Temperature-responsive Cation-exchange Membranes Prepared by Graft Polymerization of N-isopropylacrylamide and Poly(vinyl alcohol)

Mitsuru Higa[1], Koji Matsusaki[2], Kenji Hori[1], Akio Kamimura[1] and Nobutaka Endo[1]

[1]Department of Applied Chemistry and Chemical Engineering, , Yamaguchi University
[2] Applied Medical Engineering Science, Graduate School of Medicine, Yamaguchi University

Summary

We describe the design and preparation of a novel temperature-responsive cation-exchange membrane that has a fast and reversible charge density response to temperature changes. We also demonstrate, in a dialysis system consisting of the membrane and mixed electrolyte solutions, that the membrane can control the transport modes of specific ions.

In order to prepare temperature-responsive cation-exchange membranes, *in situ* polymerization of N-isopropylacrylamide in poly (vinyl alcohol) (PVA) was carried out. A mixture of dimethyl sulfoxide solution of the polymer obtained, a polyanion and PVA was cast on teflon plate. The membrane obtained was crosslinked in an aqueous solution of glutaraldehyde at 25℃ for 1 day. The charge density was estimated by fitting membrane potential data to the Teorell, Meyer and Sievers theory. The membrane potential was measured at various temperatures between 10 °C and 60 °C, using an acrylic plastic cell of two parts separated by the membrane. One chamber of the cell was filled with KCl solutions of various concentrations (0.01, 0.03, 0.1M), C_o. The other chamber was filled with KCl solutions whose concentrations were 5 times higher than those in the first chamber. Permeation experiments were performed, using an acrylic plastic cell of two parts separated by the membrane. One chamber of the cell was filled with a mixed salt solution of 0.15M NaCl and 2×10^{-3} M LiCl, 2×10^{-3} M $CaCl_2$ and 2×10^{-3} M $LaCl_3$, the other chamber a mixed salt solution of 5×10^{-4}M NaCl, 5×10^{-4} M LiCl, 5×10^{-4}M $CaCl_2$ and 5×10^{-4}M $LaCl_3$. The solution in the chamber at the low-concentration side was sampled to measure the concentration of K^+ and Ca^{2+} ions using an ion chromatograph (Hitachi Co. L-3710).

The water content of the membrane decreased with increasing temperature because the NIPAAm chains on PVA matrix become hydrophobic at temperatures above the lower critical solution temperature (32 °C). The ion-exchange capacity was independent of temperature. Hence, the charge density increased with temperature.

Permeation experiments showed that: (1) at 10°C, La^{3+} ion is transported against its concentration gradient (*uphill* transport) and both Ca^{2+} ion and Li^+ ion are transported along with their concentration gradient (*downhill* transport); (2) at 32 °C, the *uphill* transport of both La^{3+} ion and Ca^{2+} ion occur; (3) at 50°C, the *uphill* transport of all the cations occur. These results indicate that the temperature-responsive cation-exchange membrane can be applied for removing multi-valent ions such as heavy metal ions from industrial wastewater in a system of Donnan dialysis.