

# Studies on syntheses and permeabilities of special polymer membranes: 50. Transport of metal ions against their concentration gradient through water-insoluble poly(styrene sulphonic acid) membrane

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(Received 3 November 1981; revised 20 September 1982)

Water-insoluble cation exchange membranes were prepared by heat treating membranes made of poly(styrene sulphonic acid) and poly(vinyl alcohol). Transport of metal ions through the above cation exchange membrane against their concentration gradient was investigated under various conditions. The transport in this system, where one side of the membrane in a diaphragm cell was acidic and the other alkaline, was influenced significantly by the initial  $H^+$  ion concentration on the acidic side. The selectivity of metal ions in diffusive transport depended on the size of their hydrated ions and that in transport against their concentration gradient was due to the affinity between the metal ions and the carrier fixed to the membrane.

**Keywords** Cation exchange membrane; transport; metal ion; selectivity; concentration gradient; pH difference

## INTRODUCTION

Active transport and selective transport of metal ions through liquid membranes containing a carrier have been investigated by many workers. Recently, the active transport of metal ions<sup>1-5</sup>, anions<sup>6,7</sup> and organic cations<sup>8</sup>, and the selective transport of metal ions<sup>1-5</sup> through synthetic polymeric membranes with a fixed specific functional carrier, have been studied. The functions of the specific carriers fixed to the membrane, carriers such as lactone rings, *N*-hydroxyethyl amide groups and carboxyl groups, were shown by reversible and rapid changes of chemical structure of their carriers with pH change. Sulphonic acid groups are probably the simplest of such functional carriers.

Here, the transport and selectivity of metal ions through cation exchange membranes made of poly(styrene sulphonic acid) and poly(vinyl alcohol), which had sulphonic acid groups as the fixed functional carrier, are discussed from various viewpoints.

## EXPERIMENTAL

### Materials

Poly(styrene sulphonic acid) (PSA) synthesized by the method reported in the previous paper<sup>9</sup>, having an ion exchange capacity of 5.05 mEq/g, and poly(vinyl alcohol) (PVA) produced by Kurary Co. Ltd, having an average degree of polymerization  $1725 \pm 25$  and degree of saponification  $88 \pm 1$  mol%, were employed as the membrane substances. All reagents used in this work were from pure commercial sources.

### Preparation of membrane

Casting solutions were prepared by mixing the desired amounts of 5 wt% PSA and 5 wt% PVA aqueous solutions. Membranes were made by pouring the casting solution onto a rimmed glass plate and allowing water to evaporate at 25°C for 3 days. Since the membranes obtained were soluble in water, water-insoluble membranes were made by heat treating the membranes at 100°C for the desired period. After immersion for 24 h in 2 N HCl, the membranes were washed repeatedly with pure water and kept in pure water (25°C).

### Apparatus and measurements

The transport apparatus used, the experimental procedure and the determination of the concentrations of metal ions and chloride ion have been described in an earlier paper<sup>5</sup>. The electric potential difference between right-hand side and left-hand side of the membrane in a diaphragm cell was measured by a potentiometer (Hitachi-Horiba F-7SSII type). All experiments were carried out at 25°C.

## RESULTS AND DISCUSSION

### Transport of metal ion

Changes in the concentration of the  $K^+$  ion with time on the left-hand side (l.h.s.) and the right-hand side (r.h.s.) of the membranes in a diaphragm cell are shown in *Figure 1*, with various periods of heat treatment of membranes at 100°C. The l.h.s. was 0.1 M KOH and the r.h.s. 0.1 M KCl and 0.1 M HCl. In all membranes, the concentration of the

