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WATER ADSORPTION AND DESORPTION ON MICROPOROUS SOLIDS AT ELEVATED TEMPERATURE

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An accurate gravimetric method was used to explore water adsorption/desorption isotherms between 105 and to 250°C for a number of synthetic and natural porous solids including controlled pore glass, activated carbon fiber monoliths, natural zeolites, pillared clay, and geothermal reservoir rocks. The main goal of this work was to evaluate water adsorption results, in particular temperature dependence of hysteresis, for relatively uniform, nano-structured solids, in the context of other state-of-the-art experimental and modeling methods including nitrogen adsorption, spectroscopy, neutron scattering, and molecular simulation. Since no single method is able to provide a complete characterization of porous materials, a combination of approaches is needed to achieve progress in understanding the fluid-solid interactions on the way to developing a predictive capability.

Keywords: *adsorption, carbon fiber, gravimetric, high-temperature, pillared clay, porous glass, water, zeolite*

Introduction

Adsorption of fluids on solid surfaces has been a subject of steadily increasing research throughout the last century, especially since simple models of fluid–solid interactions were put forward by Langmuir and later Brunauer, Emmet and Teller [1]. Besides a purely scientific interest, the adsorption research was motivated by the usefulness of adsorption in many branches of chemical industry, such as catalysis and separation processes. Adsorption is also important in gas, oil and geothermal technologies, since most rocks and soils tend to develop pore systems, often with substantial specific surface areas as a result of hydrothermal reactions and weathering. Understanding solid-fluid interactions is crucial in the field of environmental technology for pollution remediation and prevention. Possibilities for efficient reversible storage of hydrocarbons and hydrogen fuel for vehicles in the form of adsorbate under reduced pressure is being actively investigated.

The recently increasing focus on the properties of fluids in confined geometries can be attributed to the progress of the technologies used for fabrication of new engineered porous materials with consistent pore systems properties, such as synthetic zeolites, pillared clays, aerogels, carbon nanotubes, controlled-pore glasses, activated carbon fibers, and nanoparticles. Also significant are simultaneous advances in the methods used for characterization of porous solids, such as atomic-scale resolution microscopy, X-ray and neutron scattering, and molecular-level, computational approaches to simulation and theoretical description of confined systems. Advanced porous adsorbents have been the subject of a multidisciplinary project at Oak Ridge National Laboratory investigating fluids in confined geometries using a number of experimental and computational approaches.

The capacity of a porous solid for fluid adsorption depends on pore system geometry including total internal surface area, pore size distribution, pore shapes, and pore connectivity, and on the chemical properties defining the character of solid-fluid and fluid-fluid interactions. Although there is no universal model of the behavior of fluids in a close proximity to solid surface, a variety of contributing phenomena have been described in the literature. The mechanisms invoked most often include chemical adsorption, multi-layer adsorption, cooperative pore filling, capillary condensation, phase transitions, molecular ordering in the adsorbate, and heterogeneity of the solid surface if active centers are present. Due to the lack of accurate characterization of pore system geometries and the diversity and complexity of fluid–solid interactions, even for the most uniform adsorbents and simple fluids, prediction of adsorption behavior is difficult.

Most adsorption measurements available in the literature were made at one temperature, usually am-

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bient, or at cryogenic temperatures corresponding to the boiling point of nitrogen or noble gases. Temperature-dependent data are scarce. Measurements of water adsorption are an important complement to inert gas results, but they are more difficult, and commercial instruments that can be operated over wide temperature ranges are only beginning to appear [2]. In this work we describe an exploration of water adsorption/desorption behavior of several classes of porous materials at temperatures between 105 and 250°C using an accurate gravimetric method. Analysis of adsorption results in a range of temperatures is expected to allow for differentiation between some adsorption mechanisms (e.g. capillary condensation *vs*. multilayer adsorption) and investigation of the 'hysteresis phase diagram' for the confined fluid.

Experimental

Three basic experimental approaches have been used for a vast majority of adsorption measurements: the static volumetric method, the dynamic (gas flow) method, and the static gravimetric method. By far the most popular method for obtaining adsorption isotherms is the static volumetric method, where the amounts of the adsorbate are determined from pressure drops measured in a calibrated cell holding the sample. This method is most often used for determination of BET surface areas using nitrogen, argon, xenon, and other gases, at temperatures close to their boiling points, but in principle other adsorbates, such as water or carbon dioxide can be used in modified equipment. While the operation of these instruments is often fully automated, and the results can be obtained rapidly [3], they are not easily adapted for measurements over a range of temperatures at pressures exceeding atmospheric. One of the most serious problems is maintaining the valves and connections leak-free. Degassing of the samples during temperature changes can not be monitored. Similar limitations, apply to the fast, but less accurate, dynamic method.

