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Phase Transition and Dynamics of Water Confined in Hydroxyethyl Copper Rubeanate Hydrate

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This paper reports the results of the heat capacity (C_p) and quasi-elastic neutron scattering (QENS) measurements on hydroxyethyl copper rubeanate hydrate and its deuterated analogues. These materials accommodate water in their nano-pores and exhibit large proton conductivity at room temperature. The C_p data revealed that the adsorbed water gives rise to a glass transition and a first-order transition at 170 K and 260 K, respectively. The QENS data clarified that the adsorbed water consists of the free water apart from the pore wall and the bound water condensed on the pore wall. The diffusion coefficients of both waters are smaller than those of copper rubeanate hydrates owing to the steric hindrance caused by the hydroxyethyl group. The free water transforms to the condensed water through the transition at 260 K as in the case of copper rubeanate hydrates.

KEYWORDS: Hydroxyethyl copper rubeanate, Confined water, Quasi-elastic neutron scattering, Heat capacity, Phase transition

1. Introduction

Copper rubeanate [1], $H_2C_2N_2S_2Cu$ abbreviated as H_2*dtoa*Cu, is one of porous coordination polymers (PCP), and, in more general category, one of metal organic frameworks (MOF) attracting much attention in recent years. It forms a tetragonal structure with rectangular pores of ca. 0.7 nm on a side. Water is readily adsorbed in the pore and, under a relative humidity RH = 100%, the hydrate sample H_2*dtoa*Cu•4H_2O exhibits a proton conductivity (0.01 Scm^{-1}) as large as Nafion® membrane. We have

investigated the structures, phase transitions, and dynamics of H_2*dtoa*Cu•*n*H_2O (*n* = 0, 1.3, 2.1, 3.7) by means of calorimetric and neutron scattering techniques [2,3]. The water confined in the pores exhibits a glass transition and a first-order transition at 150 K and 260 K, respectively. The QENS work revealed that the adsorbed water consists of the free water with a similar diffusion coefficient to that of bulk water and the condensed water with much smaller (ca. 1%) diffusion coefficient. On cooling the sample, the free water transforms to condensed water through a first order transition at 260 K. This transition is regarded as a sort of liquid-liquid transition.

Hydroxyethyl copper rubeanate, $(C_2H_4OH)_2$*dtoa*Cu, is a derivative of H_2*dtoa*Cu in which the hydrogen atom of the amino group is substituted with a hydroxyethyl group (C_2H_4OH). This compound has a similar tetragonal structure to that of H_2*dtoa*Cu and traps water in its nano-pores. The proton conductivity work [1] has demonstrated that the hydrate sample $(C_2H_4OH)_2$*dtoa*Cu•*n*H_2O exhibits a phase transition with large change of proton conductivity at 290 K. In the present study, we have investigated $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O (full hydration sample) by use of the heat capacity and QENS techniques. The introduction of the hydroxyethyl group provides not only reduction of the pore space but also hydrophobic nature of the pore wall. It is interesting how the hydroxyethyl group changes the transitions and dynamics of the two kinds of water observed in the original material H_2*dtoa*Cu•*n*H_2O.

2. Samples and Experiments

2.1 Samples

Hydroxyethyl copper rubeanate $(C_2H_4OH)_2$*dtoa*Cu and its partially deuterated analogue $(C_2D_4OH)_2$*dtoa*Cu were synthesized along with the method described elsewhere [1]. The hydrated and deuterated samples were prepared by keeping the samples for more than 5 h in a glove bag which was saturated by the vapor of H_2O or D_2O. The hydration number was determined to be 1.7 by a weighing method. The samples prepared were $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O, $(C_2D_4OH)_2$*dtoa*Cu•1.7H_2O and $(C_2H_4OD)_2$*dtoa*Cu•1.7D_2O. For comparison, the dry sample of $(C_2H_4OH)_2$*dtoa*Cu was also prepared.

