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ADSORPTION AND DIFFUSION OF FLUIDS IN WELL- CHARACTERIZED ADSORBENT MATERIALS

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1. Introduction

This report outlines the work carried out during the period 8/1/95 to 1/31/98 under DOE grant DE-FG02-88ER13974. The original proposal called for modeling and simulation studies of: (1) the adsorption of simple fluids and mixtures in well-characterized materials, (2) water and aqueous solutions in carbons and aluminophosphates, and (3) chain molecules in porous media. Considerable progress has been made in each of these areas, as described below. The work has so far (January 1998) resulted in 28 publications and 21 presented papers during this period.

2. Research Accomplishments

2.1. Adsorption of Pure Fluids and Mixtures in Aluminophosphates, Buckytubes, Zeolites, MCM-41 and Oxides

A long range goal of our work is to develop molecular modeling techniques for well-characterized micro- and meso-porous materials. In particular, we are interested in materials which satisfy the constraints: (a) pores of uniform shape and size, with minimum structural defects, (b) pore sizes that can be accurately controlled in manufacture, and (c) pore sizes in the range 6-100 Å (larger than most currently used zeolites). For such materials molecular modeling should be able to predict optimum pore sizes, materials and state conditions for particular purposes, e.g. removal of a particular constituent from a mixture. With this in mind we have carried out studies of four classes of materials: aluminophosphates, buckytubes (tubular carbons), selected zeolites and MCM-41 (a new zeolite first synthesized by Mobil in late 1992).

Aluminophosphates. For aluminophosphates, in collaboration with Dr. C.A. Koh and coworkers of King's College, London, we have carried out an experimental and simulation study of CO₂/X gas mixtures in VPI-5 and ALPO₄-5 [1], where X is either methane, propane or isobutane, and also for propane/isobutane mixtures. Strong selectivity was observed for both adsorbents for propane in propane/CO₂, and for isobutane in isobutane/CO₂, mixtures. Little selectivity was observed in the case of propane/isobutane mixtures in both solids, and for methane/CO₂ in ALPO₄-5, while for the latter mixture CO₂ was selectively adsorbed in the case of VPI-5. These experimental results were in general agreement with predictions of the molecular simulations. In-situ diffuse reflectance infrared spectroscopy was used to provide information on the adsorbate-adsorbent interactions for trace amounts of these gases in VPI-5. Separation of these CO₂/alkane mixtures is of interest in connection with tertiary oil recovery, where carbon dioxide is used under pressure to remove the hydrocarbons.

A grand canonical Monte Carlo molecular simulation study of the adsorption of CO_2/CH_4 mixtures in micropores having both slit and cylindrical geometries, and different adsorption energies has been carried out [2]. For realistic choices of the potential parameters and material characteristics, the adsorption selectivity was found to vary over a range from 4 (CO_2 preferentially adsorbed) to $\frac{1}{4}$ (methane preferred), depending on the geometry and choice of parameters. The variations in selectivity were explained in terms of a balance between energetic and entropic factors. Energetic factors included both the adsorbate-adsorbent and cooperative adsorbate-adsorbate interactions. Entropic considerations were associated with the constraints on rotational freedom of the CO_2 molecules imposed by the geometry of the pore spaces. Energetic factors dominated in the larger pores and led to a preferential adsorption of CO_2 . However, for a small range of diameters for cylindrical pores, entropic factors were dominant and led to a preferential adsorption of methane. The results suggest that methane might be preferred by certain small pore aluminophosphates, and this possibility is being investigated experimentally.