The static gravimetric approach, although not easy to implement, is simple in principle, universal, and accurate. It allows for investigation of slow processes over a wide range of temperatures. The ORNL isopiestic apparatus with in situ weighing, described in detail previously [4, 5], was designed for measurements of vapor pressure as a function of molality for aqueous solutions of nonvolatile electrolytes at temperatures to 250°C. The relative (isopiestic) method [6] using standard solutions, and the direct method [7], using precise Digiquartz® gauges (Paroscientific Inc.) were used. The apparatus was also adapted for measurements of adsorption on porous solids. Adsorption isotherms were determined for rock samples taken from geothermal reservoirs (the Geysers, California, USA [5], and Awibengkok, Indonesia). The method was proven to be reliable and useful for porous solids with specific surface areas as small as 1 $m^3 g^{-1}$.

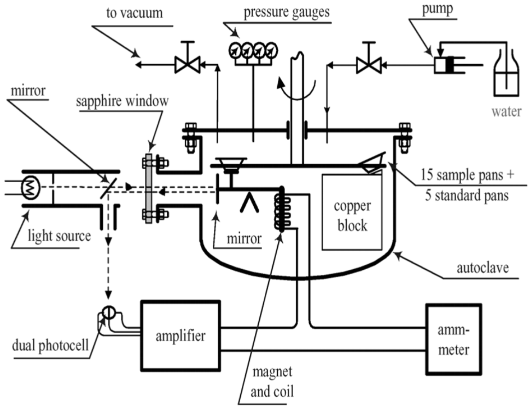

Fig 1. Schematic of the ORNL isopiestic apparatus with internal weighing

The apparatus, shown in Fig. 1, allows for monitoring the mass of 15 samples (usually 3 to 15 g) simultaneously with the accuracy better than 1 mg. Isotherms of adsorption and desorption were obtained by changing the vapor pressure inside the autoclave stepwise as water was injected or withdrawn, so that the vapor pressure increased from vacuum to the saturation pressure at each temperature, and then returned back to vacuum. The samples, placed in titanium dishes fitting in a circular sample holder were placed in turn on the pan of the internal electromagnetic balance. The position of the balance beam was maintained automatically using a light source, a platinum mirror, and photoresistors. The relationship between mass and electric current was nearly linear. Mass standards, placed in the sample holder between the samples, were used for calibration. Buoyancy corrections were applied using steam densities and solid matrix densities. Changes of sample masses in vacuum were monitored at each temperature in order to detect chemical adsorption or chemical reactions resulting in volatile products.

The samples included:

- sol-gel controlled-pore glass with nominal pore diameters given as (2.5, 5.0, 7.5, and 20.0) nm by the manufacturer (Geltech), and Vycor 7930 porous glass (pore width 35 nm);
- four activated carbon fiber monolith samples and a granular activated carbon sample fabricated at ORNL with varying burn-off ratios (33% to 49%) and bulk densities (1.11 to 1.67 g cm^{-3});
- natural zeolites clinoptilolite and mordenite, including samples exchanged with Na and K;
- aluminum-pillared montmorillonite clay (Fluka/Sigma Aldrich).

Results and discussion

Adsorption equilibrium in a range of temperatures can be most directly expressed in function of water activity *a* defined as the ratio of water fugacities over the system under investigation and over pure, bulk liquid at the same temperature, f/f_0. In this work, all results are presented and discussed in terms of relative pressure p/p_0, synonymous with relative humidity RH (usually expressed as a percentage), where p_0 is the vapor pressure of pure water. The difference between relative pressure and activity increases with pressure, as steam increasingly deviates from ideal gas behavior, and may become noticeable for sections of high temperature isotherms close to saturation.

Each of the above four groups of porous materials represents different water adsorption behavior. The isotherms for both porous glasses and activated carbons show rapid filling of the predominant pores in a narrow pressure range, while adsorption at other pressures contributes relatively little to the total capacity. For the porous glass the relative pressure where the isotherm slope was the steepest was close to p/p_0=0.9, even for the sample with the finest, 2.5 nm, pores. For the carbons, the relative pressure where pore filling occurs was much lower, $0.55<p/p_0<0.65$.