2.2 Experiments

2.2.1 Heat capacity measurement

The C_p measurements were performed using a custom-built adiabatic calorimeter [4]. The precision and accuracy ($\Delta C_p/C_p$) are 0.05% and 0.2%, respectively. The samples were wrapped with films made of tetrafluoroethylene/hexafluoropropylene copolymer to avoid reactions between the samples and the calorimeter cell. The wrapped samples were loaded into the cell with helium gas for heat exchange, and the cell was sealed with an indium gasket. The sample weight was 2.2672 g corresponding to 7.5454 mmol. The temperature range for the C_p measurements was from 5 K to 300 K.

2.2.2 Neutron scattering measurements

The neutron scattering measurements were performed by means of AGNES [5] with an energy resolution ΔE = 120 μeV and HFBS [6] with ΔE = 0.8 μeV. AGNES is

owned by the Institute for Solid State Physics, The University of Tokyo and is installed at the cold neutron guide (C3-1) of the research reactor, JRR-3 of Japan Atomic Energy Agency (JAEA). HFBS is installed at the NG2 of the guide hall at the NIST Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST, USA). The samples were loaded into concentric double cylinder aluminum cells whose outer diameter is 14 mm in a globe bag filled with helium gas and saturated H_2O or D_2O vapor. The thickness of the sample was adjusted to obtain 90% of neutron transmission.

First, the intensity of an elastic peak was measured as a function of temperature for the two partially deuterated samples. This measurement is called the fixed window scan (FWS) since the elastic intensity reflects the stationary parts of constituent atoms measured within a timescale (energy resolution) of the instrument. The FWS measurements on AGNES were performed at every 10 K from 100 K to 330 K, taking 1 h for each point. The FWS measurements on HFBS, with a narrower timescale than on AGNES, were performed continuously with ramping of 1 K min^{-1} in the temperature range from 4 K to 330 K. The DAVE software was used for the reduction of the HFBS data [7]. The QENS data on AGNES were recorded at 150 K (for the energy resolution), 320 K and 340 K taking a counting time of 8 h for each. The QENS measurement on HFBS did not provide reliable widths of the QENS peaks since the selected energy window (-17 μeV < E < 17 μeV) was not sufficient. The time range of HFBS was covered by NSE.

2.2.3 Neutron Spin Echo

Neutron spin echo (NSE) experiments were performed using the NG5-NSE spectrometer installed at NCNR, NIST [8]. The fully protonated sample ($(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O) was chosen in order to measure the incoherent scattering from H atoms as in the AGNES and HFBS measurements; the partially deuterated samples cannot be measured owing to the limited beamtime. The sample was loaded into a double concentric aluminum cylinder cell with 30 mm outer diameter and 28 mm inner diameter in a glove bag following the procedure used for the AGNES and HFBS experiments.

The measurements were carried out at 50 K (for the energy resolution), 200 K, 220 K, 240 K, 270 K, 300 K, and 330 K. The selected neutron wavelength was 0.6 nm and the scattering angle was 47 deg, corresponding to the Q value of 8.5 nm^{-1}. This Q value was chosen in order to avoid the effects of the direct beam and the diffraction peaks from the sample. The intermediate scattering functions $S(Q,t)$ were obtained from the raw data by use of the DAVE software [7].

3. Results and Discussions

3.1 Heat capacity measurements

Fig. 1 shows the C_p of $(C_2H_4OH)_2$*dtoa*Cu and $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O. The C_p of $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O exhibited a glass transition and a first order transition at 170 K (= T_g) and 240 K (= T_{trs}), respectively. The first order nature was confirmed from slow thermal equilibration after heating the sample. Both transitions should be caused by the adsorbed water since the dry $(C_2H_4OH)_2$*dtoa*Cu exhibited no anomaly. The T_g of this sample is 20 K higher than that of H_2*dtoa*Cu•*n*H_2O [2]. This indicates that the

