Structure, Properties, and Na$^+$ Transport Membrane of Polyelectrolyte Complexes Consisting of Glycol Chitosan and Poly(vinyl sulfate)

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Glycol chitosan (GC) was allowed to react with poly(vinyl sulfate) (PVSK) to form many different water-insoluble polyelectrolyte complexes (PECs) in aqueous solution at various hydrogen ion concentrations. According to elemental analyses, IR spectroscopy, and solubilities of PECs, molecular structures of each PEC depend on [H$^+$]. This result is attributable to change with [H$^+$] in the degree of dissociation and conformation of GC and PVSK. PEC membranes were made by casting solutions of all kinds of PECs, and transport phenomena through a membrane of the PEC prepared in a solution of 4 v/v% HCl were investigated under various conditions. The transport ratio of Na$^+$ and the electric potential difference between the left and right sides of the membrane were measured, with a result that the higher value the membrane potential difference was long allowed to maintain, the higher the transport ratio became. According to this result, the driving force of transport is dependent on the membrane potential, Donnan potential and diffusion potential, between both sides of the membrane. The Cl$^-$ exclusion (Donnan exclusion), however, is small due to the small cation-exchange capacity, so that the membrane potential difference is caused to decrease rather rapidly by Cl$^-$ permeation.

Polyelectrolyte complexes (PECs) are expected to find many-sided applications$^{1-3)}$ because of the diversity of their structures and properties. For example, PECs may be prepared in the form of cationic or anionic as well as neutral polymer complex because of the applicability of a variety of components, mixing ratios, and solvent pHs, and may be cast into membranes with various ion-exchange capacities (0—2 mequiv g^{-1} dry membrane).$^{4)}$ Consequently, when PEC membranes with high permeability$^{5)}$ are used, it is possible to control the active transport of alkali metal and halide ions, of which a great number of studies have recently been made.$^{6-11)}$ Investigation on PEC membrane is, however, confined almost to synthetic polymers, and there have been only a few papers on PEC membranes of naturally occurring polysaccharides. We have already reported that PEC membranes of glycol chitosan–poly(vinyl sulfate),$^{12)}$ methyl glycol chitosan–(carboxymethyl)dextran–poly(vinyl sulfate),$^{13)}$ and [2-(diethylamino)ethyl]dextran hydrochloride–(carboxymethyl)dextran–poly(vinyl sulfate)$^{14)}$ systems are capable of active and selective transport of alkali metal ions.

This paper deals with chemical reactions of glycol chitosan (GC) with poly(vinyl sulfate) (PVSK) and general characteristics of resulting PECs. In addition, a description will be made on active transport of Na$^+$ through a membrane of PEC prepared in 4v/v% HCl solution, with particular reference to the relationship between transport ratio and membrane potential.

Experimental

Glycol chitosan (GC) (nitrogen content, 6.09%; intrinsic viscosity, 1.68 dl g^{-1} in 1 mol dm^{-3} NaCl solution at 25 °C) as a polycation and poly(vinyl sulfate) (PVSK) (sulfur content, 18.67%; intrinsic viscosity, 0.66 dl g^{-1} in 1 mol dm^{-3} NaCl solution at 25 °C) as a polyanion were used to prepare PECs. Sodium poly(*p*-styrenesulfonate) (NaSS) and poly(*p*-styrenesulfonic acid) (HSS) with molecular weights 1.0×10^4 and 5.0×10^5 were adopted in the active transport experiment. Reactions were run in 7, 4, and 1% HCl, at pHs 2.0, 4.5, 6.5, 11.0, and 13.0, and in 5% NaOH, considering that the degree of dissociation of polyelectrolytes and their conformation are influenced by hydrogen ion concentration. GC solution (2 g dm^{-3}) was added dropwise to PVSK solution (2 g dm^{-3}) and vice versa, for the adjustment to the same [H$^+$], at a rate of 50 cm^3/30 min with stirring at ca. 22 °C. Water-insoluble PECs were thus obtained. After 30 min, the precipitate was separated by centrifugation. Then, it was washed with methanol, and dried in vacuo at room temperature until there occurred no further decrease in weight. Estimation of the nitrogen in PEC was carried out by the Kjeldahl method, and quantitative analysis of sulfur was performed at the Institute of Physical and Chemical Research. IR spectra of PEC in a KBr pellet were taken with a Hitachi 285 spectrophotometer. The miscibility of GC, PVSK, or PEC with the ternary solvent system, NaBr/acetone/water, was examined as previously described.$^{15)}$

