

Restricted Hydration Structures of Rb and Br Ions Confined in Slit-Shaped Carbon Nanospace

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The progress in scanning probe microscopy and development of nanoporous materials have stimulated research in chemistry at the nanomolecular level. An intensive confinement of molecules or ions in nanoscale space is expected to provide new trends in chemistry. Kaneko et al. showed that such confinement in slit-shaped carbon nanospaces leads to the self-organized assembly structure of even small molecules such as N₂, O₂, and NO.¹ Water and alcohol molecules adsorbed in the slit nanospaces form highly ordered structures even at 303 K.²

Remarkable progress in nanoporous materials, after publications about carbon nanotubes³ and MCM-41,⁴ has attracted a great deal of research on both the fundamental and practical aspects of these materials. Ichikawa et al. showed that monometallic and bimetallic nanowires can be easily produced in cylindrical nanospace, especially in organic–inorganic mesopores for bimetallic nanowires.⁵ Molecular simulation studies by Miyahara and Gubbins predicted an unusual elevation of the freezing point temperature.⁶ This prediction was then supported by the evidence of the DSC experiment.⁷ Thus, nanospace has been offering new topics for research in chemistry and physics.

The chemistry of ionic solutions has contributed to a variety of fields; electrochemistry, biochemistry, catalysis, and synthetic chemistry are some examples. The predominant efforts in ionic solution chemistry are to determine precisely the hydrated structure.⁸ Recently, Fulton et al. reported the anomalous hydration structures around Rb ions in supercritical water solutions; they reported that the coordination distance between the cation and oxygen atom of water was reduced by 0.01 nm and the coordination number decreased by 40% compared with that of RbBr aqueous solution in ambient conditions.⁹ This study indicates that even the first hydration shell can vary with the local environment. The aqueous hydration structures, therefore, should be sensitive to the nanoscale structure around ions, because hydrogen-bonding interaction among water molecules depends on the molecular-scale environment. We examined a fundamental question concerning the stability of the hydrated structure of an ion in the nanospace. Although hydration stabilizes the ions in the bulk solution, it should increase the repulsive interaction with the nanospace walls.

Now, we have determined the local structures around ions in solution with the aid of the extended X-ray absorption fine structure (EXAFS). An explicit anomaly in the hydrated structure of rubidium bromide solution confined in slit-shaped carbon nanospaces of a slit-width of about 1 nm is described in this paper.

Pitch-based activated carbon fiber (ACF) (AD'ALL Co. Ltd.) was used as a nanoporous carbon having nanoscale slit-shaped

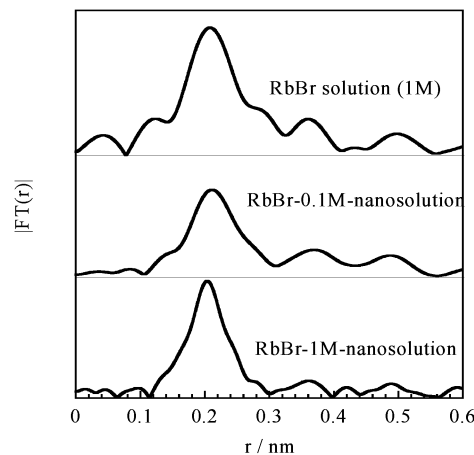


Figure 1. Rb-centered RSFs of RbBr nanosolutions and aqueous bulk solution of 1 M.

spaces. Authors have published much evidence that ACF has considerably uniform slit-shaped carbon nanospaces.¹⁰ The high-resolution N₂ adsorption isotherm of ACF at 77 K was measured, and the average width of the slit-space was evaluated to be 1.1 nm.¹¹ We used RbBr as the electrolyte, because the EXAFS technique is effective for determining the local structures around a cation or anion of a large atomic number. The electrolyte solution of 0.1 and 1 mol dm⁻³ was introduced into the slit-nanospaces and dried by evacuation at 0.1 mPa and 383 K for 2 h. Highly dispersed RbBr was evidenced by the absence of the Rb–Rb or Br–Br coordination using EXAFS in advance. After the deposition, water vapor was adsorbed to provide the corresponding solution only in the carbon nanospaces.

In this report, we denote the system of RbBr and adsorbed water in the nanospace as “nanosolution”. The RbBr nanosolution-sealed ACF created by using the 0.1 M RbBr electrolyte is denoted as RbBr-0.1 M-nanosolution.

