Macromolecular Complexes Consisting of Poly(aluminum Chloride), [2-(Diethylamino)ethyl]dextran Hydrochloride, and Potassium Poly(vinyl Sulfate)

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Synopsis

The mixture of poly(aluminum chloride) (PAC) and [2-(diethylamino)ethyl]dextran hydrochloride (EA) were allowed to react with potassium poly(vinyl sulfate) (PVSK) to form many different water-insoluble macromolecular complexes (MCs) in aqueous solution at various hydrogen ion concentrations. According to elemental analyses, IR spectroscopy, and solubilities of MCs, molecular structures of each MC depend on $[H^+]$. It is suggested that the MCs obtained at pH 1.0 are products consisting of EA, PVSK, and aluminum aquo-complex having coordination water whereas the MCs at pH 4.0 are higher molecular products consisting of EA, PVSK, and basic aluminum maltidentate complex. This result is attributable to change with $[H^+]$ in the degree of dissociation and conformation of EA, PVSK, and the dissociation of hydrated coordination of PAC. MC membranes were made by casting solutions of all kinds of MCs, and active, selective transport phenomena through a membrane of the MC prepared in a solution of pH 1.0 HCl were investigated under various conditions. 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. It was also suggested that the affinity of the carrier and both the chemical and physical properties of the MC membrane controlled the selective transport through the membrane.

INTRODUCTION

The mixing of oppositely charged polyelectrolytes in solution leads to the formation of macromolecular complexes (MCs).[1-3] To date, however, the papers on the polyion interaction between inorganic and inorganic and/or organic macromolecule except for our papers have not been investigated in spite of their importance concerning the field of macromolecules.

We have reported the structure and properties of MC[4-7] and clot formation on MC in vitro,[8,9] and also we have reported a novel chemical reaction of forming MC consisting of inorganic and two or three organic and/or inorganic macromolecules.[10-15] Moreover, MC membranes were found to be capable of active and selective transport of alkali metal ions.[12-15] This paper deals with a novel chemical reaction of potassium poly(vinyl sulfate) with the mixture of poly(aluminum chloride) as inorganic macromolecule and [2-(diethylamino)ethyl]dextran hydrochloride, and general characteristics of re-

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sulting MCs. In addition, a description will be made on active and selective transport of alkali metal ions through a membrane of MC prepared at pH 1.0 HCl solution, with particular reference to the relationship between transport and membrane potential.

EXPERIMENTAL

Synthesis of Macromolecular Complex

Poly(aluminum chloride) (PAC) {Kurosaki Kagaku Co. Ltd., compositional formula $[Al_2(OH)_nCl_{6-n}]_m$, $n = 3$, $m = 2.5$ at pH 2.7, aluminum content as Al_2O_3 10.3%} and [2-(diethylamino)ethyl]dextran hydrochloride (EA) (Meito Sangyo Co. Ltd., nitrogen content 5.33%, intrinsic viscosity 1.49 dL/g in 1 mol dm^{-3} NaCl soln at 25°C) and potassium poly(vinyl sulfate) (PVSK) (intrinsic viscosity 0.59 dL/g in 1 mol dm^{-3} NaCl soln at 25°C, sulfur content 18.91%) were used.

The precipitate of $Al(OH)_3$ in PAC solution produced at pH above 4.3 and also the MC consisting of three materials did not form at pH below 0.9. Therefore, the reactions were carried out at pH 1.0, 2.0, and 4.0. The molar ratio of the reactive group of Al (PAC) to that of N(EA) in the mixture were 1 : 1, 5 : 1, and 50 : 1 (written below as Al to N in the mixture). The PVSK solutions (2 g dm^{-3}) were added dropwise to the mixture solutions (2 g dm^{-3}) of PAC and EA (written below as mixture solution) or vice versa, both adjusted to the same hydrogen ion concentration at a rate of 50 mL/30 min with stirring (Table I). A water-insoluble MC was thus obtained. After standing for 30 min, the precipitate was washed with hydrochloric acid solution, water, and methanol. Then, it was separated by centrifugation and dried *in vacuo* at room temperature until a constant weight was attained. Molar ratio of reactive group of S(PVSK) to that of the mixture [Al(PAC) + N(EA)] in the reaction mixture at end point of coagulation of both mixing order (Fig. 1) were listed in Table I.