PEC membrane was obtained from a PEC prepared in 4% HCl solution by casting. The method of casting into membrane and the experimental conditions were described in a previous paper.$^{12)}$ A diaphragm type cell, made of poly(methyl methacrylate) and consisting of two chambers, was used in the active transport experiment for Na$^+$. After well washing with water, the PEC membrane was fixed tightly with silicone rubber between both chambers of the cell having an effective area of 4.0 cm^2. In the right-side chamber of the cell was placed 25 cm^3 of 0.1 mol dm^{-3} NaOH solution, and simultaneously 25 cm^3 of HCl (or HSS) solution of one of various concentrations containing 0.1 mol dm^{-3} NaCl (or 0.1 mol dm^{-3} NaSS unit) in the left-side chamber. The cell was then put in a thermostat controlled at 30 °C. At proper intervals, 0.1 cm^3 samples from both the side chambers of the cell were withdrawn and analyzed for the concentration of Na^+ with an atomic absorption spectrophotometer (Shimadzu AA-640). At the same time, the concentration of Cl^- was determined by volumetric titration with $Hg(NO_3)_2$, and the concentration of SS^- from the absorbance at 260 nm (Hitachi 100-10 spectrophotometer). The electric potential difference between the left and right sides of the membrane was obtained by measurement with a Horiba F-7 potentiometer and Ag–AgCl electrodes. The ion-exchange capacity of the membrane was determined as follows.[16] The PEC membrane was first immersed in 1 mol dm^{-3} HCl solution. After washing with water, this membrane was in turn immersed in 30 cm^3 of 1 mol dm^{-3} NaCl solution three times every two hours. After washing with water again, washings and immersing solvents were titrated with 0.05 mol dm^{-3} NaOH solution. The ion-exchange capacity was evaluated by dividing the measured value by the dry membrane weight.

Results and Discussion

Polyelectrolyte Complex. Figure 1 shows the dependence, upon hydrogen ion concentration, of the molar ratio of the reacting groups in PVSK and GC in a reaction mixture solution at the start and end of coagulation of PEC. The molar ratio, S(PVSK)/N(GC), increased with increasing $[H^+]$ and no coagulation was observed in solutions of lower $[H^+]$ than pH 6.5, i.e., larger amounts of PVSK solution were necessary to coagulate GC solution containing PEC as the hydrogen ion concentration was increased. The reason for above is that the degree of dissociation of GC decreases with decreasing $[H^+]$ and reaches zero eventually, whereas that of PVSK remains unchanged. In the pH 6.5 solution, the following strange phenomenon was observed. A coagulation occurred when PVSK solution was added to GC solution, while none when GC solution was added to PVSK solution. A probable reason for this phenomenon is that the concentration of PEC and the ionic strength in the reaction mixture for which PVSK solution was added to GC solution, were initially higher than those in the reaction mixture for which GC solution was added to PVSK solution.[3] Further investigation on this point should be made. Experimental conditions, yields of products, and results of elemental analyses for each PEC prepared after coagulation are given in Table 1. As seen in Table 1, the sulfur and nitrogen contents in the PECs which reflect the molar ratio of PVSK to GC are roughly equal, except for the PEC prepared in pH 6.5 solution. As a result, it appears that the reactions proceeded in the same manner when PEC was prepared after coagulation in the solutions of

