

Active Transport and Selective Transport of Alkali Metal Ions through Polyelectrolyte Complex Membranes Consisting of the Three Materials [2-(Diethylamino)ethyl]dextran Hydrochloride, Sodium Carboxymethyldextran, and Sulfate of Poly(vinyl Alcohol)

YASUO KIKUCHI and NAOJI KUBOTA, *Faculty of Engineering, Ōita University, 700-Dannoharu, Ōita-shi 870 Japan*

Synopsis

Active and selective transport of alkali metal ions through the polyelectrolyte complex membranes consisting of [2-(diethylamino)ethyl]dextran hydrochloride, sodium carboxymethyldextran, and sulfate of poly(vinyl alcohol) have been investigated for the first time. The transport behavior was much affected by the hydrogen ion concentration. The driving force for the active transport of alkali metal ions was considered to be the hydrogen ion concentration. It was suggested that both the appropriate changes of chemical and physical properties of polyelectrolyte complex membrane and the affinity of the carrier fixed to the membrane for alkali metal ions controlled the active transport and selectivity through the membranes.

INTRODUCTION

The transport of specific ions is a common function of a biomembrane. The term active transfer was defined as the transfer which overcame the gradient barrier of electrochemical potential by Rosenberg.¹ That is to say, the dissipation function is smaller than zero. It is observed in the active and the selective transport of metal ions through protoplasmic liquid,²⁻⁴ and synthetic membranes carrying a fixed functional group.⁵⁻⁷ The research of such synthetic membranes is an important objective in macromolecule field.

To date, however, active and selective transport through polyelectrolyte complex membrane carrying a fixed of functional group have not been investigated. We have studied for several polyelectrolyte complexes,⁸⁻¹⁰ and it has been found that the membranes of polyelectrolyte complex consisting of [2-(diethylamino)ethyl]dextran hydrochloride, sodium carboxymethyldextran, and sulfate of poly(vinyl alcohol) for the first time were capable of active and selective transports of alkali metal ions. This paper deals with the study of these phenomena.

EXPERIMENTAL

Synthesis of Polyelectrolyte Complex

[2-(Diethylamino)ethyl]dextran hydrochloride (EA) (Meito Sangyo Co. Ltd., degree of substitution 1.06 mol/AGU,* nitrogen content 4.85%, intrinsic viscosity 1.51 dL/g in 1M NaCl at 25°C), and sodium carboxymethyl dextran (CMD) (Meito Sangyo Co. Ltd., degree of substitution 0.70 mol/AGU,* sodium content 7.38%, intrinsic viscosity 1250 c in 1% aqueous solution at 20°C), and sulfate of poly(vinyl alcohol) (PVSK) (sulfur content 18.80%, intrinsic viscosity 0.59 dL/g in 1M NaCl at 25°C) were used.

The reaction was carried out at 4% hydrochloric acid solution. The mole ratio of the reactive group of PVSK ($-\text{OSO}_3\text{K}$) to that of CMD ($-\text{OCH}_2\text{COONa}$) in the mixture was 1:1. The EA solution (2 g/L, 40 mL) was added dropwise to mixture solution (2 g/L, 100 mL) of PVSK and CMD, both adjusted to the same 4% hydrochloric acid solution at about 22°C, at a rate of 50 mL/30 min with stirring as described previously.⁸ A water-insoluble polyelectrolyte complex (PEC) was thus obtained. After being left to stand for 30 min, the PEC was washed with hydrochloric acid solution, water, and methanol. Then it was separated by centrifugation and dried in room temperature until a constant weight was attained. The sulfur and nitrogen contents of the PEC prepared were 8.09% and 2.64%, respectively. Experimental conditions and some results elucidated the structure, and the properties of PEC are given in further detail in a previous paper.¹¹

Membrane Application

The PEC was dissolved in the ternary solvent mixture (HCl/1,4-dioxane/ H_2O , 16:47:37 wt %). The solution was poured onto a teflon plate, allowing the solvent to evaporate at room temperature for about 2 days. In addition, a uniform and yellow transparent film was obtained on a teflon plate by evaporating the solvent under 60% or 90% humidity for 1 or 2 days. The thickness of membrane was about 100 μm . The membrane dipped in 0.1M NaOH or 0.1M HCl solution were not damaged even after 2 days.