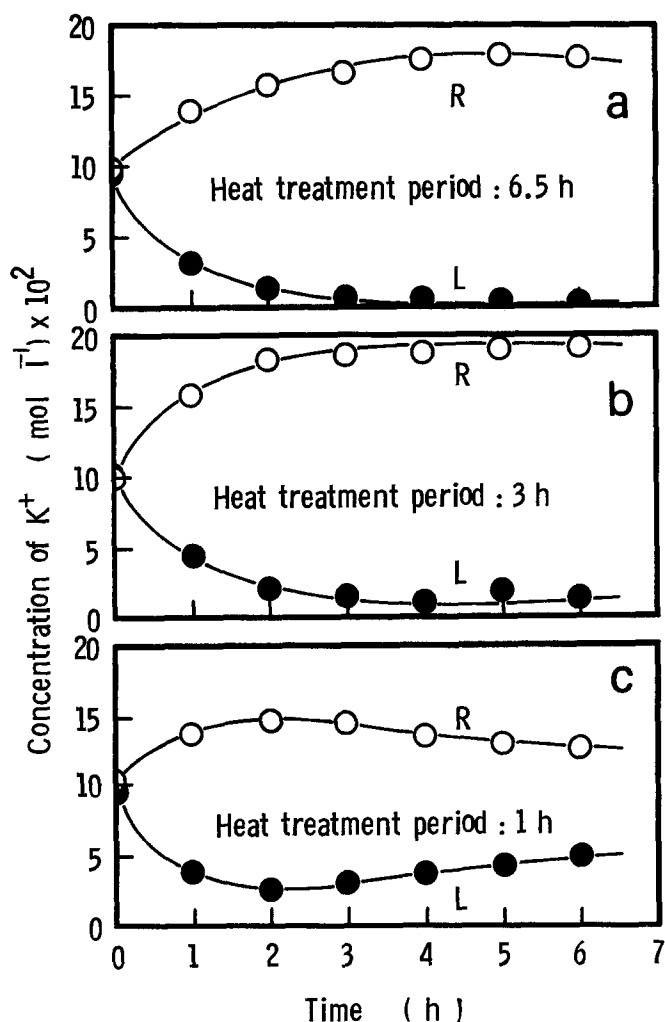


Figure 1 Changes of the  $K^+$  ion concentration on both sides of the membranes with time with various heat treatment periods. Membrane, PSA/PVA = 2/3; temperature of heat treatment,  $100^\circ\text{C}$ ; l.h.s., ●; r.h.s., ○. Heat treatment periods: (a) 6.5 h, (b) 3 h, (c) 1 h

$K^+$  ion on the r.h.s., which was acidic, increased up to a maximum and then decreased; in contrast, that on the l.h.s. decreased and then increased with time.

Since the initial concentration of the  $K^+$  ion was the same on both l.h.s. and r.h.s., the increase of the  $K^+$  concentration on the r.h.s. suggests active transport of the  $K^+$  ion from the alkaline side to the acidic side through the membrane. Such results are similar to the transport of alkali metal ions through a membrane prepared from polymers containing lactone rings<sup>1-4</sup>, that of metal ions<sup>5</sup> and organic ions<sup>8</sup> through a membrane made of polymer having carboxyl groups, and that of chloride ions through membranes having *N*-hydroxyethyl amide groups<sup>6</sup> and amino groups<sup>7</sup>.

In order to estimate the extent of transport of metal ion, the transport fraction was defined as:

$$\text{transport fraction}(\%) = (C_{\text{max}} - C_0) \times 100 / C_0 \quad (1)$$

where  $C_0$  ( $\text{mol l}^{-1}$ ) and  $C_{\text{max}}$  ( $\text{mol l}^{-1}$ ) are the initial and maximum concentrations of metal ions on the r.h.s., respectively. Figure 2 shows the relationship between the transport fraction of  $K^+$  ion and the heat treatment

period. The transport fraction of  $K^+$  was higher in membranes treated with heat for longer periods. These results imply the participation of sulphonic acid groups in the membrane in the transport of  $K^+$  ion.

When  $K^+$  ion transported actively, a difference of  $K^+$  ion concentration occurred between the two sides, Therefore the diffusion of  $K^+$  ought to occur, according to the concentration gradient of the  $K^+$  ion, in the reverse direction to its active transport. Actually, when the membrane was heat treated at  $100^\circ\text{C}$  for 1 h, at first since the reverse diffusion of  $K^+$  ion from the r.h.s. to the l.h.s. balanced the active transport of  $K^+$  ion from the l.h.s. to the r.h.s., a maximum value of  $K^+$  ion concentration was observed, then the reverse diffusion predominated, and after 24 h the  $K^+$  ion concentration was equal in both sides. In the membranes with heat treatment periods of 3 and 6.5 h, however, even if the transport time was 24 h, the reverse diffusion of  $K^+$  ion by the concentration gradient was very small but an increase of the volume of the solution on the r.h.s. was observed. This is due to the transfer of  $\text{H}_2\text{O}$  through the membrane from the lower to the higher concentration side because an osmotic pressure occurred across the membrane, which was very dense.

The membrane prepared from PSA/PVA in the ratio 2/3 and heat treated at  $100^\circ\text{C}$  for 3 h was used for all subsequent studies.

