative of the adsorption isotherm; i.e.

$$I_1 = \frac{f'_d(C) - f'_u(C)}{f'_u(C)}$$  \hspace{1cm} (1)

where $f'_d(C)$ and $f'_u(C)$ are the first derivatives of the functions describing the adsorption and desorption branches, respectively, at C. Implicit in the denominator of eq 1 is the first derivative of the zero desorption branch, which is zero. Equation 1 is self-correcting for curvature of the whole
adsorption isotherm since it is normalized to \( f_0(C) \). For a single-point, infinitesimal desorption, eq 1 is equivalent to the ratio of mass that fails to desorb because of hysteresis to the mass expected to desorb if sorption were completely reversible.

For benzene in charcoal, the slope of each branch could only be estimated since the branches are not highly defined and fit to traditional isotherm functions was poor (see below). The slope of each desorption branch was obtained by fitting the available data (mean of several adsorption points plus one or two desorption points) to a linear equation. (Curvature should be minimal over the observed change in concentration, which was always <3-fold.) The adsorption branch was fit section-wise to a polynomial expression (third to sixth order, depending on the range: 0–0.01, 0.01–1.0, 0.75–25, 25–1000 \( \mu g/mL \)), and the slope at \( C_i \) was evaluated by differentiation. The curves near each \( C_i \) were tightly fit by the expression and very close to being linear.

Results

Adsorbent Characterization. Elemental analysis of the charcoal gives atomic ratios C/H equal to 2.13 and C/N equal to 165. The C/O ratio is ~4.2 if the balance of mass (~23%) is assumed to be O. [For comparison, a pine charcoal prepared in a similar way except at 600 K (34) gave a C mass content of 68.6% vs 71.97% for our sample—and a C/N atomic ratio of 46.] The clear dominant peak at 130 ppm in the 13C NMR spectrum (Figure 3) indicates that the charcoal is composed primarily of elemental (aromatic) C. There are no significant aliphatic resonances. Small peaks at 150 and 160–190 ppm reveal the presence of phenolic and carboxyl carbons. The FTIR spectrum (not shown), which probes a few tens of nanometers into the solid, gives strong peaks corresponding to carbonyl stretch (1610, 1700 cm\(^{-1}\)), C–O stretch (broad, centered at 1320 cm\(^{-1}\)), and hydrogen bonded -OH (broad, centered at ~3450 cm\(^{-1}\)). The presence of oxygenated functional groups indicated by the 13C NMR and FTIR spectra is consistent with the high O content by elemental analysis. These groups are likely due to oxidation of carbons at the edges. The lack of aliphatic 13C NMR resonances indicates the comparative absence of incompletely pyrolyzed lignocellulose structures.

The N\(_2\) and Ar adsorption isotherms at 77 K on a sample vacuum-outgassed at 573 K (Figure 4) are classic type I (23), indicating microporous material with no significant mesoporosity. Despite long equilibration times (e.g., for Ar it took ca. 60 h to acquire the first three data and 70 more h for subsequent data), the isotherms are irreversible and exhibit a hysteresis loop, whose shape is not associated with capillary condensation in mesopores (23, 48) but indicates that equilibrium was not fully achieved. Nonequilibrium may be due to severe diffusion limitation to passage through constricted pores at such a low temperature, or by structural rearrangement/relaxation of the adsorbent during sorption. A small plateau on the Ar isotherm at low relative pressures indicates very narrow micropores, whose equilibrium filling pressure is below the minimal measurable pressure. N\(_2\) and Ar adsorption isotherms on a sample vacuum-outgassed at 373 K (not shown) were qualitatively similar to those for the sample outgassed at higher temperature but exhibited about half the sorption, indicating some residual amount of volatile substances blocking pores at the lower outgasing temperature. By contrast, CO\(_2\) adsorption isotherms on charcoal
and Ar are in good agreement; however, CO₂ gives
neglected. CO₂ adsorption at 273 K is known to be much less
isotherms exhibit very small hysteresis, which can thus be
14% and give essentially the same pore size distribution. The
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The 82 data were collected over 36 h.