A PMMA cell consisting of two chambers was used to study the active and selective transports. The membrane, having effective area of 4.0 cm^2 , was fixed tightly with rubber between two chambers of the cell.^{6,7} The cell was immersed in air bath at 30°C. Figure 1 shows a schematic representation of the cell. The concentration of alkali metal ions, K^+ and Na^+ , in both left and right side cells (chambers) was determined by atomic absorption.

RESULTS AND DISCUSSION

Active transport experiments were carried out at 30°C. Initially, the Na^+ or K^+ concentration (0.1M) in the left side cell was the same as in the right side cell. The left side cell also contained HCl, while the right side cell contained NaOH or KOH.

Figure 2 shows the concentration change of both Na^+ and K^+ ions in both the side cells at pH 1.0 through the membrane cast under 60% hu-

* Anhydroglucose unit.

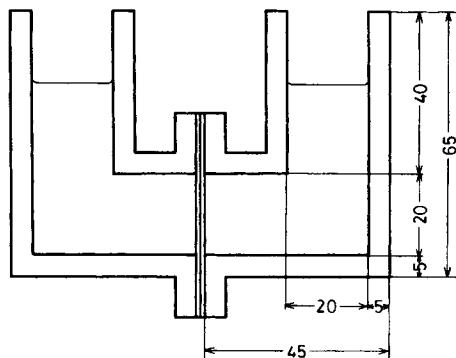


Fig. 1. Separation cell for active and selective transports.

midity. The concentration of alkali metal ions in the left side cell, which was acidic, increased up to a maximum and then decreased with reaction time, while that in the right side cell was just the reverse change. A back transfer of the concentrated alkali metal ions was due to the decrease of the H^+ concentration on the left side.

As shown in Figure 3, the transport ratio¹² $\{([M^+]_{max} - [M^+]_0)/[M^+]_0\} \times 100$ of alkali metal ions (Na^+ , K^+) were proportional to the concentration of hydrogen ion in the left side cell as well as the transport rate¹² $\{([M^+]_{max} - [M^+]_0)/T_{max}\}$ ($M h^{-1}$) in Figure 4.

Since the initial concentration of alkali ion was originally the same in both left and right cells, the increase of the alkali concentration in the left cell suggests the active transport of alkali metal ion through the membrane. The transport rate was proportional to the initial hydrogen ion concentration. Accordingly, the driving force for transport was different in hydrogen ion concentration and was considered to be the hydrogen ion concentration gradient. The pH value in the left and right side cells changed with reaction

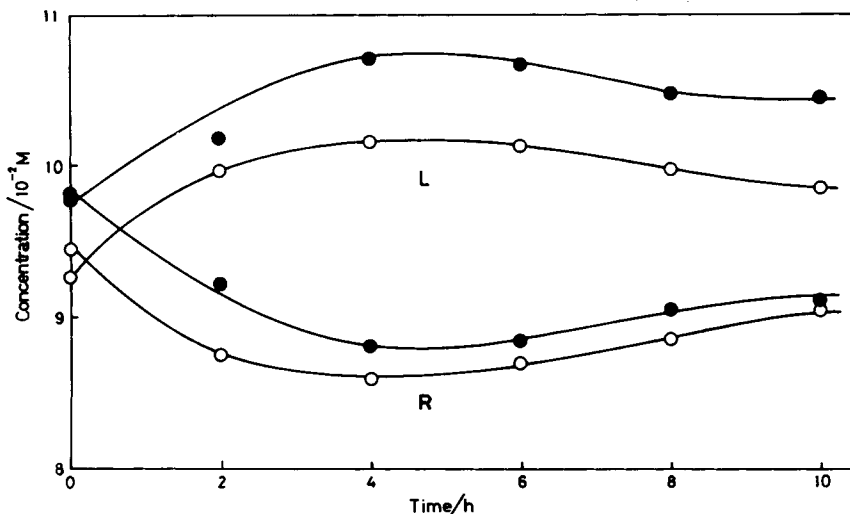


Fig. 2. Time-transport curves of Na^+ and K^+ of the active transport at $30^\circ C$: (●) Na^+ ; (○) K^+ .

