MLF Experimental Report	提出日 Date of Report 2017/8/2
課題番号 Project No. 2017A0075 実験課題名 Title of experiment The determination of mixing state of binary solution is confined spaces (4): immiscible small clusters 実験責任者名 Name of principal investigator Taku Iiyama 所属 Affiliation Shinshu University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/(BL No.) BL-21 実施日 Date of Experiment 2017.05.11 09:00 – 2017.05.13 09:00

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.

An original designed measurement cell which keeps a hermetically closed condition was used for BL21 measurement. The ground activated carbon fiber A10 (Ad'all Co. Ltd.; pore width is 0.82 nm) was used as adsorbent. We measured the ND of water–cyclohexane mixture on adsorbed states. The molar fraction of water ϕ_w = 0 (pure cyclohexane), 0.25, 0.5, 0.75, 1.0 (pure water). The deuterium substitution samples, C_6D_{12} and D_2O were used as adsorbate for reduction the recoil factor. Adsorbed amounts on A10 were controlled at unity of fractional filling the pore (ϕ = 0.9). The measurement time was 300 m for each adsorbed condition.

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 the proposal, we had a plan to measure the water –cyclohexane (D_2O–C_6D_{12}) mixture as immiscible system at low fractional filling (ϕ = 0.5) in the micropore to investigate the small clusters. But we decide to change the measurement about the saturated condition of the pore (ϕ = 0.9), because the previous beam time used to other adsorption system (water–ethanol), and we need the data of saturated condition (ϕ = 0.9) to compare with the miscible system. The small cluster system will measure in next period.

For adsorbed condition samples, the carbon sample introduced in the cell of 10 mm diameter, and preheated for 8 h at 383 K and 1 mPa before the measurements. Then each adsorbate was introduced via vapor with the adsorbed amount controlling. The sample cells were hermetically closed, and keep over 3 days for the equilibrium. For bulk samples, cell of 6 mm diameter was used.

All data show the broad peak feature due to the liquid like structures of adsorbed phases even at low fractional filling conditions. The subtraction of carbon peaks well done. It can be confirmed smooth profile feature and continuous and systematic change of profiles with molar fraction of mixture.

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

Fig. 1 shows the structure factors of adsorbed water–cyclohexane mixture in the carbon micropore with different molar fractions. These profiles were obtained by subtracting the diffraction from carbon sample itself after the data correcting. The all profiles show the broad features, and show gradual change with molar fraction. This gradual change indicate that the both of molecules introduce to the pore even the immiscible combination. We compared the experimental profiles of middle fraction and the weighted averages of pure water and cyclohexane profiles. In the high Q region (Q > 40 nm^{-1}), the experiment profile and averaged profile are similar. It indicates that the short range structure such as intramolecular structure of cyclohexane does not change in the micropore. However, around of the first sharp diffraction peak (FSDP) of micro–mixture profile does not coincide the average profile. It is indicate clearly, that the water and cyclohexane form a strange mixture in the carbon micropore.

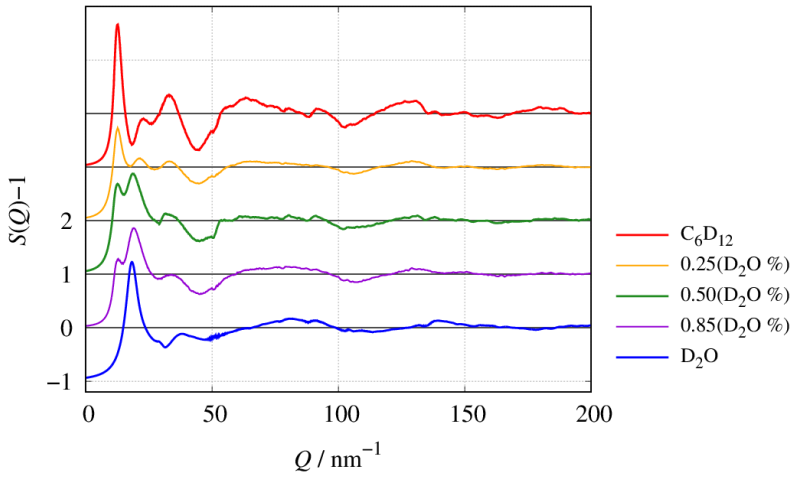

Fig.1 Comparing of structure factors of adsorbed water-cyclohexane mixture with different molar fractions.

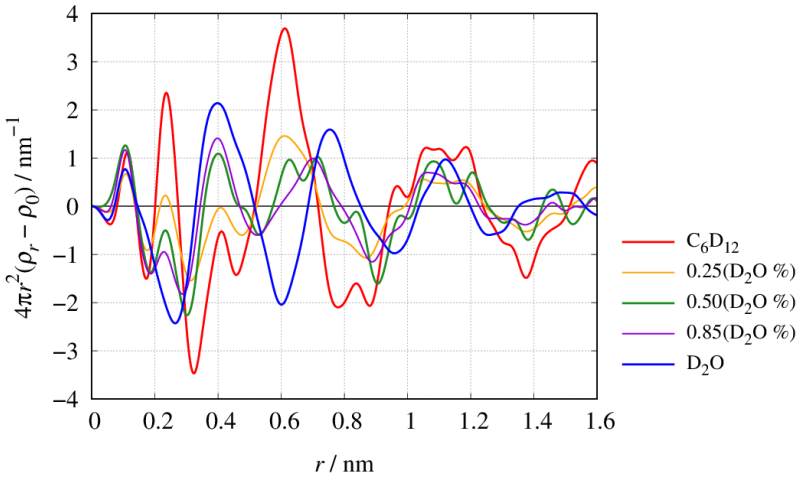

Fig.2 The radial distribution functions of adsorbed water-cyclohexane mixture with different molar fractions.

Fig. 2 show the radial distribution functions of pure cyclohexane, water and these mixture in the micropore. Unfortunately, we cannot find new peaks in the micro–mixture. The interatomic peak between different molecules should be small or overlapped to the pure component peaks. The change of peak intensities of pure component, such as 0.40 nm for water, 0.61 nm for cyclohexane are not proportional to molar fraction. The profiles suggests the forming the micro–domain structure of each component in the micropore. However, the domain size is not so large and is strongly affected the molar fraction.

We will combined XRD data of same systems and analysis the mixture by using reverse Monte Carlo simulation. By the using of both of ND and XRD profiles, the detailed structure included the domain size and shapes of water and cyclohexane mixture should be elucidated.