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# Active and Selective Transport of Alkali Metal Ions through a Polyelectrolyte Complex Membrane Consisting of Glycol Chitosan and the Sulfate of Poly(vinyl alcohol)

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Polyelectrolyte complex (PEC) membranes consisting of glycol chitosan and the sulfate of poly(vinyl alcohol) have been prepared. The membrane of the polyelectrolyte complex under a 50% humidity prepared in a 4% hydrochloric acid solution was stable in basic and acidic solutions. The membranes of the PECs under a 90% humidity prepared at pH 1.0 were not stable in an alkaline solution. The active and selective transport of $K^+$ and $Na^+$ were observed in the PEC membrane prepared in a 4% hydrochloric acid solution. The transport behavior of alkali metal ions through this membrane was much affected by the hydrogen-ion concentration, which acted as a driving force. A proton-pump mechanism was suggested for the acive transport of $Na^+$ and $K^+$. It was also suggested that the affinity of the carrier and changes in both the chemical and physical properties of the PEC membrane with the hydrogen-ion concentration controlled the selective transport through the membrane.

The specific transport of ions is a common function of a biomembrane. An active transport process is usually defined as one that can bring about a flow of a substance against an electrochemical potential gradient of the substance; the name implies that specific biological activity is involved in the process described by Rosenberg.[1] That is to say, the dissipation function is smaller than zero. This is observed in the active and selective transport of metal ions through a protoplasmic liquid[2–4] and synthetic membranes carrying a fixed functional group.[5–7] Research into such synthetic membranes is an important objective in the field of macromolecules. Active and selective transport through a polyelectrolyte complex membrane carrying a fixed functional group has not yet been investigated. However, for several polyelectrolyte complexes[8–10] we have reported that the polyelectrolyte complex membranes consisting of [2-(diethyl-amino)ethyl]dextran hydrochloride, sodium carboxymethyl dextran, and the sulfate of poly (vinyl alcohol) were capable of the active and selective transport of alkali metal ions.[11,12] This paper will deal with the similar phenomena of membranes consisting of glycol chitosan and the sulfate of poly (vinyl alcohol).

## Experimental

Glycol chitosan (GC)(nitrogen content, 4.32%; inherent viscosity, 1.79 dl/g in a 0.1 M† NaCl solution at 25 °C) and the sulfate of poly(vinyl alcohol)(PVSK)(sulfur content, 18.91%; inherent viscosity, 0.67 dl/g in a NaCl solution at 25 °C) were used.

The reaction was carried out in a hydrochloric acid solution, 4% (v/v) and pH 1.0, considering the conformational change in the materials. The polyelectrolyte complex (PEC) was not formed at hydrogen-ion concentrations above pH 4.0. The GC solution (2 g/L) or PVSK (2 g/L) solution was added dropwised to a PVSK or GC solution, and the pH values of both solutions were adjusted to that of a 4% hydrochloric acid solution, pH 1.0 at about 22 °C at a rate of 50 ml/30 min under stirring.[11] A water-insoluble PEC was thus obtained. After being left to stand for 30 min, the PEC was washed with the hydrochloric acid solution, water, and then methanol. Then it was separated by centrifugation and dried at room temperature until a constant weight was attained. The details of the expermental conditions were described in a previous paper.[11]

The PEC was dissolved in a ternary solvent mixture ($HCl/1,4\text{-dioxane}/H_2O$, 16:47:37 wt-%). The solution was poured onto a Teflon plate; about 2 d latter the solvent was removed at room temperature. In addition, a uniform and yellowish transparent film was obtained on the Teflon plate by further evaporating of the solvent under 50 or 90% humidity for one or 2 d. The thickness of the membrane was about 100 µm. The resistence of the membranes against acid and base were examined by immersing them in a acidic (0.1 M HCl) or an alkaline solution (0.1 M NaOH). A PMMA cell consisting of two chambers was used in the active and selective transport. The membrane, having an effective area of 4.0 cm$^2$,was fixed tightly with rubber between two chambers of the cell.[12] The cell was then immersed in a constant-temperature bath set at 30 °C. The concentrations of the alkali metal ions, $K^+$ and $Na^+$, in both the left and right sides of the cell (chambers) were measured by means of atomicabsorption spectrophotometer.

