doi:10.1246/cl.2012.159

Editor's Choice

Small- and Large-angle X-ray Scattering Studies of Nanometer-order Sulfuric Acid Solution in Carbon Micropores

Ryusuke Futamura, Taku Iiyama,* Atom Hamasaki, and Sumio Ozeki
Faculty of Science, Shinshu University, Asahi, Matsumoto, Nagano 390-8621

(Received November 4, 2011; CL-111076; E-mail: tiiyama@shinshu-u.ac.jp)

The structure of nanometer-order sulfuric acid solution in carbon micropores is investigated by large- and small-angle X-ray scattering experiments. The electron radial distribution function of the nanosolution is different from that of bulk solution. The intermolecular structure of nanosolution does not change with fractional filling. These results and the dependency of density fluctuations of the system with fractional filling showed that the nanometer-order sulfuric acid solutions in carbon micropores form a small molecular assembly with a hydration structure at low fractional filling.

In recent times, the rapid progress in nanoscience and nanotechnology[1] has led to the design, development, and application of various new porous materials to many scientific and industrial fields. Furthermore, extensive investigations of the adsorbate behaviors on the surfaces as well in the pores have been ongoing over the last few decades.[2,3] The in situ measurements have been performed to examine the structures and behaviors of adsorbed molecules.[4–8]

Multicomponent adsorptions, for example, the adsorption of a solution in micropores, are not only of scientific interest but also extremely attractive for many industrial applications. The adsorption of nanometer-order sulfuric acid solution in micropores is important in environmental chemistry[9] and electric double-layer capacitor (EDLC) applications.[10] EDLCs are one of the most attractive next-generation energy storage devices because they have high electrical power and can be used almost indefinitely. However, a microscopic understanding of the formation of the electrical double layers in carbon micropores is required for improving the capacitance performance.[10,11] Chmiola et al.[11] and Lin et al.[12] have demonstrated the possibilities of desolvation or distortion of the solvation structures of ions in carbon micropores by electrochemical measurements. These results indicate that the solution structures in carbon micropores could be considerably different from those under bulk conditions.

Computer simulations have been employed for investigating nanometer-sized solutions[13–15] primarily because of experimental difficulties. A few experimental studies have also been conducted; for example, Kittaka et al. investigated the phase behavior of water and acetonitrile mixtures in MCM-41 by employing infrared spectra (IR),[16] while Ohkubo et al. investigated the hydration structure of metal ions in carbon micropores by extended X-ray absorption fine structure (EXAFS).[17] However, even though their results have shown the importance of understanding multicomponent states in nanometer-order spaces, such experimental approaches are rare.

X-ray scattering curves directly provide wide-ranging geometric information from intermolecular to colloidal distances; hence, they are indispensable to describe multicomponent adsorption behaviors in nanospaces. In this paper, we describe our investigations into nanosized sulfuric acid solutions in carbon micropores by employing X-ray scattering methods; we have been able to describe the intermolecular- and colloidal-order structures of the solution confined in micropores.

Table 1. Pore structure of A25 activated carbon fiber

	Pore width (w/nm)	Micropore volume (W_0/mL g^{-1})	Specific surface area (a_α/m^2 g^{-1})
A25	1.36	1.29	1970

In this paper, an activated carbon A25 (Ad'all Co., Ltd., Uji, Japan) was used as the absorbent. The micropore structure of A25 was determined by a N_2 adsorption isotherm at 77 K using a gravimetric apparatus with the α_s-plots,[18] which are listed in Table 1. The pore width of the A25 micropore (1.36 nm) corresponds to the sizes of the second hydrated shell of the sulfate ions under the bulk condition.