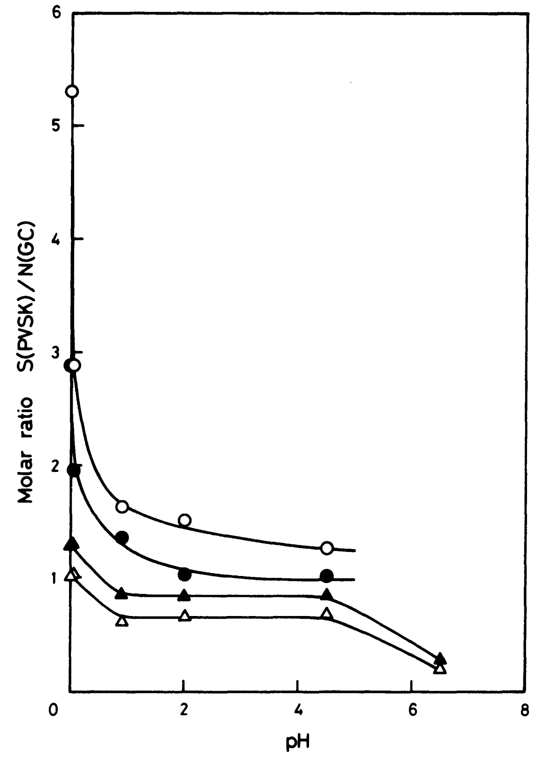

Fig. 1. Starting and end points of coagulation.
○△: Starting point of coagulation, ●▲: end point of coagulation, ○●: GC solution was added dropwise to PVSK solution, △▲: PVSK solution was added dropwise to GC solution.

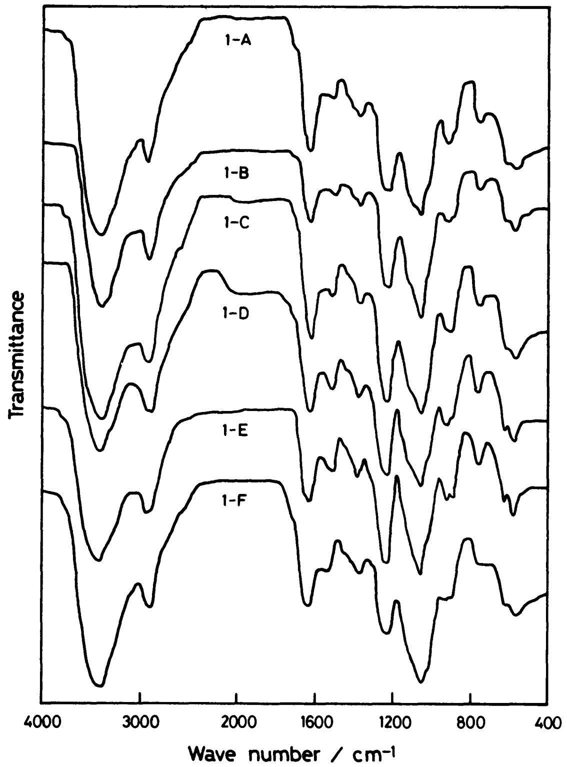

Fig. 2. IR spectra of the PEC. Sample codes correspond to those in Table 1.

$[H^+]$>pH 6.5. Thus, the hydrogen ion concentration in this system plays an important role in determining the ratio of PVSK/GC in the PEC.

Since the IR spectra of the PECs prepared in the cases where PVSK solution was added to GC solution are identical with those in the cases where GC solution was added to PVSK solution, only the former are shown in Fig. 2. The IR spectra of the PECs are almost the same as that of a mixture of PVSK and GC, differing from one another only in details. The absorption band at 1540 cm^{-1} assigned to $-NH_3^+$ in GC is present in all PECs, whereas that assigned to $-NH_2$ which should appear at 1590 cm^{-1} is absent. The absorption bands at 1230 and 800—600 cm^{-1}, which are also present in each PEC, are assigned to $-OSO_3^-$ in PVSK. The intensity of these absorptions is nearly equal in all PECs except the one prepared in pH 6.5 solution, whose absorbances at 1230 and 800—600 cm^{-1} are weak. These results imply that the PECs were produced in the same way, and this viewpoint coincides with the result of elemental analyses in Table 1. Furthermore, the absorption bands around 3500 cm^{-1} assigned to -OH groups are found in every PEC, and this proves that inter- and intramolecular hydrogen bonds between -OH groups are formed. These IR spectra have revealed that the PECs prepared in 7% HCl—pH 4.5 solutions consist of a greater fraction of PVSK, whereas the PVSK contents in the PECs prepared in pH 6.5 solution are low.

