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Distinct Dynamic Behaviors of Water Molecules in Hydrated Pores

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Received May 9, 2006; E-mail: jdmartin@iiq.csic.es

Water plays a decisive role in the transport of molecules and ions across cell membranes.[1] It either solvates the permeators and the inner surfaces of the organized pores[2] or acts as the permeant species itself, as in the aquaporin family of water pores.[3] In the latter, the narrowest pore inner diameter, 3.0 Å, is only slightly larger than the diameter of the water molecule, 2.8 Å.[4] The observation that water travels through these channels at bulk diffusion rates[5] is, therefore, still puzzling. It seems that a delicate balance of polar and nonpolar environments leading to a special arrangement of the water molecules is a prerequisite.[6]

Much of the progress achieved in our understanding of functionalized water-filled pores has come from theoretical studies.[6,7] Furthermore, numerous experimental self-assembly processes of organic and inorganic compounds induced by water have been reported.[8] In these materials, water molecules generally form well-defined clusters stabilized by H-bonding to the inner surface of the cavity created by the host.[9] However, water molecules confined in the clefts of biological macromolecules or in cavities near surfaces exposed to nonpolar moieties are presumed to be less ordered.[10] We reasoned that, in the self-assembly processes of host−guest systems, water molecules may play two different roles: either an active role in the assembly of the host structure or simply filling the voids left by the host aggregate. Knowledge of both types of water molecules is therefore important in order to understand the packing and function of water pores. We have designed, synthesized, and studied in the solid state porous organic self-assemblies suitable as models for studying such phenomena. In these models, water molecules exhibit different dynamics. Furthermore, we found that the decrease of the pore diameter induces a substantial structuring of confined water molecules.

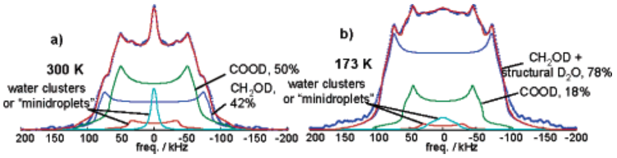

Figure 1. Superposition of static ^2H NMR spectra of **1** and simulations of individual signals at 300 and 173 K, respectively. Assignment of deuterated water, alcoholic and acidic functions, as well as relative intensity percentages are depicted. The incorporation of a structural water signal to the spectrum at low temperatures produces an increase in the alcoholic OD signal intensity.[12]

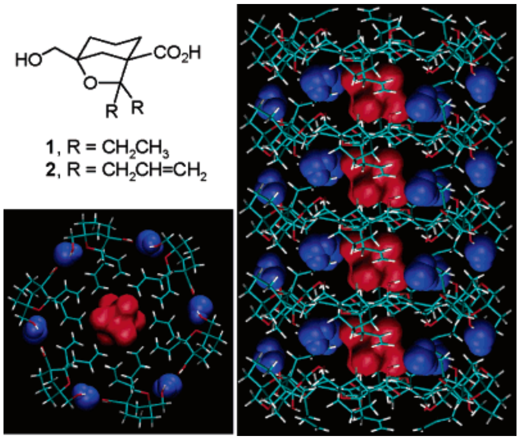

Figure 2. Crystal structure of (±)-**2**·$2H_2O$ (obtained from H_2O/CCl_4). Front and side views of the open pore. Compound **2** in capped-stick, water in space-filling representation: structural water (blue), clusters (red).