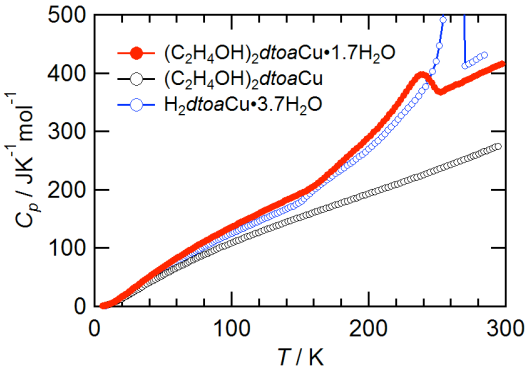

Fig. 1. Molar heat capacities of $(C_2H_4OH)_2$ *dtoa*Cu•1.7H_2O (red filled circle), $(C_2H_4OH)_2$ *dtoa*Cu (black open cirle) and H_2*dtoa*Cu•3.7H_2O [2] (blue open circle).

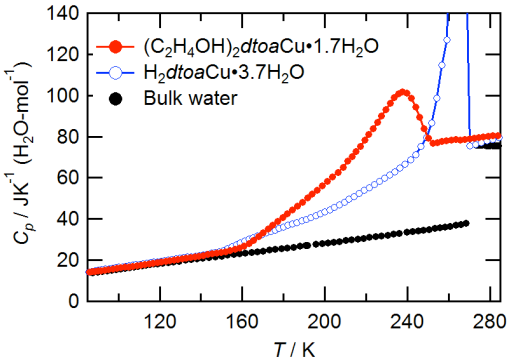

Fig. 2. Molar heat capacities of water in $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O (red filled circle), in H_2*dtoa*Cu•3.7H_2O (blue open circle) [2], and bulk water (black filled circle) [9].

motion of the adsorbed water slows down due to the steric hindrance by the hydroxyethyl group. The first order transition of $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O has a lower T_{trs} and broader peak shape than that of H_2*dtoa*Cu•3.7H_2O. These results may be associated with the effect that the low temperature phase, water condensed phase, is destabilized by introducing hydroxyethyl group with hydrophobic nature.

Fig. 2 shows the C_p of the adsorbed water derived as the difference between $(C_2H_4OH)_2$*dtoa*Cu and $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O. This C_p is close to that of bulk ice below 120 K within the discrepancy of 3%, indicating that vibrational heat capacity of the water in the pores is similar to that of ice. The transition entropy was calculated by the following equation.

$$\Delta S(273.15) = \int_{T_i}^{T_{trs}} \frac{[C_p - C_p(\mathrm{LT})]}{T} \mathrm{d}T + \int_{T_{trs}}^{T_f} \frac{[C_p - C_p(\mathrm{HT})]}{T} \mathrm{d}T + \int_{T_{trs}}^{T_{273.15}} \frac{[C_p(\mathrm{HT}) - C_p(\mathrm{LT})]}{T} \mathrm{d}T \quad (1)$$

where T_i and T_f are starting and ending temperatures of the transition, respectively. C_p(LT) and C_p(HT) are the baselines in the low and high temperature regions, respectively. The obtained transition entropy was 19.4 JK^{-1}mol^{-1}, which is comparable with those of bulk water (22 JK^{-1}mol^{-1}) [9] and H_2*dtoa*Cu•3.7H_2O (20.8 JK^{-1}mol^{-1}) [2]; 12% smaller than that of bulk water and 7% smaller than that of H_2*dtoa*Cu•3.7H_2O. The above thermodynamic outcomes suggest the following situation of water confined in the $(C_2H_4OH)_2$*dtoa*Cu framework: The water molecules are condensed and ordered by intermolecular hydrogen-bonds, and they are molten and disordered with partial hydrogen-bonds, though their degrees are somewhat different from bulk water (ice).