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14% and give essentially the same pore size distribution. The
isotherms exhibit very small hysteresis, which can thus be
neglected. CO₂ adsorption at 273 K is known to be much less
susceptible to diffusion limitations often encountered at
cryogenic temperatures. The upper limit of pores probed by
CO₂ at 273 K below 1 atm is ~10 Å (ultramicropores).
The pore size distributions (Figure 6) calculated from the
adsorption branch using NLDFT model for Ar and N₂ and
CO₂ at 273 K below 1 atm is ~10 Å (ultramicropores).
The pore size distributions (Figure 6) calculated from the
adsorption branch using NLDFT model for Ar and N₂ and
using MC model for CO₂ indicate that at least 50% porosity
exists in pores <10 Å, with peak porosity occurring at ~4–6 Å.
The pore size here is defined to the “edges” of the carbon
atoms in the pore wall, taking 3.4 Å as the size of the carbon
atom (41). The pore size distributions obtained from CO₂
and Ar are in good agreement; however, CO₂ gives ~60%
higher volume of pores <10 Å because not all of these
micropores are accessible to N₂ and Ar at 77 K. [It should be
noted that activated carbon fibers, having most pores between
~4 and 10 Å, give very similar pore volume distributions for
N₂, Ar and CO₂ (41).] The N₂ and Ar pore size distributions
agree well and indicate that the charcoal is ca. 80% mi-
croporous (pores <20 Å). The total pore volume of charcoal
vacuum-outgassed at 573 K from N₂ and Ar measurements is ~0.15
cm³/g; the total surface area (plot not shown) is ~400 m²/g.
The true numbers are likely to be greater, as not all of the
porosity could be accessed at 77 K. For comparison, the BET
surface area (49) based on N₂ is 340 m²/g with nonphysical,
strongly negative constant C. It should also be noted that the
total pore volume of ~0.15 cm³/g determined with N₂ and
Ar agrees very well with the capacity of the charcoal for water
(0.13 g of water/g; see below) assuming that the water density
in pores is 1 g/cm³.

**Benzene Adsorption–Desorption Hysteresis.** A 768-h
(32-day) equilibration period was used to construct the
adsorption and desorption branches of the isotherm—far
longer than it took for the solution concentration to reach
stasis (Figure 1). Figure 7 shows the adsorption isotherm on
log-scale which spans 7 orders of magnitude in benzene
concentration. Popular models such as Freundlich and
Langmuir did not provide good fits. Figure 8 reproduces the
adsorption isotherm on linear scale, zooming progressively
from panel a to panel d. Note (panel a) the sharp rise in the
isotherm beginning at about 1000 µg/mL or about 60% of
benzene’s water solubility. This rise was reproduced in an
independent experiment. At about 1150 µg/mL (~69% of
solubility), the charcoal is sorbing its own weight in benzene.
Figure 8 also includes the desorption branches coming
off each adsorption equilibrium point. The desorption points
correspond to 40% or 70% replacement of the liquid phase
with clean simulant water. The isotherm shows pronounced
hysteresis along almost the entire range of dissolved benzene
concentration tested—from 1 × 10⁻⁴ µg/mL, which is close
to the limit of quantification, to 1020 µg/mL, which is 61%
of solubility. Above ~1050 µg/mL, hysteresis appears
negligible.

Figure 9 shows the index of irreversibility (Iₚ) as a function
of the log of dissolved benzene concentration. The index
ranges from 0.9 to 1.0 at concentrations below ~10⁻⁴ of
solubility and then gradually decreases to ~0.6 by ~10⁻⁶ of
solubility. Above ~1050 µg/mL, the index was disregarded
because of the steepness and lack of definition in the
adsorption branch, but Iₚ in that region appears from Figure
8 to be close to zero.

**Sorbate-Induced Alteration of Charcoal Particles.** Two
different methods demonstrate that benzene causes swelling
of the charcoal and, thus, deformation of the charcoal pore structure. Both methods are necessarily restricted to the high-concentration end of the benzene isotherm ($2 \times 10^4 \mu g/g$) because of their low sensitivity.

The first is based on the method of specific gravity (44) and simply gives the displacement of aqueous fluid by charcoal or by charcoal sorbed with benzene. Figure 10 shows that sorption of benzene causes an increase in the volume occupied by the charcoal. There is also a corresponding decrease in the apparent specific gravity of the pure charcoal (not including adsorbate mass) from 1.65 for the original material to 0.73 for the sample exposed to the highest benzene concentration. The changes were complete within 24 h and reproducible (legend to Figure 10). The volumetric increases can be attributed to swelling. The swelling is slightly less than that calculated from the sum of the original charcoal and pure liquid benzene volumes (dashed line in Figure 10). Thus, at these (high) concentrations, benzene molecules swell the charcoal by an amount almost equal to their liquid volume. We reiterate that no nonaqueous-phase benzene was observed in the test vessel at equilibrium. The possibility that the volumetric changes are due merely to displacement of water by benzene in fixed pores can be ruled out because the capacity of the charcoal for water at 24 °C and 100% relative humidity is only 0.13 g of water/g, which places an upper limit on the ratio of “swelled” volume to initial volume of 1.21, a value that was clearly exceeded at benzene concentrations above ~0.1 g/g (Figure 10). Looked at another
way, the maximum observed swelling (2.3 at 0.72 g of benzene/g) corresponds to a water capacity of 1.39 g of water/g or 10.7 times more than measured. The validity of the fixed pore concept of charcoal—at least with respect to benzene—is weakened further by noting that, if it is assumed that the density of benzene condensed in pores approximates that of liquid benzene (0.8765 g/cm³), the “porosity” of the charcoal reaches unity—i.e., the matrix occupies no volume at all—at ~0.53 g of benzene/g, which is half or less of the charcoal’s ultimate capacity for benzene.