In Figure 3, where the l.h.s. was 0.1 M KOH and the r.h.s. was 0.1 M KCl in aqueous HCl, the transport fraction of  $K^+$  ion is plotted against the initial  $\text{H}^+$  ion concentration on the r.h.s. The transport fraction of  $K^+$  ion concentration increased as pH went to pH 1.0 on the r.h.s. and then remained approximately constant at 90% as the initial pH on the side decreased below unity. In Figure 4, some examples of the pH changes in both l.h.s. and r.h.s. with time are shown. These results suggest that  $\text{OH}^-$  ions in the l.h.s. and  $\text{H}^+$  ions in the r.h.s. diffused

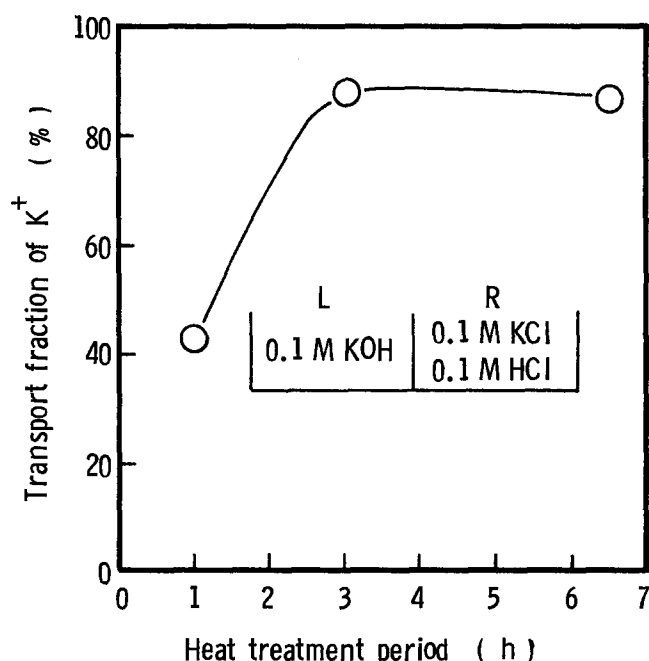


Figure 2 Effect of heat treatment period on the transport fraction of  $K^+$  ion. Membrane, PSA/PVA = 2/3; temperature of heat treatment,  $100^\circ\text{C}$ ; l.h.s., 0.1 M KOH; r.h.s., 0.1 M KCl and 0.1 M HCl

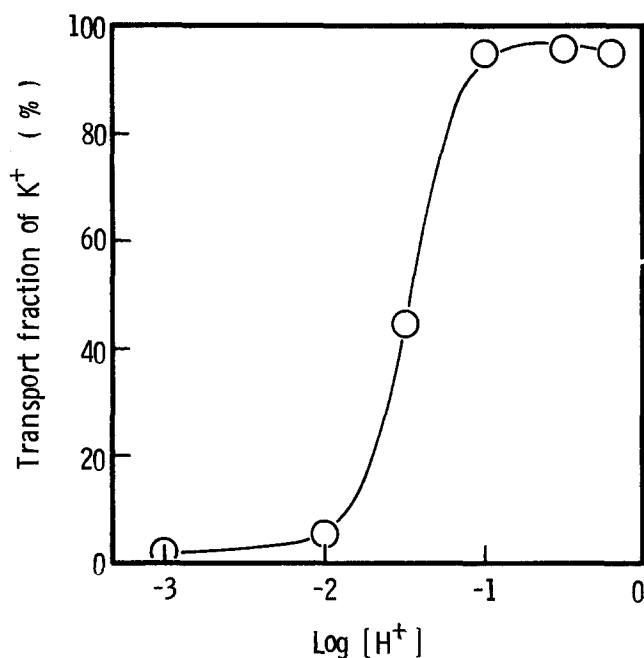


Figure 3 Transport fraction of  $K^+$  ion plotted against the initial  $H^+$  ion concentration on the r.h.s. Membrane, PSA/PVA = 2/3; conditions of heat treatment, 100°C, 3 h