Membrane and Procedure Application

The MC was dissolved in ternary solvent mixture (HCl/1,4-dioxane/H_2O 16 : 47 : 37 wt %). The solution was poured on to a Teflon plate. In addition, a uniform film was obtained on the Teflon plate by further evaporating of the solvent under 50% humidity for 1 or 2 days. The thickness of membrane was 100 ± 20 μm.

The resistance of the membranes against acid and base was examined by immersing them in acidic (pH 1.0) or alkaline solution (pH 13.0).

A PMMA cell consisting of two chambers was used to study 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. The cell was immersed in air bath at 30°C. The concentration of alkali metal ions, K^+ and Na^+, in both left and right side cells (chambers) was determined by atomic absorption. The miscibility of polyanion, polycation, or MC in a three-component system was examined by the procedure described in the previous papers.[12-15] Electric conductivity was measured by the method of Fourterminal, which passes constant current between two platinum leads on the outside and so measures the potential difference resulting from two platinum leads on the inside by a voltmeter of high impedance.[16] The details of experimental conditions and additional procedures and methods were identical with those described in the previous papers.[12-15]

RESULTS AND DISCUSSION

Macromolecular Complex

Experimental conditions, yield, and elemental analyses for the MC prepared after coagulation of MC as well as the conditions of mixing order of the solutions are given in Tables I and II. The MC of 1-A, 1-B, 1-C, 1-D, 1-E, 1-F, 2-A, 2-B, 2-D′, and 2-F′ listed in Table I were white and powdery products and those of 2-C, 2-D, 2-E, and 2-F were yellowish and viscous products. Yellowish and viscous MC were prepared by adding PVSK solution in Al to N 5 : 1, 50 : 1 in mixture solution except for the MC of 2-D′ and 2-F′. When the mixture solution was added dropwise to the PVSK solution of Al to N 5 : 1, 50 : 1 in the mixture at pH 4.0, two kinds of precipitate were produced. One was the material precipitated in the side of vessel, and another one was suspended in reaction system. The MC of 2-D, 2-D′ and 2-F, 2-F′ in Table I correspond to those mentioned above. Such iteration among them did not occur in other reaction systems. The aluminum and sulfur contents, reflecting the PAC and PVSK contents in each MC, are higher with increasing the ratio

TABLE I

Conditions and Yield for Preparation of Macromolecular Complexes[a]

Sample code	Concentration of hydrogen ion (pH)	Molar ratio of reactive group of N(EA) to that of Al(PAC) in the mixture [N(EA)/Al(PAC)]	Molar ratio of reactive group of S(PVSK) to that of the mixture [Al(PAC) + N(EA)] in the reaction mixture	Amount of complex (g)
1-A	1.0	1 : 1	0.67	0.22
1-B	4.0	1 : 1	0.67	0.31
1-C	1.0	1 : 5	0.56	0.31
1-D	4.0	1 : 5	0.56	0.16
1-E	1.0	1 : 50	0.44	0.14
1-F	4.0	1 : 50	0.44	0.51
2-A	1.0	1 : 1	0.67	0.20
2-B	4.0	1 : 1	0.67	0.32
2-C	1.0	1 : 5	0.56	0.14
2-D	4.0	1 : 5	0.56	0.21
2-D′	4.0	1 : 5	0.56	0.03
2-E	1.0	1 : 50	0.44	0.25
2-F	4.0	1 : 50	0.44	0.09
2-F′	4.0	1 : 50	0.44	0.04

[a] Concentration of sulfate of poly(vinyl alcohol) (PVSK) and those of the mixture of poly(aluminum chloride) (PAC) and [2-(diethylamino)ethyl]dextran hydrochloride (EA) were 2.0 g/L each. 1 series: PVSK solution was added dropwise to mixture solution (100 mL). 2 series: Mixture solution was added dropwise to PVSK solution (100 mL). PAC: The molecular formula $[Al_2(OH)_nCl_{6-n}]_m$, $n = 3$, $m = 2.5$ at pH 2.7, aluminum content as Al_2O_3 10.3%. EA: $[\eta] = 1.49$ dL/g in 1 mol dm^{-3} NaCl soln at 25°C, nitrogen content 5.33%. PVSK: $[\eta] = 0.59$ dL/g in one mol dm^{-3} NaCl soln at 25°C, sulfur content 18.91%.