The second method is a sedimentation technique (45) in which the height of a unit mass of charcoal in a column after centrifugation is determined as a function of sorbed benzene concentration. Figure 10 indicates that benzene causes a volumetric change in the charcoal in relation to its concentration according to this method. Swelling is significant (at the 95% level) even at the lowest concentration tested, 0.02 g of benzene/g. Thus, sedimentation confirms the trends obtained by the specific gravity method. The greater swelling obtained by sedimentation could be due to buoyancy effects not overcome by centrifugation (45) as the particles become imbibed with benzene.

Discussion

Hysteresis of benzene in this sample of charcoal is not due to common artifacts like degradation, the colloids effect, or rate-limiting diffusion (see Experimental Section); it therefore represents spontaneous (irreversible) mechanisms associated with pore filling and emptying. Since pronounced irreversibility exists while benzene is filling micropores—even down to $10^{-7}$ times solubility—it cannot be attributed to capillary condensation phenomena that are characteristic of fixed mesopore systems (23). The most likely explanation for the hysteresis of benzene in this charcoal is irreversible pore deformation by the sorbate. This produces a situation in which adsorption and desorption occur to/from different microenvironments. The pore deformation hypothesis is supported by liquid displacement and sedimentation measurements that conclusively demonstrate swelling. Swelling means that the internal matrix expands in response to the presence of the adsorbate. A linkage between swelling and hysteresis in this material is rational given the behavior of microporous standards. Sorption hysteresis of polar compounds in dry smectite clays and nonpolar compounds in organo-substituted clays has been attributed to irreversible expansion of the interlayer (24). Hysteresis in glassy polymers has been attributed to irreversible deformation by the sorbate of internal nanopores inherent in such materials (26, 27). We have proposed the latter type of hysteresis in soil organic matter based on isotherms of trichloromethane and other compounds (16, 17).

The pore structure of BC particles is not well-understood and probably depends greatly on formation conditions. Gas adsorption shows the charcoal to have a heterogeneous micropore structure, including pores <4 Å in width. Transmission electron micrographs of an anthracene soot (29) clearly show the presence of open and closed micropores, most only 3–4 Å in width. In some diesel soots, the ratio of N₂ BET surface area to the calculated smooth-sphere external surface area based on electron microscopy was close to unity (10, 28, 50). This and the observation that diesel soot uptake of PAHs occurs within hours to days (10) led some authors to suggest that accessible soot micropores might extend only a short distance into the solid and that sorption occurs on the external skin of the particles (10, 28). Evidently, however, charcoal (this study; 51) and perhaps diesel soots (10) (see below) can be swelled by the solute. Swelling may open up previously inaccessible pores. If this occurs, it could provide a basis for irreversible sorption. We propose the following mechanism for irreversible pore deformation.

The original elementary charcoal particle may reasonably be considered to contain open sectors and closed sectors with respect to an adsorbate (Scheme 1B). Open sectors are understood to have pores that have a high degree of connectivity and that are in thermodynamic contact with bulk solution. Closed sectors are understood to have the opposite. As benzene enters the solid, it adsorbs in micropores in the open sectors. In response to the presence of the adsorbed benzene, some rearrangement of polyaromatic sheets making up the pore wall occurs, causing expansion of some of the pores. This behavior is expected because (a) pressure is exerted by the adsorbate on the pore walls and (b) sheets bounding the pore are held together in part by noncovalent weak forces. Expansion of the pores now opens up new pathways for benzene molecules to penetrate into previously closed sectors. In some instances (Scheme 1A), the “door shuts behind the adsorbate”, trapping it in the closed sector until further rearrangement at some future time opens up a pathway for its escape. Closed sectors would then contain adsorbate that has leaked in but is unable to leak out on short time scales. Although swelling is confirmed only in the bulk sample at high concentrations, it is reasonable to expect it to occur at the local level at low concentrations because pore expansion is a function of local benzene concentration, which can be high in a narrow hydrophobic pore even at low solute concentration; thus, hysteresis is observed throughout the isotherm.