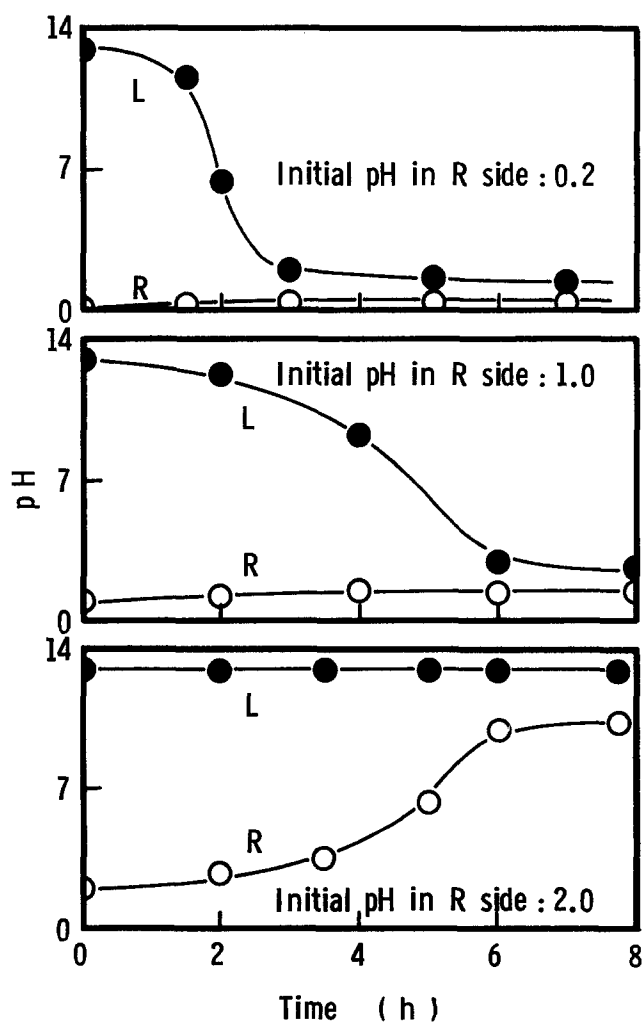


Figure 4 Changes of pH on both sides with time: l.h.s., ●; r.h.s., ○. Initial pH on r.h.s.: (a) 0.2, (b) 1.0, (c) 2.0

through the membrane according to the concentration gradients of their ions and consequently neutralization occurred. Under the condition of initial pH 1.0 on the r.h.s., both sides became acidic with time because the acidic equivalent was greater than the alkaline equivalent. When the initial pH on the r.h.s. was higher than unity, in contrast, both sides became alkaline with time. From these results, it is expected that the transport of  $K^+$  ion through the membrane is attributed to the pH difference between the two sides.

In Table 1, the decreased amount of  $H^+$  ion on the r.h.s.,  $\Delta[H^+]$ , and the transported amount of  $K^+$  ion from the l.h.s. to the r.h.s.,  $\Delta[K^+]$ , are summarized against the initial  $H^+$  ion concentration in the r.h.s. Also Table 1 includes the relationship between the ratio  $\Delta[H^+]/\Delta[K^+]$  and the initial  $H^+$  ion concentration. Both values of  $\Delta[H^+]$  and  $\Delta[K^+]$  increase with increase of initial  $H^+$  ion concentration in the r.h.s., and these values were equal except at pH 0.2.

When  $H^+$  ion transfers from the r.h.s. to the l.h.s. it would be expected that  $Cl^-$  ion, which is a counter-ion for  $H^+$  ion, would also diffuse from the r.h.s. to the l.h.s. because of the concentration gradient. The diffused amount of  $Cl^-$  ions from the r.h.s. to the l.h.s. was very small compared with that of  $H^+$  ions. This is mainly caused by the Donnan membrane relationship. However,  $H^+$  ions transferred easily by a proton-jump mechanism<sup>10</sup>.

Since the membrane used here had fixed charges, Donnan equilibrium was set up between both sides and the membrane. It is expected that an electric potential difference between the two sides occurs and that this potential difference may be related to the transport of metal ions. The changes of electric potential difference with time are shown in Figure 5. In all conditions, other than the initial pH 3 on the r.h.s., where the transport of  $K^+$  ion was not observed as shown in Figure 3, an electric potential difference occurred between the two sides. When the extent of this potential difference became higher, the transport fraction of  $K^+$  ion increased. This result suggests that transport of  $K^+$  ion is influenced significantly by the electric potential difference between the two sides.

From the above results, the tentative mechanism of active transport of alkali metal ions is shown in Figure 6. When one side was alkaline and the other side was acidic, on the alkaline side ( $OH^-$  side) metal ions were incorporated into the membrane by the ion exchange reaction (2), and  $H^+$  ions became  $H_2O$  by neutralization with  $OH^-$  ions:

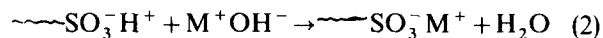


Table 1 Effect of  $H^+$  ion concentration on  $\Delta[K^+]$ ,  $\Delta[H^+]$  and  $\Delta[H^+]/\Delta[K^+]$

$\text{Log}[H^+]$	$\Delta[K^+]$ ( $\text{mol l}^{-1}$ ) $\times 10^3$	$\Delta[H^+]$ ( $\text{mol l}^{-1}$ ) $\times 10^3$	$\Delta[H^+]/\Delta[K^+]$
-0.2	1.70	2.90	1.7
-0.5	1.75	1.75	1.0
-1.0	1.65	1.63	1.0
-1.5	0.55	0.56	1.0
-2.0	0.15	0.16	1.1

