Studies on Syntheses and Permeabilities of Special Polymer Membranes. XLVII. Active Transport and Selective Transport of Metal Ions through Membranes from Poly(isobutylene-Alternative Co-Maleic Anhydride) and Poly(vinyl Alcohol)

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Synopsis

When a cation exchange membrane having carboxyl groups, made of poly(isobutylene-alternative co-maleic anhydride) and poly(vinyl alcohol), was set in a diaphragm type cell, in which one side of the solution was adjusted to be acidic and the other side alkaline, metal ions were actively transported from the alkaline side to the acidic side across the membrane against the concentration gradient of metal ions between both sides. The driving force of the transport of metal ions was the difference in H^+ ion concentration between both sides. It was presumed that the active transport was carried out chemically and physically. In the selective transport of metal ions, the selectivity was dependent on both the hydrated ionic radius for the metal ions and the affinity between the carrier fixed to the membrane, the carboxyl group, and the metal ions.

INTRODUCTION

Mass transfer through polymeric membranes is explicable by the difference of pressure, concentration, and potential, etc. across the membrane. However, many complex phenomena which cannot be understood by physicochemical mechanisms are found in biomembranes. For example, they are the active transport of ions against the osmotic pressure, concentration, and potential gradients and the selective transport of K^+ and Na^+ ions in the cell membrane. These transports play important roles for the function of the life.

We have a deep interest in the development of synthetic polymeric membranes having similar functions to the biomembranes such as the active and the selective transports. Active transport of metal ions and anions across liquid membranes containing carrier, such as stearic acid,[1] dithizone,[2] trioctylamine,[2] β-diketone,[2] monensin,[3] polyanion,[4] kelex 100, etc.,[5] and hexadecylbutylammonium,[6] and selective transport of metal ions through liquid membranes containing carrier, such as crown ether[7] and macrocyclic ligands composed of tetrahydrofuran,[8] have been investigated. Active transport and selective transport of metal ions and anions through synthetic polymeric membranes having a fixed functional carrier, such as poly(amine sulfone) derivative membranes,[9] polyamide membranes made of bicyclic oxalactam,[10] several lactone-containing polymer membranes,[11-14] polymer membranes having the N-hydroxyethyl amide group,[15] thermal re-

generation ion–exchange resin membranes,[16] and poly(isobutylene-alternative co-maleic anhydride) membranes,[17] have been studied. The functions of these membranes were depended on to transport metal ions and anions through the membranes owing to the carrier functions, for example, caused by reversible opening–closing of the lactone ring and tautomerism of the N-hydroxyethyl amide group with pH changes. Polymers having the simplest functional groups which can be changed reversibly and rapidly by pH changes have been applied to the ion exchange membranes. We have studied active and selective transport of metal ions and anions through ion exchange membranes.[18,19] We reported that it was possible to transport actively and selectively metal ions through the membrane made of poly(isobutylene-alternative co-maleic anhydride) cross-linked with poly(vinyl alcohol).[17] In this paper, these phenomena are discussed in detail from various viewpoints.

EXPERIMENTAL

Poly(isobutylene-alternative co-maleic anhydride) (ISBN, ISBN-10 from Kurary Co., Ltd.) and poly(vinyl alcohol) (PVA, PVA-217 from Kurary Co., Ltd.) were employed as the membrane substance. All reagents used in this work were pure commercial sources.

Preparation of Membrane

ISBN (15 g) was dissolved in an aqueous solution consisted of water (131 g) and NaOH (4 g). In this solution maleic anhydride units in ISBN opened, and one carboxyl group of its unit was a sodium carboxylate. Casting solutions were prepared by adding with well stirring 10% PVA aqueous solution to ISBN solution containing a desired amount of $1N$ H_2SO_4. The membranes were made by pouring these casting solutions onto a plate made of silicon rubber, allowing evaporation of water at 80°C for 5 h in an oven, and immersing the membranes into $1N$ HCl aqueous solution. After immersion for 3 days in $1N$ HCl, the membranes were washed repeatedly with water and kept in water (25°C).