These ACF samples were installed in an EXAFS glass cell with windows of Lumirror film (350 μm; Toray Ind. Inc.). The EXAFS measurements were performed on both Rb and Br K-edges for the deposited and nanosolution-sealed ACF samples at the National Laboratory for High Energy Accelerator Research Organization (KEK) in Tsukuba. The EXAFS spectra of the corresponding solutions were measured for comparison. The radial structure functions (RSFs) for Rb and Br were obtained from the EXAFS. In addition, the data were analyzed by an FEFF8 procedure¹² with a Fourier-filtering method.¹³

Figure 1 shows RSFs of RbBr nanosolutions of 0.1 and 1 M for the Rb center. In the figure, RSF of bulk 1 M RbBr solution is shown for comparison. The highest peak is assigned to the Rb–O

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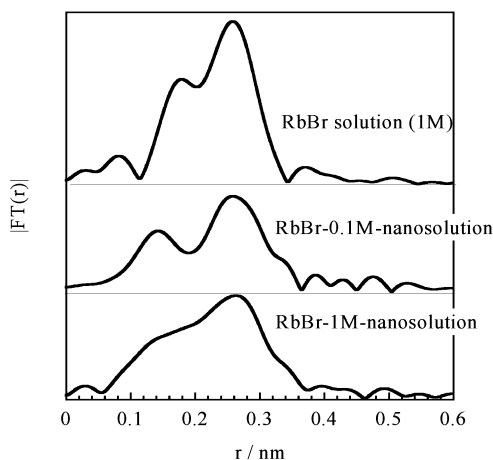
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Table 1. Structural Parameters Obtained by a Least-Squares Fit of Fourier-Filtered EXAFS Spectra

sample	RbBr-1 M-nanosolution	RbBr-0.1 M-nanosolution	RbBr solution (1 M)
$r_{\text{Rb-O}}$ (nm) ^a	0.281	0.282	0.283
$r_{\text{Br-O}}$ (nm) ^a	0.323	0.329	0.325
$N_{\text{Rb-O}}$ ^b	5.1	2.3	6
$N_{\text{Br-O}}$ ^b	2.4	1.3	6
$\sigma_{\text{Rb-O}}$ (nm) ^c	0.0070	0.0069	0.0111
$\sigma_{\text{Br-O}}$ (nm) ^c	0.0182	0.0121	0.0197

^a Distance between two atoms. ^b Coordination number. ^c DW factor. The first and second elements in the subscripts denote the central and scattering atoms, respectively.

**Figure 2.** Br-centered RSFs of RbBr nanosolutions and aqueous bulk solution of 1 M.

coordination of the nearest hydration shell. Before discussion of the detailed structure, the obtained RSFs must be analyzed with FEFF8 that will provide a reliable coordination distance, coordination number, and Debye–Waller (DW) factor. The figure shows that the Rb–O distance of the RbBr nanosolution well agrees with that of the bulk RbBr solution (0.282 ± 0.001 nm). However, the relative coordination numbers of water molecules around a Rb ion in the nanosolution are 2.3 and 5.1 for 0.1 and 1 M nanosolutions, respectively.

Here, the relative coordination number was obtained from the assumption that a Rb ion of the bulk 1 M RbBr solution is 6. Hence, the hydration number around a Rb ion in the nanospace should be less than that in the bulk solution. As the DW factor is a scale of the mean-square fluctuation in the coordination distance for a Rb shell, a small DW factor suggests the presence of an ordered structure. The DW factors are summarized in Table 1. The DW factor around a Rb ion in the nanosolution is much smaller than that in the bulk solution. Therefore, there should be an ordered structure in the nanosolution compared with the bulk solution. This should stem from the highly ordered structure of water confined in the nanospace observed by means of the preceding X-ray diffraction study.²

Figure 2 shows the Br-centered RSFs of RbBr nanosolution and the bulk solution. All samples have a main peak at 0.26 nm, which we assign to the hydration structure (Br–O). The RSFs were analyzed with FEFF8 to assign precisely the main peak and shoulder. The results are shown in Table 1. The main peak at 0.26 nm gives 0.32–0.33 nm after the FEFF8 analysis, agreeing with the literature value of the Br–O distance in bulk solution (0.29–0.34 nm).^{8,14} Consequently, the main peak can be assigned to the Br–O coordination. The hydration number around a Br ion in the nanosolution is quite small compared with that in the bulk solution,

which was 6. Also the DW factor of the nanosolution is smaller than that of the bulk solution. Accordingly, the hydration structure around a Br ion is completely unique compared with that in the bulk solution. Nevertheless, the hydration structure around a Br ion must be stabilized in the nanospace. These results also indicate that the hydrated structure of nanosolution sensitively depends on the electrolyte concentration. The lower the concentration of RbBr, the more highly an ordered structure of water molecules resulting from self-organization with a hydrogen bond will occur. This is because the coordination number of the RbBr-0.1 M-nanosolution around both Rb and Br ions was significantly reduced compared with that of RbBr-1 M-nanosolution samples. As the concentration of 1 M in the bulk solution corresponds to 1 nm of the double-layer thickness, the concentration of electrolytes in the nanosolution should affect the hydration anomaly. This concentration effect will be discussed in another article. Thus, the confinement of ionic solutions in the nanoscale space indicates the explicit anomaly of their hydration. As water molecules tend to form a highly ordered structure in the carbon nanospace, ions cannot form their hydration structure in the same way as in the bulk solution.