TABLE II
Elemental Analyses and Composition of Macromolecular Complexes

Sample code[a]	Aluminum content[b] (%)	Nitrogen content[c] (%)	Sulfur content[d] (%)	Molar ratio of S(PVSK)/Al(PAC) + N(EA)
1-A	0.78	2.92	8.53	1.14
1-B	3.02	1.19	9.85	1.53
1-C	1.62	1.81	10.00	1.63
1-D	5.97	1.32	11.01	1.08
1-E	2.26	0.82	15.19	3.38
1-F	13.80	0.39	11.12	0.65
2-A	1.75	1.77	10.50	1.64
2-B	3.61	1.52	12.20	1.58
2-C	2.65	1.43	11.98	0.79
2-D	6.62	0.62	15.15	1.65
2-D′	4.86	1.96	13.92	1.34
2-E	3.35	0.13	15.29	3.64
2-F	9.42	0	15.20	1.38
2-F′	3.74	0.40	13.58	2.50

[a] Sample code correspond to those in Table I.
[b] Analyses carried out according to JIS 1475-1978.
[c] Analyses carried out according to Kjeldahl method.
[d] Analyses performed at the Institute of Physical and Chemical Research.

of reactive group of Al(PAC) to that of N(EA) in the mixture, whereas the contents of EA are smaller than that. The PAC and PVSK contents in each MC prepared at pH 4.0 are higher than those at pH 1.0 except for the MC of sulfur contents of Al(PAC) to N(EA) 50 : 1 in the mixture. The content of EA, on the contrary, are smaller than that.

Figure 1 shows the dependence of the molar ratio of reacting groups in PVSK and the mixture of PAC and EA in the reaction mixture solution at starting and end points of coagulation of the MC upon the hydrogen ion concentration. Inspection of Figure 1 shows that the structure and properties of MC differed from one another in experimental conditions. It is obvious from the properties of MC that the MC prepared at pH 1.0 and 2.0 were yellowish and viscous materials and those at pH 4.0 were white and powdery materials.

Hydrolysis of aluminum ions has been widely investigated by many methods. It was revealed that many kinds of aluminum complexes such as ionic, nonionic, aluminum aquo-complex, and aluminum multidentate complex are present in solution. However, those are in doubt because of complicating features. Aluminum ion in solution is not bare aluminum ion Al^{3+}, but that in stable complex ion is called aluminum aquo-complex ion with six to ten coordination water molecules $\{[Al(OH_2)_n]^{3+}, [Al(OH_2)_{n-1}]^{2+}, n = 6\text{–}10\}$, and the aquo-complex ion is stable in the concentration below pH 3.0.[17] Hydrated coordination of PAC is promoted with increasing of hydrogen ion concentration and basic aluminum multidentate complex which was higher than the molecular weight of aluminum aquo-complex is produced in the polymer condensation between OH groups for PAC.[17] Therefore, the MC prepared at pH 4.0 and 1.0 appears to consist of basic aluminum multidentate