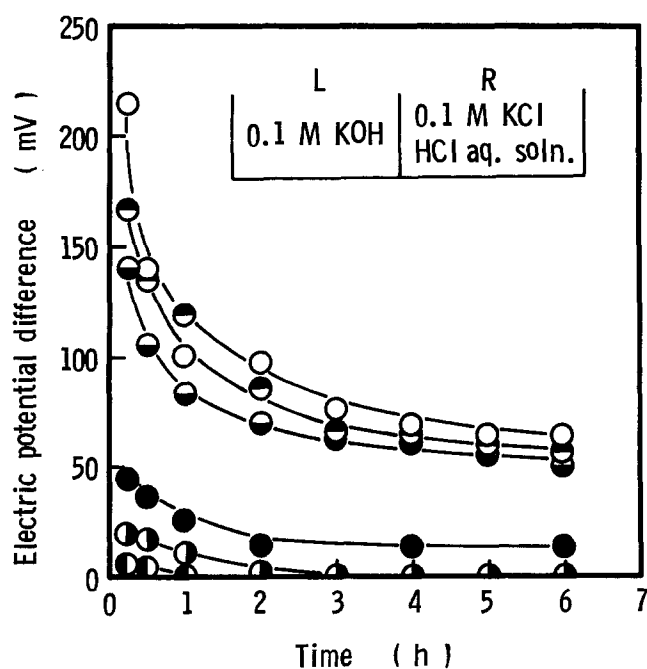


Figure 5 Changes of electric potential difference between the two sides with time: l.h.s., 0.1 M KOH; r.h.s., 0.1 M KCl, HCl aq. soln. Initial pH on r.h.s.: ○, 0.2; ●, 0.5; ◐, 1.0; ●, 1.5; ●, 2.0; ●, 3.0

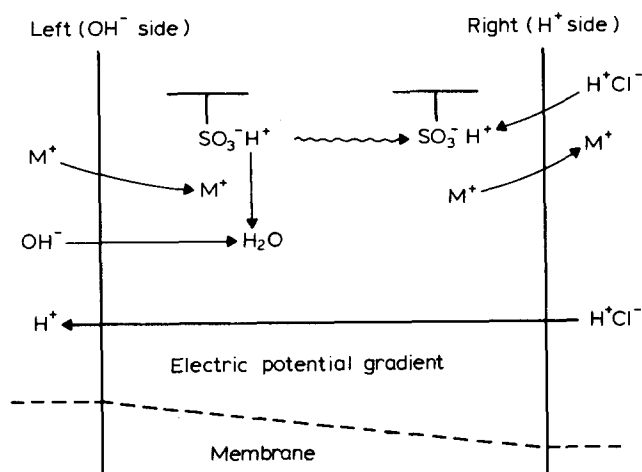


Figure 6 Tentative mechanism of transport of metal ions through a cation exchange membrane containing sulphonic acid groups

Then metal ions were transferred through the membrane by the sulphonic acid groups fixed to it. On the other hand, since the dissociation of sulphonic acid groups on the acidic side ( $H^+$  side) was very low compared with that on the alkaline side, the membrane surface on this side was very dense. Therefore, it was difficult for metal ions and in particular  $Cl^-$  ions to permeate into the membrane. However,  $H^+$  ions could be transferred through the membrane from the acidic side to the alkaline side by a proton-jump mechanism<sup>10</sup>. When such  $H^+$  ions reached the region where the metal sulphonate was formed, metal ions were released by the ion exchange reaction (3):



The metal ions released were transferred to the acidic side by the electric potential gradient between the two sides as described above.

If the transport of metal ions proceeded by the above mechanism, it is presumed to be influenced significantly by two factors: (1) the reversible adsorption-desorption cycle reaction of metal ions by the sulphonic acid groups in the membrane and (2) the occurrence of an electric potential gradient between the two sides caused by the impermeability of the membrane to  $Cl^-$  ions. In considering factor (1), it was required to give transport conditions which showed the difference in the dissociation of sulphonic acid groups in the membrane. In the systems investigated here, when the l.h.s. was an alkaline aqueous solution of constant concentration and the r.h.s. was an acidic aqueous solution the effect of factor (1) could be maximized. On the other hand, for factor (2) it was important to prevent the diffusion of  $Cl^-$  ions into the membrane by forming a membrane which was denser and had many fixed charges. The membrane used here, which was prepared with PSA/PVA in the ratio 2/3 and heat treated at  $100^\circ\text{C}$  for 3 h, was very dense and even the diffusion of  $K^+$  ions through the membrane caused by their concentration gradient was not easy, and the ionic concentration in this membrane was relatively high (4.2 mEq/g  $H_2O$ ). Therefore, it was expected that  $Cl^-$  ions did not transfer completely across the membrane. However,  $Cl^-$  ions on the r.h.s. transferred to the l.h.s. through the membrane as described above. The effect of factor (2) may be supported by using more bulky anions, such as alkylbenzene sulphonate which cannot permeate physically through the membrane, as the anionic species instead of  $Cl^-$  ion in the acidic side.