## Results and Discussion

The experimental conditions for the PEC prepared before and after the coagulation of PEC and the mole ratio of the reactive group S(PVSK) to that of N(GC) in the mixture solution before and after the coagulation of the PEC produced are given in Table 1. The details of the experimental conditions were described

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† 1 M=1 mol dm$^{-3}$.

Table 1. Preparation of polyelectrolyte complexes

| Sample code | Concentration of hydrogen ions | Order in mixing | Molar ratio of reactive group of S(PVSK) to that of N(GC) in the mixture |
|---|---|---|---|
| 1-A | 4v/v% HCl | PVSK $\xrightarrow{\text{into}}$ GC solution | 1.00 |
| 1-a | 4v/v% HCl | PVSK $\xrightarrow{\text{into}}$ GC solution | 1.57 |
| 1-B | 4v/v% HCl | GC $\xrightarrow{\text{into}}$ PVSK solution | 3.61 |
| 1-b | 4v/v% HCl | GC $\xrightarrow{\text{into}}$ PVSK solution | 2.49 |
| 2-A | pH 1.0 | PVSK $\xrightarrow{\text{into}}$ GC solution | 0.83 |
| 2-a | pH 1.0 | PVSK $\xrightarrow{\text{into}}$ GC solution | 1.30 |
| 2-B | pH 1.0 | GC $\xrightarrow{\text{into}}$ PVSK solution | 2.52 |
| 2-b | pH 1.0 | GC $\xrightarrow{\text{into}}$ PVSK solution | 1.62 |

The polyelectrolyte complexes (PEC) of 1-A, 1-B, 2-A, and 2-B were prepared before the starting point of coagulation. The molar ratios of S/N at the starting point of coagulation were 1.04, 3.57, 0.89, and 2.39 respectively. The PECs of 1-a, 1-b, 2-a, and 2-b were prepared after the end point of coagulation. The molar ratios of S/N at the end point of coagulation were 1.51, 2.56, 1.24, and 1.67 respectively. The concentration of glycol chitosan (GC) and that of sulfate of poly(vinyl alcohol) (PVSK) were both 2.0 g/l. GC: Nitrogen content 4.32%, inherent viscosity 1.79 dl/g, in 0.1 M NaCl solution at 25 °C. PVSK: Sulfur content 18.91%, inherent viscosity 0.67 dl/g, in 1 M NaCl solution at 25 °C.

Table 2. Stabilities of membranes immersed in acidic (0.1 M HCl) and alkaline (0.1 M NaOH) solutions

| Sample code[a] | Acidic solution | Alkaline solution |
|---|---|---|
| 1-A | ○ | △ |
| 1-a | ○ | △ |
| 1-B | ○ | △ |
| 1-b | ○ | ○ |
| 2-A | — | — |
| 2-a | — | — |
| 2-B | ○ | × |
| 2-b | ○ | × |

a) Sample code corresponds to that in Table 1. The PEC membranes were prepared under 50% humidity. ○: Stable, △: Slightly unstable, ×: Soluble in alkaline solution, —: Soluble in water

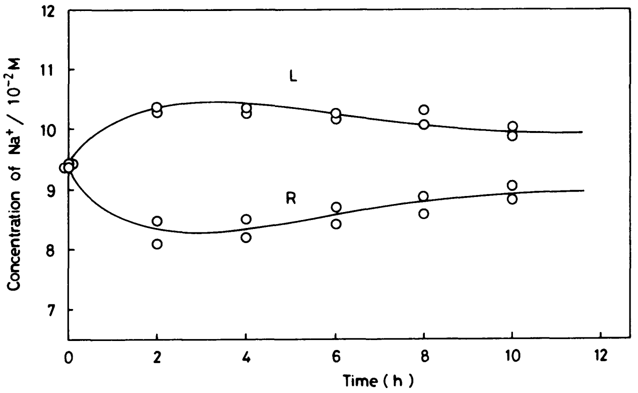


Fig. 1. Time-transport curve of Na$^+$ of the active transport at 30 °C.

