Structural Understanding of Water Confined in Hydrophobic Nanopores

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INTRODUCTION

Molecules in small space

The molecules constituted the system which have small number of molecules by spatial limitation

Different behavior from bulk state

- Unique phase transition
- Ordered structure formation

The molecules in small space is different from bulk state.

- Enhanced solid-admolecule interaction
  Molecules affected by solid-admolecule interaction. Especially, in micropore (w<2 nm), it is strongly enhanced.
- Spatial Restriction
  Molecules should constitute the system with small number of molecules

Water in 1.63 nm slit pore at 298 K (by XRD and Reverse Monte Carlo)

INTRODUCTION

Water in hydrophobic small space

Water-activated carbon system show the strange and unique phenomena.

- Different hydrogen-bonding structure
- Cluster formation?

The behavior of \textit{water molecules} in hydrophobic small space.
- \textbf{Hydrophobic effect} that the water molecules form an ordered structure around non-polar molecule, which acts as main factor in the dissolution of non-polar molecules in water.
- \textbf{Hydration structure} in the small space is also important because it will affect strongly to the heat of hydration and solubility of ions in the small space.

Water in 1.63 nm slit pore at 298 K (by XRD and Reverse Monte Carlo)

**Confined Spaces**

**Activated Carbons**
- $w: 0.75 \sim 2 \text{ nm}$
- Hydrophobic surface, single element (C)

**Carbon Nanotubes**
- 1-dimentional space

**Mesoporous Silica**
- $w: 1.5 \sim 7 \text{ nm}$
- Controllable Pore (Cylindrical)

**Zeolite**
- $w: 0.4 \sim 1.2 \text{ nm}$
- Small pore, high heat durability

**Metal organic Framework (MOF) / Porous Coordination Polymer (PCP)**
- Designable Pore by metal and organic ligands
Microporous Carbon

- Microporous $w \approx 1.0$ nm
- Large pore volume
  - Water adsorbed amount 1 g/g
- Amorphous Structure
  → Advantage for applying liquid structure analysis

Microporous Activated Carbon Fiber (ACF) $w: 0.7\sim 1.5$ nm

- $\text{CCl}_4$ $d = 0.59$ nm
- $\text{H}_2\text{O}$ $d = 0.28$ nm

Schematic model of activated carbon

TEM image of 002 lattice of activated carbon
**Adsorption System = 3 phase mixture system**

SAXS is sensitive to the distribution of electron in the system.

→ isolated particle, two-phase liquid mixture.

The adsorption system must be regard as the 3-phase mixture,

**adsorbent solid**, **adsorbed molecules**, and **vacant space**.

SAXS profile from 3-phase mixture is so complicated…

If we assume that the structure of solid phase remains unchanged with adsorption,

We can deduce informations of adsorbed phase and vacant space from SAXS measurement.
Scattering and Diffraction Techniques applied to the adsorption system

- **Small angle X-ray scattering (SAXS)**: \(2\theta = 0.3\sim 8^\circ\)
  → The size and shape of adsorbed molecular assemblies
- **X-ray diffraction (XRD)**: \(2\theta = 5\sim 90^\circ\), Neutron diffraction (ND)
  → The intermolecular structure of adsorbed water assemblies

Structure Understanding of Water Confined in Hydrophobic Spaces

Contents:

- Interaction between water and hydrophobic surface
- Cluster Formation of confined water (SAXS)
- Density Changing with T of confined water (SAXS)
- Intermolecular Structure of confined water (XRD, ND)
- Deducing 3-dimensional structure of confined water (RMC)
IUPAC classification of adsorption isotherm

Type I (Langmuir-Type)
Micropore Filling

Type II (BET)
Multilayered Adsorption

Type III
Interaction between solid-admolecule is less than between admolecule-admolecule.

Type IV
Capillary Condensation

Type V
In pore case, type III

Type III and V are the special behavior of water

Adsorption, Surface Area and Porosity, S. J. Gregg, K.S. W. Sing, Academic Press 1982
Water adsorption isotherm of Mesoporous Silica (MPS) (IUPAC Type IV)

Adsorption Hysteresis occur by the formation of water meniscus in the pore which have different curvature in adsorption and desorption processes. (Capillary Condensation)

\[
\ln\left(\frac{P}{P_0}\right) = \frac{2\gamma V_m \cos \theta_c}{RT} \frac{\cos \theta_c}{r_m}
\]

(Kelvin equation)

Water adsorption isotherms of MPS at 298K.
Activated carbon fiber (ACF)

- Pitch based Activated carbon fiber (ACF) (Ad’all Co., Ltd.)
  - Large surface and pore volume
  - Hydrophobic surface
  - Pore width ~ 1nm.
  \[ \rightarrow = 3\sim 4 \text{ water molecular-layers thickness} \]