#### Selective transportability of metal ion

The changes of  $K^+$  and  $Na^+$  ion concentrations on both sides of the membrane with time are shown in Figure 7, where the l.h.s. was a mixed solution of  $5 \times 10^{-2}$  M KOH and  $5 \times 10^{-2}$  M NaOH and the r.h.s. was aqueous HCl of different concentration. When the initial pH on the r.h.s. was 0.2 and 1.0, both  $K^+$  and  $Na^+$  ions permeated from the l.h.s. to the r.h.s., the concentrations of these metal ions on the two sides then becoming equal. Furthermore, these ions were transferred between the two sides against their concentration gradients. When the initial pH on the r.h.s. was 3.0, in spite of the fact that there were concentration gradients of these ions between the l.h.s. and r.h.s., the permeation of both  $Na^+$  and  $K^+$  ions from the l.h.s. to the r.h.s. was rather small. This is caused by the fact that the membrane was denser.

Permeation fractions and selectivities at 3 h, which were calculated from equations (4), (5) and (6) respectively, in the  $K^+-Na^+$ ,  $Li^+-Na^+$ ,  $K^+-Li^+$  binary systems are summarized in Table 2:

$$\text{permeation fraction}(\%) = ([M_1^+]_{R,t} / [M_1^+]_{L,0}) \times 100 \quad (4)$$

$$\text{permeation fraction}(\%) = ([M_2^+]_{R,t} / [M_2^+]_{L,0}) \times 100 \quad (5)$$

$$\text{selectivity} = ([M_1^+]_{R,t} / [M_1^+]_{L,0}) / ([M_2^+]_{R,t} / [M_2^+]_{L,0}) \quad (6)$$

where  $M_1$  and  $M_2$  are each cation in the mixed aqueous solution and  $R,t$  is the concentration on the r.h.s. at time  $t$  and  $L,0$  is the initial concentration on the l.h.s.

The permeation fraction of alkali metal ions in all binary systems increased with an increase in the initial  $H^+$  ion concentration in the r.h.s. and was approximately constant at pH less than 1.0. The trend of the permeation fraction was similar to that of the transport fraction of  $K^+$  ion shown in Figure 3. Under the condition of higher  $H^+$  ion concentration on the r.h.s., it is suggested that both alkali metal ions in all binary systems were actively transported through the membrane from the l.h.s. to the r.h.s.