Table 3. Stabilities of membranes immersed in acidic (0.1 M HCl) and alkaline (0.1 M NaOH) solutions

| Sample code[a] | Acidic solution | Alkaline solution |
|---|---|---|
| 1-A | ○ | × |
| 1-a | ○ | △ |
| 1-B | ○ | × |
| 1-b | ○ | △ |
| 2-A | — | — |
| 2-a | — | — |
| 2-B | △ | × |
| 2-b | △ | × |

a) Sample code corresponds to that in Table 1. The membranes were prepared under 90% humidity. ○: Stable, △: Slightly unstable, ×: Soluble in alkaline solution, —: Soluble in water.

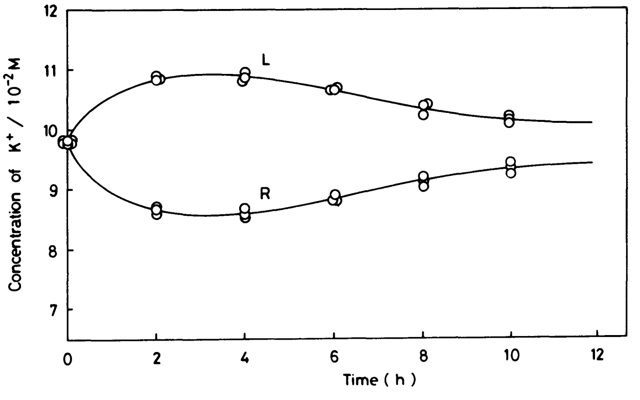


Fig. 2. Time-transport curve of K$^+$ of the active transport at 30 °C.

in a previous paper.[11]

The properties of the membranes in acidic and basic solutions are shown in Tables 2 and 3 respectively. The membranes formed under 50 and 90% humidity except for 2-A and 2-a, which were formed at pH 1.0, resisted an acidic solution. On the other hand, the membranes except 1-b formed in a 4% hydrochloric acid solution at 50% humidity were not resistant to a basic solution. The 1-b membrane was not damaged in either a 0.1 M NaOH or 0.1 M hydrochloric acid solution, even after 5 d. This membrane was used in the study of the transport of alkali metal ions. The sulfur and nitrogen contents in the PEC used to prepare the membrane were 9.55 and 3.73% respectively. The active-transport experiment was carried out at 30 °C. The concentration of the $Na^+$ or $K^+$ ion both the left and right sides of the cell was kept identical initially. In the left side, the cell also contained HCl, while the right-side cell contained NaOH or KOH.

Figures 1—2 show the concentration change in the $Na^+$ or $K^+$ ion against the reaction time in both cells at pH 1.0 through the membrane. The concentration of alkali metal ions in the left-side cell, which was acidic, increased up to a maximum and then decreased with the reaction time, while the change in the right-side cell was just the reverse. A back transfer of the concentrated alkali metal ions was due to the decrease in the hydrogen ion concentration on the left side. The changes in the concentration of $Na^+$ in the NaOH system were somewhat smaller than those of $K^+$ in the KOH system.