Table: The pore structures of the ACF

<table>
<thead>
<tr>
<th>Samples</th>
<th>micropore volume (ml g(^{-1}))</th>
<th>Surface Area (m(^2) g(^{-1}))</th>
<th>Pore Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>0.34</td>
<td>900</td>
<td>0.75</td>
</tr>
<tr>
<td>A10</td>
<td>0.66</td>
<td>1510</td>
<td>0.82</td>
</tr>
<tr>
<td>A20</td>
<td>0.97</td>
<td>1770</td>
<td>1.13</td>
</tr>
</tbody>
</table>
CCl₄ – ACF adsorption system

CCl₄ adsorption isotherms of ACFs at 303K

A5 (w = 0.75nm)

A10 (w = 0.82nm)

A20 (w = 1.13nm)

CCl₄ filled micropore at low relative pressure (IUPAC Type I)

Saturated adsorbed amount corresponded to the micropore volume

No hysteresis

CCl₄ is spherical and has no dipole.

CCl₄ adsorption system

CCl₄ adsorption isotherms of ACFs at 303K

CCl₄ is spherical and has no dipole.
Water – ACF adsorption System

The adsorption mechanism is not clearly elucidated.

Steep adsorption uptake has been believed to associate with the cluster formation.

Water is not adsorbed at low $P/P_0$, indicating the hydrophobicity of carbon surface.

Water adsorption isotherms of ACF at 303K
Adsorbed Potential in micropore

Pitch-based activated carbon fiber (ACF)

W15 (Ad’all, Co. Ltd., Uji, Japan)
Average Pore width $w = 1.63\text{nm}$

A10
Average Pore width $w = 0.84\text{nm}$

Carbon-admolecular potential

- $\text{H}_2\text{O} - \text{carbon} \quad 850 \text{ K}$
- $\text{C}_2\text{H}_5\text{OH} - \text{carbon} \quad 2700 \text{ K}$
- $\text{CHCl}_3 - \text{carbon} \quad 4100 \text{ K}$
- $\text{N}_2 - \text{carbon} \quad 1250 \text{ K}$

Inter-molecular potential

- $\text{H}_2\text{O} - \text{H}_2\text{O} \quad 1800 \text{ K}$
- $\text{C}_2\text{H}_5\text{OH} - \text{C}_2\text{H}_5\text{OH} \quad 3500 \text{ K}$
- $\text{CHCl}_3 - \text{CHCl}_3 \quad 1100 \text{ K}$
- $\text{N}_2 - \text{N}_2 \quad 95 \text{ K}$
Symmetrical Cluster Models

Single  Dimer  Trimer  Tetramer

Pentamer  Octamer  Decamer  Dodecamer

(Interaction from other molecules) + (surface-molecule interaction) = Total Potential

For Slit-pore model
T. Ohba et al
Total Potential Profiles for a Molecule in Cluster

Potential / kJ mol\(^{-1}\)

z / nm

-40 -30 -20 -10 0 10 20 30 40

single

4 Tetramer

8 Octamer
Isosteric heat of adsorption of water on various ACF

Temperature 290 K (+1 K)

Isosteric heat is almost constant, and it have near value with heat of condensation of bulk water (44 kJ mol\(^{-1}\)).

↓

The adsorbed water form a hydrogen bond with other water molecules even in micropore.
Water Vapor Adsorption Isotherm of Nonporous Carbon Black

at 303 K

No predominant adsorption

Flat surface
Very weak

No predominant adsorption
Carbon Aerogel – Typical Mesoporous Carbon

Addition of 0.8nm-pores with CO₂ activation

FE-SEM

Capillary condensation

N₂ isotherm
Water adsorption amount at 303 K corresponds to nanopore volume

\[ w = 0.8 \text{ nm} \]

Water filling occurs only in micropores of \( w < 2 \text{ nm} \)

Dependence of Adsorption Hysteresis on “Equilibration” Time at 303 K

ACF
1.1 nm

Solid symbol; adsorption, Open symbol; desorption
$P_{ad1/2}$ and $P_{ds1/2}$ against equilibration time at 303K

Equilibration time / min

$P/P_0$

$P_{ad1/2}$

$P_{ds1/2}$

> 2000 years

(more) Stable

Time dependence from non-equilibrium measurement

metastable
Remarks

- Cluster forming process is a key of water adsorption in hydrophobic process.
- “Micropore” is needed for adsorption of water in hydrophobic space.

Adsorption hysteresis is enough stable for structural measurement.
Structure Understanding of Water Confined in Hydrophobic Spaces

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Molecular Assemblies in the Micropore

The information of …
- Intermolecular structure
- Size and Shape of molecular Assemblies

Size and Shape of molecular assemblies are important for understanding the adsorption mechanism.

