

## Affinity Transformation from Hydrophilicity to Hydrophobicity of Water Molecules on the Basis of Adsorption of Water in Graphitic Nanopores

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**Abstract:** The interaction of water with hydrophobic surfaces is quite important in a variety of chemical and biochemical phenomena. The coexistence of water and oil can be realized by introduction of surfactants. In the case of water vapor adsorption on graphitic nanopores, plenty of water can be adsorbed in graphitic nanopores without surfactants, although the graphitic surface is not hydrophilic. Why are water molecules adsorbed in hydrophobic nanopores remarkably? This work can give an explicit insight to water adsorption in hydrophobic graphite nanopores using experimental and theoretical approaches. Water molecules are associated with each other to form the cluster of 1 nm in size, leading to a significant stabilization of the cluster in the graphitic nanopores. This mechanism can be widely applied to interfacial phenomena relating to coexistence of water and nanostructural materials of hydrophobicity.

Carbon nanotubes, in particular, single wall carbon nanotubes (SWNT) have promising potential for applications in sensor technology, electronic devices, energy storage, and medical technology.<sup>1–4</sup> The affinity of SWNT to water is particularly significant for potential applications.<sup>5</sup> As the purity of SWNT is insufficient to obtain reliable data on the interaction of water with SWNT, only molecular dynamics and molecular simulation have been applied to the interfacial subject of SWNT and water.<sup>6,7</sup> Graphite nanopores are expected to show interfacial properties for water, which is similar to carbon nanotubes (CNT). Therefore, reconsideration of the water-graphite system is required in order to understand the water-CNT system. A typical example is water adsorption in graphite nanopores, which can be referred to for water adsorption on CNT. In the case of slit-shaped graphite nanopores, microporous carbon of high purity offers reliable experimental data even on its water adsorption. Water adsorption in graphite slit nanopores can be simulated using interaction potential models.<sup>8–10</sup> Thus, water adsorption on graphite nanopores can be studied by both experimental and molecular simulation techniques, the results of which are applicable to understanding the water–SWNT interaction. In the case of water adsorption on nanoporous carbon, there is the well-known hysteresis subject, which has

been challenged by many scientists. For example, McBain attempted to understand it 70 years ago.<sup>11</sup> Dubinin proposed the growth of water clusters on the oxidized sites using phenomenological theory.<sup>12</sup> However, previous nanoporous carbons had many oxidized sites, missing the most important point that even quite pure nanoporous carbon shows almost vertical adsorption of water near medium relative pressure, accompanied with an explicit hysteresis. This point cannot be understood by the widely spread model of the cluster growth on oxidized sites.<sup>13</sup> These authors showed that nanoporous carbon almost free of surface oxygen by H<sub>2</sub> treatment has a vertical adsorption uptake with the hysteresis. In addition, the evidence of the cluster formation and their growth of water molecules was shown by in situ small-angle X-ray scattering.<sup>14</sup> Recently, single wall carbon nanohorn (SWNH) assemblies, being materials analogous to SWNT, which were prepared by Iijima et al. without any metallic catalysts, have been shown to adsorb water molecules with an adsorption hysteresis.<sup>15,16</sup> Kaneko et al. showed the possibility of affinity change of water molecules through cluster formation to explain experimental results.<sup>17,18</sup> This article describes that a considerably large cluster of water molecules interacts strongly with a graphite nanopore

- (1) Zhou, G.; Kawazoe, Y. *Chem. Phys. Lett.* **2001**, *350*, 386.
- (2) Frackowiak, E.; Béguin, F. *Carbon* **2002**, *40*, 1775.
- (3) Saito, Y.; Uemura, S. *Carbon* **2000**, *38*, 169.
- (4) Gevorgian, L. A.; Ispirian, K. A.; Ispirian, R. K. *Nucl. Instrum. Math. Phys. Res. B* **1998**, *145*, 155.
- (5) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188.
- (6) Koga, K.; Gao, G. T.; Tanaka, H.; Zeng, X. C. *Nature* **2001**, *412*, 802.
- (7) Walther, J. H.; Jaffe, R.; Halicioğlu, T.; Koumoutsakos, P. *J. Phys. Chem. B* **2001**, *105*, 9980.
- (8) Feller, D.; Jordan, K. D. *J. Phys. Chem. A* **2000**, *104*, 9971.
- (9) McCallum, C. L.; Bandoz, T. J.; McGrother, S. C.; Müller, E. A.; Gubbins, K. E. *Langmuir* **1999**, *15*, 533.
- (10) Gordillo, M. C.; Martí, J. J. *Chem. Phys.* **2002**, *117*, 3425.

