

# A STRUCTURAL ANALYSIS OF WATER-ADSORBED ACTIVATED CARBONS WITH X-RAY DIFFRACTION

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## Introduction

The behavior of water molecules restricted in a small space has attracted much attention from biology and chemistry. The surface tension of water depends strongly on the curvature of the gas-liquid interface; the depression of the freezing point of water in a small space, which has been believed to be associated with biological and geological processes. Although adsorption of water by microporous carbon has been studied for many years, the adsorption mechanism is not sufficiently established yet. In adsorption of water by activated carbon, water molecules are presumed to form clusters prior to filling of micropores without any direct evidence.

Microporous carbons can offer hydrophobic graphitic micropores of great pore volume. In particular activated carbon fibers (ACFs) and superhigh surface area carbons (HSACs) have considerably uniform micropores, compared with conventional activated carbons. The micropore-walls are mainly composed of micrographitic crystallites and thereby the micropores are of slit-shape. The pore width-controlled ACF is available in the range of 0.7 to 1.5 nm. Therefore, the graphitic micropores of ACF can be regarded excellent hydrophobic nanospaces.

The authors showed the effectiveness of the X-ray diffraction method for determination of the molecular assembly structure of water in the graphitic micropore due to a good transparency of carbon against X-ray[1]. The electron radial distribution function (ERDF) analysis for X-ray diffraction data showed the presence of a well-organized structure of water in micropores of HSAC at 303K; the adsorbed water has a more ordered structure than liquid, but less than ice. Furthermore the reliability of the ERDF analysis was examined for the  $\text{CCl}_4$ -graphitic micropore system[2]. This paper describes the structure of the water molecular assembly in the hydrophobic slit-shaped micropore at low temperature with in situ X-ray diffraction analysis using the pore width-controlled ACFs[3].

## Experimental

Two kinds of pitch-based activated carbon fibers (PIT-5 and PIT-20) were used. The micropore structure was determined by the high resolution  $\text{N}_2$  adsorption isotherm at 77 K. The X-ray diffraction of water adsorbed in

micropores of ACFs was measured by the transmission method using  $\text{MoK}\alpha$  at 50 kV and 30 mA in the scattering parameter  $s(=4\pi\sin\theta/\lambda)$  range of 0.7 to  $12 \text{ \AA}^{-1}$ . We used an in situ X-ray diffraction chamber[4]. The sample chamber was connected to the vacuum-adsorption system for controlling the adsorption conditions. Samples can be cooled by flowing liquid  $\text{N}_2$  down to 90 K without condensation of water vapor using an indirect cooling device. X-ray diffraction of the water-adsorbed ACF at 143-255 K were measured. The temperature of the sample was kept constant within  $\pm 0.1$  K for 303 K and within  $\pm 5$  K for 143-255 K during the X-ray diffraction measurement.

## Results and Discussion

$\text{N}_2$  adsorption isotherms at 77 K were of Type I. The micropore widths  $w$  of PIT-5 and PIT-20 determined by the subtracting pore effect method using the high resolution  $\alpha_s$  plots were 0.75 and 1.13 nm, respectively. The X-ray diffraction data were corrected by the method mentioned in previous paper[4]. Figure 1 shows X-ray diffraction patterns of water-adsorbed PIT-20 ( $w = 1.13$  nm) as a function of the measuring temperature. The X-ray diffraction patterns for all temperatures have broad peaks. There are no sharp peaks due to the bulk ice formation even at 143 K. It indicates that the water molecular assembly do not crystallize even at 143 K. Both of the first peak (A) at  $s = 1.8$  and second peak (B) at  $s = 3.1$  change gradually with temperature even across the freezing point of bulk water. On the contrary the broad diffraction patterns of water-adsorbed PIT-5 having a narrow pore ( $w = 0.75$  nm) change slightly with temperature in the range of 143 - 303K.

The difference of diffraction intensities between the water-adsorbed ACF and ACF itself is assigned to the adsorbed water molecular assemblies themselves with the assumption that the interference between adsorbed molecules and carbon walls can be neglected. The diffraction patterns of adsorbed water were Fourier transformed to the electron radial distribution function (ERDF). Figure 2 shows the ERDFs of water adsorbed in the 1.13 and 0.75 nm slit space at different temperatures. Each ERDF of water adsorbed has the highest peak (D) and shoulder one (C) at 0.42 and 0.35 nm, respectively. In the 1.13 nm-slit space case, the feature at this region sensitively varies as lowering the temperature. The peak or shoulder