Buckytubes. We have used GCMC simulations to study the adsorption of argon, nitrogen and hydrocarbons in carbon tubes ranging in diameter from 10 to 50 Å [3,4]. Tube sizes and walls were chosen to model buckytubes prepared by Iijima [5]. The structure of the tubules is known from scanning and transmission electron microscopy, and the solid-fluid potentials are known with some confidence for simple fluids from studies of planar graphite surfaces. The adsorption isotherms and heats show several interesting phase transitions, including layering transitions (0 to 1, 1 to 2, 2 to 3) and capillary condensation [3,4]. Typical isotherms for argon in a double buckytube (i.e. a tube with two graphite layers) of 4.78 nm internal diameter are shown in Figure 1. In these simulations argon is modeled as a Lennard-Jones molecule, and the fluid-wall interaction is the cylindrical pore analog of the (10,4,3) potential. At 77 K (Fig. 1a) the adsorption isotherm has a step-like character, indicating the buildup of successive adsorbed layers on the walls, up to 3 layers, followed by capillary condensation. This temperature is clearly somewhat above the critical temperature for the layering transitions, but below the capillary condensation critical temperature. Desorption exhibits the usual hysteresis behavior for monodisperse pores. At the lower temperature of 55 K the hysteresis loop becomes broader, and the layering occurs as sharp first-order transitions; the critical temperatures for these transitions is 58 K. A two-dimensional freezing transition is observed in the first adsorbed layer at this lower temperature. There are no experimental data yet with which to compare our results, but measurements are in progress by several research groups. These materials seem to be very promising for adsorption and separations. We have also carried out simulations for several methane/X mixtures in buckytubes, where X is another paraffin hydrocarbon such as ethane or propane [4,6].

The results described above and shown in Fig. 1 are for carbon tubes of infinite length. We have also studied adsorption in open-ended carbon tubes of internal diameter 4.78 nm. For tubes whose length exceeds 30 nm the effects of the open ends of the tube were negligible; only a small fraction of adsorbate molecules are near enough to these

Figure 1. Simulated adsorption isotherms for argon in a double buckytube of 4.78 nm internal diameter at (a) 77 K and (b) 55 K [3].

Figure 2. Adsorption isotherms for argon in a semi-infinite and in an open-ended buckytube of 4.78 nm diameter at 77 K [3].

Figure 3. Adsorption isotherms for nitrogen at 77 K in MCM-41 of pore diameter 4.3 nm, from experiment and from simulations for 3 models of the fluid-solid interaction. Models 1a and 1b assume a homogeneous wall, while Model 2 accounts for the heterogeneity [7].

open ends to feel a reduced fluid-solid interaction. For shorter tubes the end effects became pronounced. Adsorbate (argon or nitrogen) molecules within 2 nm of the end of the tube experience an appreciably different fluid-solid interaction from those in the interior of the tube, and this affects the adsorption isotherm and heat of adsorption. A buckytube that is 4 nm long is affected by the open ends throughout its length. Results for argon adsorption in an open-ended buckytube of length 7.7 nm and internal diameter 4.78 nm are shown in Fig. 2. Results for the infinite tube are also shown for comparison. The open ended tube is seen to result in (a) lower adsorption, particularly at high pressures where the pore is full, when the adsorption is reduced by about 10%; and (b) a substantial change in the shape and width of the hysteresis loop, the loop being much narrower and more rounded, with no first-order capillary evaporation on desorption. These changes result from the roughly hemispherical meniscus that forms at the ends of the open-ended tube during capillary condensation and evaporation [3].

MCM-41. We have used simulation methods to study several pure gases and gas mixtures in MCM-41 [4,6]. This new material seems especially promising as an adsorbent, since it adsorbs strongly and selectively, and can be prepared with uniform cylindrical pores. Moreover, the pore diameter can be controlled in the range 15-100 Å. GCMC simulation studies have been carried out to study the adsorption and selectivity for argon/nitrogen and several methane/X mixtures in buckytubes, where X is another paraffin hydrocarbon or nitrogen [4,6]. Very large increases in selectivity for the preferentially adsorbed component were found on tuning the pore size and pressure of the bulk gas, suggesting ways to improve selectivity in practice. Good agreement with ideal adsorbed solution theory was found for the mixtures considered. No experimental data on mixtures in MCM-41 seems to have been reported so far.