- (11) McBain, J. W.; Porter, J. L.; Sessions, R. F. *J. Am. Chem. Soc.* **1933**, *55*, 2294.
- (12) Do, D. D.; Do, H. D. *Carbon* **2000**, *38*, 767.
- (13) Mowla, D.; Do, D. D.; Kaneko, K. *Chem. Phys. Carbon* **2003**, *28*, 229.
- (14) Iiyama, T.; Ruike, M.; Kaneko, K. *Chem. Phys. Lett.* **2000**, *331*, 359.
- (15) Iijima, S.; Yudasaka, M.; Yamada, R.; Bandow, S.; Suenaga, K.; Kokai, F.; Takahashi, K. *Chem. Phys. Lett.* **1999**, *309*, 165.
- (16) Bekyarova, E.; Hanzawa, Y.; Kaneko, K.; Silvestre-Albero, J.; Sepulveda-Escribano, A.; Rodriguez-Reinoso, F.; Kasuya, D.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2002**, *366*, 463.
- (17) Iiyama, T.; Ruike, M.; Kaneko, K. *Chem. Phys. Lett.* **2001**, *331*, 359–364.
- (18) Iiyama, T.; Nishikawa, K.; Otowa, T.; Kaneko, K. *J. Phys. Chem.* **1995**, *99*, 10075–10076.

by the interaction potential calculation using the advanced potential function. This stabilization of its water cluster in the graphite nanopore indicates that the clusterization transforms the chemical affinity of water molecules from hydrophilicity to hydrophobicity. This cluster-associated hydrophilicity to hydrophobicity transformation is helpful in understanding a variety of functions of water molecules in the life activities of animals and plants.

The intermolecular interaction of water molecules was calculated using the TIP-5P model proposed by Mahoney et al.<sup>19</sup> The interaction between oxygen atoms in the water molecules is given by the Lennard–Jones potential. The potential between two water molecules is calculated from Coulomb interaction and the Lennard–Jones term between the centers of the water molecules.

$$\phi_{ff}(r) = 4\epsilon_{ff} \left[ \left( \frac{\sigma_{ff}}{r} \right)^{12} - \left( \frac{\sigma_{ff}}{r} \right)^6 \right] + \sum_i \sum_{j(\neq i)} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (1)$$

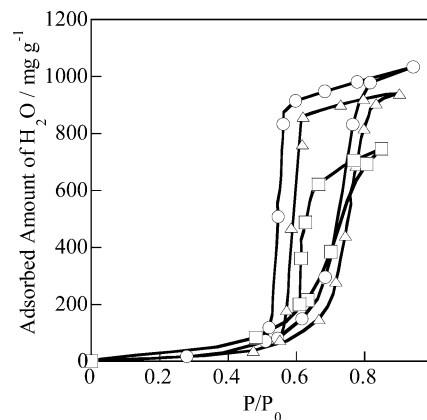
Here  $\epsilon_{ff}$  and  $\sigma_{ff}$  are the water–water potential well depth ( $\epsilon_{ff}/k_B = 80.5$  K) and the effective diameter ( $\sigma_{ff} = 0.312$  nm), respectively. The absolute value of the electric charge,  $|q|$ , of hydrogen and a lone pair of oxygen is  $3.86 \times 10^{-20}$  coulomb. The O–H and O–lone pair distances are 0.0957 and 0.0700 nm, respectively. Steele's 10–4–3 potential function was used for the interaction of a water molecule with a single graphite slab.<sup>20</sup>

$$\phi_{sf}(z) = A \left[ \frac{2}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta_C(z + 0.61\Delta_C)^3} \right] \quad (2)$$