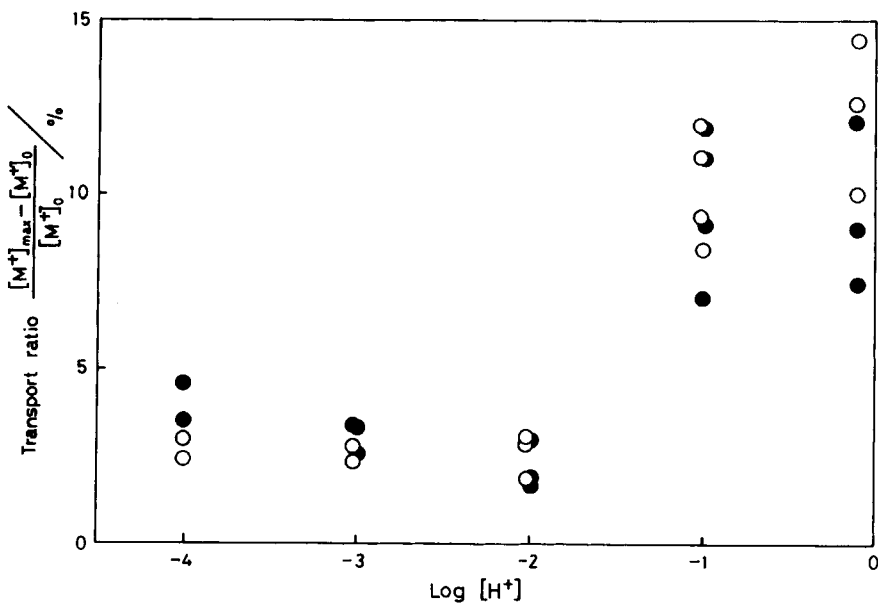


Fig. 3. Influence of $[H^+]$ concentration on the transport ratios of alkali metal ions at 30°C : (●) Na^+ ; (○) K^+ .

time. This pH change is attributed to a transport of H^+ and OH^- , alkali metal ions as well as Cl^- ion⁶ in both side cells.

Changes of pH in both side cells are shown in Figure 5. A maximum in alkali metal ion concentration appeared because of the neutralization of the aqueous solution in both cells.

As shown in Figure 6, the transports of Na^+ ion with the hydrogen ion

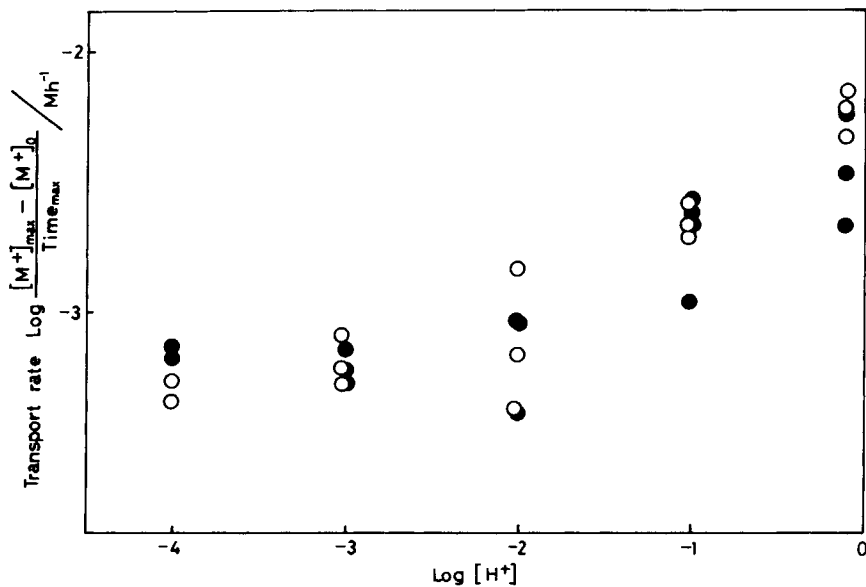


Fig. 4. Influence of $[H^+]$ concentration on the transport rates of alkali metal ions at 30°C : (●) Na^+ ; (○) K^+ .

