Solid-state ^{2}H NMR Study of Nanocrystal Formation of D_2O and Their Dynamic Aspects in ACF Hydrophobic Nanospaces

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Molecular motion of heavy water confined in activated carbon fiber (ACF) was investigated using solid-state ^{2}H NMR. The ^{2}H NMR spectrum indicated that π-flip motion as well as tetrahedral jump of D_2O was active below 190 K, suggesting the formation of nanocrystal of D_2O in the ACF nanoslits.

Physicochemical properties of water in nanospace have attracted intense interest from specialists in industry, chemical engineering, and life and earth sciences.[1] Especially, the microscopic features of water in hydrophobic nanospace are very important to understand the local structure and dynamics of water in a nonfreezing water layer, which is closely related to life and earth sciences.

Recently, the peculiar cohesion structure of water has been reported in the hydrophobic nanospace of carbon nanotubes.[2] In the novel condensed system, the molecule–surface interaction is emphasized by the restricted space in nanometer-order instead of the intermolecular interaction in bulk. Particularly, cooperative phenomena of water confined in the hydrophobic nanospace, as exhibited in phase transition, melting, and crystallization, are closely related to fluctuation of the local structure of water in the manner of hydrogen bonding and/or disorder of molecular orientation. Information related to molecular dynamics of water in the restricted space also aid understanding of the specific behavior of water confined in a porous medium as well as interstices of huge proteins or polypeptides.

Activated carbon fiber (ACF) is a kind of porous carbon in which nanometer-sized graphite sheets form a hydrophobic and uniform slit-shaped nanospace.[3] The ACF micropore is regarded as a quasi-two-dimensional nanospace that exhibits strong affinity to many organic molecules. In the ACF nanospace, a hexatic phase of carbon tetrachloride (CCl_4) has been observed using nonlinear dielectric effect.[4] This intermediate phase resembles smectic B liquid crystal; it appears specifically in the two-dimensional molecular arrangement, as predicted by KTHNY theory.[5] Furthermore, cluster formation of water molecules has been proposed in the ACF nanospace on the basis of small-angle X-ray scattering (SAXS) measurement and GCMC simulation.[6–8] However, the molecular motion of the guest molecules confined in the ACF nanospace has not yet been examined in detail. In this letter, we report the molecular motion of D_2O confined in the ACF nanospace studied by ^{2}H NMR measurements.

Pitch-based activated carbon fibers ACF10A (slit width 0.7 nm) and ACF20A (slit width 1.1 nm) were supplied by Osaka Gas Co., Ltd. Heavy water (D_2O 99.9 wt %) was purchased from Cambridge Isotope Laboratories Inc. and was used without further purification. The ^{2}H NMR spectra were measured using a spectrometer (DSX200; Bruker Analytik GmbH) at a Larmor frequency of 30.7 MHz. The free induction decay (FID) signals were recorded using the solid-echo pulse sequence, which comprises two $\pi/2$-pulses of 3-μs length, a pulse interval of 20 or 40 μs, and a repetition time of 4 s. The spectral simulation was carried out using the MXQET program.[9] Differential thermal analysis (DTA) measurements were performed using a homebuilt apparatus.

Figures 1a and 1b show the temperature dependence of the ^{2}H NMR spectrum of D_2O saturating the ACF nanopore with different pore size. The spectra were observed on heating. Below 190 K, both specimens gave a powder pattern broadened by ^{2}H quadrupolar interaction, but the spectrum was somewhat asymmetric. Since ACFs have unpaired electrons originated from dangling bonds (Figure S1),[10] the paramagnetic shift due to electron spins may cause the distortion of the powder patterns.[11] However, the detuned spectrum (Figure S2)[10] suggested that this artifact is mainly caused by inhomogeneity of rf-pulses.

In the case of ACF20A, the powder pattern below 167 K showed the Pake doublet characterized by 220 kHz of quadrupole coupling constant (QCC) and 0.1 of the asymmetry parameter of electric-field-gradient (EFG) (η). As temperature increased, the narrower component was growing up. Above 193 K, the spectrum showed an isotropic peak, suggesting the rapid isotropic rotation of D_2O, as in the liquid phase. This temperature dependence could be nearly explained by tetrahedral jump of D_2O.

Wittebort et al. reported that, in polycrystalline hexagonal ice (Ih), the Pake doublet at 220 K gives a set of parameters of QCC = 216 kHz and $\eta = 0.1$.[12] This powder pattern is averaged by a tetrahedral jump of water, engendering an isotropic resonance peak in the fast exchange region of 220–260 K. The mechanism of the molecular jump between the possible configurations in a tetrahedron in hexagonal ice is accepted widely, and two kinds of the orientational defect of water, D (two hydrogen atoms between oxygen atoms) and L (no hydrogen atoms between oxygen atoms), make it possible to reorient the water molecule in the tetrahedron.[13] Figure 1c shows the simulation of the powder pattern based on tetrahedral jump. This pattern is consistent with the observation of the spectrum from water-saturated ACFs below 185 K in ACF20A. This aspect indicates that D_2O in the ACF nanoslits forms an analogous local structure to that of the tetrahedron of water in the hexagonal ice: the nanometer-sized crystals form in the ACF nanoslits in ACF20A. Surprisingly, the resonance line was already isotropic in the temperature region below 200 K, even though a DTA curve showed a broad endothermic peak at about 230 K on heating (Figure S3).[10] This probably corresponds to the melting of water in ACF20A.