The sample was ground and preheated at 393 K and 1 mPa for 3 h before the adsorption isotherm measurements. Sulfuric acid (96 wt %, Kanto Chemical Co., Inc., Tokyo, Japan) was mixed with milli-Q water (Nihon Millipore K. K., Tokyo, Japan), and a 10 wt % solution was prepared. The solution was used as the adsorbate without additional treatment. The A25 sample was mixed well with 10 wt % sulfuric acid, and the mixture sample was kept in hermetically closed condition at 298 K for 2 days without stirring. We confirmed that XRD data does not change after 10 days storage (at $\phi = 0.5$). The weight of dried A25 is 100 mg, and the weights of sulfuric acid solution are 26.9 and 119 mg for fractional filling $\phi = 0.2$ and 0.9 samples, respectively. The ϕ was determined by using of micropore volume W_0 and bulk density of sulfuric acid solution ($\rho = 1.07\,\mathrm{g\,mL^{-1}}$). Large-angle X-ray scattering (Mo Kα, 40 kV, 100 mA) and small-angle X-ray scattering (SAXS) (Cu Kα, 40 kV, 30 mA) measurements were performed by transmission using angle-dispersion diffractometers (AFC5R and Ultima III, Rigaku Co., Tokyo, Japan) at 298 K. The sample was packed into a 2-mm-thick slit-shaped cell with PET polymer film (Lumirror; Toray Industries, Inc. $t = 4.5\,\mu\mathrm{m}$) windows. The bulk liquid solution was also measured using the same sample cell.

Figure 1 shows the results of the X-ray diffraction (XRD) profiles of 10 wt % H_2SO_4 in A25 when ϕ is 0.2 and 0.9. The XRD profiles of water in A25 when ϕ is 0.9 and 10 wt % H_2SO_4 under the bulk condition are also shown. In the case of the bulk solution, we observed one peak and two shoulders at $2\theta = 13$, 20, and 32°; they are derived from the intermolecular structures of solution. Although the shape of the X-ray scattering curve of the confined solution resembles that of the bulk, detailed observations reveal differences, for example, in the peak positions. These differences remained even after the scattering

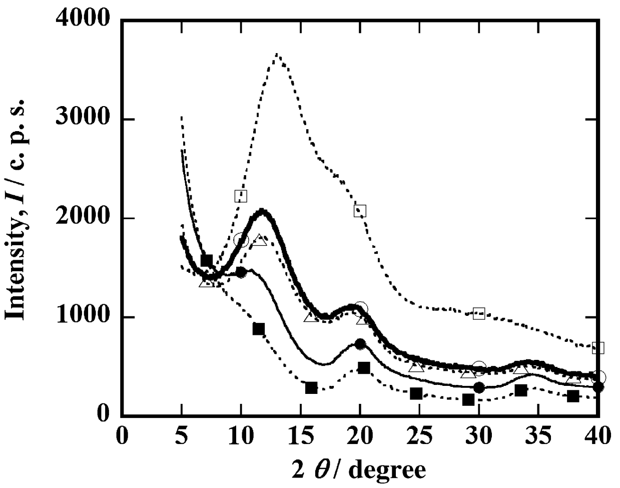

Figure 1. Changes of XRD profiles of 10 wt % H_2SO_4 solution adsorbed A25 at 298 K. ■: A25 in vacuum, ● (thin): H_2SO_4 adsorbed by $\phi = 0.2$, ○ (bold): by $\phi = 0.9$, △: confined water by $\phi = 0.9$, and □: bulk H_2SO_4 solution.

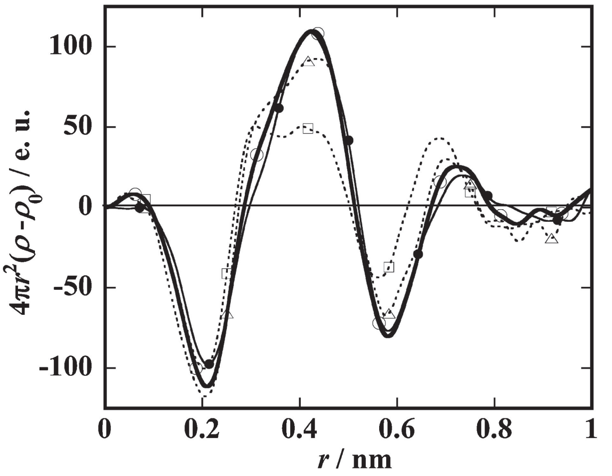

Figure 2. Electron radial distribution functions of confined 10 wt % H_2SO_4 solution. ● (thin): by $\phi = 0.2$, ○ (bold): by $\phi = 0.9$, △: confined water by $\phi = 0.9$, and □: bulk 10 wt % H_2SO_4 solution.

from A25 was subtracted (see Supporting Information; SI, Figure S1[27]).