3.2 Fixed Window Scan

Fig. 3 and Fig. 4 show the temperature dependence of the normalized elastic

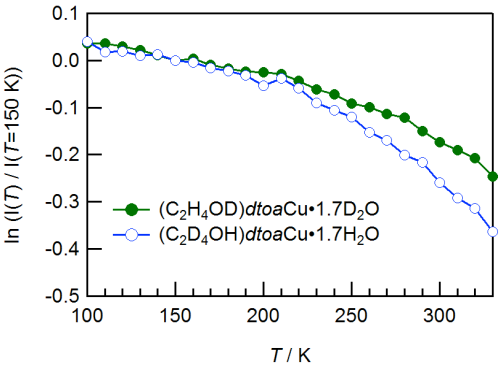

Fig. 3. Normalized elastic scattering intensities of $(C_2H_4OD)_2$ *dtoa*Cu•1.7D_2O (green filled circle) and $(C_2D_4OH)_2$*dtoa*Cu•1.7H_2O (blue open circle) obtained by AGNES as functions of temperature.

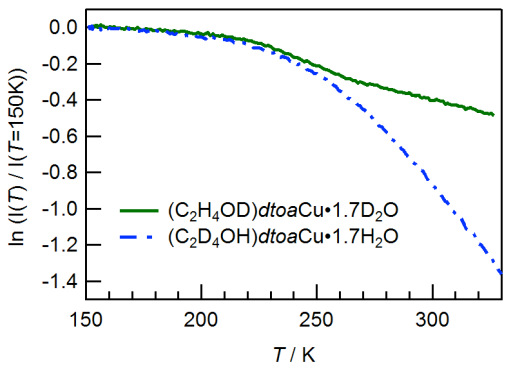

Fig. 4. Normalized elastic scattering intensities of $(C_2H_4OD)_2$ *dtoa*Cu•1.7D_2O (green solid line) and $(C_2D_4OH)_2$*dtoa*Cu•1.7H_2O (blue dashed dotted line) obtained by HFBS as functions of temperature.

scattering intensities of partially deuterated hydroxyethyl copper rubeanate hydrates obtained by AGNES and HFBS, respectively. Owing to large incoherent scattering from hydrogen atoms (σ_{inc} = 80 barn), one can observe the motions of water molecules in $(C_2D_4OH)_2$*dtoa*Cu•1.7H_2O, while those of hydroxyethyl groups in (C_2H_4OD)2*dtoa*Cu•1.7D_2O. The logarithmic elastic intensity will be linear with respect to temperature for a harmonic oscillator, and so the deviation from a straight line provides a measure of anharmonic vibrations and/or relaxations in atomic displacements. Both AGNES and HFBS data show deviation from straight lines around the transition temperature (240 K). The extent of deviation on HFBS is larger than that of AGNES due to the time window effect; HFBS has a narrower elastic (or wider quasielastic) window than AGNES. However, the onset temperature of the deviation is almost the same for both AGNES and HFBS. This implies that the deviation is due to the onset of diffusive motions caused by the transition at 240 K. The degree of the deviation for $(C_2D_4OH)_2$*dtoa*Cu•1.7H_2O is much larger than that of $(C_2H_4OD)_2$*dtoa*Cu• 1.7D_2O, clearly showing that the first order transition is due to the adsorbed water. It is noteworthy that considerable amount of intensity change was observed in $(C_2H_4OD)_2$*dtoa*Cu•1.7D_2O at T_{trs}. This indicates that the motion of the hydroxyethyl group is coupled with the adsorbed water. The NSE results, as shown below, clarified that hydroxyethyl group does not relax in the present temperature range. Hence, the anomaly at T_{trs} might be due to the increase of the mean square displacement of the libration of hydroxyethyl group.

3.3 QENS Fitting

Fig. 5 shows an example of the QENS data of the $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O obtained at Q = 14 nm^{-1} and 320 K on AGNES. The observed spectra were fitted by the same procedure as that of H_2*dtoa*Cu•*n*H_2O [3]. The scattering function is expressed by the following equation,

$$S(Q,\omega) = \{\delta(\omega) + L_{\mathrm{trans}}(Q,\omega) \otimes L_{\mathrm{rot}}(Q,\omega)\} \otimes R(Q,\omega) + \mathrm{BG} \qquad (2)$$