Apparatus and Measurements

Transport experiments were carried out at 25°C under magnetic stirring, using a diaphragm type cell consisting of two detachable parts made of poly(methyl methacrylate), as shown in Figure 1. The membrane was set in the middle of the two parts of the cell, which were clamped and sealed tightly with silicon rubber packings. The effective membrane area in the cell was 4.0 cm². Since the system was not closed, volume changes in both sides occurred with time. Therefore, the concentration of metal ions in both sides was corrected.

The concentrations of metal cations, in both left and right cells, were determined by atomic absorption photometry. The concentration of Cl⁻ ion in both cells was determined indirectly by measuring the amount of Ag⁺ ion by means of atomic absorption photometry. That is, a given sample solution was added to a known concentration of AgNO₃ aqueous solution (A mol/L), a precipitation of AgCl was removed completely by the filtration, and a residual amount of Ag⁺ ion in the filtrate (B mol/l) was determined.
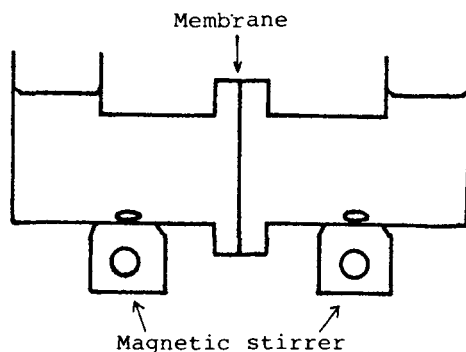
Membrane

Magnetic stirrer

Fig. 1. Sketch of diaphragm cell: volume 20 cm^3, effective membrane area 4.0 cm^2.

$$\text{concn of Cl}^- \text{ ion} = A - B$$

The weighed dry membranes consisted of ISBN and PVA were immersed into 0.2N NaOH at 25°C for 3 days in order to completely convert the carboxyl groups in the membranes into the sodium carboxylate and then the Na$^+$ ion concentration in the solution was determined by atomic absorption photometry. The ion exchange capacities per weight of the dry membranes were calculated from the following equation:

$$\text{ion exchange capacity (meq/g)} = (C_0 - C)V/W \tag{1}$$

where C_0 (mol/L) and C (mol/L) are the Na$^+$ ion concentration in the blank test and in the NaOH solution with the membrane, respectively. V (mL) is the volume of 0.2N NaOH aqueous solution immersed the membrane and W (g) is the weight of dry membrane.

The amount of metal ions in the membrane, washed the surface with water, was determined by reducing the membrane to ashes in a crucible.

RESULTS AND DISCUSSION

Active Transport of Alkali Metal Ions

Some examples of the concentration changes of K$^+$ ions and pH changes in the L side and the R side through the membrane are shown in Figure 2. In all systems, the concentration of K$^+$ ion in the R side up to a certain hour increased and the concentration change in both sides was just the opposite, while Cl$^-$ ions were scarcely transferred during the experiment. These results suggest that K$^+$ ions were actively transported across the membrane against its concentration gradient between both sides. The membranes used in this work swelled in alkaline pH and contracted in acidic pH. This phenomenon is similar to those observed in water-insoluble films of poly(acrylic acid), poly(methacrylic acid), and poly(L-glutamic acid) crosslinked with glycerol or poly(vinyl alcohol)[20,21] and depends on a degree of dissociation of the carboxyl groups in the membrane. The active transport of K$^+$ ion across the membrane may be related to a swelling and contracting of the membrane, too.