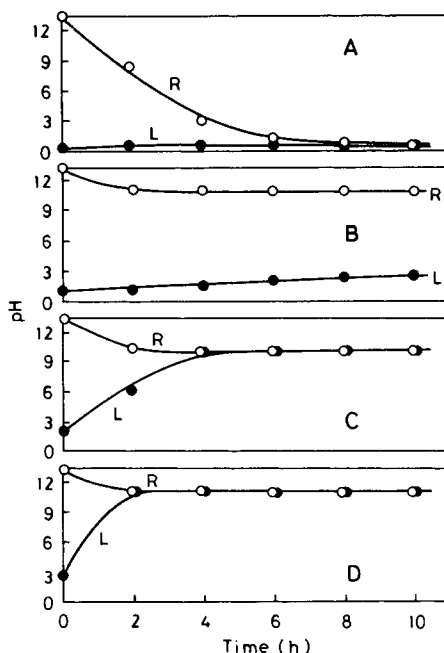


Fig. 5. Changes in hydrogen ion concentration through membrane: (A) 1M HCl; (B) 0.1M HCl; (C) 0.01M HCl; (D) 0.001M HCl.

concentration in both cells through the membranes cast under 60% and 90% humidity were different and also that under low humidity was greater than that under high humidity because of the changes of some physical and chemical properties in the membrane. Hydrogen ion concentration governs the degree of PEC opening and closing in the membrane (described later) and plays the important roles of driving force and controlling the properties of the membrane.

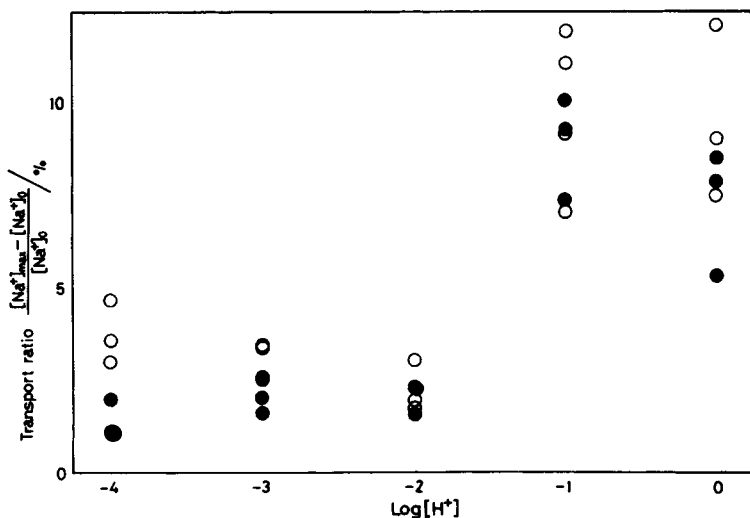


Fig. 6. Influence of $[H^+]$ concentration on the transport ratios of membranes cast under different humidities at 30°C: (○) 60%; (●) 90%.

Selective transport from the right side cell to the left side cell through the membrane was observed under 0.05M concentration of both NaOH and KOH solutions in the right side cell at the different hydrogen ion concentration in the left side cell at 30°C. The ratios of transported ions selectivity^{5,6} were calculated from the following equation:

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

The concentration change of alkali metal ions on the time of transport in both cells at pH 1.0 and the selectivity of the transport after 4 h at different hydrogen ion concentration through the membrane which was cast under 60% humidity is shown in Figures 7 and 8, respectively. The ratio of the permeated K^+ to the permeated Na^+ changed with the hydrogen ion concentration. Under the condition that the initial hydrogen ion concentration was low, the selectivity was close to unity. In this region, the alkali metal ions diffused without great specific interaction with the membrane. In this region where the hydrogen ion concentration was high $> 1.0 \times 10^{-2}M$, more K^+ permeated than Na^+ ion. The optimum hydrogen ion concentration was $1.0 \times 10^{-1}M$ with 0.05M concentration of NaOH and KOH solutions in the right side cell. These results suggest that contributing factors in the selectivity in alkali metal ions transport are the hydrogen ion concentration.