While low-pressure slopes, which reflect fluid-solid affinity, were steeper for the porous glasses than for the carbons, there was no distinct knee corresponding to the completion of the monolayer. The isotherms for both porous glasses and carbons were of type V in the classification adopted by IUPAC [8], with type H1 hysteresis loops, characterized by hydrophobic adsorption at low pressures, a narrow hysteresis loop, and a flat section close to saturation. Water content at p/p_0=1 (total pore volume) was well defined, indicating no large-pore tail in pore size distribution, as should be expected for uniform pore systems. Low water uptake at low pressures indicated that the surfaces of silica and fibrous carbon were relatively pure, with relatively few polar groups able to promote the adsorption of water. At the opposite end, water adsorption isotherms for the zeolites were of type I, with the steepest slope near p/p_0=0, and a nearly flat plateau at higher pressure, indicating hydrophilic surface and microporosity. Finally, the isotherms for the pillared clay were of type IV with a type H3 hysteresis loop, usually associated with slit-shaped pores. The most interesting results for each of the four groups of adsorbents are described below.

Porous glass

The most noticeable feature of water adsorption on porous glass samples was 'negative hysteresis', characterized by desorption branches falling below the adsorption branches. This behavior is interpreted as evidence of partial destruction of the structure by dissolution of silica. Since the total volume of the pores remained unchanged, and the two samples with the widest pores (the Geltech sample with the widest pores, and Vycor 7930) did not show 'negative hysteresis', apparently only the finest pores with little volume, but a major contribution to the specific surface area, were affected. Nearly all dissolution probably took place at the lowest temperature, 105°C, so that the next isotherm at 150°C showed nearly no hysteresis. However, due to the increasing solubility of silica with increasing temperature, the reduction of the specific surface area continued at higher temperature, as indicated by a decrease in low-pressure adsorption at 200°C. The isotherms of nitrogen adsorption measured by Robens *et al.* [9] on samples of controlled pore glass were similar to the water adsorption isotherms obtained in this work. This is caused by the purity of glass surface and the weakness of interactions between glass and water.

Activated carbons

The five activated carbon samples were of two types. Four samples were carbon fiber monoliths fabricated at Oak Ridge National Laboratory from an isotropic pitch derived carbon fiber (Ashland Petroleum) and a powdered phenolic resin (Occidental Chemicals). The fibers and resin were combined in water at a mass ratio of four parts fiber and one part resin to form dilute slurry. Water slurry was molded, pressed, and dried for 24 h at 60°C in a process somewhat similar to papermaking. In the next step the resin was allowed to cure as the billets were either heated to 120 to 130°C for a further 24 h, or hot pressed at 300°C to markedly increase their density. The billets were carbonized in nitrogen atmosphere at 650°C (four hours at the final temperature). In the final step the carbon was activated at 850°C in a CO_2 atmosphere until the desired burn-off (mass loss) was attained.

The samples obtained in this process are called 'monolithic' because the carbon matrix is strongly interconnected and for this reason exhibits high thermal conductivity. The additional sample used in this work was a granular, non fibrous, activated carbon. The features of adsorption isotherms were found to correlate with the methods of preparation of the samples. The low pressure slopes of the adsorption isotherms, sensitive to the presence of small amounts of hydrophilic impurities, decreased with increasing burn-off ratio for the fibrous-carbon samples. In the case of the granular carbon sample, low-pressure adsorption was much higher, indicating the least hydrophobic, most heterogeneous surface. In this case the shape of the adsorption isotherm was closer to type IV than V. Since the interaction between pure carbon surface and water is known to be strongly hydrophobic, there is little doubt that these differences are caused by adsorbed surface groups and atoms that promote initial adsorption of water clusters. Oxidation of the surface is an important factor significantly influencing adsorption of polar, hydrogen-bonded molecules [1, 10] However, elemental analysis has shown that the oxygen/carbon and hydrogen/carbon ratios (below 2 and 13%, respectively) were not well correlated with the burn-off ratio. The sensitivity of adsorption to unknown surface heterogeneities makes it difficult to compare experimental results with molecular simulation assuming pure carbon surface and uniformity of the pores [11].