Figure 3 shows the effect of initial H$^+$ ion concentration in the R side on a mean
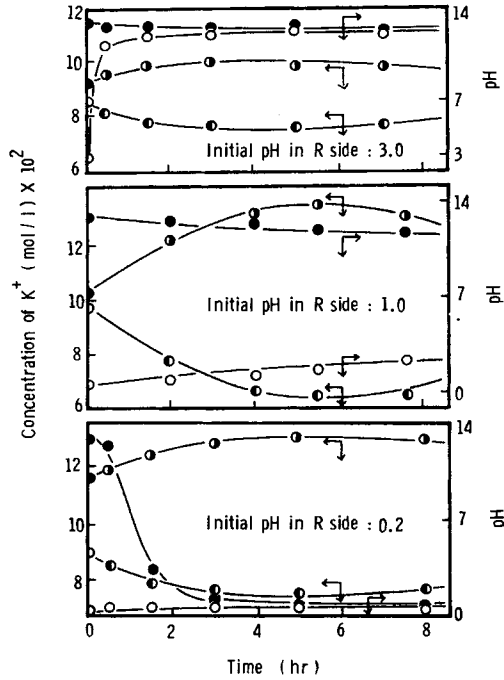
Fig. 2. Changes of the K^+ ion concentration and pH in both sides with time through the membrane: ISBN/PVA = 1/9, ($\mathbb{O}$) K^+ ion in the L side; ($\mathbb{O}$) K^+ ion in the R side; (O) pH in the R side; (●) pH in the L side; (L) 0.1M KOH; (R) 0.1M KCl, HCl aq. soln

transport rate (mol/L·h) and transport fraction (%) of K^+ ion, which are defined as eqs. (2) and (3).

$$\text{mean transport rate} = \frac{[K^+]_{max} - [K^+]_0}{t_{max}} \qquad (2)$$

$$\text{transport fraction} = \frac{[K^+]_{max} - [K^+]_0}{[K^+]_0} \times 100 \qquad (3)$$

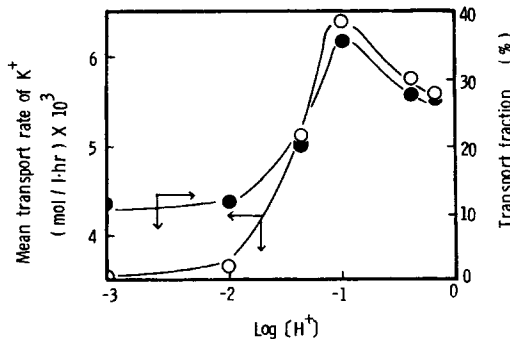where $[K^+]_{max}$, $[K^+]_0$, and t_{max} are as shown in Figure 4.

Fig. 3. Effect of the initial H^+ ion concentration in the R side on the mean transport rate and transport fraction of K^+ ion.
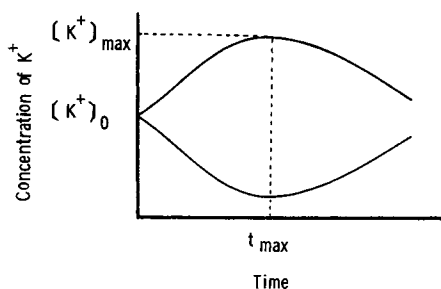
Fig. 4. Scheme of active transport of K^+ ion.

The mean transport rate and the transport fraction had maximum values at the initial pH 1.0 in the R side. These results are due to the fact that under these conditions the L side and the R side kept alkaline pH and acidic pH, respectively, during a long transport period as shown in Figure 2. In the conditions other than the initial pH 1.0 in the R side, both the L and R sides became rapidly alkaline or acidic. Even after such pH changes of both sides, however, up to 4 h, K^+ ions were actively transported from the L side to the R side. This active transport of K^+ ion is due to very slight pH difference between the L side and the R side. After 4 h, the K^+ ion concentration started to decrease in the R side. This is simply due to a diffusive transport caused by the concentration gradient. As can be seen from Figure 3, the mean transport rate and the transport fraction at lower pH than the initial pH 1 in the R side were greater than those for over pH 1. This is dependent on a reverse diffusion of K^+ ions from the R side to the L side based on a remarkable swelling of the membrane, because both the L and R sides became alkaline.

