Dynamics of Water in Dioxane-Water Binary Solutions Confined in Mesoporous Materials

Toshio Yamaguchi, Toshio Urabe, Koji Yoshida, Shigeharu Kittaka, Fanni Juranyi, Marie-Claire Bellissent Funel
Fukuoka University, Okayama University of Science, Paul Sherrer Institute, Laboratoire L on Brillouin

Organic solvents - water binary solutions in confined geometry have play a vital role in separation of compounds by chromatography, synthesis of new materials, and nanotechnology. The properties of confined solutions are perturbed by confinement and the interaction of solutions with wall surface and thus different from those in bulk solutions. 1,4-Dioxane-water binary solutions are unique in dielectric constant which can be varied from 80 to 2 with an increase in dioxane concentration. Previous X-ray diffraction measurements of 1,4-dioxane-water binary solutions have shown a structural transition from tetrahedral-like water structure to a neat dioxane arrangement at a dioxane mole fraction (xdio) of around 0.3. It is interesting to see how structural transition and dynamic properties change in MCM-41 C18, compared with those in bulk.

In the present study, quasielastic neutron scattering measurements were made on fully deuterated 1,4-dioxane-water (H2O) binary solutions confined in MCM-41 C18 pores with xdio of 0.18 and 0.70 over a temperature range of 263-310 K on a time-of-flight spectrometer FOCUS at Paul Scherrer Institute. The samples were sealed in a rectangular Al cell of a 2-mm sample thickness.

A typical quasi-elastic neutron scattering spectrum of 1,4-dioxane-water binary solution is shown in Fig. 1. The data were analyzed with a jump-diffusion model in which only translation motion was taken into account. The diffusion coefficient of translational motion of water molecules in 1,4-dioxane-water binary solutions in MCM-41 C18 was obtained. The corresponding activation energy obtained from Arrhenius plots of the diffusion coefficient was derived as 14.2 $\pm$ 1.6 kJ/mol and 8.5 $\pm$ 2.0 kJ/mol at xdio = 0.18 and 0.70, respectively, which are smaller than a value of 17.9 $\pm$ 0.9 kJ/mol for bulk water.

The present results suggest that at xdio = 0.18 most of water molecules are hydrogen-bonded to the silanol groups of silica wall, whereas at xdio = 0.70 a large amount of dioxane molecules tend to break the hydrogen bonds between water molecules and the silanol groups, resulting in formation of water clusters in the central part of pores.

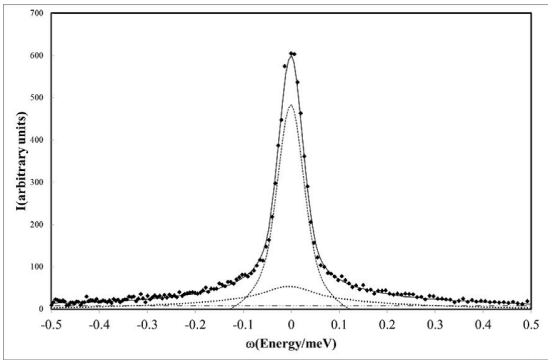

Fig. 1. Fitting results of quasi-elastic neutron scattering spectrum S(Q,w) of 1,4-dioxane-water binary solution with xdio =0.18 confined in MCM-41 C18 at 310 K.