The samples with higher degree of burn-off showed higher total adsorption capacities (total pore volume) and higher pore–filling pressures, as expected. The hysteresis loops of the two samples with less burn-off (the finest pores) were very narrow at 105 and disappeared at 150°C. The remaining samples had somewhat wider loops at 105°C, which were still noticeable at 150°C. Adsorption/desorption isotherms at 105 and 150°C for an activated carbon fiber sample with a high (49%) burn-off ratio are shown in Fig. 2. The 200°C isotherm, not shown in Fig. 2, was very close to the 150°C adsorption isotherm (continuous line). Temperature dependence was greater on the desorption branches than on the adsorption branches. This is consistent with the results of water adsorption on geothermal reservoir rocks [5], which showed clearly that the temperature dependence of physical adsorption isotherms is useful for determining the contribution of the capillary condensation mechanism (characterized by curved liquid-gas interfaces) to the total water adsorption capacity. Very narrow hysteresis loops occurring at low pressure, and little change with temperature indicate that at elevated temperature the water adsorption mechanism in these materials is far removed from the well known model of capillary condensation in mesoporous materials.

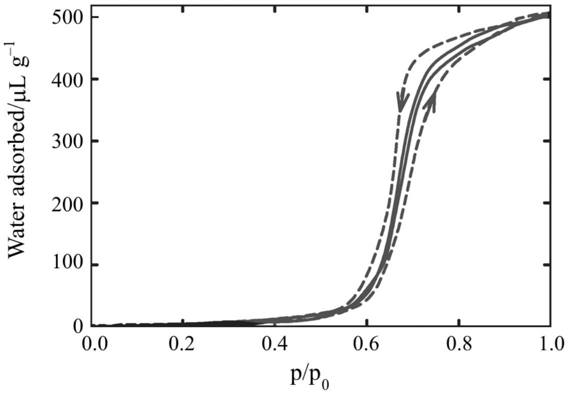

Fig 2 Volumetric water adsorption and desorption isotherms at - - - – 105 °C and —– 150 °C for an activated carbon fiber monolith sample with 49% burn-off ratio

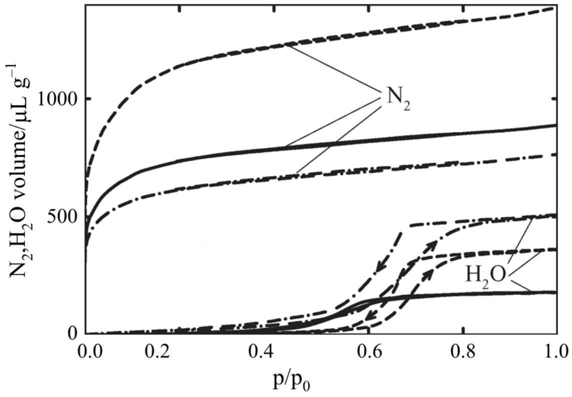

Fig 3. Volumetric water and nitrogen adsorption and desorption isotherms at 105°C for three activated carbon samples: carbon fiber monolith with —– 35% burn-off, with - - - – 49% burn-off, and - · - · – non-fibrous granular carbon. The higher curves are for nitrogen

In contrast to water adsorption, isotherms of nitrogen adsorption on activated carbon samples are of type I, with only a small slope at relative pressure greater than 0.2. Such isotherms are usually associated with microporous materials and liquid-solid interactions that are stronger than fluid–fluid interactions, as is also the case for water on zeolites. As shown in Fig. 3, water adsorption isotherms are not only of different shape, but they also show significantly smaller total pore volume. The smaller accessible pore volume for water, clearly due to the energy of dipole–dipole interactions and hydrogen bonding, demonstrates the difference in pore structures between carbon fiber monoliths (water volume equal to 71% of nitrogen volume) and the non–fibrous activated carbon sample (water volume below 50% of nitrogen volume). The ratio of water and nitrogen volumes V_{H_2O}/V_{N_2} is the lowest (0.22) for the sample which also shows the most pronounced microporosity, as indicated by the lowest pore filling pressure range and the lowest total water adsorption capacity. Note that, as shown by the examples in Fig. 3, and also by the remaining results, water adsorption capacities can not be predicted from nitrogen adsorption capacities.