The selectivity with the change of hydrogen ion concentration in the membrane cast in 60% or 90% humidity is shown in Figure 9, and that cast under the low humidity was greater than that under the high humidity. This might be ascribed to the difference of some chemical and physical properties in the membrane which the membrane was cast at different humidity.

The IR spectra of the PEC membranes, which were immersed in acidic and basic aqueous solution and were dried, are shown in Figure 10. The spectrum of membrane immersed in acidic solution exhibit weak absorptions, assigned to the $-OSO_3H$ group¹³ at $800-900\text{ cm}^{-1}$ in the presence of

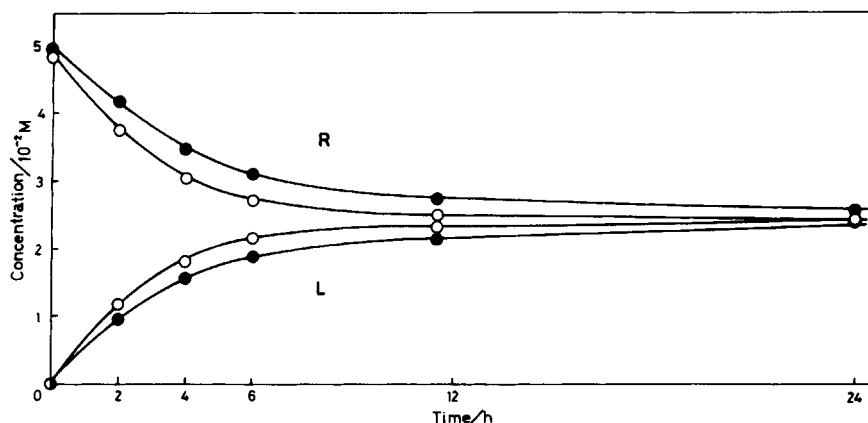


Fig. 7. Time-transport curves of Na^+ and K^+ through PEC membrane at pH 1.0: (●) Na^+ ; (○) K^+ .

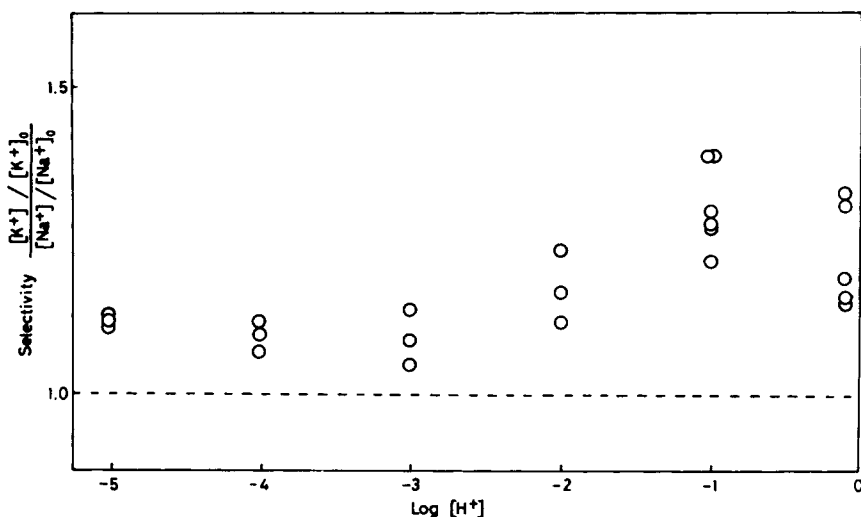


Fig. 8. Influence of $[H^+]$ concentration on selectivities in transport of Na^+ and K^+ ions after 4 h.