As is shown in Figs 3—4, the transport ratio[13], $([M^+]_{max}-[M^+]_o/[M^+]_o)\times 100$, of the alkali metal ions ($Na^+$, $K^+$) was proportional to the concentration of hydrogen ions in the left-side cell. Since the initial concentration of the alkali ion was originally the same in both left and right cells, the increase in the alkali concentration in the left cell suggests the active transport of the alkali metal ion through the membrane. It is of important significance in saving energy and resources that a PEC membrane carrying a fixed functional group is capable of the active transport of alkali metal ions. The difference in the transport ratios of $Na^+$ and $K^+$ against the hydrogen-ion concentration of the two systems are hardly discernible in hydrogen-ion concentrations below pH 2.0, whereas that of $Na^+$ is larger than that of $K^+$ in hydrogen-ion concentrations above pH 1.0. The transport rate,[13] $[M^+]_{max}-[M^+]_o/T_{max}$ in $Mh^{-1}$ was proportional to the initial hydrogen-ion concentration. The pH values in the left- and right-side cells changed with the passing of time.

The change in the pH in both side cells is shown in Fig. 5. A maximum in the alkali metal-ion concentration appeared because of the neutralization of the aqueous solution in both cells. Accordingly, the driving force for transport was a gradient of the hydrogen-ion concentration. This pH change is attributed to a transfer of $H^+$, $OH^-$ and alkali metal ions as well as the $Cl^-$ ion[6] in both side cells. A proton-pump mechanism was considered for the concentration of alkali-metal ions.[5]

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

$$\text{Selectivity} = \frac{[K^+]_{Lt}/[K^+]_{R,o}}{[Na^+]_{Lt}/[Na^+]_{R,o}}$$

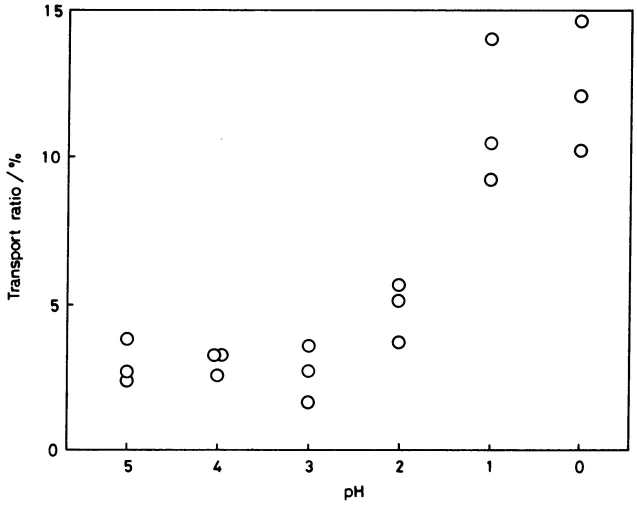


Fig. 3. Influence of hydrogen ion concentrations on the transport ratio of $Na^+$ ion at 30 °C.

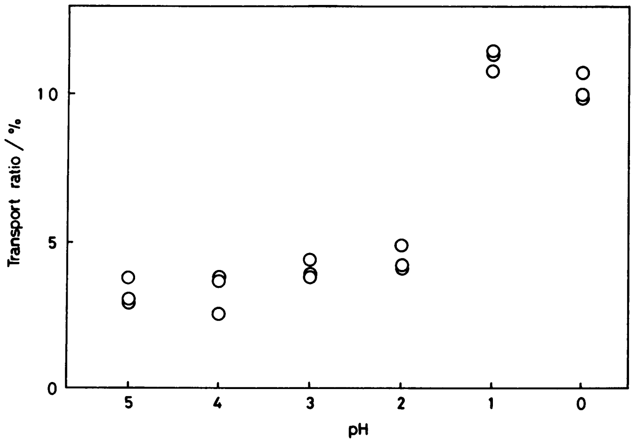


Fig. 4. Influence of hydrogen ion concentrations on the transport ratio of $K^+$ ion at 30 °C.