(C) at 0.35 nm is assigned to the nearest-neighbor water molecules, whereas peaks (D) and (E) are attributed to the second and third nearest-neighbor molecules, respectively. Hence these three peaks provide the detailed information on the short range structure of the water molecular assembly in the micropore. As bulk liquid water has an interstitial molecule at the nearest-neighbor position, and thereby the peak (C) is higher than the peak (D) in case of bulk liquid water[5]. It is shown that the adsorbed water even at 303 K has a more ordered structure than bulk liquid[1]. The ERDFs of water molecules in 1.13 nm slit space show the strong dependence on temperature. The shoulder (C) at 303 K becomes the peak as lowering the temperature and at the same time the intensity decreases markedly. The intensity of the peak (E) increases with the decrease of the temperature. The position of the peak (C) shifts to a smaller value and the positions of the peaks (D) and (E) shift to a greater value with the decrease of temperature. The positions of peaks (C) and (D) at 143K are 0.282 and 0.456 nm, respectively. These values are close to those of the bulk ice of  $I_h$  form, because the distances to the first and second nearest neighbor molecules ice are 0.275nm and 0.449nm, respectively. This agreement indicates that the water molecular assembly in the 1.13 nm-carbonaceous slit space has a similar structure to the bulk ice.

However, it should be stressed the fact that water molecules in micropores even at 143 K have higher mobility than bulk ice, which is shown by broad peaks. The electron radial distribution function of water adsorbed at 143 K has an ordered structure up to 1.3 nm at best. This ordered structure range of the adsorbed water is plausible for the horizontal direction of the slit space. Although the structure of the water adsorbed was examined over the wide temperature range of 143 to 273 K, we could not observe a clear phase transition behavior of water adsorbed in the micropore.

On the contrary, in the 0.75 nm-slit space of PIT-5 case, the peak intensities of (D) and (E) which are assigned to the second and third nearest-neighbor molecules increase slightly with the decreases of temperature. The intensity difference between 143 and 303 K is much smaller than that of the wide pore system of PIT-20. Water molecules form a well-ordered structure and they cannot move easily even at 303 K in the 0.75 nm-slit space.

Thus the structure of water adsorbed in the narrower space has a completely different temperature dependence from that in the wider space. This X-ray diffraction study showed clearly that water molecules confined in the hydrophobic nanospace have an ice like structure of the different molecular mobility. The ordering of the water molecular assembly structure depends sensitively on the pore width. We need the X-ray diffraction simulation in order to understand the water molecular assembly structure more precisely in future.

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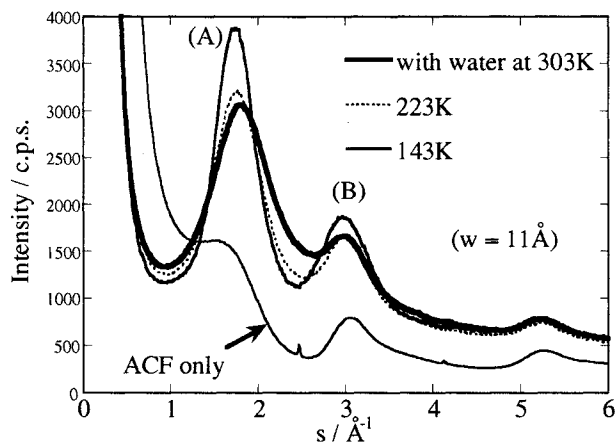


Fig.1 Temperature dependence on XRD patterns of water adsorbed ACF

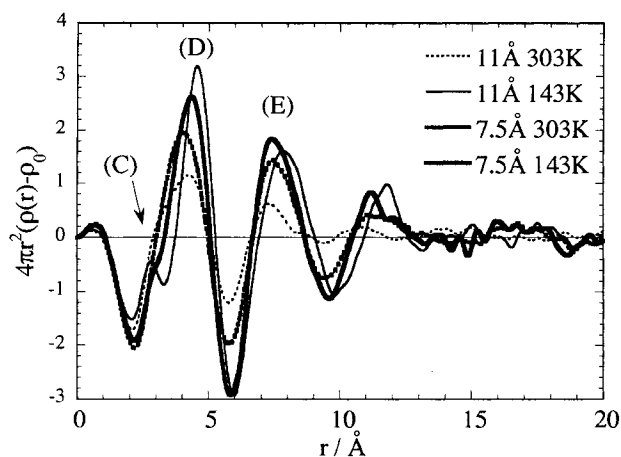


Fig.2 Radial distribution function of adsorbed water at 303K and 143K

### References

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