PVSK as well as $-OCH_2COOH$ group¹⁴ at around 1740 cm^{-1} in the presence of CMD. On the basic side, this characteristic absorption bands disappeared. Therefore, it was concluded that the PEC moiety was opened on the alkaline side and close on the acidic side. Furthermore, this conclusion has been well confirmed by the experimental result of lengthening or shrinkage of membrane immersed in basic or acidic solution. In this system, hydrogen ion concentration plays the role of controlling reagent for the properties of the membrane as well as driving force. Therefore, it is confirmed that the PEC membrane achieved the following reaction on the basis of pH changes in solution:

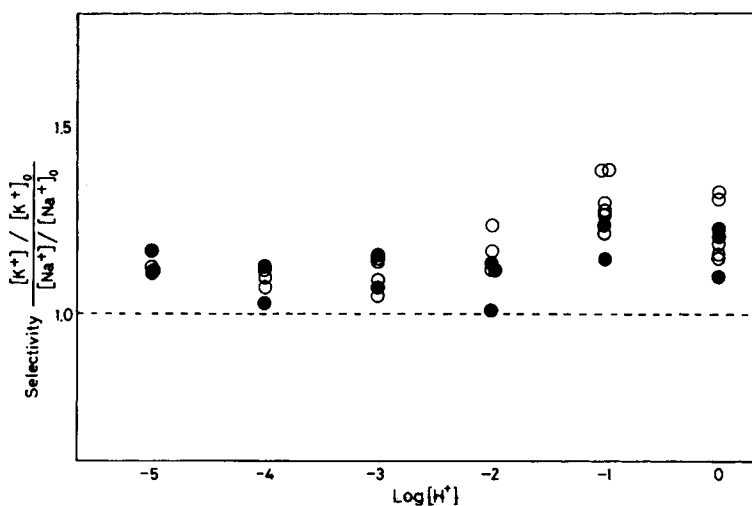


Fig. 9. Influence of $[H^+]$ concentration on the selectivities of membranes cast under different humidities at 30°C after 4 h: (○) 60%; (●) 90%.

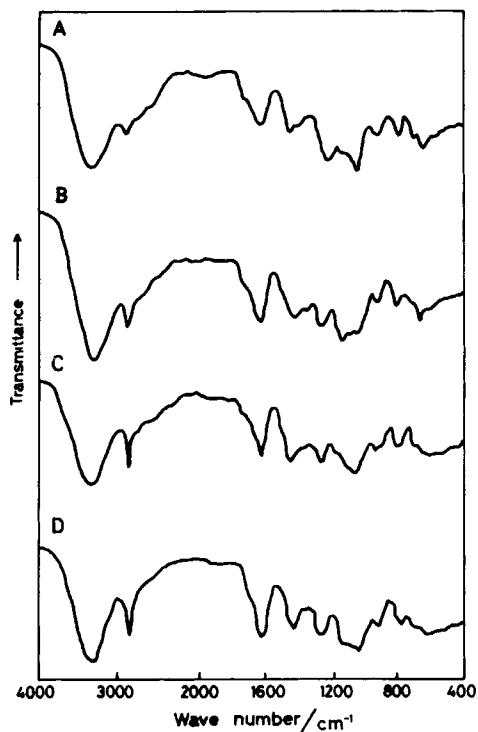


Fig. 10. IR spectra of PEC membranes: (A) PEC powder; (B) PEC membrane; (C) treated with HCl solution; (D) treated with NaOH solution.

