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43. Active and Selective Transports of Alkali Metal Ions through Crosslinked Poly (isobutylene-alternating co-maleic anhydride) Membrane

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Summary

An ion exchange membrane containing carboxyl groups, insoluble in acidic and alkaline aqueous solutions, was prepared from poly(isobutylene-alternating co-maleic anhydride) and poly(vinyl alcohol). Using the membrane in a diaphragm cell, one side being adjusted to be acidic and the other alkaline, it was possible to transport actively and selectively alkali metal ions through the membrane from the alkaline side to the acidic side.

Introduction

The active transport of ions and the selective transport of K^+ and Na^+ ions in biomembranes play the important roles for the function of the life. A simulation for such functions of the biomembranes was shown by liquid membranes containing carrier such as monensin[1] and crown ether[2], etc. However, the liquid membranes are rather unstable during the transport experiment. Therefore, functional carriers, such as a specific functional group, were fixed to a synthetic polymer membrane. For example, polymers having a lactone ring[3] and a N-hydroxyethyl amide group[4] were synthesized. Membranes prepared from these polymers were able to transport metal ions and anions owing to the carrier functions caused by the reversible opening-closing of the lactone ring and the tautomerism of the N-hydroxy-

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ethyl amide group with pH changes. This paper deals with the active and selective transport of alkali metal ions through an ion exchange membrane containing carboxyl groups, prepared by poly(isobutylene-alternating co-maleic anhydride) crosslinked with poly(vinyl alcohol).

Experimental

Materials Poly(isobutylene-alternating co-maleic anhydride)(ISBN, from Kurary Co. Ltd.) and poly(vinyl alcohol)(PVA, from Kurary Co. Ltd.) were employed as the membrane substance. All reagents used were of pure grade from commercial sources.

Preparation of membrane Casting solution was prepared by adding during well stirring a desired amount of 1N H_2SO_4 and PVA aqueous solution (10 wt%) to ISBN solution (10 wt%) in NaOH aqueous solution. The membrane was prepared by pouring the casting solution onto a plate made of silicon rubber, allowing to evaporate the solvent (water) at 80°C for 5 h in an oven, and then immersing the membrane into 1N HCl. After immersion for 3 days in 1N HCl, the membrane was washed repeatedly with water and kept in pure water (25°C).

Apparatus and measurements Transport experiments were carried out at 25°C under magnetic stirring, using a diaphragm cell consisting of two detachable parts made of poly(methyl methacrylate). The membrane was fixed in the middle of the two parts of the cell, which were clamped and sealed tight with silicon rubber packings. The concentrations of alkali metal ions in both left and right part of the cell were determined by atomic absorption photometry.

Results and Discussion

An example of the concentration change of Na^+ ion in the L side and the R side with time due to the transport through the membrane is shown in Figure 1. The concentration of Na^+ ion in the R side increased with time, the concentration change in both sides being just the opposite. This result suggests that Na^+ ions were actively transported across the membrane from the L side to the R side against the concentration gradient between both sides.

The mean transport rate and transport fraction of Na^+ ion are defined by the following equations:

Mean transport rate (mol/l·h)

$$= ([Na^+]_{max} - [Na^+]_o)/t_{max} \qquad (1)$$

Transport fraction (%)

$$= ([Na^+]_{max} - [Na^+]_o) \times 100/[Na^+]_o \qquad (2)$$

where $[Na^+]_o$ and $[Na^+]_{max}$ are the initial and maximum concentrations of Na^+ ion in the R side, respectively, and t_{max} is the transport time for $[Na^+]_{max}$.

In Figure 2, the mean transport rate and transport fraction of Na^+ ion, determined by eq. (1) and (2) respectively, are plotted against the initial H^+ ion concentration in the R side. Both had maximum values at the initial pH 1.0 in the R side. These results are attributed to the fact that the L side and the R side kept alkaline and acidic, respectively for a long time. Both the L and R sides under conditions other than the initial pH 1.0 in the R side became rapidly alkaline or acidic. However, even after such pH changes in both sides, Na^+ ions were actively transported from the L side to the R side. This transport of Na^+ ion is dependent on very slight pH difference between both sides. When the initial pH in the R side was lower than unity, both the mean transport rate and the transport fraction were greater than those for over pH 1.0. This is due to a reverse diffusion of Na^+ ions from the R side to the L side caused by a remarkable swelling of the membrane, because both the L side and the R side became alkaline. The experimental fact that the membrane used elongates in alkaline pH and contracts in