PECs are insoluble in general organic solvents, e.g., *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and dimethyl sulfoxide, but soluble in ternary solvent mixtures, e.g., NaBr/acetone/H_2O and $CaCl_2$/1,4-dioxane/H_2O, and also in 36% HCl solution without heating. Phase diagrams were obtained for all kinds of PECs in the system of NaBr/acetone/H_2O and are shown in Fig. 3. There is a small region in the solvent composition field where PEC remains in the solution to form a homogeneous, viscous sirup. The miscibility limit of each PEC is approximately constant except for the PEC prepared in the solution of pH 6.5.

These experimental results support the concept that the PECs prepared in 7% HCl—pH 4.5 solutions have common constituents and similar compositions, but that the PEC prepared in pH 6.5 solution is different from them. This concept is in turn reduced to the dependence that the degree of dissociation of GC and PVSK changes with $[H^+]$.

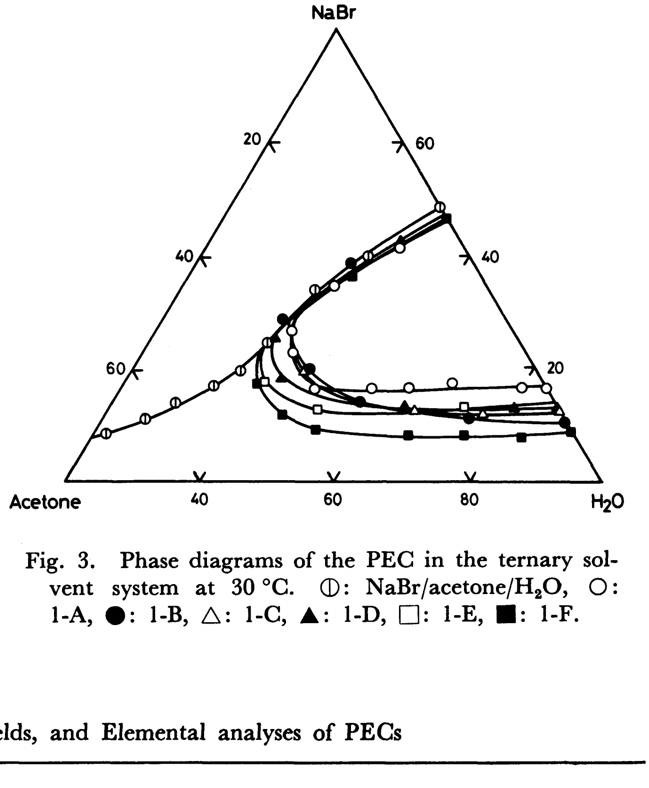

Fig. 3. Phase diagrams of the PEC in the ternary solvent system at 30 °C. ⦶: NaBr/acetone/H_2O, ○: 1-A, ●: 1-B, △: 1-C, ▲: 1-D, □: 1-E, ■: 1-F.

Table 1. Experimental Conditions, Yields, and Elemental analyses of PECs

Sample code[a]	Conditions		Yield/g	Sulfur content/%	Nitrogen content/%	Molar ratio of S(PVSK)/N(GC) in PEC
	Hydrogen ion concentration	Molar ratio of S(PVSK)/N(GC) in mixture				
1-A	7 v/v% HCl	2.00	0.304	7.03	2.67	1.15
1-B	4 v/v% HCl	1.60	0.314	7.40	2.59	1.25
1-C	1 v/v% HCl	1.10	0.282	7.73	2.29	1.48
1-D	pH 2.0	1.00	0.281	7.61	2.18	1.53
1-E	pH 4.5	0.90	0.293	7.41	2.10	1.54
1-F	pH 6.5	0.50	0.079	4.64	5.19	0.39
2-A	7 v/v% HCl	2.00	0.221	7.04	2.15	1.43
2-B	4 v/v% HCl	1.60	0.246	6.51	2.02	1.41
2-C	1 v/v% HCl	1.10	0.322	7.01	2.07	1.48
2-D	pH 2.0	1.00	0.409	7.85	2.43	1.41
2-E	pH 4.5	0.90	0.438	8.13	2.60	1.37

a) Series 1: PVSK solution was added dropwise to GC solution (100 cm^3). Series 2: GC solution was added dropwise to PVSK solution (100 cm^3).