We need direct informations on molecular assemblies.
in situ Small Angle X-ray Scattering (SAXS)

- Fractional filling, $\phi = 0 \sim 0.9$
  - Adsorbed amount was measured by volumetric method and simultaneously SAXS measurements were carried out.
- Measurement Temperature, $T = 303$ K (fixed)
- X-ray range, $s (=4\pi \sin \theta / \lambda) = 0.035 \sim 1.2$ Å$^{-1}$ ($2\theta = 0.5 \sim 5^\circ$)  
  (using Synchrotron Radiation $s = 0.012 \sim 0.16$ Å$^{-1}$)


Sample thickness: 0.5~1 mm (samples were used after ground)
X-ray source: CuK$\alpha$, 35 kV, 15 mA.
Measurement time: 1 ~ 1.5 hr
Preheating: 383 K, <10$^{-5}$ Torr, 2 hr
Transmission method
Principle of small angle scattering

Scattering intensity $I$

$$I(2\theta) = A \cdot \left( \sum_k f_k \cdot \exp\left(-\frac{2\pi i}{\lambda} \cdot \delta(2\theta)\right) \right)^2$$

When the scattering angle $2\theta$ is small, $(\delta<\lambda)$ scattering intensity $I$ arise.

- **Intercept ($I(0)$)**
  - Density fluctuation (density difference between particle and surrounding)

- **Peak width**
  - Size of particle

- **Peak shape**
  - Shape of particle

Particle (which have different density from other region)

X-ray

Path difference

2 $\theta$
The sum of waves can be understood by the add-up vectors.

\[ \sin\{\pi \cdot x\} + \sin\{\pi \cdot (x + 0.5)\} \]
Scattering from small particle

Small Particle (which have different density from other region)

Waves which have different phases

At small $2\theta$, total scattering is not zero.

Sensu, Japanese hand fan
Principle of small angle scattering

When the scattering angle $2\theta$ is small, $(\delta<\lambda)$ scattering intensity $I$ arise.

$$I(2\theta) = A \cdot \left( \sum_k f_k \cdot \exp\left(-\frac{2\pi i}{\lambda} \cdot \delta(2\theta)\right) \right)^2$$

- **Intercept ($I(0)$)**
- **Density fluctuation (density difference between particle and surrounding)**
- **Path difference**
- **Small particle**
- **Different shape**
- **Peak width → Size of particle**
- **Peak shape → Shape of particle**
- **Particle (which have different density from other region)**
- **X-ray**
- **X-ray path difference**
SAXS profiles of A20 - CCl₄ adsorption

At various fractional filling, $\phi$.

The scattering intensities decrease with $\phi$.

With CCl₄ micropore filling.

ACF itself show the strong scattering due to the density difference between the vacant and carbon crystallites.

$\phi$: fractional filling
SAXS profiles of A20 - water adsorption

\[ s = \frac{4\pi\sin\theta}{\lambda} \text{ / Å}^{-1} \]

scattering intensity, \( I \) / a.u.

\[ \phi = 0 \text{ (carbon only)} \]

\[ \phi = 0.3 \]

\[ \phi = 0.7 \]

\[ \phi = 0.8 \]

The SAXS curve is non-linear in the higher \( \phi \) region.

The SAXS curves for adsorption and desorption processes do not agree.

This hysteresis indicates that structure of water assembly is different at adsorption and desorption processes.

SAXS profiles of water adsorbed ACF(A20) at various fractional filling, \( \phi \).
Debye-Bueche Analysis

- This theory developed for porous materials, which assumed the exponential correlation function.

\[ I(s) = \frac{I_0}{(1 + \xi^2 s^2)^2} \]

\( I(s)^{-1/2} \) vs. \( s^2 \) plot (so called Debye-Bueche plot)

\[ I_0 = \frac{1}{\text{(intercept)}^2} \quad \xi = \sqrt{\frac{\text{slope}}{\text{intercept}}} \]

\( I_0 \): zero angle X-ray scattering intensity
\( \xi \): correlation length
\( <(\Delta N)^2>/N \): electron density fluctuation

\( I_0 \) is associated with electron density fluctuation of whole system

\[ \frac{I_0}{N} = Z^2 \frac{\langle(\Delta N)^2\rangle}{N} \]

Debye-Bueche plot for A10-water system

\[ I^{1/2} / \text{a.u.} \]

\[ s^2 / \text{Å}^{-2} \]

\( \phi = 0.9 \)

\( \phi = 0.7 \)

\( \phi = 0.4 \)

\( \phi = 0 \) (Carbon)
The zero-angle X-ray scattering intensities, $I_0$, of CCl$_4$ adsorbed ACF as a function of fractional filling, $\phi$.

$I_0$ decreases monotonically and concavely with CCl$_4$ adsorption.

Simulated value using volume fraction of A20.

CCl$_4$ form no multilayers in the micropore because the diameter of CCl$_4$ is very close to the pore width.

A20 ($w = 1.13\text{ nm}$)  A5 ($w = 0.75\text{ nm}$)
The zero-angle X-ray scattering intensities, $I_0$, of water adsorbed ACFs against the fractional filling, $\phi$.

The hysteresis loop of $I_0$ is consistent with adsorption hysteresis.