On the other hand, in the case of ACF10A, the spectrum at 144 K showed a Pake doublet (QCC = 220 kHz, $\eta = 0.1$), but at

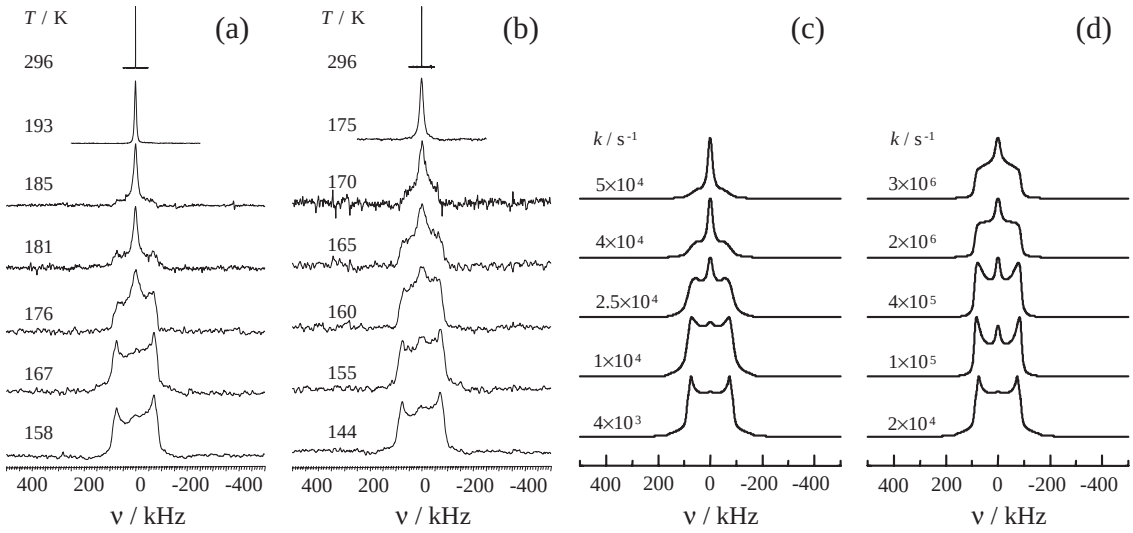

Figure 1. Temperature-dependence ^{2}H NMR spectrum of D_2O in ACF20A (a), ACF10A (b), and simulated spectra based on a tetrahedral jump (c), and a π-flip (d) with different exchange rates. k is exchange rate (s^{-1}), which is given by inverse of the resident time of molecule in an orientation.

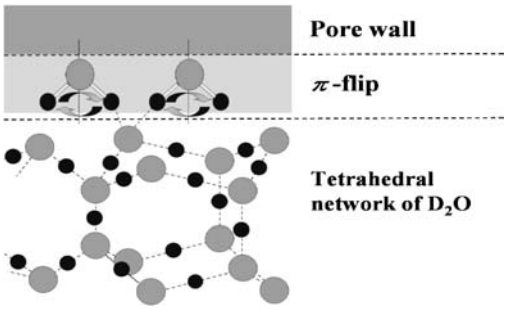

Figure 2. Schematic representation of D_2O local structure in ACF hydrophobic nanospace.

165 K it was well-characterized by 110 KHz of QCC and 1 of η. In D_2O, this characteristic powder pattern is caused by partially averaging of the quadrupolar interaction due to a rapid π-flip motion as shown in Figure 1d. A π-flip motion of D_2O molecules indicates anisotropy of the water occupation sites. In fact, lone-paired electrons on an oxygen atom of water are favorable to interact with π-orbital of graphene sheets, leading to the oriented D_2O molecules on the ACF nanoslit surface. The anisotropic orientation of D_2O near the pore walls prevents the hydrogen-bond network from growing. Water molecules in the vicinity of the pore surface are not able to participate completely in the construction of the tetrahedron structure during growth of the ice-like nanostructure as depicted in Figure 2.

Above 170 K, further narrowing was observed in the spectrum, indicating that additional mode such as tetrahedral jump contributes to the motional averaging of the spectrum. This implies that D_2O undergoes chemical exchange between the interfacial and tetrahedral sites. In the narrower pore of ACF10A, the contribution of the interfacial water becomes large in comparison with that of ACF20A. Water (sphere of 0.28 nm diameter) makes it possible to form 4 molecular layers in ACF20A, but only 2.5 layers in ACF10A. Therefore, the contribution of a π-flip motion due to interfacial water is emphasized on the spectrum in ACF10A.

This result supports the previous X-ray diffraction study by Iiyama et al.[6] and the simulation of a water structure at the hydrophobic planar wall with a central force model.[14] This result will also support a peculiar motional model for reaction dynamics in a restricted space, e.g., a surface, a porous catalyst, and a lipid bilayer. The refinements of the lineshape simulation and further experiments in other molecular systems are now in progress.

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