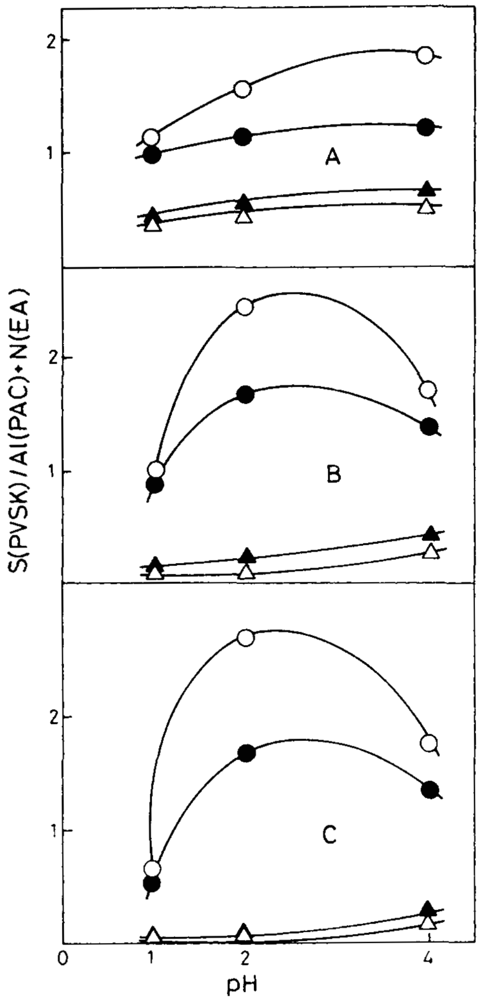

Fig. 1. The starting and end points of coagulation: (△, ○) starting point of coagulation; (▲, ●) end point of coagulation; (△, ▲) PVSK solution was added dropwise to mixture solution; (○, ●) mixture solution (PAC + EA) was added dropwise to PVSK solution; (A) molar ratio of reactive group of Al(PAC) to that of N(EA) in the mixture 1 : 1; (B) molar ratio of reactive group of Al(PAC) to that of N(EA) in the mixture 5 : 1; (C) molar ratio of reactive group of Al(PAC) to that of N(EA) in the mixture 50 : 1; S = mole number of sulfur (PVSK) in the reaction mixture; Al = mole number in aluminum (PAC) in the reaction mixture; N = mole number of nitrogen (EA) in the reaction mixture.

of high molecular weight, PVSK and EA, and aluminum aquo-complex, PVSK and EA, respectively.

The IR spectra of MC prepared at pH 1.0 and 4.0 except for that of 1-E, 2-E, and 2-F in Table I are shown in Figures 2 and 3. The IR spectra for 1-E, 2-E, and 2-F could not be measured because of viscous materials. The IR spectra of MC are roughly similar to that of the mixture of PAC, EA, and PVSK, differing from each other only in detail. The MC prepared at pH 1.0, 4.0 in molar ratio of active group Al(PAC) to that of N(EA) 1 : 1 in the mixture, are similar to one another in IR spectra. The intensity of absorption

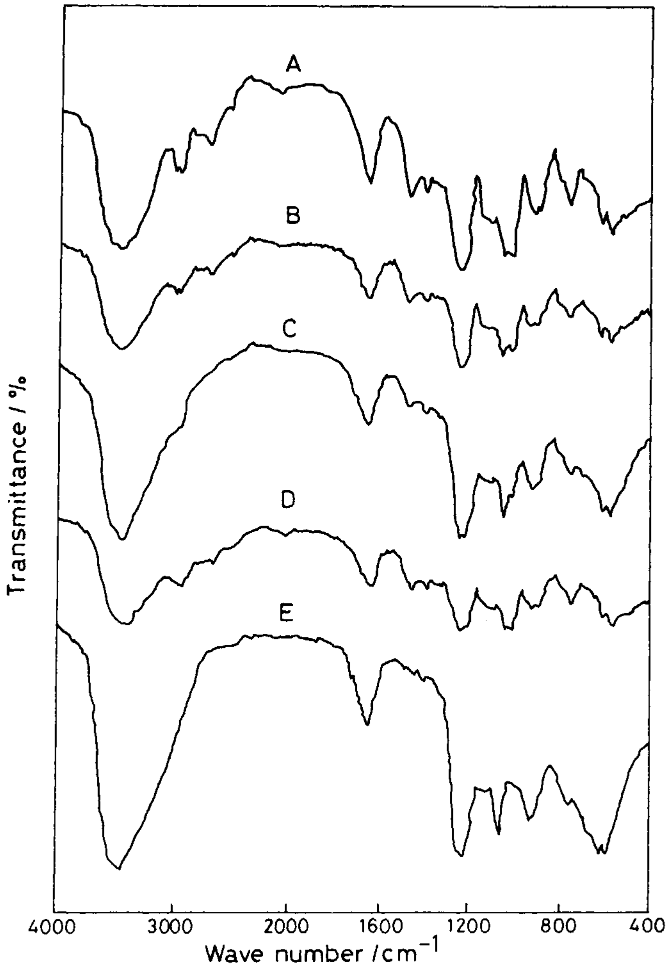

Fig. 2. IR spectra of macromolecular complexes: (A) 1-A, (B) 1-B, (C) 1-C, (D) 1-D, (E) 1-F, in Table I.

