

A Fundamental Study on Selectivity for Monovalent Ions of Ion-exchange Membranes

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Summary

Selectivity for monovalent ions of charged membranes is determined through interaction among solvated charged groups and counterions. According to our studies on counterion binding in solution and gel systems, the ion- and solvent-specific binding is affected not only by the dielectric constant but also by factors such as acceptor number (AN) and donor number (DN) that is a measure of solvation energies for anions and cations, respectively. In the present study, we employed poly(allylamine) (PAIAm) gel to investigate the anion-specific binding through observation of the swelling behaviors in water/organic solvent mixtures.

PAIAm gel of rod-type was prepared by irradiation of the aqueous solution with γ -rays. The gel diameter was measured in various kinds of water/organic solvent mixtures. By ion-exchange, gel samples with many kinds of counterion species were prepared to find any counterion-specific binding.

Solvent-specific swelling behavior was investigated for HCl and HNO₃ systems, in which PAIAm should be fully protonated. For the former system, PAIAm gel deswelled first in aqueous acetone while in aqueous MeOH for the latter. This difference may be ascribed to the selective interaction of Cl⁻ with solvents. Namely, acetone with lower AN must be a poor solvent to Cl⁻. For NO₃⁻, because of the weak interaction with solvents, an effective decrease in the local dielectric constant in aqueous MeOH, which has a high dielectric constant and can easily approach to the polymer, seems to be more essential for the gel deswelling.

The above results suggest an approach for anion exchange membrane design; In order to make a membrane with high selectivity for Cl⁻ and Br⁻, for example, introduction of functional groups of high or low AN may be effective. For actual development of such membranes, further examinations on the ion-solvent interaction would be necessary.