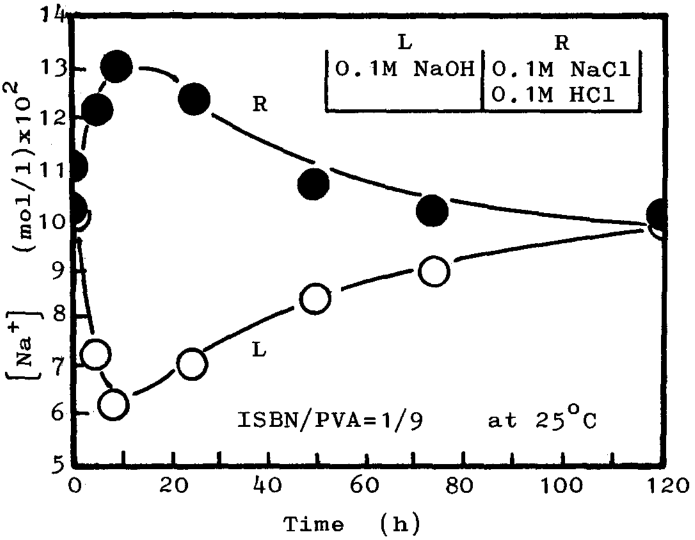

Figure 1. Change in the concentration of Na^+ ion through the membrane

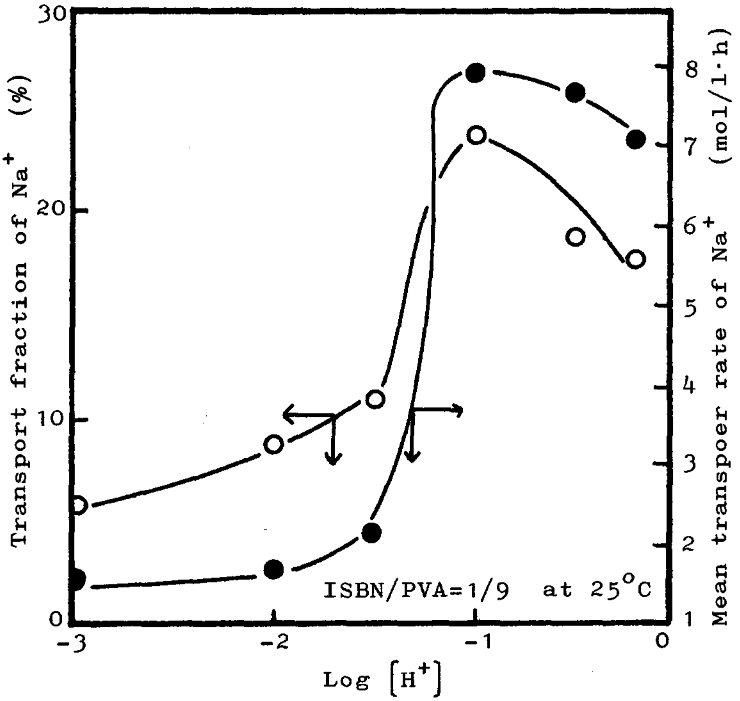

Figure 2. Effect of H^+ ion concentration in the R side on the transport fraction and the mean transport rate of Na^+ ions

acidic pH similarly to water-insoluble films of polyacids, such as poly(acrylic acid), poly(methacrylic acid), and poly(L-glutamic acid) crosslinked with glycerol or poly(vinyl alcohol)[5,6], explains the above swelling of the membrane.

The mechanism of the active transport of metal ions is shown in Figure 3. Metal ions are incorporated into the membrane in the alkaline side (L side), transferred by the functional carrier fixed on the membrane through the membrane, and released by H^+ ions in the acidic side (R side), while H^+ ions are easily counter -flowed by a proton-jump mechanism[7]. Furthermore, a swelling-contracting cycle of the membrane is related to the transport of metal ions from the L side to the R side. Consequently, H^+ ions play the role of driving force in the transport of metal ions and of controlling reagent for the physical and chemical structures of the membrane.

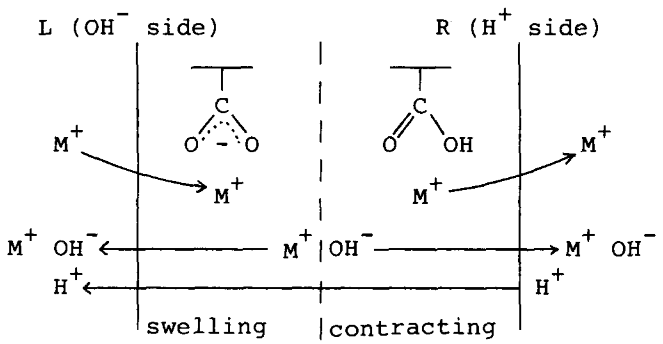

Figure 3. Tentative mechanism of the transport of metal ions through the polymer membrane containing carboxyl group

The selectivity, K^+/Li^+, against the initial H^+ ion concentration in the R side is summarized in Table 1, where the initial concentration of KOH and LiOH in the L side were kept constant at 5.0×10^{-2} M. The selectivity, K^+/Li^+, was always greater than unity and increased as the H^+ ion concentration increased. These results are attributed to the difference of the degree of swelling of the membrane and the hydrated size of each ion.

Table 1. Effect of H^+ ion concentration on the selectivity, K^+/Li^+

Log $[H^+]$	K^+/Li^{+*}
-0.1	1.75
-0.5	1.63
-1.0	1.32
-1.5	1.15
-2.0	1.25
-3.0	1.26

* $K^+/Li^+ = ([K^+]_{R,t}/[K^+]_{L,0})/([Li^+]_{R,t}/[Li^+]_{L,0})$ R,t is the concentration in the R side at time t and L,0 is the initial concentration in the L side

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