It is not likely that the difference in pore volumes shown in Fig. 3 can be explained solely on the basis of the differences in sizes and shapes of water and nitrogen molecules. Alternatively, the observations can be rationalized by assuming that the average density of the adsorbed phase is much less for water than for nitrogen. However, it seems more plausible that the finest pores are not accessible to water at all, due to the hydrogen bonding favoring the proximity of a water molecule to its neighbors in the liquid state over the proximity of solid surface. It is interesting to note that compressing the samples to higher bulk densities increased the ultimate pore volume for water adsorption, but decreased the ultimate pore volume for nitrogen. The reason for this is not clear without further research, but it should be noted that besides the increase in density, hot pressing the billets at 300°C also had an effect of increasing the degree of graphitization of the carbon.

As the temperature increases, the pressure range where pore filling occurs would be expected to shift towards lower values because of the decrease in hydrogen bonding and the dielectric constant, and at the same time tend to move towards higher values, as observed for most mesoporous materials, due to the decreasing surface tension of water. Since the two effects partially cancel, the temperature dependence of the pore-filling pressure is small.

Zeolites

Although the first systematic studies of water sorption on zeolites were carried out by Barrer *et al*. [12] more than forty years ago, measurements over a wide range of temperature are not common in the literature. Measured variations of water adsorption with temperature have been used by Carey and Bish [13] and Wilkin and Barnes [14] to obtain general thermodynamic quantities for zeolite hydration. While there is a general agreement that the water adsorbed at higher pressures is 'zeolitic water' which fills the molecular-size channels and does not contribute to the stability of the zeolite framework, in some cases dehydration of zeolites at elevated temperature leads to reversible or irreversible changes in the crystal lattice. Such changes are visible as breaks on the characterisctic curves of adsorption and can be also detected using X-ray diffraction [15] . The mechanism of water adsorption in zeolite channels at low pressure is not clear. Apparently water molecules adsorb with a range of interaction energies to a variety of locations, including sites directly on the O-atom lined framework and sites close to exchangeable cations. The localization and migration of water molecules and cations in zeolite channels in various hydration states have been investigated using X-ray diffraction and calorimetry [16, 17]. It appears that the nature of the cations present in the channels should influence the capacity for water adsorption. Indeed the results of Wilkin and Barnes suggest that hydration numbers are higher for Na-cpt than for K-cpt by about 35% at 200°C. This is in qualitative agreement with the present work which showed that for clinoptilolite the order of adsorption capacity was Na-cpt>natural cpt>K-cpt, however, with much a smaller difference. On the other hand, the present results indicate that water adsorption capacity is greater for K-mordenite than for Na-mordenite. Measuring this effect for different samples is difficult and carries a high uncertainty, due to a large influence of physical and chemical adsorption in the extremely steep low-pressure region, and consequently, possible variations in initial state of the surface for different samples.

While the initial state of the surface at different temperatures may be still difficult to compare, determination of the temperature dependence of the hydration of zeolites is more reliable, since variations between samples are eliminated. The present results exhibited only very slight, if any, influence of temperature on the hydration of the investigated zeolite samples to 250°C. This finding does not agree with the data of Wilkin and Barnes [14] who found at least 25% difference in hydration between 150 and 250°C, but it is consistent with our earlier observations, based on temperature-dependent adsorption results for various adsorbents. A marked temperature dependence can be usually seen only on the desorption branch of hysteresis loops associated with capillary condensation. The temperature effect in these cases due to capillary condensation and limited by the extent of hysteresis, since with increasing temperature the desorption branch tends to approach the adsorption branch, which is essentially independent of temperature.

As noted above, the isotherms of water adsorption on zeolites obtained in this work were of type I, similar to the isotherms of nitrogen adsorption for activated carbon samples. The isotherms for clinoptilolite featured a swing upward at high pressures, and a small hysteresis loop decreasing with temperature. Only a trace of this behavior was observed in mordenite. There is little doubt that this is due to the presence of a relatively small-capacity mesopore system, superposed over the molecular-sized zeolitic channels. While the origin of these larger pores is unknown, they are not likely to depend on sample preparation, since the present results are consistent with those of Yamanaka *et al*. [18] obtained for similar samples at 20°C.

