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Membranes

Studies on Syntheses and Permeabilities of Special Polymer Membranes
58. Facilitation of Active Transport of Sodium Ion Through Cation Exchange Membranes

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Summary

An active transport of alkali metal ion through cation exchange membranes was studied under various conditions. This active transport was facilitated by using a greateranion species on an acidic side in a diaphragm cell, in which one side of the solution was adjusted to be acidic and the other side alkaline across the membrane. An active transport fraction of alkali metal ion was in order poly(styrenesulfonate)>benzenesulfonate>Cl^- >I^->Br^- of anion species on the acidic side. A rate, fraction and period of the active transport of metal ion were significantly influenced by an electric potential gradient in the membrane.

Introduction

We have reported that alkali metal ions[1,2], ammonium ion[3], and amino acids[4,5] were transported actively through cation exchange membranes such as the membranes with carboxylic and sulfonic groups. The transport in their systems, where one side of the membrane in a diaphragm cell was acidic and the other alkaline, was significantly influenced by an intial H^+ ion concentration on the acidic side and diffusivity of anions from the acidic side to the alkaline side.

The present report focuses on a facilitation of active transport of Na^+ ion through cation exchange membranes by controlling the latter factors, i. e., by changing a size of anion species.

Experimental

The membrane (ISBN/PVA) with carboxylic acid group were prepared from poly(isobutylene-alternative co-maleic anhydride)(ISBN) and poly(vinyl alcohol)(PVA) as reported in previous papers[1,4]. The PSA/PVA membranes containing sulfonic acid groups were made from poly(styrenesulfonic acid) (PSA) and PVA as described in earlier papers[2,5]. All reagents used were of pure grade from commercial sources.

The apparatus for the transport experiment[1-4], the experimetal procedure[1,2], the determination of metal ion[1,2], the measurement of halogen ions[6], and the electric potential difference between the two sides of the membrane in a diaphragm cell[1,2] have been described in the previous papers. The concentration of benzenesulfonate and poly(styrenesulfonate) anions on both sides of the membrane were determined by colorimetric methods: 262 nm for benzenesulfonate anion and 260 nm for poly(styrenesulfonate) anion.

Results and Discussion

The effect of halogen ions on the acidic side on the transport fraction of Na^+ ion on the left-hand (L) and right-hand (R) sides in the diaphragm cell with time, due to the transport through the membrane is shown in Figure 1, where the membrane used was prepared from a ISBN/PVA weight ratio of 1/9, the L side was 0.1M NaOH aqueous solution and the R side consisted of 0.1M NaX and 0.1M HX aqueous solutions in which X is halogen. The transport fraction of Na^+ ion is defined by

$$\text{Transport fraction(\%)} = \{([Na^+]_t - [Na^+]_0)/[Na^+]_0\} \times 100$$

where $[Na^+]_0$ and $[Na^+]_t$ are the initial concentration and the concentrations of Na^+ ion on the L and the R sides after t hours, respectively. Positive and negative transport fractions represent an increase of Na^+ ion on the R side and a decrease of Na^+ ion on the L side due to the transport of Na^+ ion from the L side to the R side through the membrane, respectively. These phenomena for the transport suggests that Na^+ ions were transported actively through the membrane from the L side to the R side opposite to the concentration gradient between the two sides, because the initial concentrations of Na^+ ions on the two sides were identical. The transport fraction of Na^+ ion on the R side may be dependent on halogen ion on the R sides. In Figure 2 the permeation fraction of anion from the R side to the L side due to a diffusive transport through the ISBN/PVA membrane is shown. The permeation fraction of anion from the R side to the L side is difined by

$$\text{Permeation fraction (\%)} = ([\text{Anion}]_{L,t} / [\text{Anion}]_{R,0}) \times 100$$

where $[\text{Anion}]_{R,0}$ is the initial concentration of anion on the R side and $[\text{Anion}]_{L,t}$ is the anion concentration transported from the R side to the L side after t hours.

The hydrated ionic radius for halogen ions was in the order $Cl^- > I^- > Br^-$.