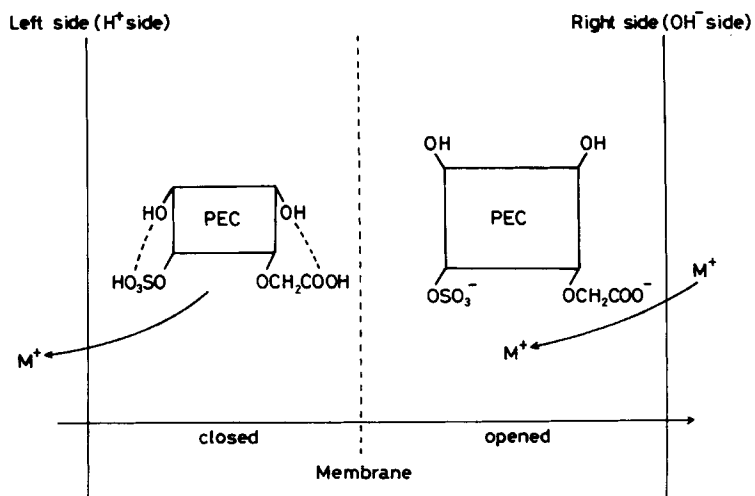
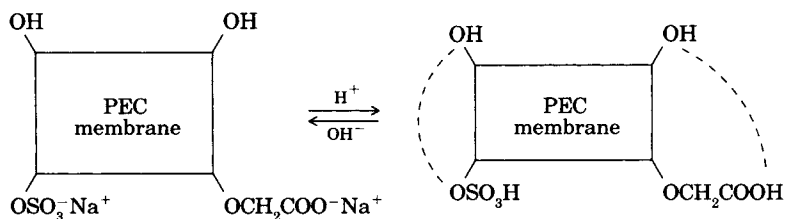


Fig. 11. Tentative mechanism of the transport of Na⁺ and K⁺ ions.



A tentative mechanism of the transport of alkali metal ions deduced from those results was shown in Figure 11. At first, when a specific functional group, $-\text{OSO}_3^-$ and $-\text{OCH}_2\text{COO}^-$ (small amount) in the membrane, were in the right side (OH^- side), the sulfate and carboxylate were formed in the presence of alkali solution. Then the sulfate and carboxylate moved through the membrane. When the sulfate and carboxylate reached the left side (H^+ side), sulfate and carboxylate changed to $-\text{OSO}_3\text{H}$ and $-\text{COOH}$ groups, and the alkali metal ions were released in the left side cell. As a result of this mechanism, alkali metal ions were transported from the basic side to the acidic side.

References

1. T. Rosenberg, *Acta. Chem. Scand.*, **2**, 14 (1948).
2. E. M. Choy, D. F. Evans, and E. L. Cussler, *J. Am. Chem. Soc.*, **96**, 7085 (1974).
3. D. K. Schiffer, A. Hochhauser, D. F. Evans, and E. L. Cussler, *Nature*, **250**, 484 (1974).
4. C. J. Pedeson, *J. Am. Chem. Soc.*, **89**, 2495 (1967).
5. T. Shimidzu, Y. Yoshikawa, M. Hasegawa, and H. Chiba, *Kobunshi Ronbunshu*, **34**, 753 (1977).
6. T. Shimidzu, M. Yoshikawa, M. Hasegawa, and K. Kawakatsu, *Macromolecules*, **14**, 170 (1981).
7. N. Ogata, K. Sanui, and H. Fujimura, *J. Appl. Polym. Sci.*, **25**, 1419 (1980).
8. Y. Kikuchi and S. Sasayama, *Makromol. Chem.*, **183**, 2153 (1982).
9. Y. Kikuchi and Y. Onishi, *Nippon Kagaku Kaishi*, **1980**, 1157.
10. Y. Kikuchi and K. Kaseda, *Nippon Kagaku Kaishi*, **1982**, 842.
11. Y. Kikuchi and N. Kubota, *Nippon Kagaku Kaishi*, **1984**, 1986.
12. H. Kakiuchi, K. Fukuda, and S. Suzue, *Polym. Prepr. Jpn.*, **30**, 2312 (1981).
13. M. Tanaka, T. Oba, and S. Toda, *IR Absorption Spectroscopy*, Hirokawa, Tokyo, 1970, p. 39.
14. K. Nakanishi, *IR Absorption Spectroscopy*, Namkodo, Tokyo, 1960, p. 49.

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