The ratio R_{H^+}/R_{K^+}, where R_{K^+} is the mean transport rate of K^+ ion from the L side to the R side and R_{H^+} is the mean diffusion rate of H^+ ion from the R side to the L side during the active transport of K^+ ions, against the initial H^+ ion concentration in the R side is summarized in Table I. Over pH 1, the transport rate of K^+ ions decreased because of the small differences of H^+ ion concentration between both sides, and the diffusion rate of H^+ ion from the R side to the L side also decreased. Consequently, the R_{H^+}/R_{K^+} ratio was kept constant at about 2.5. This implies that in order to transport one K^+ ion from the L side to the R side, two and a half H^+ ions migrated in the reverse. On the other hand, when pH became lower than unity, the diffusion of H^+ ion from the R side to the L side increased with the increase of initial H^+ ion concentration in the R side. However, the transport rate of K^+ ions decreased as shown in Figure 3. Therefore,

TABLE I
Effect of Initial H^+ Ion Concentration in the R side on the ratio R_{H^+}/R_{K^+}

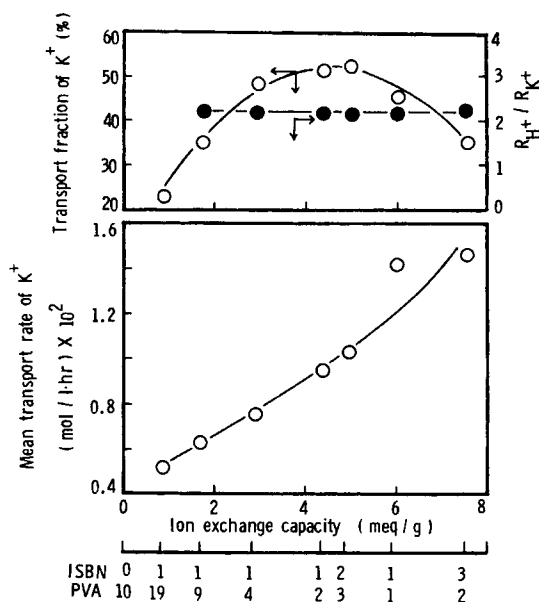| $\log [H^+]$	R_{H^+}/R_{K^+}
-3.0	2.1
-2.0	2.7
-1.5	2.5
-1.0	2.5
-0.4	7.1
-0.1	11.2

Fig. 5. Relation among the mean transport rate and transport fraction of K^+ ion, the ratio R_{H^+}/R_{K^+}, and the ion exchange capacity of the membrane. (O) pH in the R side; (●) pH in the L side. (L) $0.1M$ KOH; (R) $0.1M$ KCl, $0.1M$ HCl.

the R_{H^+}/R_{K^+} ratio became larger. This increase of R_{H^+}/R_{K^+} suggests an increase of free diffusion of H^+ ion from the R side to the L side.

Figure 5 shows the mean transport rate of K^+ ions, transport fraction, ratio R_{H^+}/R_{K^+}, and ion exchange capacity of the membranes prepared by changing the ratio ISBN/PVA. The mean transport rate increased with an increase in the ion exchange capacity of the membrane. This is attributed to the fact that the swelling and contracting of the membrane due to alkaline solution and acidic solution occurred significantly with an increase of charge groups in the membrane which are fixed carrier. The transport fraction had a maximum value at the ratio ISBN/PVA of 2/3. The increase of transport fraction up to this maximum value is caused by the increase of carboxyl group in the membrane. A decrease of transport fraction over the maximum value is dependent on a reverse diffusion of K^+ ions from the R side to the L side due to the diffusive flow through micropores because of remarkable swelling of the membrane. The ratio R_{H^+}/R_{K^+} kept approximately constant regardless of the ion exchange capacity of membrane and was greater than unity. These results imply that the transport of K^+ ions through the membrane was not due to only the ion exchange reactions.