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Supporting Information Available: RSFs of deposited RbBr confined in ACF (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Kaneko, K.; Shimizu, K.; Suzuki, T. *J. Chem. Phys.* **1992**, *98*, 8705. (b) Kanoh, H.; Kaneko, K. *J. Phys. Chem.* **1995**, *99*, 5746. (c) Kaneko, K. *Colloid Surf.* **1996**, *109*, 319. (d) Kaneko, K. *Carbon* **2000**, *38*, 287. (e) Iiyama, T.; Ohkubo, T.; Kaneko, K. *Membr. Sci. Technol. Ser.* **2000**, *6*, 35.
- (2) (a) Iiyama, T.; Nishikawa, K.; Otowa, T.; Kaneko, K. *J. Phys. Chem.* **1995**, *99*, 10075. (b) Iiyama, T.; Nishikawa, K.; Suzuki, T.; Kaneko, K. *Chem. Phys. Lett.* **1997**, *274*, 152. (c) Ohkubo, T.; Iiyama, T.; Nishikawa, K.; Suzuki, T.; Kaneko, K. *J. Phys. Chem. B* **1999**, *103*, 1859. (d) Ohkubo, T.; Iiyama, T.; Kaneko, K. *Chem. Phys. Lett.* **1999**, *312*, 191. (e) Ohkubo, T.; Kaneko, K. *Colloid Surf. A* **2001**, *187–188*, 177. (f) Iiyama, T.; Ruike, M.; Kaneko, K. *Chem. Phys. Lett.* **2001**, *331*, 359.
- (3) Iijima, S. *Nature* **1991**, *354*, 56.
- (4) Kresge, C. T.; Leonowicz, M. E.; Toth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (5) (a) Sasaki, M.; Osada, M.; Higashimoto, N.; Inagaki, S.; Fukushima, Y.; Fukuoka, A.; Ichikawa, M. *Microporous Mesoporous Mater.* **1998**, *21*, 597. (b) Sasaki, M.; Osada, M.; Higashimoto, N.; Yamamoto, T.; Fukuoka, A.; Ichikawa, M. *J. Mol. Catal. A* **1999**, *141*, 223. (c) Fukuoka, A.; Sakamoto, Y.; Guan, S.; Inagaki, S.; Sugimoto, N.; Fukushima, Y.; Hirahara, K.; Iijima, S.; Ichikawa, M. *J. Am. Chem. Soc.* **2001**, *123*, 3373.
- (6) Miyahara, M.; Gubbins, K. E. *J. Chem. Phys.* **1997**, *106*, 2865.
- (7) (a) Kaneko, K.; Watanabe, A.; Iiyama, T.; Radhakrishnan, R.; Gubbins, K. E. *J. Phys. Chem. B* **1999**, *103*, 7061. (b) Watanabe, A.; Iiyama, T.; Kaneko, K. *Chem. Phys. Lett.* **1999**, *305*, 71.
- (8) (a) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475. (b) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
- (9) Fulton, J. L.; Pfund, D. M.; Wallen, S. L.; Newville, M.; Stern, E. A.; Ma, Y. *J. Chem. Phys.* **1996**, *105*, 2161.
- (10) Kaneko, K.; Ishii, C.; Ruike, M.; Kuwabara, H. *Carbon* **1992**, *30*, 1075.
- (11) (a) Kaneko, K.; Ishii, C. *Colloids Surf.* **1992**, *67*, 203. (b) Setoyama, N.; Suzuki, T.; Kaneko, K. *Carbon* **1998**, *36*, 1459.
- (12) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. *Phys. Rev. B* **1998**, *58*, 7565.
- (13) Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *53*, 769.
- (14) (a) Ludwig, K. F., Jr.; Warburton, W. K.; Fontaine, A. *J. Chem. Phys.* **1987**, *87*, 620. (b) Rao, R. V. G.; Das, R. *Phys. Stat. Sol.* **1988**, *110*, 347. (c) Bertagnoli, H.; Ertel, T. S.; Hoffmann, M.; Frahm, R. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 704. (d) D'Angelo, P.; Nola, A. D.; Filippini, A.; Pavel, N. V.; Roccatano, D. *J. Chem. Phys.* **1994**, *100*, 985. (e) Ramos, S.; Barnes, A. C.; Neilson, G. W.; Thiaudiere, D.; Lequien, S. *J. Phys.: Condens. Matter* **1999**, *11*, A203.

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