Wider pore (A20), $I_0$ increases with $\phi$. It indicates the formation of large cluster of water in the micropore.

$I_0$ of water - ACF adsorption

$A20$ ($w = 1.13\text{nm}$)  
$A10$ ($w = 0.82\text{nm}$)  
$A5$ ($w = 0.75\text{nm}$)
This result show that the density fluctuation of system in the adsorption process is larger than desorption process.
Schematic model for $I_0$ of adsorption system

The difference in the size and shape of water cluster in the adsorption and desorption process should lead to the adsorption hysteresis.
Modeling of bicontinuous structure

Debye-Bueche theory

correlation length $\xi$

\[ I(s) = \frac{I_0}{(1 + \xi \cdot s^2)^2} \]

DB theory assumed the exponential correlation function, and $\xi$ mean the mixing size of each phases.

Size of solid $l_s = \frac{\xi}{\phi_v}$

Size of vacant $l_v = \frac{\xi}{\phi_s}$

\[ P_{ss} = \phi_s + \phi_v \exp\left(-\frac{r}{\xi}\right) \]
The correlation length, \( \xi \), of adsorbed ACFs against the fractional filling, \( \phi \). The correlation length, \( \xi \), includes direct informations about size of adsorbed cluster.

Vacant space in the micropore also contributes to SAXS intensity.

We need that \( \xi \) divided into each characteristic values for solid, pore, and adsorbate.
Extend Debye-Bueche theory to the 3-phase system

The average dimensions of solid ($l_s$), vacant space ($l_v$) and adsorbed molecules ($l_a$)

- **2 phase**
  \[ l_s = \frac{\xi}{\phi_v} \quad l_v = \frac{\xi}{\phi_s} \]
  

- **3 phase**
  - solid phase is no change
  - interface between adsorbed phase and vacant space is perpendicular on the solid surface

  \[ l_s = \frac{\xi}{\phi_v + \phi_a} \quad l_v = \frac{\xi \cdot \xi_L}{\phi_s \xi_L + \phi_a \xi} \quad l_a = \frac{\xi \cdot \xi_L}{\phi_s \xi_L + \phi_v \xi} \]

  $\xi_L$ : correlation length between adsorbed phase and vacant space
  
Average dimension $l$ of A20 - water adsorption

The average dimensions $l_a$, $l_v$ and $l_s$ of water adsorbed A20 against fractional filling $\phi$

$\phi \cdot A20$ - water ($w = 1.13\text{nm}$)

The average dimensions $l_a$, $l_v$ and $l_s$ start from near 0.4nm, increase rapidly until $\phi = 0.1$, then gradually increase with $\phi$.

$$r = \frac{\sqrt{5}}{2} l_a = 1.12 \cdot l_a$$

$r$ : radius of spherical particle that give an equivalent scattering
The average dimensions $l_a$, $l_v$ and $l_s$ of water adsorbed A10 against fractional filling $\phi$. 

$l_a$ increase linearly with $\phi$. 

A10-water ($w = 0.82\text{nm}$)
The average dimensions $l_a$, $l_v$ and $l_s$ of water adsorbed A5 against fractional filling $\phi$

The average dimensions $l_a$, $l_v$ and $l_s$ of water adsorbed A5 against fractional filling $\phi$.

$l_a$ is almost constant with $\phi$. The size of water cluster does not change during adsorption, and water molecule fill the micropore by the number increasing of water cluster in small pore case.
Cluster size, $l_a$ on water - ACF adsorption

The average dimensions of adsorbed phase $l_a$ of water adsorbed ACFs against fractional filling $\phi$

Water would adsorb, when the cluster over 0.4nm in radius is formed.

$$r = \frac{\sqrt{5}}{2} l_a (= 1.12 \cdot l_a)$$

0.4 nm radius is corresponding to about 10 molecules, when assuming sphere for cluster, and bulk density.
Remarks

• The \textit{in situ} SAXS elucidate the structure of molecular assemblies.
• Water forms a cluster-like molecular assemblies in hydrophobic microspace.

✓ A direct evidence of cluster formation of the water molecules is given from measurement of density fluctuation.

✓ The difference in the size and shape of water cluster in adsorption and desorption processes should lead to the adsorption hysteresis.

$$m / \text{mg g}^{-1}$$

$$P/P_0$$

Micropore filling seems to progress by increasing number of cluster.

growth of cluster.

Size of cluster is different.
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Density Changing of bulk water with $T$

The temperature dependency of density is a one of most characteristic future of bulk water.

Water shows the negative thermal expansion between 273 – 277 K, super-cooled region, and below 70 K.

Water density increases when the melting.

$\rho (\text{LDA}) = 0.94 \text{ g cm}^{-3}$

$\rho (\text{HDA}) = 1.17 \text{ g cm}^{-3}$

The temperature dependence of density of confined water on activated carbon A25 ($w = 1.36 \text{ nm}$).
Temperature dependency of **density** of confined water

Liu et al. reported the density of confined water in mesoporous silica (MCM-41), and template synthesis mesoporous carbon (CMK-1).