Polyelectrolyte Complex Membrane. The membrane obtained by casting the PEC prepared in 4% HCl solution was adopted for the study on the transport of alkali metal ion Na^+, because this membrane was most stable in acidic and alkaline solutions. The concentrations of Na^+ in the left- and right-side chambers of the cell were set the same initially. The left-side chamber contained HCl as well, while the right-side chamber NaOH. Figure 4 shows concentration changes for Na^+, Cl^-, and H^+ with time in both the side chambers containing 0.1 mol dm^{-3} HCl. Despite the fact that both the sides of the membrane were originally equal in the concentration of Na^+, an increase of Na^+ in the left side was observed and the change in the right side was quite reverse. This suggests that the active transport of Na^+ took place from the right side, alkaline solution, to the left side, acidic solution, through the membrane. The concentration of Na^+ in the left side increased up to a maximum, and then decreased with the passage of time. This back transport of concentrated Na^+ is due to decrease in the hydrogen ion concentration difference between both sides of the membrane and to the permeation of Cl^-. The ratios of the transported ions are calculated by

$$\text{Transport ratio } (\%) = \frac{[Na^+]_{max} - [Na^+]_0}{[Na^+]_0} \times 100, \qquad (1)$$

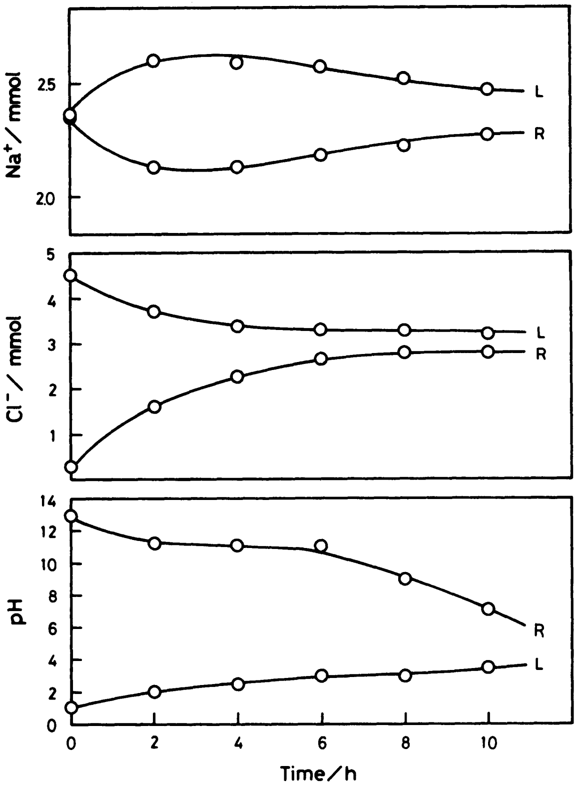

Fig. 4. Changes in the concentration of Na^+, Cl^-, and H^+ at the active transport

where $[Na^+]_{max}$ is the mole number of Na^+ in the left-side chamber at the maximum, and $[Na^+]_0$ is the mean of the initial mole numbers of Na^+ in both the side chambers. The dependence of the transport ratio of Na^+ on the concentration of H^+ in the left-side chamber is shown in Fig. 5. The transport ratio corresponds to the $[H^+]$, and it is high at $[H^+]$ above pH 1.0, whereas low at $[H^+]$ below pH 2.0. Hence, it is thought that the driving force for the transport of Na^+ will be the hydrogen ion concentration difference between both the side chambers which causes an electric potential gradient. Accordingly, the membrane potential difference needs to be measured. Figure 6 indicates that the membrane potential difference gets greater as the concentration of HCl in the left side is increased, and this tendency is consistent with the result in Fig. 5. The membrane potential difference, however, decreases with time. This decrease in the potential difference is not only due to the transport of Na^+ from the right to left side

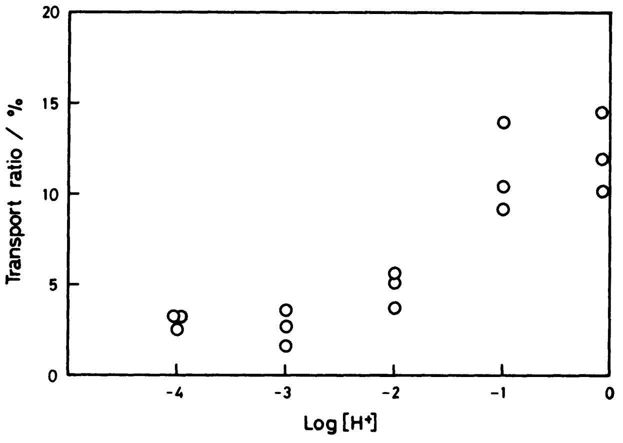

Fig. 5. Effect of the hydrogen ion concentration on the transport ratio of Na^+ in the case HCl was used.