Figure 6 shows the tentative transport mechanism during the active transport of metal ions through the membrane. When one side was alkaline and the other side acidic across the membrane, the carboxyl groups in the membrane dissociate in the alkaline side (OH^- side), and metal ions are incorporated into the membrane by the ion exchange between H^+ ions in the carboxyl groups and metal ions on the alkaline side. Their metal ions are migrated by the carboxyl groups fixed to the membrane matrix. On the other hand, the dissociation of the carboxyl groups in the acidic side (H^+ side) is very low. Therefore, the membrane surface on the acidic side is very dense, and consequently a permeation of metal ions and, in particular, Cl^- ions into the membrane becomes very difficult.
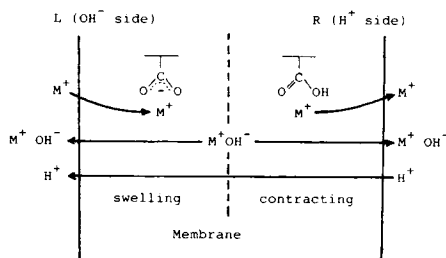
Fig. 6. Tentative mechanism of the transport of metal ions through the cation exchange membrane having the carboxyl group.

However, H$^+$ ions can be easily transferred from the acidic side to the alkaline side through the membrane by a proton-jump mechanism[22] as shown in Figure 7. When such H$^+$ ions reach the region where metal carboxylate exists, metal ions are released by the ion exchange between metal ions in the metal carboxylate and H$^+$ ions. The released metal ions are transferred to the acidic side by an electric potential gradient between the acidic and alkaline sides. We named "chemical active transport" the transport of metal ions from the alkaline side to the acidic side due to the above mechanism.

When the carboxyl groups in the membrane become the carboxylate groups in alkaline pH, the membrane swells remarkably because of an electrostatic repulsion between the carboxylate anions. Therefore, metal cation and OH$^-$ ion in the alkali side can easily enter into a swollen region of the membrane, physical space. When H$^+$ ions, transferred by the proton-jump mechanism, reach the swollen region in the membrane, such H$^+$ ions exchange with metal ions in metal carboxylate and simultaneously the membrane contracts rapidly. By such steep contracting of the membrane, metal ions and OH$^-$ ions that exist in a willful state in the membrane are physically turned to the acidic and alkaline sides. We called "physical active transport" another transport of metal ions from the alkaline side to the acidic side due to this mechanism. It is concluded that the active transport of metal ions from the alkaline side to the acidic side across the membrane is due to the above two processes.

In this active transport system, where one side was acidic and the other alkaline, H$^+$ ions play the roles of driving force in the transport of metal ions and controlling reagent for physical and chemical structures of the membrane.[13]

Selective Transport of Metal Ions

The selectivity, K$^+$/Na$^+$, of the transport after 8 h shows in Figure 8(a) where the initial concentrations of potassium hydroxide and sodium hydroxide in the L side were kept constant at $5.0 \times 10^{-2} M$ and that of hydrochloric acid in the R side was changed. The ratios of transported metal ions from the L side to the R side through the membrane were calculated from the following equation.

$$\text{selectivity} = ([\text{K}^+]_{R,t}/[\text{K}^+]_{L,0})/([\text{Na}^+]_{R,t}/[\text{Na}^+]_{L,0}) \qquad (4)$$
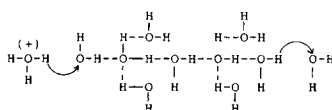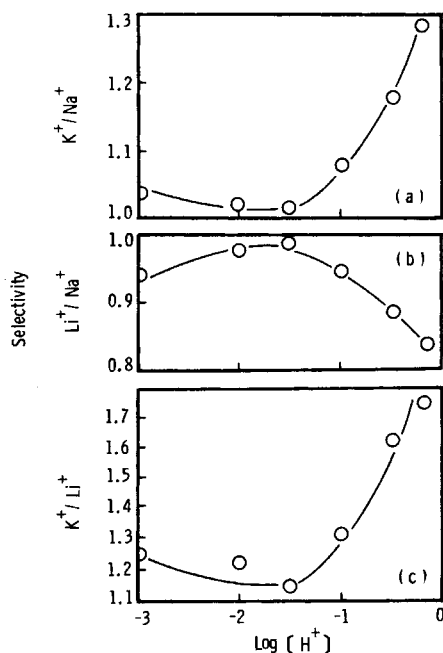

Fig. 7. Proton jump mechanism.