They use the **Bragg peak** of SANS profiles.

\[
Q = 0.27 \text{A}^{-1}
\]


**Figure 3.** Comparisons of densities of different isotopic species of water in different confinements.
The SAXS intensities decrease monotonously with increase temperature (except 277-298 K).

Average density of confined water increase continuously with increasing $T$.

**Figure 2** The corrected SAXS profiles of water adsorbed on A25 by $\phi = 0.85$ at 20 K (red), 120 K (blue), 200 K(black), 225 K(green), 250 K(sky blue), 277 K(purple) and 298 K (light green)
Convert SAXS profile to density of adsorbed phase

\[ I(s) = 4\pi V \phi_s \phi_a (\rho_s - \rho_a)^2 \int_0^\infty r^2 \exp \left( -\frac{r}{\xi} \right) \frac{\sin(sr)}{sr} \, dr \]

\[ I(s) = 4\pi V \phi_s \phi_a (\rho_s - \rho_a)^2 \frac{2\xi^3}{(1 + \xi^2 s^2)^2} \]

\[ I(s) = \frac{I_0}{(1 + \xi^2 s^2)^2} \quad \text{(Debye-Bueche equation)} \]

Zero angle scattering \( I_0 \) contain the density information about confined water.

We can convert \( I_0 \) and \( \xi \) to density

\[ \rho_a = \rho_s - \sqrt{\frac{I_0}{8\pi V \phi_s \phi_a \xi^3}} \]

\( \rho_s \): electron density of solid phase (1.135 mol cm\(^{-3}\))

\( \phi_s = 0.260, \phi_a = 0.636 \)
Density Changing of confined water with $T$

The temperature dependence of density of confined water on activated carbon A25 ($w = 1.36$ nm).

Temperature dependence of SAXS profiles of water adsorbed ACF

Confined water shows negative thermal expansion over a wide $T$ range.

Density Changing of confined water with $T$

$w = 1.36 \text{ nm, } \phi = 0.85$

Confined water shows negative thermal expansion over a wide $T$ range.

The temperature dependence of density of confined water on activated carbon A25 ($w = 1.36 \text{ nm}$).

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**X-ray diffraction (XRD):**

scattering angle $2\theta = 5$~$90^\circ$

**diffraction**

Intermolecular structure

0.1~$2 \text{ nm order}$

Intermolecular structure of confined water

Phase transition phenomena of confined water

X-ray diffractometer

MoK\(\alpha\) (\(\lambda = 0.71\text{Å}\))
XRD profiles of water adsorbed activated carbon

X-ray diffraction patterns of water adsorbed activated carbon ACF(A20) at 303K

- Black line: A20 in vacuo at 303K
- Blue line: Water adsorbed at 303K

Intensity / c.p.s.

$\sin \theta / \lambda = \frac{4\pi}{\lambda} \sin \theta / \lambda$ (Å$^{-1}$) ($\lambda = 1.13$ nm)

(002) (10) (11)

Water adsorbing

Activated carbon in vacuum
Radial distribution functions of bulk and confined water

The 2nd neighbor peak intensity is strongest → Ice like structure

Radial distribution functions of bulk and adsorbed water in the 1.13nm slit space at 303K.

\[ 4\pi r^2 (\rho(r) - \rho_0) = \frac{2r}{\pi \Sigma z^2} \int s \cdot i(s) \sin(sr) \, ds \]

\[ i(s) = I_{coh}(s) - \sum f_i^2(s) \]

Temperature dependence of XRD profile

Changes in the X-ray diffraction patterns of water adsorbed ACF(P-20) with temperature.

Radial distribution function of adsorbed water in 1.13nm nanospace

The amplitude of function increase with temperature decreasing.

Gradual structure change between 143 – 303 K

Bulk ice (I_h)

<table>
<thead>
<tr>
<th>Distance (nm)</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.275</td>
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</tr>
<tr>
<td>0.448</td>
<td>12</td>
</tr>
<tr>
<td>0.456</td>
<td>1</td>
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<tr>
<td>0.525</td>
<td>9</td>
</tr>
<tr>
<td>0.635</td>
<td>12</td>
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<tr>
<td>0.690</td>
<td>9</td>
</tr>
</tbody>
</table>

Changes in the radial distribution function of adsorbed water molecules in the 1.13nm slit space with temperature.
Water in Hydrophobic Nanopores

Changes in the radial distribution function of adsorbed water molecules in the 0.75 nm slit space with temperature.

In wider pore case ($w = 1.36$ nm), the relatively sharp peaks appear under 225 K.