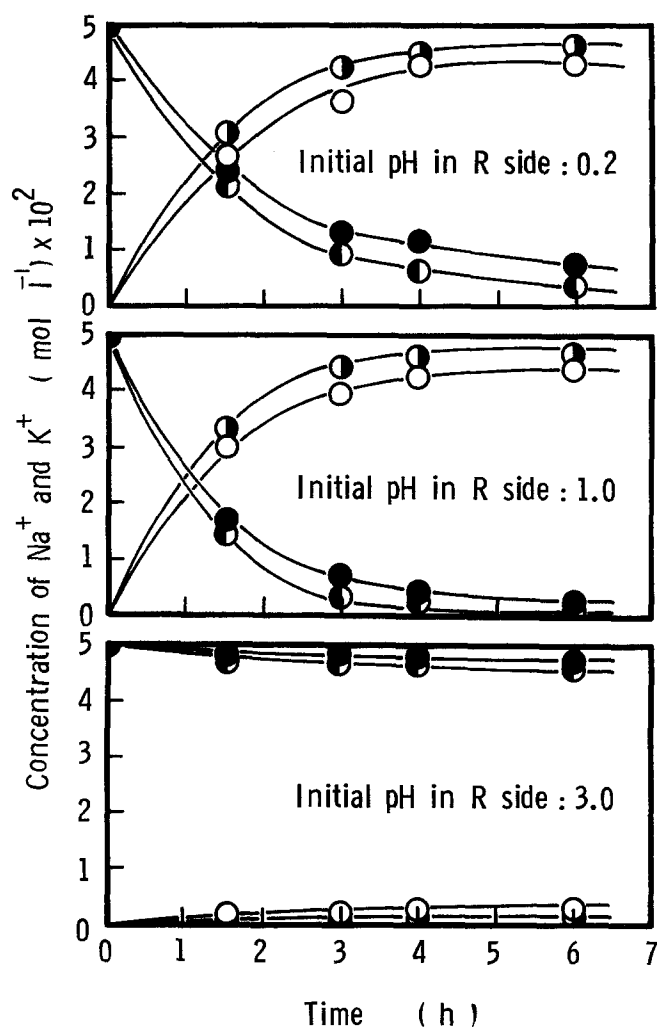


Figure 7 Changes of the  $Na^+$  and  $K^+$  ion concentrations on the two sides of the membrane with time. Membrane, PSA/PVA ratio of 2/3 in the  $Na^+-K^+$  binary system: ●,  $Na^+$  ion on l.h.s.; ○,  $Na^+$  ion on r.h.s.; ●,  $K^+$  ion on l.h.s.; ○,  $K^+$  ion on r.h.s. Initial pH on r.h.s.: (a) 0.2, (b) 1.0, (c) 3.0

The selectivities,  $K^+/Na^+$  and  $K^+/Li^+$ , were always greater than unity, that is,  $K^+$  ion permeated preferentially to  $Na^+$  ion or  $Li^+$  ion. In the  $Li^+-Na^+$  binary system, the selectivity,  $Li^+/Na^+$ , was smaller than unity, that is,  $Na^+$  ion permeated more rapidly than  $Li^+$  ion. As mentioned above, if the transport of metal ions was dependent on the reversible adsorption-desorption reaction of metal ions, it is expected that the selective transportability of metal ions may be governed by affinity between the membrane and the metal ion. The amount of metal ions adsorbed on the membrane in various metal binary systems is summarized in Table 3. The difference of amount of metal ions adsorbed corresponded to the selectivity for each metal binary system. That is, it is found that metal ion which was selectively adsorbed into the membrane was permeated preferentially.

In the  $K^+-Li^+$  binary system, the selectivity,  $K^+/Li^+$ , increased as the initial  $H^+$  ion concentration on the r.h.s. decreased and was higher than those of the  $K^+-Na^+$  and  $Li^+-Na^+$  binary systems. Since the hydrated ionic radius for these alkali metal ions was in the order<sup>11</sup>  $K^+ < Na^+ < Li^+$ , this is attributed to the difference between the hydrated ionic radii of  $K^+$  and  $Li^+$  being greater than those of the other two binary systems. In particular, when the initial  $H^+$  ion concentration on the r.h.s. became lower, the permeation of metal ions depended on diffusion through the membrane due to the concentration gradient between the two sides, as shown in Figure 7. Therefore, under such conditions a metal ion which had a larger hydrated ionic radius decreased the permeation fraction because the permeation resistance between the membrane and the hydrated ion increased.

It is found that the selectivity of permeation for alkali metal ions through the membrane from the alkaline side to the acidic side is given by the following order:



This order of selectivity was identical to that for alkali metal ions through a cation exchange membrane containing carboxyl groups, made of poly(isobutylene-co-maleic anhydride) alternating copolymer and poly(vinyl alcohol)<sup>5</sup>.

In Figure 8, the permeation fraction and the selectivity at 3 h in the  $Ca^{2+}-Na^+$  binary system are plotted against the initial  $H^+$  ion concentration on the r.h.s. The permeation fraction increased with increase of the initial  $H^+$  ion concentration on the r.h.s.

The selectivity,  $Ca^{2+}/Na^+$ , reversed at initial pH 2.0 on the r.h.s., i.e. when the initial  $H^+$  ion concentration was lower than pH 2.0,  $Na^+$  ion permeated more selectively than  $Ca^{2+}$  ion and the selectivity for these ions reversed at