Fig. 8. Effect of the initial H^+ ion concentration in the R side on the selectivities in the transport of alkali metal ions. (a) K^+–Na^+ binary system: $[KOH]_0 = [NaOH]_0 = 5.0 \times 10^{-2}\,M$; (b) Li^+–Na^+ binary system: $[LiOH]_0 = [NaOH]_0 = 5.0 \times 10^{-2}\,M$; (c) K^+–Li^+ binary system: $[KOH]_0 = [LiOH]_0 = 5.0 \times 10^{-2}\,M$; (L) M_1OH, M_2OH ($M_1 = K^+$ or Li^+; $M_2 = Na^+$ or Li^+); (R) HCl.

where R,t is the concentration in the R side at time t and the $L,0$ is the initial concentration in the L side. The permeation ratio of K^+ ion to Na^+ ion changed with the initial H^+ ion concentration in the R side. In the lower initial H^+ ion concentration, the selectivity K^+/Na^+ was close to unity, but it was larger than unity in the higher H^+ concentration. In the former region both K^+ and Na^+ ions diffused simply without physical interaction with the membrane such as a permeation resistance in the membrane; but in the latter region a frictional resistance between each ion and the membrane occurred because the membrane became denser, and consequently the increase of selectivity was due to the difference of hydrated size of each ion.

In Figure 8(b), the selectivity of the transport of Na^+ and Li^+ ions from the L side to the R side after 8 h, which was calculated from eq. (5), is plotted against the initial H^+ ion concentration in the R side. In this Li^+–Na^+ binary system, the selectivity was always

$$\text{selectivity} = ([Li^+]_{R,i}/[Li^+]_{L,0})/([Na^+]_{R,8}/[Na^+]_{L,0}) \qquad (5)$$

smaller than unity; i.e., Na^+ ion permeated more preferentially than Li^+ ion. A decrease of selectivity in the higher initial H^+ ion concentration in the R side is caused by the fact that hydrated Li^+ ion was larger than that of Na^+ ion.

The relationship between the initial H^+ ion concentration in the R side and the selectivity of the transport of K^+ and Li^+ ions from the L side to the R side, which was calculated from eq. (6) at 8 h, is shown in Figure 8(c):

$$\text{selectivity} = ([K^+]_{R,8}/[K^+]_{L,0})/([Li^+]_{R,8}/[Li^+]_{L,0}) \qquad (6)$$

In this K^+–Li^+ binary system, the selectivity was always larger than unity; i.e., K^+ ion was transported more preferentially than Li^+ ion. In the K^+–Na^+ and the Li^+–Na^+ systems, the selectivities were close to unity in the lower initial H^+ ion concentration in the R side, as shown in Figures 8(a) and 8(b), but in this K^+–Li^+ binary system it was not. This result is attributable to the fact that the permeation of K^+ ion was not hindered by the hydrated Li^+ ion which was the most bulky, because the difference between the hydrated ion sizes of Li^+ and K^+ is greater than that between Li^+ and Na^+.

From the above results, the selective transportability for the alkali metal ions from the alkaline side to the acidic side across the membrane was given by the following series:
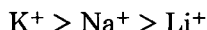
$$K^+ > Na^+ > Li^+$$

The ionic radius for these metal ions was in the order $K^+ > Na^+ > Li^+$.[23] This order agreed with that of the above selective transportability but was not a measure for the selectivity of the metal ions because, in aqueous solution, the alkali metal ions were certainly hydrated. Therefore, the selective transportability had to be compared with the hydrated ionic radius for the alkali metal ions, whose order was $K^+ < Na^+ < Li^+$.[24] It is suggested that the selective transportability for the alkali metal ions was governed by the hydrated size of these metal ions. Also a contribution of hydrated ionic size to the selective transportability implies the physical factors took part mainly in the selectivity of the metal ions.