We have also carried out a detailed study of the adsorption of nitrogen in MCM-41, in collaboration with Dr. J. Olivier of Micromeritics Corp. (one of the two main instrument companies making sorptometers). Although experimental data has been reported for this system recently by other groups, the experiments were not carried out at sufficiently low pressures to test our fluid-solid interaction models. This has now been remedied by Dr. Olivier, who carried out careful and accurate adsorption measurements on this system for pressures down to P/P^0 of about 2×10^{-6} , well into the Henry Law regime, where only fluid-solid interactions are important. Comparisons of our simulation results with this new experimental data have shown [7] that the models used previously, having homogeneous walls as suggested by the synthesizers of this material, cannot fit the experimental adsorption data. Based on this new data we have developed a heterogeneous surface model, which is in excellent agreement with the existing adsorption isotherm data for all pressures and temperatures. Comparison of this new heterogeneous surface model (model 2) with the experimental data is shown in Figure 3; agreement is excellent over the entire pressure range of 6 orders of magnitude. The heterogeneous model is also in good agreement with data of other workers for this system [7]. By contrast, two previously proposed models (1a and 1b) that assume a homogeneous surface give poor agreement, particularly at low and intermediate pressures. The heterogeneous model has been used to develop a new and more accurate

method for characterizing MCM-41 materials [7]. This recent work suggests that some residue of the synthesis chemicals remain on the surface of MCM-41. Experimental work is underway by some of our collaborators to determine spectroscopically the nature of these surface modifications.

Clinoptilolite. We have been carrying out simulation studies of the selective adsorption of nitrogen/methane mixtures in several zeolites, with particular emphasis on clinoptilolite, a naturally occurring mineral. The great majority of materials preferentially adsorb methane from this mixture; adsorbents that preferentially adsorb nitrogen could be of great value in improving the fuel content of nitrogen-rich natural gas. Our studies are aimed at determining the variables that can make selectivity for nitrogen possible. Our studies [8] so far have focussed on the silica form of clinoptilolite, and the effects of pressure and water content on the separation. We find very little selectivity when water is absent from the framework. However, the presence of even small amounts of water have a large effect and cause the selectivity to be for nitrogen; increasing water content leads to increased selectivity for nitrogen, although the adsorption capacity decreases.

Alumina. Adsorption holds out promise for improved economy and selectivity in the separation of olefin/alkane mixtures. Such separations are of great importance in the petrochemical industry, since such mixtures are present in the product stream of catalytic crackers, and olefins such as ethylene and propylene provide the monomer feedstock for polyethylene and polypropylene. Recently it has been shown that selective adsorption of olefins from such mixtures can be effected in aluminas in which suitable metal salts (e.g. CuCl, NiCl₂) have been dispersed on the pore surfaces of γ -Al₂O₃. In these systems π -complexation occurs between the metal atoms and the π electrons of the olefins, leading to strong adsorption. The system must be so designed that the bonds resulting from this complexation are strong enough to effectively separate the olefin, while being weak enough to enable subsequent removal of the olefin (e.g. by heating or lowering the pressure). Copper seems to have a suitable binding strength for ethylene and propylene.

We have successfully modeled the adsorption and separation of ethylene/ethane mixtures in both bare γ -Al₂O₃ and in CuCl/ γ -Al₂O₃ [9], using GCMC simulations. Site-site Lennard-Jones interactions were used for the (adsorbate-adsorbate) interactions of ethane and ethylene. The alumina walls were treated as structured layers of oxygen atoms which form a cylinder. The π -complexation between copper ions and ethylene molecules was modeled by placing square well sites on the copper ions; the density of sites was taken from the experimental data.

A comparison of the simulation with experimental data for the adsorption of pure ethane and ethylene on bare γ -Al₂O₃ is shown in Figure 4. Agreement between the simulation and experimental data is excellent (within a few percent). Ethane is seen to be more strongly adsorbed than ethylene; this is due to a larger dispersion interaction for ethane. Single component isotherms for ethane and ethylene on CuCl/ γ -Al₂O₃ are

Figure 4. Adsorption isotherms for ethane and ethylene on bare γ -alumina at 333 K, from simulation (points) and experiment (lines) [9].