at 1250 cm^{-1} in that of dropping to mixture solution of Al to N 5 : 1 was assigned to the —OSO_3^- group in PVSK, and was stronger than that of reverse order of mixing at pH 1.0. Inversely, that prepared by dropping to PVSK solution at pH 4.0 was stronger than that of reverse order of mixing. The absorption bands at 1405 and 1480 cm^{-1} assigned to the —CH_2 and —CH_2—N^+ groups in EA were not detected in the MC prepared in Al to N 50 : 1 in the mixture regardless of pH and order of mixing. The content of PVSK in that of dropping to mixture solution was higher than of reverse order of mixing, and those of PAC in that of dropping to PVSK solution were higher than that, compared with that of reverse order of mixing.

The MC are insoluble in *N,N*-dimethylformamide and dimethyl sulfoxide, and soluble or swell in ammonia water and hydrobromic acid, a part of MC swell in formalin, formic acid, and *n*-butylamine.

Phase diagrams in the system NaBr/acetone/H_2O are shown for MC of 1-A, 1-C, and 2-A in Figure 4. Phase diagrams were obtained for MC which

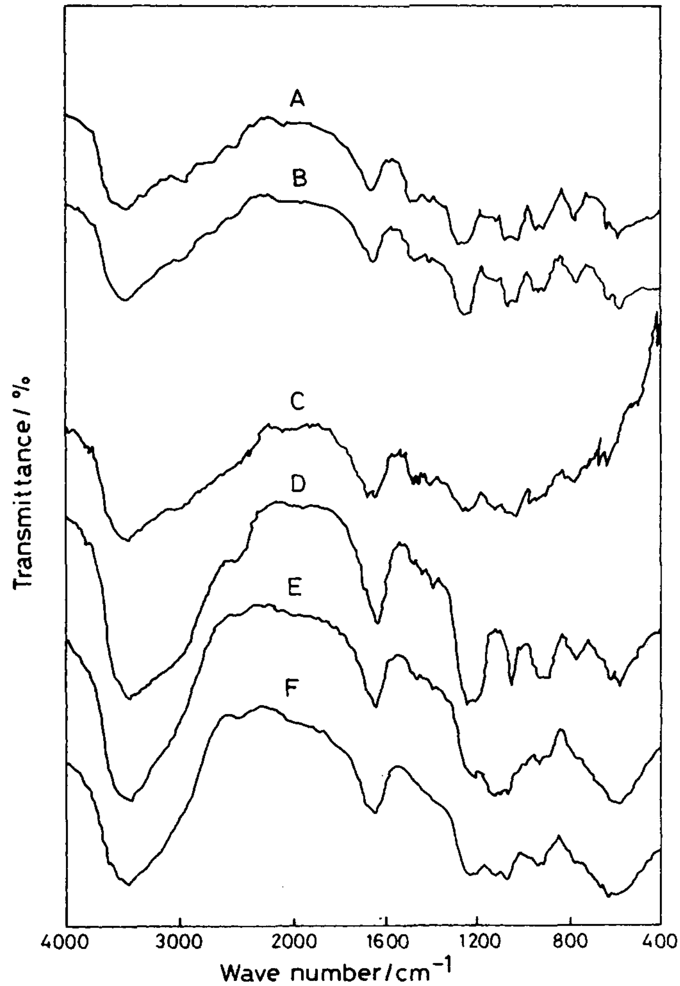

Fig. 3. IR spectra of macromolecular complexes: (A) 2-A, (B) 2-B, (C) 2-C, (D) 2-D, (E) 2-D′, (F) 2-F′, in Table I.

was prepared at pH 1.0, and those were smaller-content aluminum than that of the other MC and were not obtained for MC prepared at other experimental conditions, because of swelling to form a gel or cloudy solution or remaining insoluble. As Figure 4 shows, there is a small region in the solvent composition field where the complexes remain in solution to yield a homogeneous, viscous liquid. These experimental results support the differences in molecular structure of the MCs prepared according to the experimental conditions of hydrogen ion concentration, mole ratio of reaction mixture, and that of order of mixing, although the MC have common constituents. It appears that the degree of dissociation and conformation of EA and hydrated coordination of PAC change with the hydrogen ion concentration.

