

Structures of low-dimensional ionic solutions confined in solid nanospaces

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Introduction

It is well known that molecules form an ordered structure in solid nanospaces.^{1,2} Ionic solutions have been interested in a variety of fields in physics and chemistry. The structures of electrolytes have been studied actively. The characterization of electrolytes confined in nanospace is also important from aspects of development of industrial materials such as supercapacitor. An explicit anomaly in the hydration structure of rubidium bromide solution confined in the slit-shaped carbon nanospaces of the slit-width of about 1 nm is described in this report.

Experimental

Pitch-based activated carbon fiber (ACF, AD'ALL Co. Ltd.) was used as a nanoporous carbon having nano-scale slit-shaped space whose width was evaluated to be 1.1 nm from the nitrogen adsorption isotherm and subtracting pore effect (SPE) method. RbBr "nanosolution" confined in nanospaces of ACF was prepared by dissolution of deposited RbBr in adsorbed water. ACF having "nanosolutions" of 0.1 or 1 M RbBr were sealed in glass cell with Lumirror film (350 μm : Toray Ind. Inc.) All EXAFS spectra were recorded at BL-10B of Photon Factory, High Energy Accelerator Research Organization in Tsukuba.

Results and Discussion

Figures 1 and 2 show the Fourier transform of Rb and Br K-edge of RbBr "nanosolution" confined in ACF. The peak positions stemming from the 1st hydration shell around Rb and Br ions were similar to those of bulk aqueous solution of 1 M. The results with FEFF procedure are shown in Table 1. We used the hydration model of 2.8 \AA for Rb-O distance and 3.3 \AA for Br-O distance, respectively. The coordination number and Debye-Waller factor around both Rb and Br ions were decreased compared with those of bulk RbBr aqueous solution. These results indicate that dehydration of water molecule around both cation and anion confined in carbon nanospace is induced and cluster formation of water molecule is enhanced. This coincides that water molecules confined in hydrophobic micropores could form highly ordered structure even at 303 K.¹ Therefore, the dehydration effect in hydrophobic nanospace should be the result of strong ordering of water molecules in nanospace.

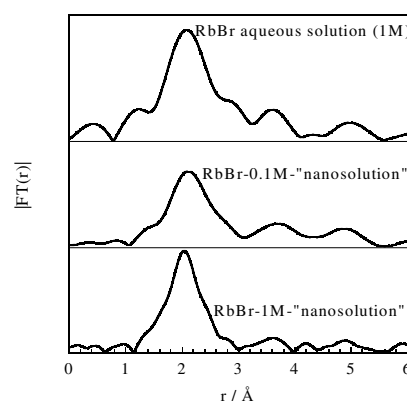


Fig. 1 Fourier transforms of Rb K-edge EXAFS of RbBr "nanosolution" and aqueous solution of 1 M.

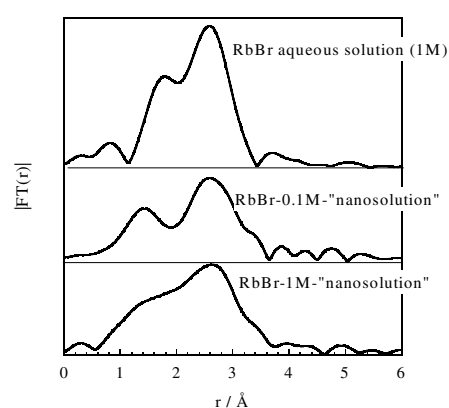


Fig. 2 Fourier transforms of Br K-edge EXAFS of RbBr "nanosolution" and aqueous solution of 1 M.

TABLE 1. EXAFS parameters from curve-fitting.

Sample	RbBr-1M-nanosolution	RbBr-0.1M-nanosolution	RbBr solution (1M)
$r_{\text{Rb-O}}$ (\AA)	2.81	2.82	2.83
$r_{\text{Br-O}}$ (\AA)	3.23	3.29	3.25
$N_{\text{Rb-O}}$	5.1	2.3	6
$N_{\text{Br-O}}$	2.4	1.3	6
$\sigma_{\text{Rb-O}}$ (\AA)	0.070	0.069	0.111
$\sigma_{\text{Br-O}}$ (\AA)	0.182	0.121	0.197

References

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