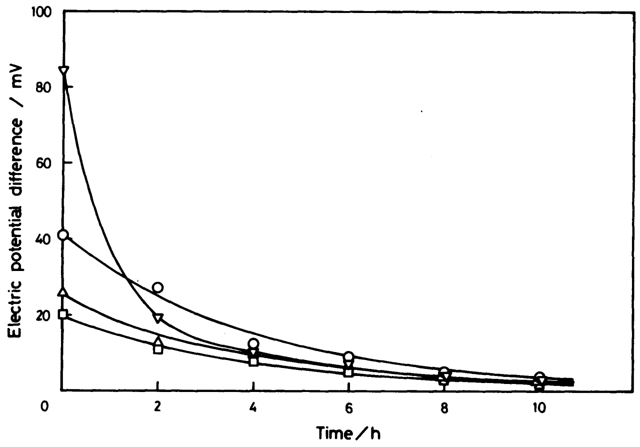

Fig. 6. Changes of the electric potential difference with time. ▽: 1 mol dm^{-3} HCl, ○: 0.1 mol dm^{-3} HCl, △: 0.01 mol dm^{-3} HCl, □: 0.001 and 0.0001 mol dm^{-3} HCl.

but also due to the permeation of Cl$^-$ from the left to right side. As shown in Fig. 4, this Cl$^-$ permeation is large, so that an investigation on the transport in cases where all negative charges are kept fixed in the left side of the membrane, was attempted, results obtained being analyzed in the light of the above conclusion.

The results in the case where HSS and NaSS were adopted instead of HCl and NaCl, respectively, are shown in Figs. 7 and 8. The transport ratios were evaluated by Eq. 1 by taking into consideration the transfer of water based on the Donnan osmosis. The concentration of Na$^+$ in the left-side chamber increased and that in the right-side one decreased with the passage of time in a similar manner as in the case of HCl. On the other hand, the concentration of SS$^-$ was unchanged, in contrast with Cl$^-$ in the case of HCl. Moreover, the transport ratios of Na$^+$ were much larger than those in the case of HCl, as shown in Fig. 8. This is compatible with the assumption that the membrane potential difference would be maintained for a long time because SS$^-$ is kept fixed well in the left side of the membrane. This assumption is supported by the result in Fig. 9. The membrane potential difference was maintained for more than 24 h.

Therefore, on the basis of the results described above we speculate that the transport of Na$^+$ will be effected in the following manner. The PEC membrane is considered to be a sort of charged membrane for which the functional groups of $-OSO_3^-$ in PVSK are responsible. The permeation phenomena in the case where a charged membrane is used or a certain ion is fixed in one side of the membrane, is explained in terms of the Donnan membrane equilibrium. It is difficult to analyze such a system as in this study comprising many kinds of ions. However, on the assumption that the membrane potential is the concentration membrane potential raised by HCl or HSS, the membrane potential $\Delta\phi$ can be regarded as the sum of the Donnan potentials $\Delta\phi_{\mathrm{Don,L}}$ and $\Delta\phi_{\mathrm{Don,R}}$ at the two solution-membrane interfaces and the diffusion potential $\Delta\phi_{\mathrm{Dif}}$ in the membrane.[17] Tentative membrane potential and transfer of Na$^+$ deduced

