Dynamics of K+ aqueous solution confined in [CuZn(CN)4]- host

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Our target material is K+ aqueous solution confined in a coordination polymer host [CuZn(CN)4]-, which was recently synthesized by our group [1]. The chemical formula is [K(H2O)n][CuZn(CN)4] where n = 7.5+/-1.0. The host has nearly-spherical "cavities" of ca. 0.63 nm in a diameter. The confined K+ solution keeps electric charge balance with the negatively charged host framework. Our DSC and 2H NMR works revealed that the K+ solution in the host is not frozen at 273 K but exhibits an ordering transition at ca. 170 K and additional transitions at higher temperatures. The quasielastic neutron scattering (QENS) data taken by AGNES (JRR-3, energy resolution: 120 micro-eV) demonstrated that the motion of water molecules in the [CuZn(CN)4]- host is as fast as that of bulk water and reproduced well by the jump-diffusion model.

The aim of this study is to investigate the dynamics of water molecules more precisely, especially at low temperatures, by means of TOFTOF which has a higher energy resolution and a wider energy window than AGNES. The QENS data as functions of momentum transfer and temperature will provide important information on not only the relaxation time but also the mechanism of the relaxation. By combining the TOFTOF and AGNES data, it will be revealed how the rotational and translational motions of water molecules are activated as a function of temperature.

QENS measurements were performed at 3 energy resolution modes, 8 micro-eV (wave length: 1.2 nm), 40 micro-eV (0.6 nm), 110 micro-eV (0.5 nm), at 10 temperatures, 170K, 185 K, 200 K, 215 K, 230 K, 245 K, 260 K, 275 K, 287 K, 300 K. Clear peak broadening owing to QENS was observed at all temperatures above 185 K, indicating that water molecules diffuse in a time scale of 1 ns in the cavities of the [CuZn(CN)4]- host. This result is quite different from that of the pure water in nanoporous materials such as MCM-41 [2]; water is much slower than in the present host and exhibits a well-known liquid-liquid transition around 220 K. This may be due to the fact that K+ ions break the hydrogen-bonded network of water and enhance the mobility of water molecules.

Figure 1 presents the result of the mode distribution analysis [3] on the QENS data at 300 K. This analysis basically gives information on the number of relaxation modes and their Q dependence. There may be 1 diffusion mode and 2 or 3 more localized modes. On the basis of this result, more precise analysis on the QENS spectra is now in progress.

[1] H. Dan et al., Dalton Trans., 40, 1168 (2011). [2] L. Liu et al., Phys. Rev. Lett. 95, 117802 (2005). [3] T. Kikuchi et al., Phys. Rev. E, 87, 062314 (2013).

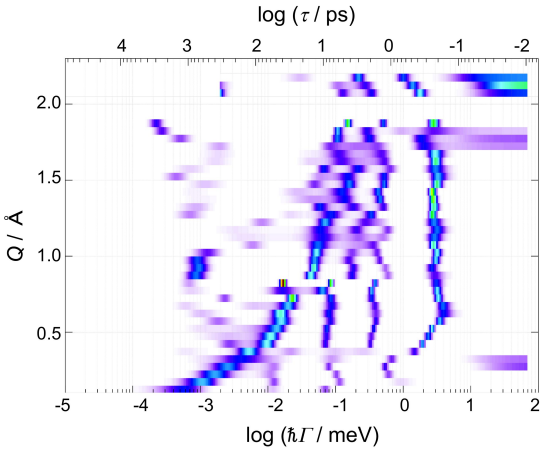

Fig. 1. Mode distribution analysis on QENS data of [K(H2O)7.5][CuZn(CN)4] at 300 K.