MLF Experimental Report	提出日 Date of Report 2015/4/15
課題番号 Project No. 2014B0020 実験課題名 Title of experiment The determination of mixing state of binary solution in confined space (2): immiscible cases 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 Toshiya Otomo 装置名 Name of Instrument/(BL No.) BL21 実施日 Date of Experiment 2015.03.06 10:00 – 2015.03.08 10:00

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–ethanol mixture on adsorbed states. The molar fraction of water ϕ_w = 0 (pure ethanol), 0.3, 0.6, 0.9, 1.0 (pure water). The deuterium substitution samples, C_2D_5OD and D_2O were used as adsorbate for reduction the recoil factor. Adsorbed amounts on A10 were controlled at half of fractional filling the pore (ϕ = 0.5). 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 in the micropore as immiscible combination. But we decide to change the measurement system to water–ethanol (D_2O–C_2D_5OD) mixture at low fractional filling (ϕ = 0.5), because we recently found that this system form a unique molecular cluster in the carbon micropore, and we can compare with the previous measurement data of saturated condition (ϕ = 0.9). The immiscible system will measure in next period (2015A).

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)

We can compared these adsorbed data at ϕ = 0.5 with the mixture on bulk condition and saturated condition (ϕ = 0.9). Fig. 1 shows the structure factors of ϕ_w = 0 (pure ethanol) at bulk and adsorbed conditions. In the high Q region (Q > 80 nm^{-1}), all profiles are almost coincide. It indicates that the short range structure such as intramolecular structure of ethanol does not change in the micropore. However, the first sharp diffraction peak (FSDP) of adsorbed state is shift to high-Q side compared with bulk clearly. Comparing in ϕ changing, the peak intensity is diminished at low ϕ (green) compared with high ϕ (red). The structure factor of adsorbed ethanol at ϕ = 0.9 (red) indicated the ordered 2d liquid structure forming of ethanol molecules. The data of ϕ = 0.5 in this experiment suggested the distortion of the 2d liquid structure at low fractional fillings.

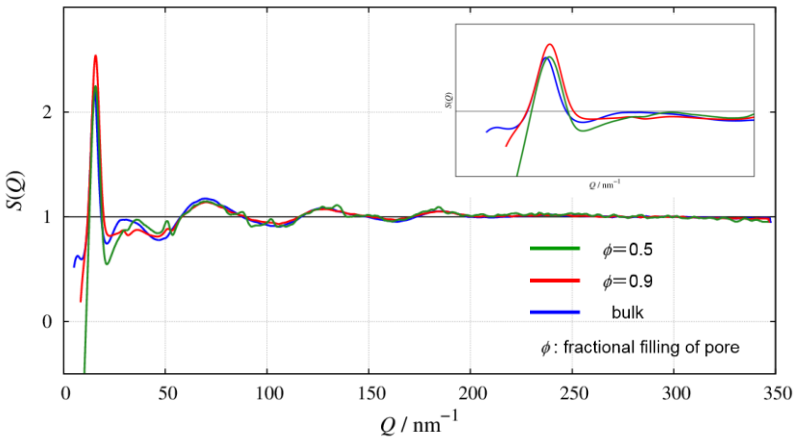

Fig.1 Comparing of structure factors of bulk (blue) and adsorbed condition (ϕ=0.5; green, ϕ=1.0; red) of ϕ_w = 0 (pure ethanol) .

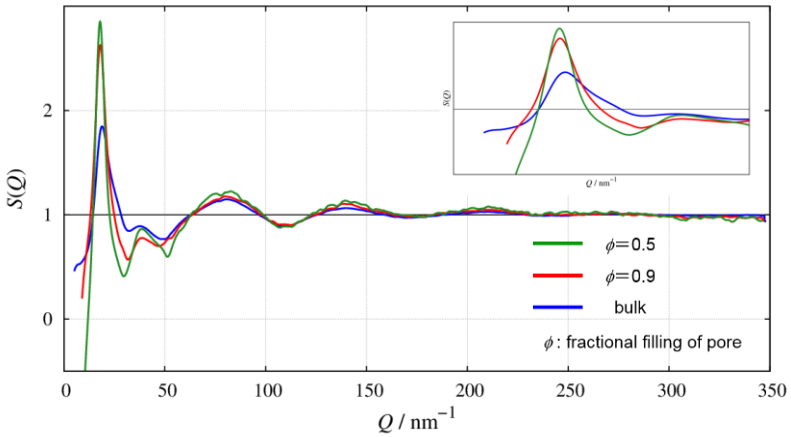

Fig.2 Comparing of structure factors of bulk (blue) and

Fig. 2 show the result of ϕ_w = 0.9. The water rich systems show the opposite tendency of ethanol rich systems. The FSDP of adsorbed state shift to low-Q side, it clearly shows the sparse structure of adsorbed water. Furthermore, the intensity of FSDP increased at low ϕ condition, it also show the opposite tendency at ethanol case. Previous investigation suggest that the water molecules form a cluster-like molecular assemblies which have a ice Ic like structure. This result suggest that the structure ordering tendency is enhanced at low fractional filling conditions. This intensity enhancement of FSDP at low ϕ condition is biggest at ϕ_w = 0.9.

The changing around 2nd peak (Q ≈ 40 nm^{-1}) is also interesting. The difference between bulk and adsorbed should be concern with hydrogen bonding. We will measured of XRD data of same systems soon, and the detailed structure analysis especially for mixture done using reverse Monte Carlo simulation. By the using of both of ND and XRD profiles, the detailed structure especially hydrogen bonding of water and ethanol mixture should be elucidated.