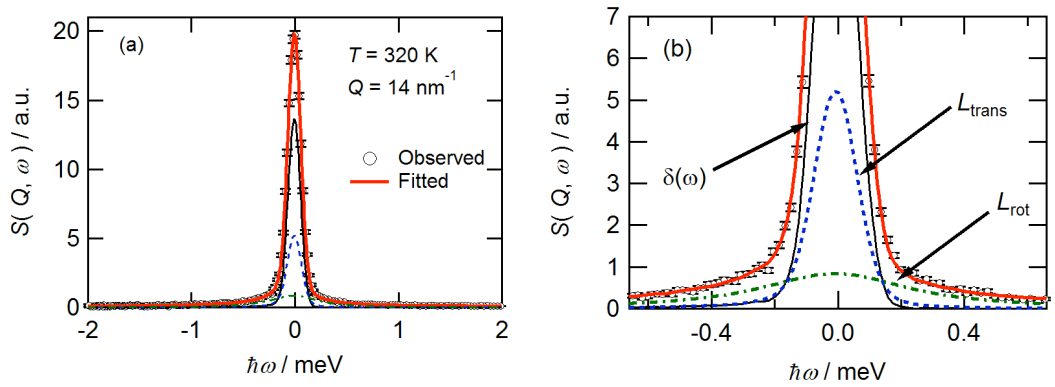

Fig. 5. QENS profile of $(C_2H_4OH)_2dtoaCu{\bullet}1.7H_2O$ at Q = 14 nm^{-1} and T = 320 K. The red solid curve is the result of the fitting to eq. (2). The black solid, blue dotted and green dashed dotted lines correspond to $\delta(\omega)$, L_{trans}, and L_{rot}, respectively. See text for the details. The scales of vertical and horizontal axes of (b) are enlarged by 3 times. The error bars represent a ±1 standard deviation throughout the paper.

The water motion was expressed by the convolution between the Lorentz functions for the translational (L_{trans}) and the rotational (L_{rot}) modes. The delta function corresponds to the scattering from the framework and/or the slow component of the water motions. $R(Q,\omega)$ is the resolution function. The data were fitted well as shown in Fig. 5. The diffusion coefficients were obtained from the Q dependence of the peak width by using the jump-diffusion model [10] as usually adopted to the water dynamics. The detail of the analysis was described elsewhere [3].

3.4 Neutron Spin Echo

Fig. 6 shows the incoherent intermediate scattering functions of $(C_2H_4OH)_2dtoaCu{\bullet}1.7H_2O$ obtained by the NSE measurements. These data clearly demonstrate that there are two relaxation modes (fast-mode and slow-mode) above T_{trs} (= 240 K) while a single relaxation mode below T_{trs}. A non-decay component also exists even at the highest temperature (330 K). Therefore, the experimental data were fitted to the following function,

$$\frac{I(Q,t)}{I(Q,0)} = f_{fast}\exp\left(-\frac{t}{\tau_{fast}}\right) + f_{slow}\exp\left\{-\left(\frac{t}{\tau_{slow}}\right)^{\beta_{slow}}\right\} + f_{non-decay} \qquad (3)$$

The terms of an exponential function, a stretched exponential function and a constant correspond to the fast-mode, slow-mode and non-decay component, respectively. The β_{slow} was fixed to be 0.5. The $f_{non\text{-}decay}$ at 330 K was 0.65. This value is close to the fraction of the H atoms in the methylene ($-CH_2-$) of the hydroxyethyl group; i.e., $(2\times4)/(2\times4+2+2\times1.7) = 0.60$. These H atoms should be slower than other H atoms in the present system. Therefore, the $f_{non\text{-}decay}$ was fixed to be 0.65 throughout the fitting. The fitting was satisfactory as shown in Fig. 6. The fast-mode disappeared and only the slow mode remained below T_{trs}. This is quite similar to the results for copper rubeanate