**Figure 6** Corrected XRD profiles of water adsorbed on A25 by $\phi = 0.85$ at 20 K(red), 120 K(blue), 200 K(black), 225 K (green), 250 K(sky blue), 277 K(purple) and 298 K(light green). XRD profile of $I_c$(upward) and $I_h$(downward) are also shown.
**Figure** Redial distribution function of adsorbed water in 1.36 nm width
X-ray Scattering and Neutron Scattering

<table>
<thead>
<tr>
<th>Scatter Power</th>
<th>O</th>
<th>D</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>64</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$n_e^2$</td>
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<td></td>
</tr>
<tr>
<td>Neutron</td>
<td>4.2</td>
<td>5.4</td>
<td>1.8</td>
</tr>
<tr>
<td>$S_{coh}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Electron**
  - Information about Oxygen Atoms mainly.

- **Nuclear**
  - Information about both of Oxygen and Hydrogen Atoms
EXPERIMENTAL SECTION

Measurement of Neutron Diffraction

**J-PARC (Tokai, Ibaraki, Japan)**
Materials and Life science Experimental Facility (MLF)
(Since 2008)

Beam intensity: 100-300 kW

\[ Q = 1.3 \sim 35 \text{ (max 80) } \text{Å}^{-1} \]

The pulsed neutron beam which was generated by using accelerator was used for the measurement.

Sample weight 1.8 g
Measurement time: 2 - 5 h.

Pretreatment: 383 K, \(10^{-3}\) Pa, 2 h
Time for equilibrium: > 24 h

Temperature: 298 - 20 K
RESULTS and DISCUSSION

XRD and ND

Diffraction profiles of D$_2$O adsorbed ACF using X-ray and neutron at 298 K.

Scattering parameter, $Q (=4\pi\sin\theta/\lambda)$

Diffraction intensity were normalized for a molecule and convert to RDF by Fourier transformation.

$w = 1.13$ nm
298 K
RESULTS and DISCUSSION

XRD and ND

Diffraction profiles of D$_2$O adsorbed ACF using X-ray and neutron at 298 K.

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$w = 1.13$ nm
298 K
Comparison of bulk and adsorbed D$_2$O by ND

The structure factors of adsorbed and bulk D$_2$O by ND at 298 K.

RESULTS and DISCUSSION

Comparison of bulk and adsorbed D$_2$O by ND

The structure factor does not change in high $Q$ region ($Q > 10$ Å$^{-1}$). However, it dramatically changed in low $Q$ region ($Q < 10$ Å$^{-1}$).

High-$Q$ region: short range (O-D, D-D) structure.
Low-$Q$ region: long range ($1^{st}$, $2^{nd}$, $3^{rd}$ nearest neighbor) structure.

Temperature dependence of structure factor of adsorbed D$_2$O by ND

$w = 1.34$ nm, $\phi = 0.9$
The sharp peaks come from the crystallization of partially water at outside of micropore. (Bulk ice $I_h$)

Amount of desorbed water is estimated less than 10% (by intensity in high-Q region).

$w = 1.34 \text{ nm, } \phi = 0.9$

Structure function of adsorbed $\text{D}_2\text{O}$ in A25 micropore.
Structure function of adsorbed D$_2$O in A25 micropore.

Main peak shift to low angle with temperature decreasing.

Ic peaks appear under 225 K.
Morishige reported that the disordered stacking sequence along [100] direction on very small ice crystallites in mesoporous silicas give rise to ice Ic peaks.

RESULTS and DISCUSSION

Low fractional filling

The zero-angle X-ray scattering intensities, $I_0$, of water adsorbed ACFs against the fractional filling, $\phi$.

($\phi = 0.5$)
The small cluster forming is expected.

ND profiles of adsorbed D$_2$O ACF at different $\phi$. 

$w = 1.34$ nm
RESULTS and DISCUSSION

Low fractional filling

The intensity of main peak \((Q = 1.9 \text{ Å}^{-1})\) and amplitude of middle-\(Q\) range increase at low \(\phi\) data.

Ordered structure was formed at the low \(\phi\).

ND profiles of adsorbed D\(_2\)O ACF at different \(\phi\).
Remarks

- The *in situ* XRD elucidate the intermolecular structure of water.
- Ice-like structure was formed even at room temperature, and it gradually change with temperature decreasing.

✓ Long-range ordered structure forming is restricted by the pore-space.

✓ The structure and its changes of water are strongly depended on the pore width.

- **w** = 0.75 nm: structure change is very small
- **w** = 1.13 nm: structure gradually change with T
- **w** = 1.36 nm: bulk I₁c peaks appear under 225 K
Structure Understanding of Water Confined in Hydrophobic Spaces

Contents:

- Interaction between water and hydrophobic surface
- Cluster Formation of confined water (SAXS)
- Density Changing with T of confined water (SAXS)
- Intermolecular Structure of confined water (XRD, ND)
- **Deducing 3-dimensional structure of confined water (RMC)**
The RDF obtained by XRD (red) denote the contribution of oxygen atom mainly.