where  $A$  is  $2\pi\sigma_{sf}^2\epsilon_{sf}\rho\Delta_C$  and  $z$  is the vertical distance of the molecule from the graphite surface.  $\rho$  is the carbon atomic number density, and  $\Delta_C$  is the interlayer distance of the graphite.  $\epsilon_{sf}$  and  $\sigma_{sf}$  are fitted parameters of the H<sub>2</sub>O–carbon potential depth and effective diameter, respectively, which were obtained using the Lorentz–Berthelot rules. This is because the carbon wall is presumed not to induce charge separation on adsorption of water. However, we assume the presence of water clusters in the graphite slit pore. Consequently, the interaction of a water cluster of different structure to the graphite slit pore was calculated. Here, the most stable conformation of each cluster in the slit pore geometry was obtained in advance. Then, the interaction potential profile of the cluster in the pore was determined by summation of the interaction between the pore walls and a molecule in the cluster. The water adsorption isotherm was simulated using grand canonical Monte Carlo (GCMC) simulation. In the potential calculation, the physical pore width,  $H$ , is expressed by the distance between atomic positions of both surfaces, which differs from the experimental pore width,  $w$ .<sup>21</sup>  $H$  and  $w$  are related to each other through eq 3.

$$w = H - (2z_0 - \sigma_{ff}), z_0 = 0.856\sigma_{sf} \quad (3)$$

The isosteric heat of water adsorption,  $q_{st}$ , was calculated using eq 4.



**Figure 1.** Adsorption isotherms of H<sub>2</sub>O at different temperatures: (○) 293 K, (△) 303 K, and (□) 328 K.

$$q_{st} = N_A \left( \langle \phi_{ff} \rangle + \phi_{\text{pore}} + \frac{9}{2} k_B T \right) / \text{kJ mol}^{-1} \quad (4)$$

Here,  $\phi_{ff}$  and  $N_A$  are averaged for different configurations and Avogadro's number, respectively. We assume on the basis of in situ X-ray diffraction study that all motional freedoms of a water molecule are lost on adsorption in the nanopore.<sup>22,23</sup>

Pitch-based activated carbon fiber (ACF), which consists of nanographitic units, was used for water adsorption after pre-evacuation at 383 K. The specific surface area, nanopore volume, and pore width,  $w$ , from N<sub>2</sub> adsorption at 77 K are 1650 m<sup>2</sup> g<sup>-1</sup>, 0.91 mL g<sup>-1</sup>, and 1.1 nm, respectively. The water adsorption isotherm of ACF was measured over the temperature range of 293 K to 333 K by every 10 K.

Figure 1 shows adsorption isotherms of water on ACF at 293, 303, and 328 K. The isotherms at other temperatures are not shown for clear illustration. The vertical adsorption begins at  $P/P_0 = 0.74$  irrespective of the measuring temperature. On the course of desorption, the amount of adsorption decreases almost vertically at  $P/P_0 = 0.57 \pm 0.01$  below 315 K and  $P/P_0 = 0.64 \pm 0.03$  above 323 K. Thus, an explicit adsorption hysteresis is observed. The water adsorption isotherms at different temperatures lead to the isosteric heats of adsorption 43.2 kJ mol<sup>-1</sup> and 46.7 kJ mol<sup>-1</sup> from the adsorption and desorption branches. Figure 2 shows the interaction potential profile of the cluster with the carbon nanopore. Clusters of high symmetry were used as model clusters for calculation of the interaction. A single water molecule interacts very weakly with the graphite slit pore, as shown in Figure 2. However, the greater the cluster size, the deeper the potential depth. That is, once water molecules are associated to form a tetramer or a larger cluster, the cluster is remarkably stabilized in the nanopore to gain a marked hydrophobicity. According to the snapshot of GCMC simulation, many clusters are observed above the rising relative pressure; some clusters have a structure similar to ice I, as shown in Figure 3. In nanopores, the cluster formation is enhanced, leading to the stable adsorbed structure of water molecules. Thus, the cluster formation varies the affinity of water from hydrophilicity to hydrophobicity.

Figure 4 shows the interaction potential profile change of water molecules as a function of the clusterization. This cluster-

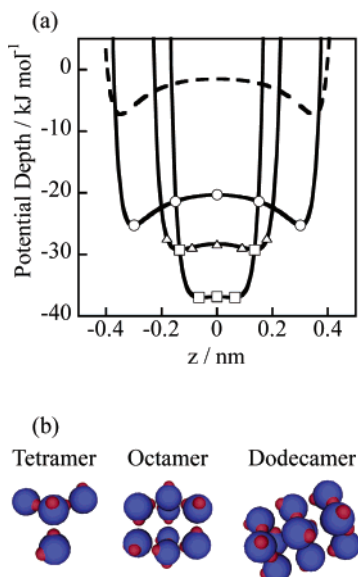
(19) Mahoney, M. W.; Jorgensen, W. L. *J. Chem. Phys.* **2000**, *112*, 8910.