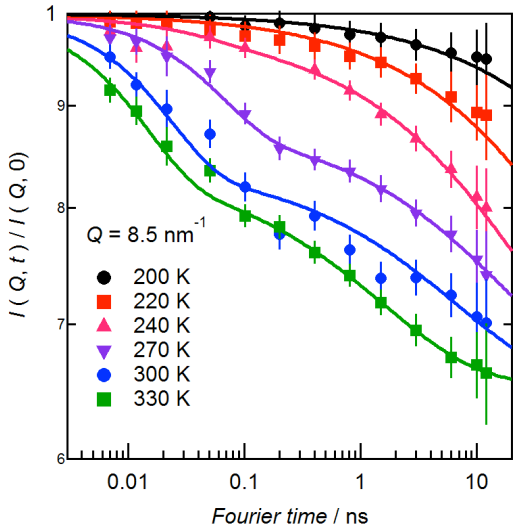

Fig. 6. Incoherent intermediate scattering functions of $(C_2H_4OH)_2$ *dtoa*Cu•1.7H_2O obtained by NSE. The solid curves are the result of the fitting to eq. (3).

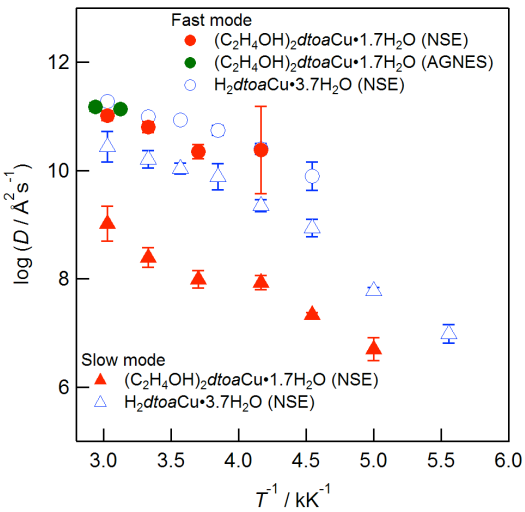

Fig. 7. Arrhenius plot of the diffusion coefficients of the fast (circles) and slow (triangles) modes of $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O obtained by NSE (red filled symbols) and AGNES (green filled symbols). Diffusion coefficients of H_2 *dtoa*Cu•3.7H_2O (blue open symbols) [3] are also plotted for comparison.

hydrates without hydroxyethyl group.

3.5 Arrhenius Plot

Fig. 7 shows Arrhenius plot of the diffusion coefficients obtained by AGNES and NSE. The diffusion coefficients by NSE were calculated by the following equation:

$$D = Q^2 \tau^{-1} \tag{4}$$

For comparison, the diffusion coefficients of water in H_2*dtoa*Cu•3.7H_2O were also plotted. The diffusion coefficients of both fast-mode and slow-mode of $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O are smaller than those of H_2*dtoa*Cu•3.7H_2O. This result indicates that the water motion slowed down by the steric hindrance of the hydroxyethyl group. This is quite consistent with the increase of T_g observed in the heat capacity measurement. Especially, the diffusion coefficient of the condensed water was decreased by one order of magnitude. The fast-mode clearly disappeared at T_{trs} on cooling. Thus the mechanism of the first order transition of $(C_2H_4OH)_2$*dtoa*Cu•1.7H_2O should be the same as that of H_2*dtoa*Cu•*n*H_2O; i.e., the condensation of the free water on the pore wall.

4. Conclusion

We have investigated the hydroxyethyl copper rubeanate hydrates by means of heat capacity and QENS measurements. The confined water exhibited a glass transition and

a first order transition at 170 K and 240 K, respectively. The QENS data revealed that the adsorbed water consists of the "free water" little affected and the "condensed water" strongly affected by the pore wall. The free water transforms to the condensed water through the first order transition on cooling. The diffusion coefficients of both free and condensed water were smaller than those of copper rubeanate hydrates, indicating that the hydroxyethyl group hinders the water motion by steric effects.

Further experiments are needed to clarify whether the first order transition observed at 240 K in this study is the same as the proton conductivity transition at 290 K mentioned in Introduction. Some sort of sample condition problems, for example the sample was presses to form a pellet for conduction measurements, might induce the difference in the transition temperature. The simultaneous measurement of the heat capacity and conductivity may be most effective.

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