Comparison the RDFs obtained by XRD and ND

Applying ND to the adsorption system

The radial distribution functions of adsorbed D$_2$O ($\phi = 1$) were obtained by XRD and ND

$w = 1.13$ nm

298 K, $\phi = 1$
Scheme of Reverse Monte Carlo (RMC) method

Calculate scattering profile \( I_{\text{old}}(s) \) of initial configuration \( p_{\text{old}} \)

**Insert**
\[ N_i = N_i + 1; \]

**Delete**
\[ N_i = N_i - 1; \]

**Move, Rotation**
\[ x_n = x_n + \Delta x, \quad y_n = y_n + \Delta y \ldots \]

Calculate XRD profile \( I_{\text{new}}(s) \) of new configuration \( p_{\text{new}} \)

Comparison with experimental scattering profile \( I_{\text{obs}}(s) \)

difference between experimental data and their simulated function \( R \)

\[
R_{\text{new}}(p) = \sum_{s} (I_{\text{new}} - I_{\text{obs}})^2
\]

- **Accept**
  - new configuration \( p_{\text{old}} = p_{\text{new}} \)
  - \( R_{\text{old}} = R_{\text{new}} \)

- **Reject**
  - trial was canceled \( p_{\text{old}} = p_{\text{old}} \)
  - \( R_{\text{old}} = R_{\text{old}} \)

\[ R_{\text{new}} < R_{\text{old}} \]

\[ \exp\left(-\frac{R_{\text{new}} - R_{\text{old}}}{\sigma_{\text{rmc}}}\right) > \xi \]

\( \xi \): random number (0~1)

RMC simulation deduces the molecular arrangement which reproduces the experimental profiles.
Reverse Monte Carlo Simulation (RMC)

adsorbent   ACF(A20)

- Slit-shaped pore by graphite layers  \( w = 1.13 \text{ nm} \)
- Periodic boundary conditions were employed to x and y axes
- 2 graphite layers (on each side)
- The position of carbon atom was averaged in graphite layer

This method used the geometrical parameters only (any potential assuming does not use) and deduce the molecular arrangement which reproduces the experimental scattering profiles.

\[
\begin{align*}
    f^X_{strf}(Q) &= \sum_i \sum_{i,j} \left( f_i(Q) f_j(Q) \frac{\sin Qr}{Qr} \right) \\
    f^N_{strf}(Q) &= \sum_i \sum_{i,j} \left( b_i b_j \frac{\sin Qr}{Qr} \right)
\end{align*}
\]


| \( \rho \) | 114 nm\(^{-3} \) | Atom density |
| \( \Delta \) | 0.335 nm | Inter-layer dist. |
| \( w \) | 1.13 nm | Pore width |
| \( L \) | 2.95 \( \times \) 2.98 nm | Width for x, y axes |

adsorbate

[\( \text{D}_2\text{O} \)]

| O-D | 0.09578 nm |
| \( \angle \text{DOD} \) | 104.478° |
XRD profile of adsorption system

\[
I_{tot}^a(s) = \frac{k}{n_s} \cdot P \cdot G \cdot A \cdot \left\{ I_{sc}^s + I_{sc}^a + I_{if}^{s-s} + I_{if}^{a-a} + I_{if}^{s-a} + I_{saxs} \right\}
\]

XRD profile of adsorption system

\[ I_{\text{tot}}^a(s) = \frac{k}{n_s} \cdot P \cdot G \cdot A \cdot \left\{ I_{s\text{c}}^s + I_{s\text{c}}^a + I_{If}^{s-s} + I_{If}^{a-a} + I_{If}^{s-a} + I_{s\text{x}s} \right\} \]

**Corrections**

- **Self-Scattering**
- **Correlations**
- **Small-angle Scattering**

\[ k : \text{intensity converting coefficient from e.u. to c.p.s.} \]
\[ n_s : \text{the number of carbon atom in the cell} \]
\[ P : \text{polarization correcting} \]
\[ G : \text{X-ray irradiation volume correcting} \]
\[ A : \text{X-ray absorption correcting} \]

\[ A(s, \frac{n_a}{n_s}) = \exp \left\{ -(1 + \frac{n_a}{n_s} \cdot \frac{\mu_a}{\mu_s}) \cdot G(s) \cdot \ln \frac{I_{\text{trans}}^s}{I_{\text{trans}}^0} \right\} \]

- \( \mu : \text{molar linear X-ray absorption coefficient} \)
- \( I_{\text{trans}} : \text{transmitting X-ray intensity} \)

The average intensity of XRD profile with the adsorption is determined by a balance of \( A(\downarrow) \) and \( I_{s\text{c}}^a(\uparrow) \).