Figure 5. Adsorption isotherms for ethane and ethylene on CuCl/ γ -alumina at 333 K, from simulation (points) and experiment (lines) [9].

Figure 6. Snapshots from simulations of water in an activated carbon pore at 300 K, showing (a) "bridging" between two water molecules which are H-bonded to sites (small dark spheres) on the carbon surface (shown as a hexagonal lattice); (b) a cluster spanning between the two carbon surfaces [13].

Figure 7. Effect of surface site density on adsorption of water on an activated carbon at 300 K. Closed circles are for $n=0$ (unactivated surface); triangles, $n=0.222$ site/nm²; squares, $n=0.444$ site/nm²; open circles, $n=1$ site/nm² [13].

shown in Figure 5. The adsorption of ethane is somewhat reduced with respect to bare γ - Al_2O_3 ; this is because of screening of the surface by copper chloride. The adsorption of ethylene is greatly increased over that for bare γ - Al_2O_3 due to the π -complexation. Agreement between simulation and experiment is again very good, being within 5% in all cases. The small deviation for ethylene at the higher pressures is believed to be due to larger pores in the alumina, which were not accounted for in the model.

Unfortunately, no mixture data have been reported for these systems. However, the results in Fig. 5 suggest a strong selectivity for ethylene in the presence of CuCl . This has been confirmed in our simulations for this mixture.

2.2. Melting and Freezing Phenomena in Buckytubes and MCM-41

We have carried out a molecular simulation study of the effect of confinement on melting and freezing transitions, using methane and nitrogen as the fluids, and buckytubes and MCM-41 as the materials [10]. The latter have the advantage that they can be prepared with a controlled range of pore diameters. We find that the phase transition is strongly dependent on (a) the degree of pore filling, (b) the strength of the fluid-wall attractive forces. For a submonolayer filling the melting temperature is much below the bulk value (a fact that has been known for some time), but for a complete monolayer we find that the melting and freezing temperatures can be above or below the bulk value; this finding seems to be new. For a filled pore the transition temperature is below the bulk value, in agreement with experimental results for porous glasses. Buckytubes offer more attractive walls than MCM-41, and generally the transition temperature is higher in such tubes.

In the above calculations the transition between fluid and solid was determined from the change in diffusion rate with temperature, which was found from Molecular Dynamics simulations. GCMC simulations to determine the change in density of the adsorbed phase with temperature were also used, and gave results for transition temperatures that were consistent with those from the diffusion method. It would be preferable to calculate the free energy of the confined phase, and from this determine the true thermodynamic transition point. Such an approach would enable us to determine if a true first order transition occurs, as well as determining the transition more reliably. Until recently this has not been possible because conventional methods for determining the free energy of solids did not work for confined phases. This is because the contact layer freezes at a different temperature to the inner layers of adsorbate, so that thermodynamic integration cannot be carried out. Recently we have developed [11] a new method for determining the free energy of confined phases which avoids this problem. We have successfully demonstrated this method for a simple fluid (methane) in slit pores for carbon and silica-like materials, and have shown that the freezing transition for both contact and inner layers is truly first order. We plan to apply this method to cylindrical pores in the future.

2.3. Water and Water/X Mixtures in Activated Carbons and Aluminophosphates

Water in Activated Carbons. Adsorbed water behaves very differently from simple fluids. In carbons the adsorption isotherms are usually of types III (non-porous materials) or V (mesoporous materials), with very little adsorption at lower pressures followed by a steep rise in adsorption at some higher pressure. In class V this rise is accompanied by capillary condensation. In materials with active groups on the surface (e.g. activated carbons, many silicas) a wide range of adsorption behavior is observed. Understanding the factors that govern the adsorption of water is important for several reasons. Small amounts of water in process streams usually have a very large effect on the performance of adsorbers, often greatly reducing the capacity and effectiveness of the process; freezing of water and aqueous mixtures in pores seems to involve novel solid structures, perhaps including hydrates at conditions where the bulk mixture is fluid; and water adsorption appears to occur by a different mechanism than that for other simpler fluids.