(20) Steele, W. A. *Surf. Sci.* **1973**, *36*, 317.

(21) Kaneko, K.; Cracknell, R. F.; Nicholson, D. *Langmuir* **1994**, *10*, 4606.

(22) Iiyama, T.; Nishikawa, K.; Otowa, T.; Kaneko, K. *J. Phys. Chem.* **1995**, *99*, 10075.

(23) Iiyama, T.; Nishikawa, K.; Suzuki, T.; Kaneko, K. *Chem. Phys. Lett.* **1997**, *274*, 152–158.



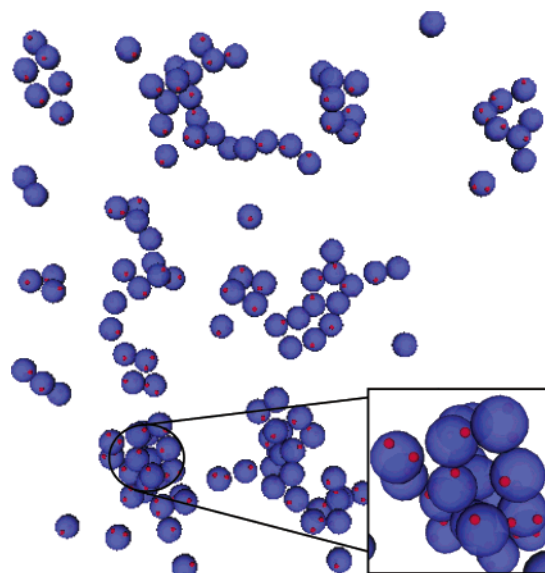
**Figure 2.** Interaction profiles of a water molecular cluster with the graphitic slit nanopore: (○) tetramer, (△) octamer, and (□) dodecamer. The dashed curve denotes the potential profile for a single water molecule (a). Here, the structures of the model clusters are shown in Figure 2 (b).

induced affinity transformation is supported by the agreement of heat of adsorption from experiment and simulation. The simulation provides the relation between  $q_{st}$  and the association number,  $N_w$ , of water molecules.

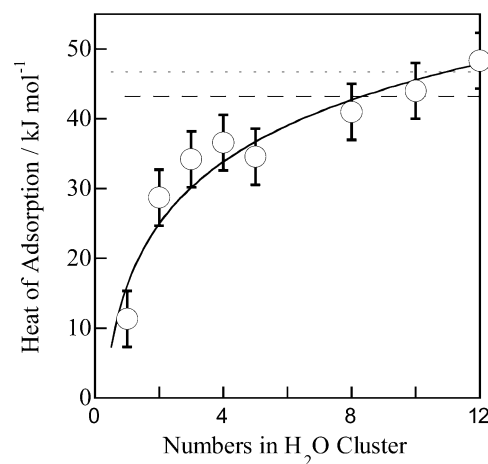
$$q_{st} = 14.0 \ln(N_w) + 12.5/\text{kJ mol}^{-1} \quad (5)$$

The experimental  $q_{st}$  value depends on adsorption and desorption courses, as mentioned above. In the way of adsorption, the experimental  $q_{st}$  (43.2 kJ mol<sup>-1</sup>) corresponds to 8–10 of the association number of water molecules. Therefore, the cluster formation of octamers to decamers is indispensable to induce a predominant adsorption of water in the graphite slit pore. As the size of octamers, nonamers, and decamers is less than 1 nm, water molecules can be adsorbed in the carbon nanopores of  $w = 1.1$  nm of ACF. The  $q_{st}$  from the desorption branch indicates the presence of undecamers in the nanopores. Accordingly, fully adsorbed water is more stabilized in the carbon nanopores due to formation of larger clusters.

Thus, the formation of water clusters of 1 nm in size induces hydrophilicity to hydrophobicity transformation, which should play an essential role in biochemical functions of animals and plants.



**Figure 3.** Snapshots of H<sub>2</sub>O molecules at  $\phi = 0.1$  in  $w = 1.1$  nm. The magnified cluster structure is shown in the inset.



**Figure 4.** Heat of adsorptions of an H<sub>2</sub>O molecule with the cluster size. Solid curve, model simulation; broken line,  $q_{st}$  in adsorption; and dashed line,  $q_{st}$  in desorption.

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