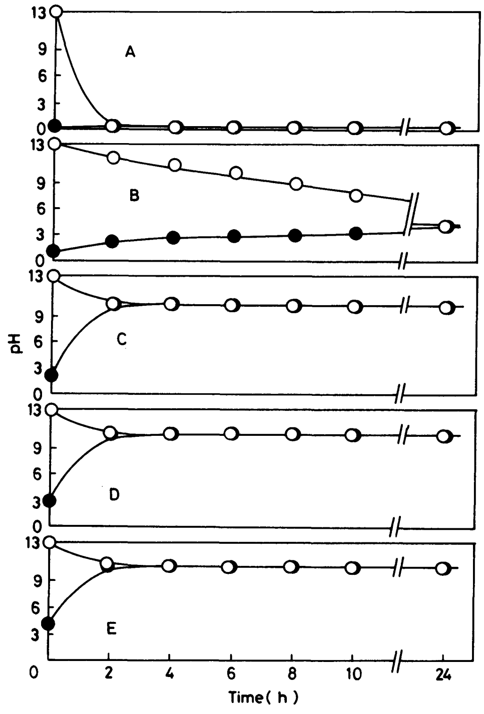


Fig. 5. Changes in hydrogen ion concentration through membrane.
A: 1 M HCl, B: 0.1 M HCl, C: 0.01 M HCl, D: 0.001 M HCl, E: 0.0001 M HCl.

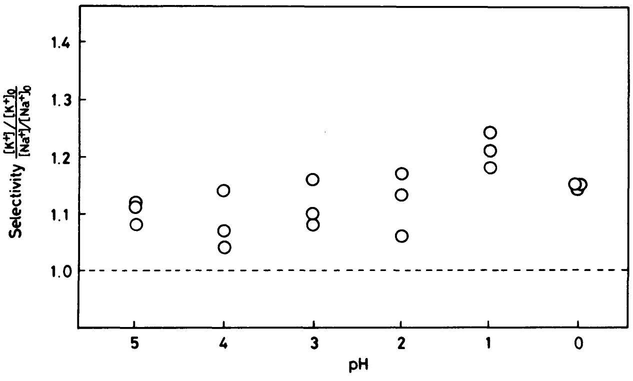


Fig. 6. Influence of hydrogen ion concentrations on selectivities in transport of $Na^+$ and $K^+$ ions after 4 h.

The selectivity of the transport through membrane after 4 h at different hydrogen-ion concentrations is shown in Fig. 6. The ratio of the permeated $K^+$ to the permeated $Na^+$ changed with the hydrogen-ion concentration. When the initial hydrogen-ion concentration was low, the selectivity was close to unity. In this region, the alkali metal ions diffused without any great or specific interaction with the membrane. In the region where the hydrogen-ion concentration was higher than $1.0\times10^{-2}$ M, more $K^+$ ions permeated than $Na^+$ ions. The optimum hydrogen-ion concentration was $1.0\times10^{-1}$ M with 0.05 M concentrations of NaOH and KOH solutions in the right-side cell. These results suggest that the main contributing factor in the selectivity in the transport of alkali metal ions is the hydrogen-ion concentration. The membrane prepared was throughly powdered in a agate mortar with a pestle. The pulverized membrane was then immersed in a basic or acidic solution for about 1 d. The IR spectrum of the pulverized membrane immersed in an acidic solution exhibited the medium absorption a 800—900 $cm^{-1}$, assigned to the $-SO_3H$ group,[14] but that immersed in a basic solution exhibited only a weak absorption. In addition, that immersed in a basic solution exhibited the medium absorption at 900—940 $cm^{-1}$, assigned to the $-SO_3$ group.[14] On the acidic side, this characteristic absorption band almost disappeared. From these IR spectra, therefore, it was concluded that the PEC moiety was opened on the alkaline side and closed on the acidic side. Furthermore, this conclusion has been well confirmed by the following experimental results of the lengthing or shrinkage of the membrane immersed in a basic or acidic solution. The horizontal and vertical lengthes of membrane immersed in the pH 1.0 and 13.0 solutions were 25 mm×28 mm and 33 mm×34 mm. When the above membrane, pretreated in a pH 1.0 or pH 13.0 solution, was further immersed in a pH 13.0 or pH 1.0 solution, the lengthes of the above two dimensions varied about 31 mm×34 mm and 30 mm×30 mm respectively, with an error of about 2 mm. That is, the membrane was elongated in a basic solution and shrunk in an acidic solution. In the region where the hydrogen-ion concentration was larger than $1.0\times10^{-2}$ M in the left-side cell, the hydrated $K^+$ permeated faster than the hydrated $Na^+$ because of the radius of the hydrated $K^+$ was shorted than that of the hydrated $Na^+$ because of the formation of small holes as a result of the closing of the channel in the membrane, whereas that of the hydrogen-ion concentration was smaller. No appreciable selectivity of transport were observed because of the indiscriminate permeation of alkali metal ions owing to the formation of large holes results of the opening of the channel in the membrane. It was suggested that the affinity of the carrier fixed to the membrane, the degree of the opening and closing of the PEC moiety, and the physical properties of the PEC membrane, as well as the hydrogen bonding between $-OH$ and $-OSO_3H$ or $-OSO_3^-Na^+$ groups with the hydrogen-ion concentration, controlled the selective transport through the membrane.[6] Therefore, on the basis of the pH change in the solution we speculate that the PEC membrane achieved the following reaction;