These structural differences can be interpreted by the electron radial distribution function (ERDF) that can be obtained from the Fourier transformation of the X-ray scattering curves. The ERDFs of 10 wt % H_2SO_4 under the bulk condition and in A25 when $\phi = 0.2$ and 0.9 are shown in Figure 2. Figure 2 also shows the ERDFs of confined water. Details of the derivation of ERDFs are provided in our previous work,[19] and the schematic procedure is described in the Supporting Information. The ERDFs of bulk water and confined water exhibit three peaks and shoulder at 0.3, 0.45, and 0.7 nm, which can be attributed to the first, second, and third nearest-neighbor water molecules, respectively.[8,20,21] We have shown that the water confined in carbon micropores has the highest peak of the 2nd nearest neighbor.[8,20] Caminiti et al. have previously demonstrated detailed analyses of the 2 M sulfuric acid solution under the bulk condition,[22] and they concluded that the hydration radii of the sulfate ions is 0.367 nm. Hence, the ERDF peaks at 0.31 and 0.41 nm for the bulk solution (Figure 2) can be derived from the hydration structures of the ions as well as the intermolecular structure of the water molecules.

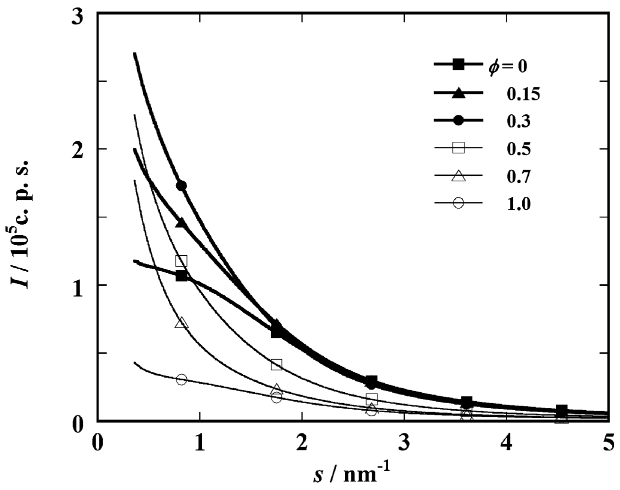

Figure 3. Corrected SAXS profiles of 10 wt % H_2SO_4 adsorbed A25 by ■: $\phi = 0$, ▲: 0.15, ●: 0.3, □: 0.5, △: 0.7, and ○: 1.0.

The ERDFs of confined solution have a highest peak at 0.42 nm and shoulder at 0.3 nm. It is completely different from the bulk solution. This suggests that the intermolecular structure of water molecules in the carbon micropore has a more ordered structure than that under the bulk condition not only for the confined water[10] but also for the confined solution. The difference in the peak intensities at 0.42 nm between the confined solution and water is a result of the hydration structures of sulfate ions. The sulfate ions form hydration structures even in narrow hydrophobic spaces. Moreover, the intermolecular structure of water in carbon micropores strongly affects the hydration structures of sulfate ions. Ohkubo et al.[17] and Ohba et al.[13] have employed experiment and computer simulations respectively and showed that the hydration structures of several ions were affected by confinements in the molecular-dimension micropores. It is interesting that the ERDFs of the confined solution at $\phi = 0.2$ and 0.9 have almost identical shapes; the sulfate ions form a hydration structure with water molecules in the micropore even when the fractional filling is low. The sulfuric acid solution is adsorbed in the form of cluster-like molecular assemblies in the micropore and not as a monolayer on the surface.