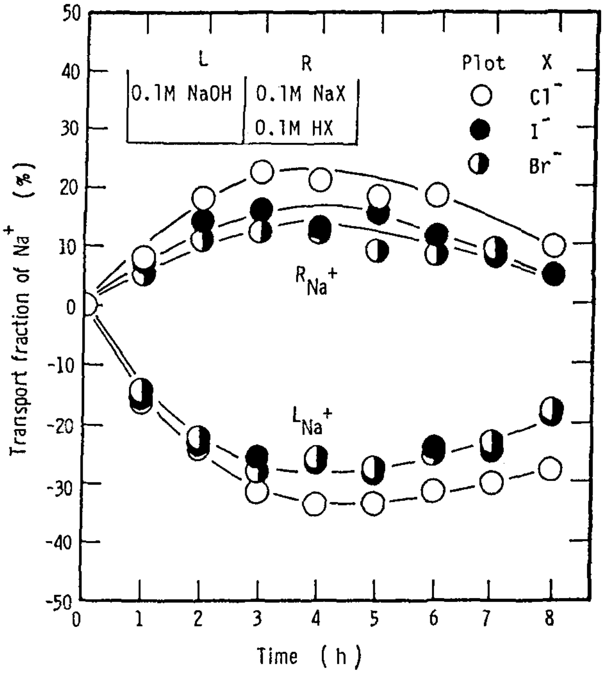

Figure 1. Changing of transport fraction of Na^+ ion on the two sides of a ISBN/PVA membrane with time.

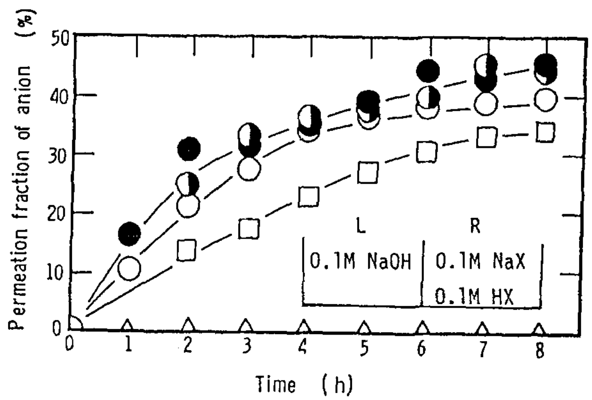

Figure 2. Effect of the anion species on the permeation fraction of anion from the R side to the L side through a ISBN/PVA membrane.

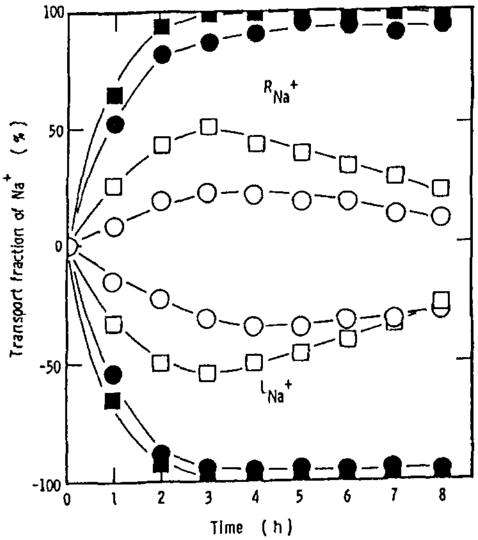

Figure 3. Effect of anion species on the transport fraction of Na^+ ion through a ISBN/PVA and a PSA/PVA membranes.

L	R
0.1M NaOH	0.1M NaX 0.1M HX

Membrane	X on R side	Plot
ISBN/PVA	Cl^-	○
	benzenesulfonate	☐
PSA/PVA	Cl^-	●
	benzenesulfonate	■

The order of permeation fraction for halogen ion in Figure 2 depended on the hydrated ionic radius. The transport fraction of Na^+ ion on the R side in Figure 1 was larger when the permeation fraction of halogen ions was smaller. From these results if the permeation of anion species from the R side to the L side can be disturbed, it is expected that the transport fraction of Na^+ ion from the L side to the R side is facilitated