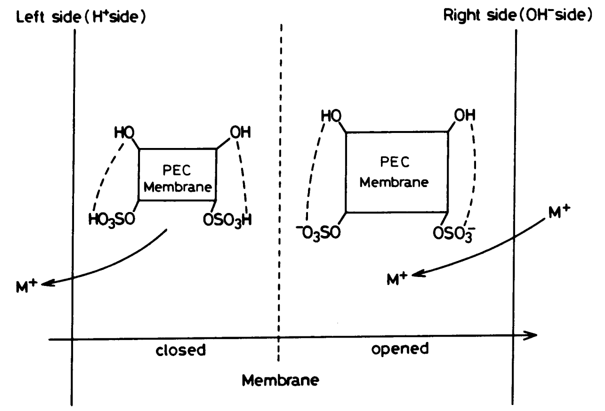
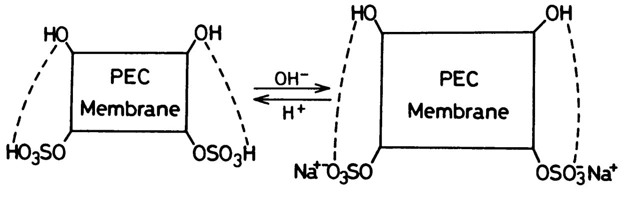


Fig. 7. Tentative mechanism of the transport of $Na^+$ and $K^+$ ions.



A tentative mechanism of the transport of alkali-metal ions, deduced from the results described above, is shown in Fig. 7. In this system, the hydrogen-ion concentration acted as the driving force and controlling reagent for the properties of the membrane.[5] At first, when a specific functional group, $-OSO_3^-$ in the membrane is on the right-side ($OH^-$ side), metal ions are bound to the sulfate group in an alkaline solution with the changes in both the chemical and physical properties of the PEC membrane described above. Then, the alkali metal ions bound to the sulfate group are transferred through the membrane and are released by the hydrogen-ion or the acidic side. As a result, alkali metal ions are transported from the basic side to the acidic side. We consider that the driving force of the active transport of alkali ions is a gradient of the hydrogen-ion concentration, while the binding of the alkali metal ions to the sulfate group is attributable to the degree of the ring opening of the PEC membrane with hydrogen bonding, which affects the selectivity.[5,6]

The suitable conditions for the formation of the PEC membrane and the PEC membrane of transport for a negative ions have scarcely been elucidated at all. Therefore, further investigation must be carried out clarify the mechanism.

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