The size of the solution cluster in the carbon micropore was investigated by SAXS analysis. Figure 3 shows the SAXS profiles of 10 wt % H_2SO_4 adsorbed A25 as a function of ϕ. The profiles were corrected for the X-ray absorption using the transmitted X-ray intensities.[23] The activated carbons exhibited strong X-ray scattering at the small-angle regions because of the electron density differences between the solid and vacant regions. When $s > 2\,\mathrm{nm}^{-1}$, the intensity of A25 containing solution decreases monotonously with ϕ, while at $s < 2\,\mathrm{nm}^{-1}$, it increases and then decreases. This result indicates that the zero-angle X-ray scattering intensity $I(0)$, which is directly related to

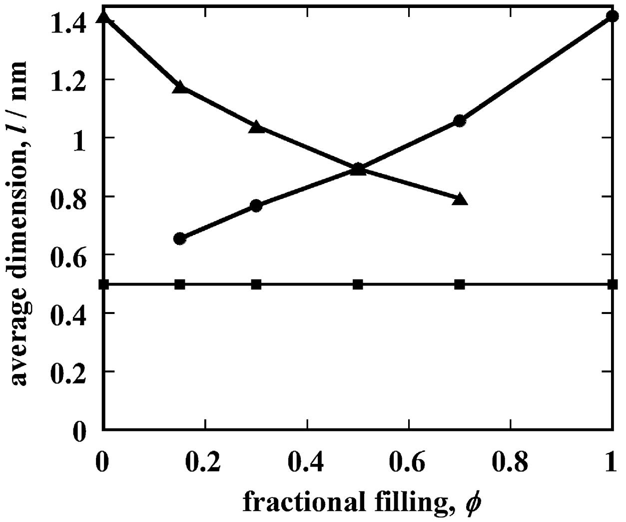

Figure 4. Changes of the average dimensions of ●: solution (adsorbed phase) l_a, ▲: vapor l_v, and ■: solid l_s on fractional filling of 10 wt % H_2SO_4.

the density fluctuations in the system,[24] increases with increasing ϕ until $\phi = 0.3$ and then decreases gradually (see SI, Figure S2[27]). Iiyama et al.[25] had reported identical tendency for $I(0)$ vs. ϕ in the case of water adsorbed on activated carbon PIT-20 ($w = 1.1$ nm); they concluded that the increase in the density fluctuations at low fractional filling is a result of the cluster formation of water molecules in carbon micropores. In our results, the cluster formation of sulfate ions with water molecules was observed in both the XRD and SAXS measurement results.

A more detailed analysis for the hydration cluster was conducted using the extended Debye–Bueche analysis.[25] Figure 4 shows the average dimensions of the adsorbed (l_a), solid (l_s), and vapor (l_v) phases as a function of ϕ. As ϕ increases, l_a increases and l_v decreases monotonously. It is noteworthy that l_a is 0.7 nm even when $\phi = 0.15$, and this is comparable to the dimensions of the sulfate ions with the first hydration shells; further, the formation of hydration clusters in hydrophobic spaces is also supported. The formation of hydration clusters in hydrophobic nanospaces can be explained in two ways: the property of water molecules in hydrophobic spaces, that is, the tendency to form clusters by hydrogen-bonding interactions and the strong interactions between water molecules and ions. The high water content region is formed around sulfate ions in carbon micropores because water prefers to be around ions rather than near hydrophobic surfaces; hence, the sulfuric acid solution forms a unique hydration cluster including hydration structures in the micropores.

It is concluded that the sulfate ions form hydration structure in micropores even at low fractional filling and that the sulfate ions and water molecules form a molecular assembly comprising a small number of molecules. The hydration structure of hydronium ion could not be described in this paper, because the X-ray scattering by hydrogen is almost negligible compared with another elements. The degree of dissociation of sulfuric acid is strongly dependent on the concentration. The investigations of higher concentration of sulfuric acid and different cation salts such as Na_2SO_4 will be discussed with reverse Monte Carlo simulation[26] which is very effective to discuss intermolecular structures of mixture in a future article. More investigations are required to elucidate the behaviors of the confined solutions in micropores, but it can be suggested that activated carbons are suitable tools for the investigation of the nanometer-sized solutions. Further, XRD and SAXS measurements are very useful techniques even for multicomponent systems in micropores, and more detailed structural information can be obtained by combining these methods.