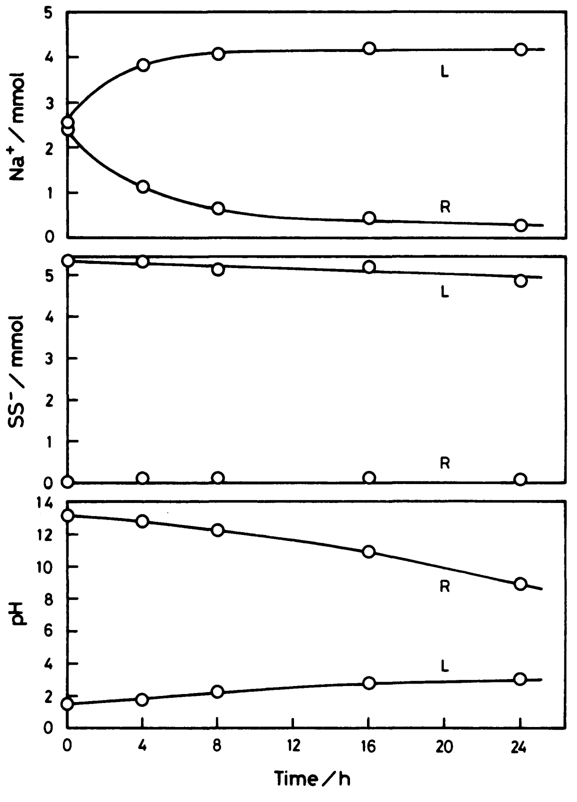

Fig. 7. Changes in the concentration of Na$^+$, SS$^-$, and H$^+$ at the active transport.

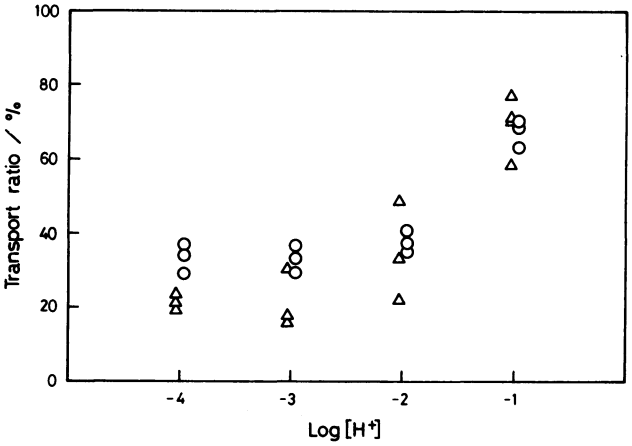

Fig. 8. Effect of the hydrogen ion concentration on the transport ratio of Na$^+$ in the case HSS was used. ○: $M_w=1.0\times10^4$, △: $M_w=5.0\times10^5$.

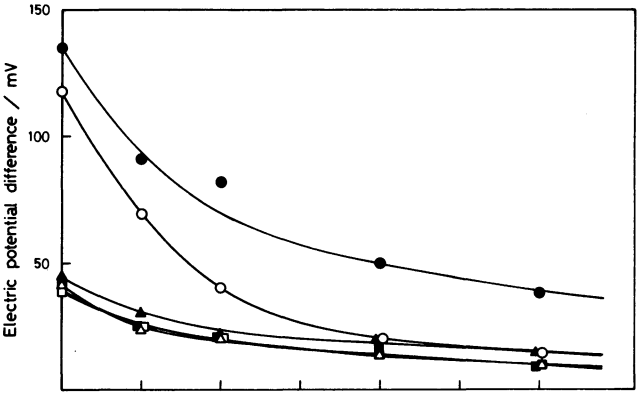

Fig. 9. Changes of the electric potential difference with time. ○: 0.1 mol dm^{-3} HSS($M_w=1.0\times10^4$), △: 0.01 mol dm^{-3} HSS($M_w=1.0\times10^4$), □: 0.001 and 0.0001 mol dm^{-3} HSS($M_w=1.0\times10^4$), ●: 0.1 mol dm^{-3} HSS($M_w=5.0\times10^5$), ▲: 0.01 mol dm^{-3} HSS($M_w=5.0\times10^5$), ■: 0.001 and 0.0001 mol dm^{-3} HSS($M_w=5.0\times10^5$).

