

## Pore-Width Dependence of Hydration Structure of RbBr Nanosolution Confined in Hydrophobic Slit Nanospaces

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### Introduction

Molecules can be strongly confined in solid nanospaces to form an ordered structure.<sup>1</sup> The structure of electrolytic solutions in bulk phase is now understood by experimental and simulation technique. However, structural analysis on ionic solution restricted in nanospaces should provide a new insight for the structure of electrolytic solutions.<sup>2</sup> Recently, we showed a characteristic hydration structure of Rb ion confined in slit-shaped solid nanospaces.<sup>3-5</sup> This report summarizes the effect of the pore width on the hydration structure of Rb and Br ion restricted in carbon nanospaces. We name the confined electrolytic solution as nanosolution (NSN) in this report.

### Experimental

Two kinds of pitch-based activated carbon fiber (ACF; P5 and P20) were used as a nanoporous carbon having nano-scale slit-shaped spaces whose widths are evaluated to be 0.7 nm for P5 and 1.1 nm for P20 from the nitrogen adsorption isotherm and subtracting pore effect (SPE) method.<sup>6,7</sup> The electrolytic solutions of RbBr (1M) were introduced into each ACF, being dried by evacuation at 0.1 mPa and 383 K for 2 hours. The RbBr-deposited ACFs were put on the glass cell with Mylar film (350  $\mu\text{m}$ : Toray Ind. Inc.), and then water vapor was re-adsorbed after drying. The pore-width dependence of the hydration structure was evaluated by EXAFS technique recorded at BL-10B of Photon Factory, High Energy Accelerator Research Organization in Tsukuba.

### Results and Discussion

Tables 1 and 2 show the structural parameters around Rb and Br ions, respectively. Here, P5-NSN and P20-NSN are NSNs formed in the nanospaces of P5 and P20, respectively. As the slit-width is an order of the molecular size, the effect of the confinement of Rb ions depends sensitively on the pore width. In the micropores of 0.7 nm, the confinement induces the contraction of the coordination distance of Rb-H<sub>2</sub>O in addition to the decrease of the hydration number. However, a part of hydration water molecules is intricate to form a stable ordered structure of water molecules in the 1.1 nm-slit spaces.

On the other hand, the confinement effect around a Br ion is different from that around a Rb ion, as the hydration to the Br ion is weaker than that to the Rb ion. The coordination number around the Br ion of NSNs

decreases in and the Br-H<sub>2</sub>O distance is relatively longer than that of bulk aqueous solution. Thus, confinement of "ionic solution" in the nano-scale space surrounded by the hydrophobic walls can provide a new concept in chemistry, which should be useful even in application.

**TABLE 1:** Structural parameters obtained by a least-squares fit of Fourier-filtered EXAFS spectra around a Rb ion.

Sample	$r_{\text{Rb-O}} / \text{nm}$	$N_{\text{Rb-O}}$	$\sigma_{\text{Rb-O}}^2 / 10^2 \text{nm}^2$	$R / \%$
P5-NSN	0.286	5.3	0.0245	6.4
P20-NSN	0.283	3.8	0.0235	7.4
RbBr solution (1M)	0.310	6*	0.0379	6.0
Literature value	0.287-0.312	4-12		

\*: Fixed parameter

**TABLE 2:** Structural parameters obtained by a least-squares fit of Fourier-filtered EXAFS spectra around a Br ion.

Sample	$r_{\text{Br-O}} / \text{nm}$	$N_{\text{Br-O}}$	$\sigma_{\text{Br-O}}^2 / 10^2 \text{nm}^2$	$R / \%$
P5-NSN	0.328	5.2	0.0236	2.5
P20-NSN	0.328	4.1	0.0196	4.9
RbBr solution (1M)	0.326	6*	0.0243	2.6
Literature value	0.29-0.34	6		

ion.

\*: Fixed parameter

### References

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