MLF Experimental Report	提出日 Date of Report 2012/07/05
課題番号 Project No. 2012A0033 実験課題名 Title of experiment The determination of mixture state of cyclohexane and water in small spaces 実験責任者名 Name of principal investigator Taku Iiyama 所属 Affiliation Faculty of Science, Shinshu University	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/(BL No.) BL20 実施日 Date of Experiment 2012/05/01-2012/05/02

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

A new designed measurement cell for the connecting with cryostat of BL20 was used. The ground activated carbon fiber A25 (Ad'all Co.; pore width is 1.36 nm) was introduced in the cell, and preheated for 4h at 393 K and 1 mPa before the measurements. We measured the neutron diffractions of D_2O adsorbed A25. Adsorbed amount was controlled at half of saturated adsorbed amount (ϕ = 0.5). The measurement time is 4h with 200 kW pulsed neutron beam, at double-flame mode. ND of D_2O adsorbed activated carbon A25 (ϕ = 0.5) was measured at 20, 200, 225, 250, 298 K

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In this experiment, we planned to investigate the molecular mixing state of cyclohexane and water in the hydrophobic small spaces at the proposing stage. However, we decide that the continuous investigation with previous project 2011B0062 was carried out which is the investigation of phase transition phenomena of water in the small spaces. Because this experiment time was very near with 2011B0062, and the proposed theme 2010B concerning with water was canceled. We measured ND of D_2O adsorbed activated carbon (AC) at low fractional filling for elucidation of the phase transition phenomena of water small clusters in hydrophobic nanospace. We choose the same temperatures with measurement of 2011B. We can used the beam time on this experiment effectively because we can use the data of BG (vacant vanadium cell) and AC in vacuum which were measured in 2011B.

We measured ND of D_2O adsorbed AC at fractional filling ϕ = 0.5. D_2O (Cambridge Isotope Laboratories, D = 99.9 %) was used as adsorbate water. The AC sample was preheated in the cell, and then D_2O vapor was introduced. Equilibrium time was 2 day. Measurement time was set 4h; it was twice of previous measurement, because the amount of water is little.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Fig. 1 shows the ND profiles of adsorbed D_2O obtained by the subtracting NDs of AC in vacuum and D_2O adsorbed AC. The both of ϕ = 0.9 (2011B) and ϕ = 0.5 (2012A) data were shown for comparison. The intensity of ϕ = 0.5 data is small as expected. However, we could obtain enough data accuracy by the long measurement time. At the high-Q end (Q = 25–35 $Å^{-1}$), the intensities at 298 K is larger than 20 K in the both cases of ϕ = 0.9, 0.5. It is indicated that the adsorbed amount of water at 298 K is larger than 20 K. This result is inconsistent with the result of adsorption experiments. It suggest that the partially of adsorbed water desorbed in the cooling process by the ununiformity temperature distribution in the cell. However, amount of desorbed water is estimated less than 10 % by the ratio of intensities, it is not serious for object of this experiment.

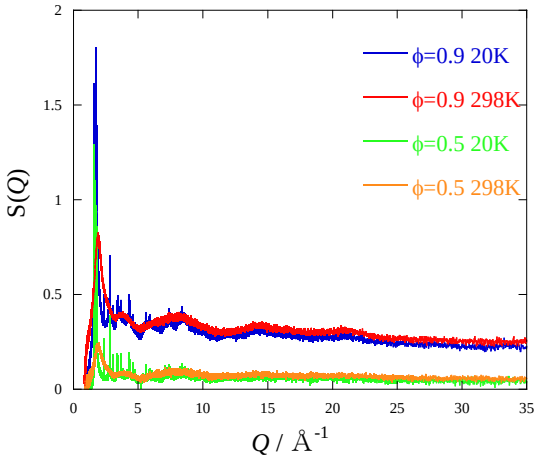


Fig.1 ND profiles of adsorbed D_2O(SE)

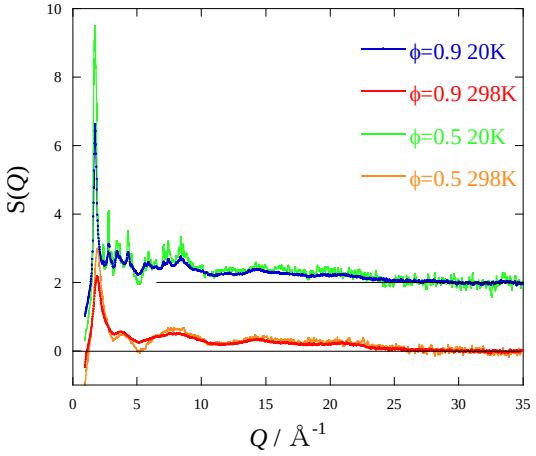
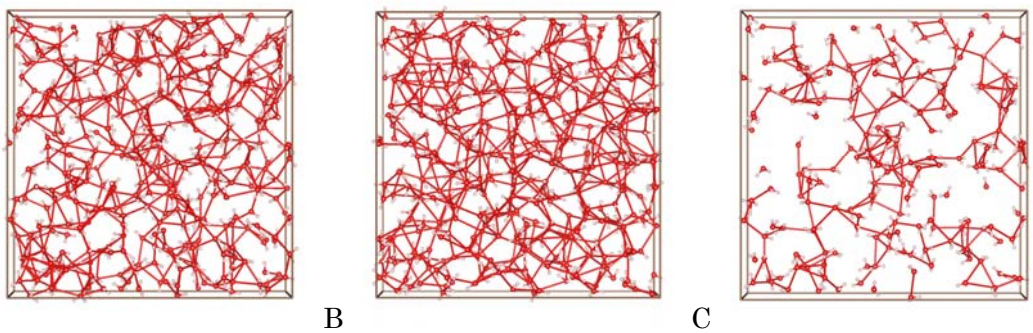


Fig.2 Structure factors of adsorbed D_2O

We transform the ND profiles (Fig. 1) to structure factors (Fig. 2) by the normalization using the intensity of high-Q end (Q = 25–35 $Å^{-1}$). The intensities gradually increase with Q decreasing; it would be come from recoil effect. The low fractional filling (ϕ = 0.5) data show the similar features of ϕ = 0.9 data. However, the intensity of main peak (Q = 1.9 $Å^{-1}$) and amplitude around middle-Q range (Q = 2–10 $Å^{-1}$) increase. It is indicated that the water molecules form high ordered structure on the low fractional filling at the both cases at 20 and 298 K.

We have tried to attempt the reverse Monte Carlo (RMC) simulation for these experimental ND data. Fig. 3 shows the snapshots of adsorbed water in slit-shaped pore (pore width is 1.36 nm). These molecular arrangements reproduce the ND profiles well, but not perfect yet. We will improve the modeling method, and deduce the phase transition phenomena of small cluster of water in the nanospaces.



A B C

Fig.3 Snapshots of adsorbed D_2O. These figures show the view along z axis (vertical direction of slit-shaped pore). A: ϕ = 0.9, 20 K, B: ϕ = 0.9, 298 K, C: ϕ = 0.5, 298 K.