

Design and evaluation of ion-exchange reactions in the nanospace underneath surface monolayers

Tetsuo Okada and Makoto Harada

Department of Chemistry, Tokyo Institute of Technology

Summary

Ion-exchange usually occurs at the interface between ion-exchange materials and solution. Separation selectivity is a function of the structure of ion-exchange groups, their density, type of matrices, the nature of a solvent, etc. The distributions of ions at such charged interface are dominated by electrostatic interaction, which is expected to influence the structures of ions as well. The Poisson-Boltzmann theory predicts that counterions are condensed in the electrical double layer and that their concentrations decrease as a function of the distance from an interface. If we can experimentally probe this area, the understanding of ion-exchange phenomena will be facilitated and a new design of separation is expected to become possible. Total reflection X-ray absorption fine structure (XAFS) is a powerful tool to investigate the concentration and local structures of ions attracted in the vicinity of surface monolayers. The typical observation depth is several nanometers, which correspond to the electrical double layer thickness in 1-10 mM 1:1 electrolyte; thus, we can access the interior of the electrical double layer by this method. A new cell, which has allowed us to measure XAFS spectra of ions attracted by the surface films at controlled surface pressures (or surface densities), has been designed to investigate ion-exchange phenomena at the surface monolayer.

When the surface monolayer of HTA or DTA is compressed on the subphase containing Br^- , the signal intensities measured at the Br K-edge should increase in a hyperbolic fashion. Although the signals follow the predicted hyperbolic curve when A is relatively large ($>130 \text{ \AA}^2$), the departures of experimental values from the curves become obvious when the surface monolayers are further compressed, and finally the signal intensities are leveled off. This is caused by the dissolution of the surface monolayer or exclusion of Br^- from the observation volume by compression. When the subphase contains both Br^- and Cl^- , XAFS measurements at Br K-edge allow us to detect ion-exchange equilibria between Br^- and Cl^- added in a subphase. The ion-exchange selectivity of Br^- over Cl^- basically increases as the monolayer is compressed, indicating that Cl^- is selectively squeezed out by compression because of its larger hydrated ionic radius. However, at $A \approx 100 \text{ \AA}^2$, an anomaly was detected both for HTA and DTA surface monolayers. This phenomenon is indicative of a change in the total reflection plane by the compression of the surface monolayer. This aspect can be utilized to the probing of ionic distribution in the electrical double layer.