In a model of a water pore with a variable inner diameter between 5.9 and 9.4 Å, created by crystallization from H_2O/CCl_4 of the organic monomer **1**,[11] we show through TGA and DSC studies that the water/monomer ratio remains at 2/1 indefinitely, even when in contact with air. Two types of water molecules can be distinguished by static ^2H NMR (Figure 1). One type, located by X-ray diffraction at specific sites, remains at the inner surface of the pore forming part of the H-bonding pattern that maintains the whole structure.[12] A second type of water molecule forms clusters or mini droplets in the pore interior and can only be partially observed by X-ray diffraction.[11b] However, combined studies of ^1H, ^2H MAS, and static ^2H NMR show that this is a highly mobile fraction of almost liquid-like water.[13] We also show through direct evidence that these pores can be reversibly filled with water from the gas phase and that the 2/1 water/monomer ratio is the minimum essential to maintain the structure. Thus, DSC studies of a new isomorphic pore formed by monomers of homologue **2**[14] also show a 2/1 water/monomer relationship. In this new pore, X-ray crystallographic data[15] account not only for the location of the water molecules H-bonded to the pore surface but also for the clusters formed by water inside the pore, which necessarily have to experience a limitation in their diffusion rate because of the narrower diameter (Figure 2). These water molecules form discrete $(H_2O)_6$ octahedral clusters that expand preferentially to the greatest possible diameter inside the pore. X-ray results give average O−O bond distances for the cage hexamer of 2.768(4) and 2.717(6) Å at 115 and 170 K, respectively, which are close to the average neutron diffraction values of 2.751(1), 2.752(1), and 2.760(2) Å in normal ice (I_h) at 60, 123, and 223 K.[16] These findings show that the degree of structuring that

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10.1021/ja063223j CCC: $33.50

Table 1. Observed Endotherms by DSC[a]

compound	interval (K)	$\Delta H°$ (J/g)	interval (K)	$\Delta H°$ (J/g)
$(\pm)$-$\mathbf{1}\cdot2\mathrm{H_2O}$	197.1−273.0	5.4	273.0−292.2	0.5
$(\pm)$-$\mathbf{2}\cdot2\mathrm{H_2O}$	196.8−226.1	2.6	257.7−286.1	1.6

[a] Temperature intervals and changes in enthalpy found when heating (rate of 10 K/min) previously cooled samples of $\mathbf{1}\cdot2\mathrm{H_2O}$ and $\mathbf{2}\cdot2\mathrm{H_2O}$ (cooling rate of 5 K/min).

can be imposed on confined water by nonpolar surroundings, or vice versa, is determined by the width of the pore. Furthermore, these results provide compelling evidence that the cage-like cluster formed by six water molecules is sufficiently hydrophobic to be stably adsorbed in such an environment. Most likely, this is because the cage structure maximizes the formation of hydrogen bonds within the cluster while interactions with the surrounding environment are ignored.

The water transport mechanism would thus involve water molecules hopping between voids until a thermodynamically favorable location is found. The water dynamics as a function of temperature were also studied by DSC. A common behavior for freshly prepared samples of $\mathbf{1}\cdot2\mathrm{H_2O}$ and $\mathbf{2}\cdot2\mathrm{H_2O}$ was found, where both position and shape of the observed peaks of repeated cooling/heating cycles are extremely reproducible. Two broad endotherms were distinguished when heating the samples, with the temperature intervals and enthalpy variations being dependent on each previous cooling rate (Table 1). The higher temperature curve was identified with freezing/melting properties of the confined water.[17] In agreement with the solid-state ^{2}H dynamics (Figure 1), the lower temperature curve was associated with arrangements of the dynamically disordered water H-bonded to the pore surface.

In summary, two types of water molecules moving with different dynamics are observed, and hence their effects can be analyzed separately. The water covering the surface of the pore remains H-bonded most of the time, preventing pore collapse. The water making up the clusters distributed along the pore produces a water-wetting path that renders the observed permeability and causes the water to reversibly fill the pore, depending on the exterior water vapor pressure. Both types of water are in slow equilibrium. Thus, when deuterated water is used in the gas phase, deuterium is slowly and reversibly incorporated into all mobile protons of the pore structure.

From this present work and future research on water clusters in other pores from this family, we ultimately hope to extract quantitative descriptions of the many-body interactions which are responsible for the complexity of water behavior and for the function of aquaporins and related natural pores.

Acknowledgment. This research was supported by the Spanish Ministry of Science and Education (Grant CTQ2004-01674/BQU), the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt. N.P.H. and M.F. thank the Spanish Ministry of Science and Education for Research Fellowships. This research was supported in part by an EU Marie Curie Fellowship (N.P.H., HPMT-CT-2000-00127).

Supporting Information Available: Crystallographic information file (CIF) and analytical data for compound **2**; experimental procedures for ^{1}H, ^{2}H MAS, and static NMR spectra of **1** at different temperatures; TGA and DSC data for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA063223J