This research was supported by a Grant-in-Aid for Young Scientists (A) (No. 19685002) of the Ministry of Education, Culture, Sports, Science and Technology, Japan and Program for Fostering Regional Innovation in Nagano, granted by MEXT, Japan.

References and Notes

1 S. Iijima, *Nature* **1991**, *354*, 56; H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
2 S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309.
3 M. M. Dubinin, *Chem. Rev.* **1960**, *60*, 235.
4 H. Omichi, T. Ueda, K. Miyakubo, T. Eguchi, *Chem. Lett.* **2007**, *36*, 256.
5 S. C. Sharma, D. Singh, Y. Li, *J. Raman Spectrosc.* **2005**, *36*, 755.
6 Y. Maniwa, H. Kataura, M. Abe, S. Suzuki, Y. Achiba, H. Kira, K. Matsuda, *J. Phys. Soc. Jpn.* **2002**, *71*, 2863.
7 T. Iiyama, K. Hagi, T. Urushibara, S. Ozeki, *Colloids Surf., A* **2009**, *347*, 133.
8 T. Iiyama, K. Nishikawa, T. Suzuki, K. Kaneko, *Chem. Phys. Lett.* **1997**, *274*, 152.
9 S. Solomon, *Rev. Geophys.* **1999**, *37*, 275.
10 L. Eliad, G. Salitra, E. Pollak, A. Soffer, D. Aurbach, *Langmuir* **2005**, *21*, 10615.
11 J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, *Science* **2006**, *313*, 1760.
12 R. Lin, P. Huang, J. Ségalini, C. Largeot, P. L. Taberna, J. Chmiola, Y. Gogotsi, P. Simon, *Electrochim. Acta* **2009**, *54*, 7025.
13 T. Ohba, N. Kojima, H. Kanoh, K. Kaneko, *J. Phys. Chem. C* **2009**, *113*, 12622.
14 L. Yang, S. Garde, *J. Chem. Phys.* **2007**, *126*, 084706.
15 S. Agnihotri, P. Kim, Y. Zheng, J. P. B. Mota, L. Yang, *Langmuir* **2008**, *24*, 5746.
16 S. Kittaka, M. Kuranishi, S. Ishimaru, O. Umahara, *J. Chem. Phys.* **2007**, *126*, 091103.
17 T. Ohkubo, T. Konishi, Y. Hattori, H. Kanoh, T. Fujikawa, K. Kaneko, *J. Am. Chem. Soc.* **2002**, *124*, 11860.
18 K. Kaneko, C. Ishii, M. Ruike, H. Kuwabara, *Carbon* **1992**, *30*, 1075.
19 T. Iiyama, K. Nishikawa, T. Suzuki, T. Otowa, M. Hijiriyama, Y. Nojima, K. Kaneko, *J. Phys. Chem. B* **1997**, *101*, 3037.
20 T. Iiyama, K. Nishikawa, T. Otowa, K. Kaneko, *J. Phys. Chem.* **1995**, *99*, 10075.
21 A. H. Narten, H. A. Levy, *J. Chem. Phys.* **1971**, *55*, 2263.
22 R. Caminiti, *Chem. Phys. Lett.* **1983**, *96*, 390.
23 T. Iiyama, M. Ruike, K. Kaneko, *Chem. Phys. Lett.* **2000**, *331*, 359.
24 P. Debye, A. M. Bueche, *J. Appl. Phys.* **1949**, *20*, 518; P. Debye, H. R. Anderson, H. Brumberger, *J. Appl. Phys.* **1957**, *28*, 679.
25 T. Iiyama, Y. Kobayashi, K. Kaneko, S. Ozeki, *Colloids Surf., A* **2004**, *241*, 207.
26 A. Tanaka, T. Iiyama, T. Ohba, S. Ozeki, K. Urita, T. Fujimori, H. Kanoh, K. Kaneko, *J. Am. Chem. Soc.* **2010**, *132*, 2112.
27 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.