The relationship between the transport fraction of metal ion, the selectivity calculated from eq. (7), the amount of metal ions in the membrane, whose thickness was 130 μm and whose area was 4.0 cm^2, after 8 h, and the initial H^+ ion concentration in the R side is shown in Figure 9, where the mixed aqueous solution of sodium chloride and calcium chloride contained in the L side and the initial pH of the L side was 6.3:

$$\text{selectivity} = ([Ca^{2+}]_{R,8}/[Ca^{2+}]_{L,0})/([Na^+]_{R,8}/[Na^+]_{L,0}) \qquad (7)$$

In this system, the metal ions were transported from the L side to the R side by both diffusive flows based on the concentration gradient and active transport caused by the pH difference between both sides as above mentioned. The transport fraction of metal ions tended to decrease with the increase in the initial H^+ ion concentration in the R side. This decrease was caused by the frictional resistance between the metal ions and the membrane because the membrane became denser with the increase in the initial H^+ ion concentration. The transport fraction for Na^+ ion was always greater than that for Ca^{2+} ion, and the selectivity was always significantly smaller than unity. In the region of over pH 1, in spite of the fact that the amount of Ca^{2+} ions in the membrane was greater than that of Na^+ ions, the transport fraction for Ca^{2+} ions was smaller than that for Na^+ ions. This is dependent on the formation in the membrane of ionomeric bonds such as

$$\underset{O}{\overset{C}{\diagup}}\overset{\diagdown}{O^-}\text{---}Ca^{2+}\text{---}\underset{O}{\overset{C}{O^-}}\diagup\overset{\diagdown}{O}$$
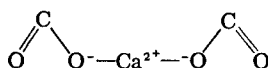
between Ca^{2+} ions and the carboxylate anions. The transport and the selectivity is related to the above ionomeric bond of Ca^{2+} ion. The amount of Na^+ ions in
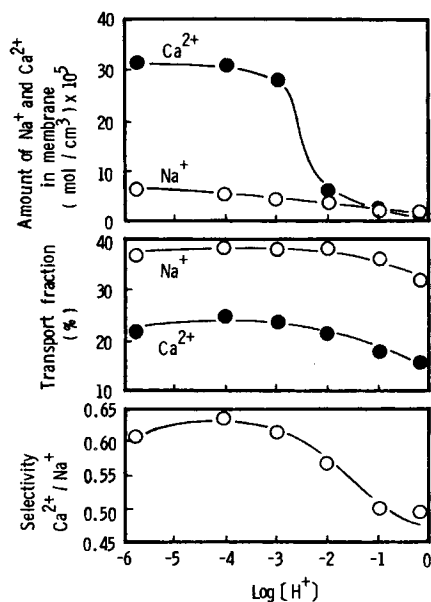
Fig. 9. Effect of the initial H^+ ion concentration in the R side on the permeation fraction and selectivity of metal ions, and the amount of metal ion in the membrane. Na^+–Ca^{2+} binary system: $[NaCl]_0 = [CaCl_2]_0 = 5.0 \times 10^{-2} M$.

the membrane increased almost linearly with the increase in pH in the R side, but that of Ca^{2+} ions increased suddenly at about pH 2–3. This is due to the fact that the carboxyl groups began to dissociate at this pH region and formed the ionomeric bonds with Ca^{2+} ions. On the other hand, the amount of Na^+ ions bound by the carboxylate could not be greatly increased in order to the formation of the ionomeric bonds between the carboxylate groups and Ca^{2+} ions.

CONCLUSIONS

The transport and selectivity of metal ions through the cation exchange membranes made of poly(isobutylene-alternative co-maleic anhydride) and poly(vinyl alcohol) were investigated under various conditions. Their membranes exhibited active transport and selective transport of metal ions. In the active transport of metal ions, H^+ ions played the roles of driving force and controlling reagent for physical and chemical structures of the membrane. The tentative mechanism for the active transport of metal ions was discussed in some details. In the selective transport of metal ions, the selectivity depended on both the hydrated ionic size and the interaction between the change groups in the membrane and the metal ions.

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