MLF Experimental Report	提出日 Date of Report 2014/7/13
課題番号 Project No. 2014A0194 実験課題名 Title of experiment The determination of mixing state of binary solution in confined space 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 2014.05.21 21:00 – 2014.05.24 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.

A new 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 both of bulk and 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 near of saturated adsorbed amount (ϕ = 0.9). The measurement times were 160 m for bulk samples, and 300 m for adsorbed conditions, respectively.

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.

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.

Fig. 1 show the ND profiles of adsorbed phases by using 45° bank data. These data were obtained by the subtraction of ND profiles of carbon sample itself (at vacuum condition) from that of adsorbed conditions.

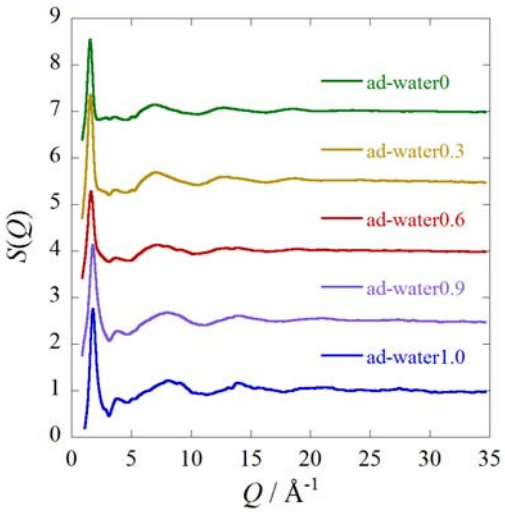

Fig.1 ND profiles of adsorbed phases

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

All data show the broad peak feature due to the liquid like structures of adsorbed phases. 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.

We can compared these adsorbed data with the mixture on bulk condition. In the high Q region (Q > 8 A^{-1}), both profiles are almost coincide. It indicates that the short range structure such as intramolecular structure of water and ethanol does not change in the micropore. However, the low Q peaks show the distinguish changes. Fig. 2 show the structure factors of various molar fraction of mixture on the adsorbed and bulk conditions. Solid lines denote the adsorbed, and broken lines denote the bulk conditions, respectively. On the water rich fractions (ϕ_w = 1.0, 0.9), the main peak of structure factors are shift to the low Q side, and intensity increases apparently. On the other hand, the main peaks of ethanol rich fractions (ϕ_w = 0.0, 0.3) shift to the high Q side. These results suggest the sparse structure of water, and dense structure of ethanol in the micropore, respectively.

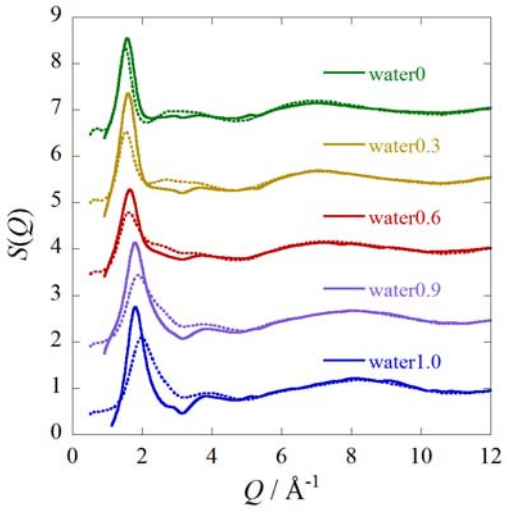

Fig.2 Comparing of structure factors of adsorbed (solid line) and bulk conditions (broken line).

The radial distribution functions (RDF) which were obtained by Fourier transformation of structure factors were shown in Fig. 3. In water rich cases, the peaks in short range (r < 0.2 nm) denote the intramolecular structure, and peaks at far from 0.2 nm denote the intermolecular structure of water. The main peak (at 0.4 nm) come from the first and second nearest neighbor molecules, and this peak shift to long distance and intensity increase in bulk condition. Furthermore, amplitude of RDF around 3rd and 4th peaks are increase and also shift to long distance. This result show the intermolecular structure of water including hydrogen bonding are strongly affected by the space restriction. On the other hand, ethanol rich case, the main peak of RDF at 0.5 nm due to the first nearest neighbor molecules does not shift in the micropore, but 2nd and 3rd molecules peaks shift to short distances.

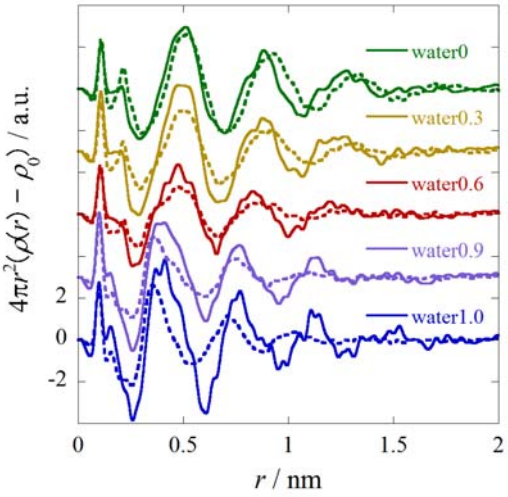

Fig.3 Radial distribution functions of adsorbed (solid line) and bulk conditions (broken line).

We already measured of XRD data of same systems, and will compare soon. 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.