Table 2 Effect of  $H^+$  ion concentration on the permeation fractions of alkali metal ions and the selectivities,  $K^+/Na^+$ ,  $Li^+/Na^+$ ,  $K^+/Li^+$

log[H <sup>+</sup> ]	Permeation fraction (%)			Permeation fraction (%)			Permeation fraction (%)		
	K <sup>+</sup>	Na <sup>+</sup>	Selectivity, K <sup>+</sup> /Na <sup>+</sup>	Li <sup>+</sup>	Na <sup>+</sup>	Selectivity, Li <sup>+</sup> /Na <sup>+</sup>	K <sup>+</sup>	Li <sup>+</sup>	Selectivity, K <sup>+</sup> /Li <sup>+</sup>
-0.2	80.8	71.5	1.13	78.9	80.5	0.98	78.2	69.8	1.12
-0.5	86.2	80.6	1.07	78.1	79.8	0.97	81.7	79.3	1.03
-1.0	90.2	83.5	1.08	76.8	81.7	0.94	86.9	80.5	1.08
-1.5	58.5	54.2	1.08	48.7	55.3	0.88	50.5	41.7	1.21
-2.0	9.0	8.1	1.11	18.4	21.4	0.86	11.7	8.2	1.43
-3.0	3.1	2.8	1.12	1.9	2.1	0.90	4.2	2.7	1.55

Table 3 Amount of metal ions adsorbed on the membrane

Solution composition <sup>a</sup>	Amount of metal ion adsorbed (mmol/g dry membrane)			
	K <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>	Ca <sup>2+</sup>
KOH/NaOH	1.28	0.97	—	—
NaOH/LiOH	—	1.08	0.95	—
KOH/LiOH	1.08	—	0.81	—
NaCl/CaCl <sub>2</sub>	—	0.13	—	0.75

<sup>a</sup> 5.0 × 10<sup>-2</sup> M aqueous solution

pH more than 2.0. Under the conditions where transport occurred, the selectivity was dependent on the affinity between the membrane and the metal ion as summarized in Table 2. However, when the initial H<sup>+</sup> ion concentration on the r.h.s. was lower, the permeation of metal ions was mainly governed by diffusion due to the concentration gradient because the driving force of the transport of metal ions decreased with decrease of the initial H<sup>+</sup> ion concentration. Consequently, Na<sup>+</sup> ion, which was smaller than the hydrated ionic radius of Ca<sup>2+</sup> and had a weaker interaction with the membrane, permeated selectively.

From the above results, the permeation of metal cations in the binary system is classified into the diffusive transport of metal ions due to the concentration gradient and the transport of metal ions caused by the pH difference between the two sides of the membrane. It is concluded that, under the conditions where the former transport is predominant, the selectivity for metal ions is governed significantly by the hydrated size of metal ions and under the latter it is mainly influenced by the affinity between the membrane and the transporting ion.

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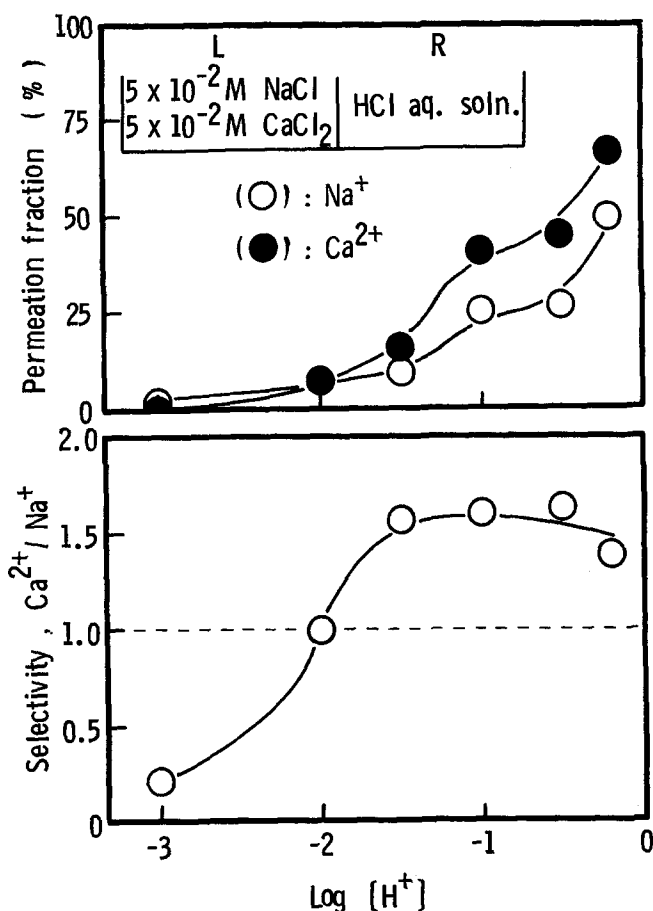


Figure 8 Effect of initial H<sup>+</sup> ion concentration on r.h.s. on the permeation fraction and the selectivity, Ca<sup>2+</sup>/Na<sup>+</sup>. R.h.s., HCl aq. soln.; l.h.s., 5 × 10<sup>-2</sup> M NaCl or 5 × 10<sup>-2</sup> M CaCl<sub>2</sub>