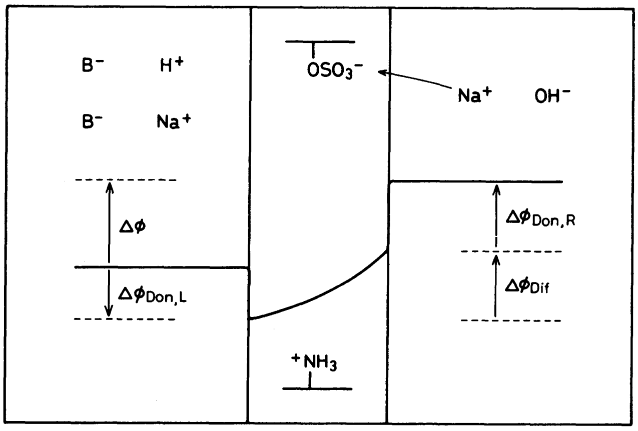

Fig. 10. Schematic representation of the membrane potential.

from the conclusions described above are illustrated in Fig. 10. In this system, the membrane surface potential is low because PEC membrane is anionic, and the potential in the membrane increases in the direction toward the right because of the large mobility of H^+. Thus, as a result, the right side is higher than the left side in electric potential. Na^+ was transported from the right to left side, i.e., from the alkaline to acidic side, through the membrane in accord with the gradient of electric potential. It seems that $-OSO_3^-$ groups in the membrane serve as carriers for Na^+.[8] However, the Donnan exclusion for Cl^- is small due to the small cation-exchange capacity (0.14 mequiv g^{-1} dry membrane) and there are $-N^+$ groups in the membrane capable of attracting Cl^-, so that the membrane potential difference is not maintained constant so long by Cl^- permeation. Then, the transport ratio of Na^+ seems low in the case of HCl. In the case of HSS, on the contrary, $\Delta\phi_{\mathrm{Don,L}}$ and $\Delta\phi_{\mathrm{Dif}}$ are larger than those in the case of HCl for the fixed SS^-, although $\Delta\phi_{\mathrm{Don,R}}$ is equal; moreover, the maintenance time of constant membrane potential difference is long. Therefore, the transport of Na^+ in accord with the membrane potential gradient is appreciable.

References

1) Y. Mori and H. Tanzawa, *Kobunshi*, **22**, 616 (1973).

2) A. Nakajima, *Kagaku To Kogyo*, **27**, 750 (1974).

3) E. Tsuchida and K. Abe, *Adv. Polym. Sci.*, **45**, 18 (1982).

4) L. L. Markley, H. J. Bixler, and R. A. Cross, *J. Biomed. Mater.*, **2**, 145 (1968).

5) H. J. Bixler and A. S. Michaels, *Encycl. Polymer Sci. Tech.*, **10**, 765 (1969).

6) T. Shimidzu, M. Yoshikawa, M. Hasegawa, and K. Kawakatsu, *Macromolecules*, **14**, 170 (1981).

7) T. Shimidzu and M. Yoshikawa, *Nippon Kagaku Kaishi*, **1983**, 958.

8) T. Uragami, R. Nakamura, and M. Sugihara, *Polymer*, **24**, 559 (1983).

9) T. Uragami, F. Yoshida, and M. Sugihara, *J. Appl. Polym. Sci.*, **28**, 1361 (1983).

10) N. Ogata, K. Sanui, and H. Fujimura, *J. Appl. Polym. Sci.*, **25**, 1914 (1980).

11) M. Yoshikawa, H. Ogata, and K. Sanui, *Polym. J.*, **15**, 609 (1983).

12) Y. Kikuchi and N. Kubota, *Bull. Chem. Soc. Jpn.*, **58**, 2121 (1985).

13) Y. Kikuchi and N. Kubota, *Nippon Kagaku Kaishi*, **1985**, 1592.

14) Y. Kikuchi and N. Kubota, *Nippon Kagaku Kaishi*, **1985**, 111; *J. Appl. Polym. Sci.*, **30**, 2565 (1985).

15) Y. Kikuchi, K. Hori, and Y. Onishi, *Nippon Kagaku Kaishi*, **1980**, 1157.

16) M. Senoo and Y. Tanaka, "Makugaku Jikkenho," ed by M. Nakagaki, Kitami Shobo, Tokyo (1984), p. 194.

17) T. Hanai, "Maku To Ion," Kagaku Dojin, Kyoto (1978), p. 232.