Matrix expansion also means that part of the work of adsorption is converted to entropy in the form of increased pore surface area. Expansion is not expected to be completely reversible because of the restricted mobility of the polyaromatic sheets. Hence, the adsorbate experiences a stronger net affinity for the adsorbent in the desorption direction than in the adsorption direction, giving rise to hysteresis.

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The original elementary charcoal particle may reasonably be considered to contain open sectors and closed sectors with respect to an adsorbate (Scheme 1B). Open sectors are understood to have pores that have a high degree of connectivity and that are in thermodynamic contact with bulk solution. Closed sectors are understood to have the opposite. As benzene enters the solid, it adsorbs in micropores in the open sectors. In response to the presence of the adsorbed benzene, some rearrangement of polyaromatic sheets making up the pore wall occurs, causing expansion of some of the pores. This behavior is expected because (a) pressure is exerted by the adsorbate on the pore walls and (b) sheets bounding the pore are held together in part by noncovalent weak forces. Expansion of the pores now opens up new pathways for benzene molecules to penetrate into previously closed sectors. In some instances (Scheme 1A), the “door shuts behind the adsorbate”, trapping it in the closed sector until further rearrangement at some future time opens up a pathway for its escape. Closed sectors would then contain adsorbate that has leaked in but is unable to leak out on short time scales. Although swelling is confirmed only in the bulk sample at high concentrations, it is reasonable to expect it to occur at the local level at low concentrations because pore expansion is a function of local benzene concentration, which can be high in a narrow hydrophobic pore even at low solute concentration; thus, hysteresis is observed throughout the isotherm.

Matrix expansion also means that part of the work of adsorption is converted to entropy in the form of increased pore surface area. Expansion is not expected to be completely reversible because of the restricted mobility of the polyaromatic sheets. Hence, the adsorbate experiences a stronger net affinity for the adsorbent in the desorption direction than in the adsorption direction, giving rise to hysteresis.
Penetration of adsorbate causes softening of the matrix, as adsorbate–adsorbent interactions develop at the expense of adsorbent–adsorbent interactions. The degree of softening depends on the local adsorbate concentration, which, in turn, depends on external solute pressure. The effect of softening is to convert closed-sector volume to open-sector volume, effectively increasing the free diffusion space of the adsorbate. Thus, as external solute pressure increases, the adsorbent volume occupied by closed sectors is reduced (Scheme 1B). This accounts for the decline in the index of irreversibility as concentration increases (Figure 9). The closed sector volume may reach zero as the particles swell to twice or more their original size at very high concentrations (Figure 10); indeed, hysteresis practically disappears at the highest concentrations (Figure 8). Softening also depends on adsorbate structure. Benzene sorption is seen to be more hysteretic than CO₂ sorption. This is because benzene interacts more strongly with charcoal than CO₂ since it is larger, more polarizable, and undergoes stronger van der Waal interactions with polyaromatic sheets.

An additional effect of pore deformation is manifested during net desorption. As the external fluid concentration is suddenly reduced, the flux of adsorbate leaving the solid causes contraction of pores and thus reversion of open-sector to closed-sector volume. During this reversion, some benzene molecules may end up trapped in the nascent closed sector as the polyaromatic scaffold around them collapses (Scheme 1C).

Hysteresis, in summary, is a consequence of the following: (i) leakage of penetrant during net adsorption into closed sectors where it is no longer in thermodynamic contact with solute in bulk solution; (ii) irreversible pore expansion; and (iii) contraction of pores during net desorption and trapping of adsorbate within the collapsed structure. The foregoing mechanism implies that intra-grain transport is dependent on matrix rearrangement processes in addition to passive diffusion of the penetrant. Since it is the former that gives rise to irreversibility, it follows that reversibility would be achieved if uptake and release were to occur over an infinite number of steps over infinite time.

Support for a pore deformation mechanism in BC also exists in the recent literature. The possibility of pore dilation in carbonaceous adsorbents caused by the packing effects of adsorbate molecules has been discussed by Olivier (52). The water–diesel soot partition coefficient of naphthalene calculated by moments analysis of elution curves was greater during net desorption. As the external fluid concentration is decreased, the water content of BC decreases, and more soot is packed into the adsorbent. This is a physical effect and not due to chemical interactions between the adsorbate and the charcoal of our study. We speculate that larger molecules may end up trapped in the nascent closed sectors where it is no longer in thermodynamic contact with the charcoal of our study. We speculate that larger molecules may end up trapped in the nascent closed sectors where it is no longer in thermodynamic contact with

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