XRD profile of adsorption system

\[
I^a_{\text{tot}}(s) = \frac{k}{n_s} \cdot P \cdot G \cdot A \cdot \left\{ I^s_{\text{sc}} + I^a_{\text{sc}} + I^{s-s}_{\text{if}} + I^{a-a}_{\text{if}} + I^{s-a}_{\text{if}} + I_{\text{saxs}} \right\}
\]

Though \( I_{\text{saxs}} \) includes the valuable information about the porous samples and shape and size of adsorbed molecular assemblies, it was removed by the parameter fitting.

\[
I_{\text{saxs}} = \exp(a \cdot \ln s + b)
\]

XRD profile of adsorption system

\[ I^a_{\text{tot}}(s) = \frac{k}{n_s} \cdot P \cdot G \cdot A \cdot \left\{ I^{s}_{\text{sc}} + I^{a}_{\text{sc}} + I^{s-s}_{\text{if}} + I^{a-a}_{\text{if}} + I^{s-a}_{\text{if}} + I_{\text{saxs}} \right\} \]

Self-Scattering

Corrections

Correlations

Small-angle Scattering

Self-Scattering and interferences are adding up all atom and all combination of the all atom-pair within the cell.

\[ I(s) = n \cdot f^2(s) + \sum_j \sum_k f_j \cdot f_k \frac{\sin sr_{jk}}{sr_{jk}} \]

We must take into account the terms concerning solid.
We assumed that the carbon structure does not change with adsorption

Application of RMC to the adsorption system

add up all atoms self-scattering and atom-pair correlation.

concerning carbon ( ), use XRD profile of a carbon sample in a vacuum.

Scheme of Reverse Monte Carlo (RMC) method

Calculate experimental profiles \( (I_{\text{old}}^s, I_{\text{old}}^X) \) of initial configuration \( (p_{\text{old}}) \)

Calculate profiles \( (I_{\text{new}}^s) \) of new configuration \( (p_{\text{new}}) \)

Comparison with experimental profiles \( (I_{\text{obs}}^s) \)

difference between experimental data and their simulated function \( R \)

\[
R_{\text{new}}(p) = \sum_s (I_{\text{new}} - I_{\text{obs}})^2
\]

Accept

\( p_{\text{old}} = p_{\text{new}} \)
\( R_{\text{old}} = R_{\text{new}} \)

Reject

trial was canceled

\( p_{\text{old}} = p_{\text{old}} \)
\( R_{\text{old}} = R_{\text{old}} \)

\( \xi \) : random number (0~1)

\( \theta_{\text{DOD \ change}} \)
\( \theta = 105 \pm 5^\circ \)

\( l_{\text{OD \ change}} \)
\( l = 0.96 \pm 0.05 \text{ Å} \)
Introducing flexible water model

Comparison with RMC configuration

Flexible water model
298 K

Simulated function by RMC

Experimental result at $\phi=1$

Structure function of adsorbed water by experiment and simulation
Introducing flexible water model

Comparison with RMC configuration

flexible water model
20 K
w = 1.34 nm

Simulated function by RMC

Experimental result at $\phi=1$

Structure function of adsorbed water by experiment and simulation
Introducing flexible water model

Comparison with RMC configuration

Structure function of adsorbed water by experiment and simulation

RMC configuration of adsorbed water obtained from ND and XRD profile at 20 K

Simulated function by RMC

Experimental result at $\phi = 1$

$w = 1.34 \text{ nm}$

ND

XRD

ND

Flexible water model

20 K
Introducing flexible water model

Separation of RDFs into O-O, O-D and D-D contributions

Radial distribution functions of adsorbed D₂O.

RMC configuration of adsorbed water obtained from ND profile
Introducing flexible water model

Separation of RDFs into O-O, O-D and D-D contributions

Radial distribution functions of adsorbed D₂O.
Introducing flexible water model

Separation of RDFs into O-O, O-D and D-D contributions

Radial distribution functions of adsorbed D$_2$O.

The 1$^{\text{st}}$ neighbor peak shift to short distance, (0.30 $\rightarrow$ 0.28 nm) and 2$^{\text{nd}}$ neighbor peak intensity increase with $T$ decreasing.
Introducing flexible water model

Separation of RDFs into O-O, O-D and D-D contributions

The amplitudes increase with $T$ decreasing in 2$\text{nd}$ and 3$\text{rd}$ nearest – neighbor distance.

Water molecule rotation is fixed (or hydrogen-bonding structure form rigidly) in low $T$.

Radial distribution functions of adsorbed D$_2$O.
Applying ND to the adsorption system

Comparison of hydrogen network structure between adsorbed and bulk states

Solid line: Adsorbed D$_2$O
Broken line: Bulk D$_2$O

Radial distribution functions of adsorbed and bulk D$_2$O.

The difference at 0.4 nm denote the **distortion of hydrogen bonding network** structure at 2$^{nd}$ nearest neighbors in the hydrophobic small space.
CONCLUSION

Cluster formation (by SAXS) and Characteristic structure changing with temperature (by XRD, ND) of confined water in hydrophobic space are elucidated.

Water is really adaptable to the surrounding.

In the hydrophobic nanospace, water property change from hydrophobic to hydrophilic by the cluster formation.

Snapshot of adsorbed D$_2$O in 1.13 nm carbon micropore by RMC simulation using flexible water model
Thank you very much for your kind attention.

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