Pillared clay

Pillared clays are obtained by intercalating large inorganic ions between the structural layers [19]. As the material is dried the pillars keep the layers separated and prevent entrapment of most adsorbates at low pressure. Interlayer sorption properties of polar-mole-

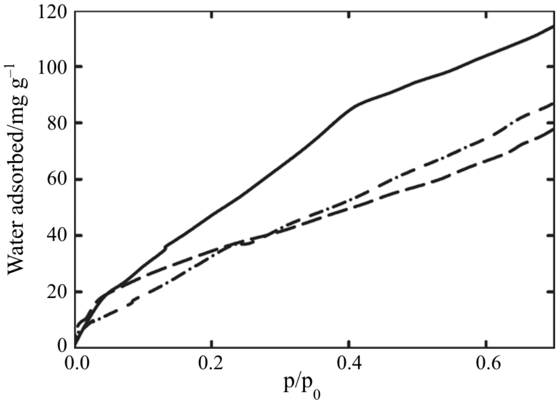

Fig 4. Water adsorption isotherms for aluminum-pillared montmorillonite at —– 105°C, - - - –150°C and - · - – 200°C

cules are modified, and possibly can be fine-tuned by a proper selection of pillaring ions. Water adsorption isotherms for the sample of aluminum-pillared montmorillonite at (105, 150 and 200)°C are shown in Fig. 4. The most interesting feature visible in Fig. 4 is the change of the shape of the isotherm at each temperature. Following the discussion by Gregg and Sing [1] of water adsorption on rutile after degassing at various temperatures, the straight-line section visible in the 105°C isotherm (continuous line) in Fig. 4 is believed to reflect adsorption on completely, or at least substantially, dehydroxylated clay surface in the initial state as supplied by the manufacturer. The second knee appearing on this isotherm at about p/p_0=0.4 corresponds to complete coverage of this surface. Additional water retention capacity is caused by subsequent physical adsorption on the first layer. Following saturation with water at 105°C, the next isotherm at 150°C has a different shape, since it represents only the physical adsorption on fully hydroxylated surface. At 200°C at least some of the surface groups are probably removed again, so that the affinity between the solid surface and water decreases. Further research is needed to fully investigate the complex sequence of surface coverage in this system.

Conclusions

We used a high-temperature gravimetric method to obtain water adsorption isotherms for a number of samples including relatively homogeneous nano-structured solids as a part of a multidisciplinary approach that is necessary to advance the understanding of confined fluids and micropore system properties. As a polar fluid with hydrogen bonding, water is a considerably more complex probing molecule than nitrogen, and it provides information about chemistry of surfaces and geometries of pore systems that are not available using simpler fluids. For many porous solids, adsorption at higher pressures, where hysteresis loops usually occur, is strongly influenced by pore system properties, while adsorption at low pressures reflects the chemistry of the surface. While it should be kept in mind that even small amount of surface groups and impurities can affect adsorption, in general, higher adsorption indicates a more hydrophilic surface. The samples investigated in this work showed significant differences in adsorption at low pressure. The features of low-pressure adsorption have nearly no relation to the varying geometries of the pore systems. For example the surfaces of carbon fiber and Vycor glass had roughly the same affinity to water. Also, the surfaces of the non-fibrous active carbon and the Geltech porous glass, composed of nearly pure silica, were equivalent as water adsorbents. The steep acceleration of adsorption occurring above p/p_0=0.3 for the fibrous carbon sample was due to the increasing penetration of water into the smallest accessible micropores.

One of the goals of this project was to obtain data necessary for construction of confined-fluid phase envelope (‘hysteresis phase diagram’) [20] analogous to the well-known vapor–liquid or liquid–liquid phase separation envelope for bulk fluid. However, extracting quantitative hysteresis data proved to be difficult for the adsorbents investigated in this work. Dissolution of silica and extremely narrow width of the hysteresis loops on the approach to the hysteresis critical temperature (Fig. 2) precluded construction of phase diagrams for porous glasses and activated carbons. However, it was possible to determine that the hysteresis critical temperatures for water in activated carbon pores are close to 150°C, and, as expected, they decrease with decreasing pore size. At present, the activated carbon fiber samples seem to be the best candidates for testing theoretical approaches, including molecular simulation [10]. The samples of carbon-fiber monoliths, fabricated at ORNL and characterized by relatively pure, homogeneous, hydrophobic carbon surfaces and a large contribution of micropores, provided an extreme example of the difference between pore system volumes for different liquids, reaching a ratio of nearly 5:1 for nitrogen and water.

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