The goal of our simulation work in this area is to understand the factors that govern such behavior, and particularly the role of temperature, pore width, type of surface, and density and type of active groups on the surface. We have carried out simulation studies [12-15] to investigate the influence of pore size and of the density and geometric location of active oxygenated sites on the surfaces of a carbon pore. In our early work in this area [16] we employed point charge models for water and for the active surface sites. Such models require very large systems and difficult long range corrections to account for the long range Coulomb forces. Subsequently, we found that, for the equilibrium properties of interest to us in the current study, the H-bonding could be modeled equally well using short range square well interactions. Thus, water is modeled using a spherical interaction for the O atoms with four off-center square well interactions for the H-bond sites (2 lone pair electron sites, 2 H sites). This model gives an excellent account of the properties of liquid water, including the coexistence and vapor pressure curves [12], and seems to be superior in this respect to existing point charge models. Active surface sites are modeled using Lennard-Jones sites with attached square well interaction sites to mimic the H-bonds.

In our first study [13], the surface sites were distributed either randomly or on a square grid on the surface, and approximate potential parameters were used for the surface sites. Parameters for water-water interactions were obtained by fitting to the properties of bulk water. Water-surface site interaction parameters were not fitted to experimental data, since we were not able to find accurate and reliable data on well-characterized carbons at sufficiently low pressures, where water-water interactions could safely be assumed to be negligible. Instead physically plausible approximate values were used for these parameters. It was found that the pore filling mechanism for water in such a pore is entirely different from that for simple fluids; water molecules adsorb (H-bond) onto the oxygenated sites and then form nuclei for the adsorption of further water molecules to form clusters. The total adsorption depends strongly on the placement of the sites. If they are suitably placed on the surface, a second cooperative adsorption

Figure 8. Comparison of experimental data (open circles) and simulation (triangles) for water adsorption on an activated carbon at 298 K [14,15].

Figure 9. Effect of surface site density, n , on selectivity for methane for water/methane mixtures in an activated carbon pore at 300 K from simulation [17].

Figure 10. Adsorption isotherms for a fluid of chain molecules of 4 mers (diameter σ) in a pore of width $H^* = H/\sigma = 10$, showing effect of association: open circles are for non-associating chains and non-associating walls; open squares, associating chains and non-associating walls; solid squares, associating chains and walls with associating surface sites [25].

mechanism can occur, by which the water molecules form 'bridges' between adsorbed waters on sites (Fig. 6a). Thus the density and placement has a major effect on the degree of adsorption [13]. As the bulk gas pressure is increased 'bridges' between water clusters form, and at somewhat higher pressures clusters that span across between the pore walls can occur (Fig. 6b). At still higher pressures the pore fills with water molecules. Capillary condensation does not occur in these systems at room temperature (Fig. 7).

In a second, more recent study [14,15] in collaboration with Prof. T. Bandosz (of City College of New York) we have carried out GCMC simulations for a more refined model and made comparisons with new and careful experimental measurements on well characterized activated carbons. In the experiments both Bohm and potentiometric titrations were used to determine the density and species of surface groups. Nitrogen adsorption measurements, coupled with density functional theory, were used to determine the pore size distribution of the carbons. Water adsorption measurements were made for pressures down to P/P° of 5×10^{-4} (and up to P/P° of 1.0). These low pressures were sufficiently small to observe the region where single water molecules bond to an active surface site. Our model of the surface was modified to account for the fact that oxygenated sites occur only at the edge of graphite microcrystals, and the experimentally determined site densities were used in the model. The H-bond strength (square well depth) for water-site interactions was adjusted to fit the lowest pressure part of the isotherm, and the remainder of the isotherm was predicted from the simulations for a range of pore sizes. The isotherm for the experimental material was then predicted from these using the known pore size distribution. The agreement between this model and the experiment was very good (Fig. 8). Some discrepancy was observed at full loading; this is believed to arise from errors in the experimentally determined pore size distribution, which appears not to account for some larger pores. Further refinement of the model to account for multiple bonding to some of the oxygenated sites is likely to lead to further improvement in the low pressure part of the isotherm.