In order to reveal the above expection, benzenesulfonate and poly(styrenesulfonate) anions whose ionic sizes larger than hlogen ions were used as anion species on the R side. The results obtained were shown in Figures 3 and 4. As can be seen from these results, the transport fractions of Na^+ ions on the R isde through both membranes of ISBN/PVA and PSA/PVA in the systems of benzenesulfonate and poly(styrenesulfonate) anions were greater than those in the system of chloride ion. In particular, the use of poly(styrenesulfonate) anion on the R side increased remarkably the transport fraction of Na^+ ion on the R side and in addition the transport rate and transport period of Na^+ ion were significantly facilitated. Figure 2 also included the permeation fraction of benzenesulfonate and poly(styrene sulfonate) anions through the ISBN/PVA membrane. It is suggested from these results that the permeation fraction of anion from the R side to the L side governs significantly the transport fraction of Na^+ ion on the R side. The transport fraction of Na^+ ion and the permeation fraction of anion may be related to an electric potential difference between the two sides of the membrane. The changes of electric potential difference with time are shown in Figure 5. This potential difference became higher as the permeation fraction of anion was smaller. The increase in this potential difference corresponded to the increase in the transport fraction of Na^+ ion[2]. This fact suggests that the rate, the fraction and the period of the active transport of Na^+ ion were significantly influenced by an electric potential gradient in the membrane.

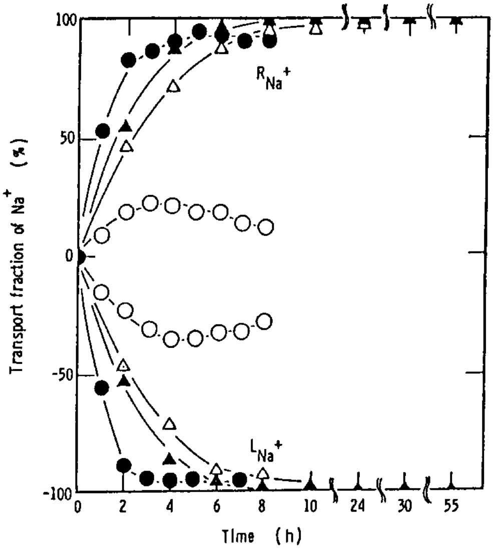

Figure 4. Effect of anion species on the transport fraction of Na^+ ion through a ISBN/PVA and a PSA/PVA membranes.

L	R
0.1M NaOH	0.1M NaX 0.1M HX

Membrane	X on R side	Plot
ISBN/PVA	Cl^-	○
	poly(styrenesulfonate)	△
PSA/PVA	Cl^-	●
	poly(styrenesulfonate)	▲

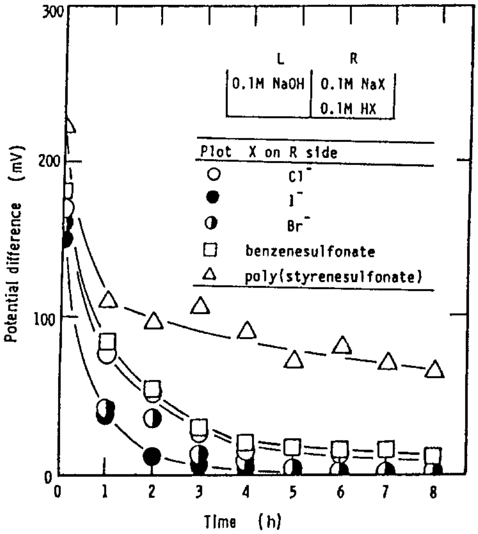

Figure 5. Changes of electric potential difference between the two sides across a ISBN/PVA membrane with time.

The PSA/PVA membrane was denser than the ISBN/PVA membrane[1,2]. Therefore, the transport fraction of Na^+ ion was larger and the permeation fraction of anion was smaller through the PSA/PVA membrane. The improvement of transport fraction of Na^+ ion through the cation exchange membranes by disturbing the permeation of anion on the R side across the membrane may be accomplished by (1) making the denser membranes, (2) preparing the membranes with higher ion exchange capacity, and (3) using anion species with larger ionic size, etc. The factors (1) and (3) are physical, and (2) is chemical. The factor (1) and (2) have their limts. The factor (3) is the simplest and favorable to improve the transport fraction of metal ions through the cation exchange membranes.

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