Water/Methane Mixtures in Activated Carbons. We have also carried out a similar study of water/methane mixtures [17], to determine the influence of site density and location on selectivity and adsorption capacity. We find that the addition of oxygenated sites to the carbon surfaces has a very large effect on selectivity. By varying the site density it is possible to effect an inversion in the selectivity of the separation, water being preferred at high site densities (Fig. 9). These results explain the large reduction in breakthrough times that occurs for industrial adsorbers when the feed gas has a high relative humidity. This work was carried out in collaboration with Prof. Erich Müller of Simon Bolivar University.

Water in VPI-5. In the adsorption of water in VPI-5 and other aluminophosphates, there is strong experimental evidence of chemisorption of water to the aluminum atoms; thus, x-ray diffraction studies show a change from tetrahedral to octahedral structure around the aluminum in the presence of water. Adsorption isotherm measurements for this system [18] show 3 distinct steps as the pressure is increased. The first step, at very low pressures (less than 1% of the bulk vapor pressure) seems to arise

from very strong adsorption at a few specific sites. The second and third steps may be due to phase transitions in the adsorbed water layer.

To investigate these intriguing phenomena, we have carried out ab initio MO quantum mechanical calculations (using Gaussian) for the VPI-5 structure in the presence of, and in the absence of, water [19,20]. Interaction energy calculations (including counterpoise correction to remove basis set superposition errors) were performed for four molecular clusters consisting of one or more $\text{Al}(\text{OH})_4$ groups plus a water molecule; these clusters differed in the type of Al atom included in the cluster (VPI-5 exhibits 4 types of Al, depending on its position in the crystal structure). In addition, energy decomposition calculations were made, using the Fock matrix fragmentation approach of Kitaura and Morokuma [21], which with more recent modifications gives a stable solution even for strong interactions [22]. The decomposition analysis provided results for the electrostatic, exchange, polarization, charge transfer, and residual term contributions.

Of the four cluster models, three showed only repulsive interactions, and so cannot explain the observed chemisorption. These were the clusters containing the $\text{Al}(\text{d}4)$, $\text{Al}(\text{d}6)$ and $\text{Al}(\text{h}6)$ aluminum atoms. Here the notation $\text{Al}(\text{XY})$ is used to distinguish the Al sites in VPI-5; $\text{X}=\text{d},\text{h}$ denotes the dehydrated or hydrated crystal, while $\text{Y}=4,6$ denotes the coordination number of the Al atom. Thus for these Al atoms oxygen atoms around the aluminum prevent any water molecule approaching the aluminum due to a large exchange interaction. For the fourth cluster, $\text{Al}(\text{h}4)$, the electrostatic and charge transfer interactions between the O in the water molecule and the aluminum atom are strong enough to overcome the exchange interaction leading to a strongly attractive net interaction of about 25 kcal/mol. Thus it is the $\text{Al}(\text{h}4)$ sites in VPI-5 that can chemisorb to water molecules, and we believe that this accounts for the both the x-ray diffraction results and the sharp rise in the adsorption isotherm at very low pressures. Recently, more accurate calculations of the interaction energy have been made using larger clusters and have been used to construct the intermolecular potential field for the water-VPI-5 system. These more extensive results have been fitted to a suitable equation for the potential. This analytical force field is suitable for use in conventional GCMC simulations to determine the adsorption isotherm and heat of adsorption.

2.4. Chain Molecules in Pores

We have completed a Monte Carlo simulation study of associating and non-associating chain molecules (chains of up to 35 Lennard-Jones mers) in slit carbon pores of various widths. The calculations have been carried out for pure fluids and mixtures, and for walls with and without association sites that can bond to the sites on the chain molecules, for a range of fluid-wall interaction strengths [23-26]. The Chain Increment Method, and also the Configurational Bias Method, were used to calculate the chemical potentials of the polymers in the pore, and from these it was possible to calculate the adsorption isotherms. Chains were modeled as made up of tangentially linked Lennard-Jones spheres. Association sites were modeled using off-center square well potentials,

Figure 11. Selectivity isotherms for a mixture of associating and non-associating chain molecules in a pore having associating surface sites for two pore widths: $H^*=7$ (circles) and 15 (squares) [24].

Figure 12. Snapshot of adsorption of a mixture of associating and non-associating chains (4-mers) in a pore of $H^*=7$. Dark and light grey spheres correspond to associating and non-associating chains, respectively, while smaller spheres indicate wall sites. Pore walls are at the top and bottom of the box [25].

for both chain molecule sites and wall sites. These were the first calculations of chemical potentials or adsorption isotherms for associating chain molecules in pores.

For pure chain fluids, adsorption was less than for fluids of small molecules. Moreover, adsorption decreases further as chain length increases. These effects are due to the loss of entropy on confinement, which is much greater for chains than for small molecules. When the chain molecules contain association sites that can H-bond to active sites on the walls, the adsorption is increased (Figure 10) as expected. However, this effect is much smaller than for small molecules, again because of entropy loss on confinement.

Typical results for mixtures of non-associating (1) and associating (2) chains for slit pores having associating sites on the walls are shown in Figure 11 for two pore widths; a snapshot of a typical configuration for one of these mixtures is shown in Figure 12. The model used is an approximate representation of alkane/alkanol mixtures in an activated carbon having oxygenated sites on the walls. The selectivity is defined as $S_2 = (x_2/x_1)/(y_2/y_1)$, where x and y represent the mole fractions in the pore phase and bulk phase, respectively. The selectivity (Fig. 11) is seen to decrease as pore width increases, as expected. It also decreases as the bulk pressure is increased. The values of S_2 found in simulations are in the same range as those reported experimentally for alkane/alkanol mixtures of this chainlength in activated carbons [27].

2.5. Experimental Studies

Experimental studies were carried out in two areas to support the modeling effort. The first was a program to study the adsorption of water on well-characterized active carbons, including measurements at very low pressures, where the adsorption is controlled by active sites on the carbon surface. The second was a study of the adsorption of nitrogen onto MCM-41, again emphasizing the important low pressure region.

Water Adsorption on Active Carbons. Although numerous reports have been made of water adsorption measurements on activated carbons, these have been unsuitable for testing molecular models since they do not reach low enough pressures to explore the initial water/active site interactions; in addition, the carbons used are usually not well characterized. In collaboration with Prof. T.J. Bandosz of City College New York, we have undertaken a careful experimental study on several active carbons, and have included low pressure measurements and characterization of both pore size distributions and surface chemistry [15]. Adsorption was measured for pressures down to P/P° of 10^{-3} at 298 K. Molecular simulations show that this pressure is low enough to explore the region where the first few water molecules adsorb onto active surface sites. Nitrogen adsorption isotherms were obtained at 77 K, and density functional theory [28-30] was used to invert these and obtain the pore size distribution. Surface groups were characterized using potentiometric and Boehm titration methods. These measurements

yielded both the surface site density and information about the concentrations of acidic and basic surface groups.

Some of the water adsorption results are shown in Figure 8, and a more complete description is given in a recent paper [15].

Adsorption of Nitrogen in MCM-41. In collaboration with Dr. J. Olivier of Micromeritics Corporation we have carried out studies of the adsorption of nitrogen in MCM-41 samples at 77 K over a wide range of pressure [7]. Particular care was taken to obtain measurements at low pressure, down to below P/P^0 of 10^{-5} , in order to explore the region where only fluid-solid interactions are important. The energy distributions were obtained by applying density functional theory methods to the experimental data. It was found that the MCM-41 surfaces exhibited significant heterogeneity, and models that did not account for this were in serious error at the lower pressures. At higher pressures capillary condensation was observed. Some of these results are shown in Figure 3.

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