The properties of the membrane in acidic and basic solutions are shown in Table III. All the membranes formed at pH 1.0 and 4.0 resisted an acidic solution. On the other hand, all the membranes were not resistant to a basic

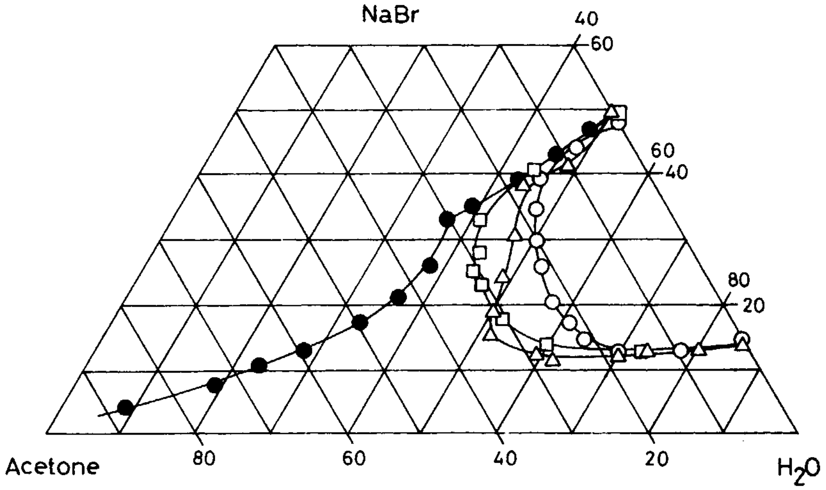

Fig. 4. Phase diagram of macromolecular complexes in the ternary solvent system at 30°C: (●) NaBr–acetone–H_2O, (○) 1-C, (△) 2-A, (□) 1-A, in Table I.

solution in the whole. The membranes of 1-A, 1-E, and 1-F were not damaged in either 0.1*M* NaOH or 0.1*M* HCl solution, even after 2 days. In addition, the electric conductivities of membranes were soaked in water, listed on the right side of Table III. The electric current did not pass through the MC in the condition of humidity of 50% and so was measured for MC soaked in water. The electric conductivities of membranes were 10^{-3}–10^{-4} s cm^{-1}.

It has become apparent that the structure and properties of the MC composed of inorganic macromolecules differed from each other according to

TABLE III
Stabilities of Macromolecular Complex Membranes in Acidic and Alkaline Solutions for 1–3 Days Duration and Electric Conductivity[a]

Sample code[b]	One day duration in pH 1.0 solution	Two days duration in pH 1.0 solution	Three days duration in pH 1.0 solution	One day duration in pH 13.0 solution	Two days duration in pH 13.0 solution	Three days duration in pH 13.0 solution	Electric conductivity of membranes[c] soaked in water ($S\ cm^{-1}$)
1-A	○	○	○	○	○	△	9.0×10^{-4}
1-B	○	○	○	△	×	×	8.1×10^{-4}
1-E	○	○	○	○	○	△	2.2×10^{-4}
1-F	○	○	○	○	○	△	2.1×10^{-4}
2-A	○	△	△	△	×	×	1.1×10^{-3}
2-B	○	○	△	△	△	×	4.9×10^{-4}
2-E	○	○	○	○	△	△	3.3×10^{-4}
2-F	○	△	△	△	×	×	3.6×10^{-4}
2-F′	○	△	△	○	×	×	1.3×10^{-3}

[a] (○) stable; (△) unstable; (×) soluble in acidic or alkaline solution.
[b] Sample code corresponds to that in Table I.
[c] The membranes were prepared in relative humidity 50%.

TABLE IV
Experimental Conditions of the Active Transport of Na^+ and Transport Ratio

Expt no	Left side	Right side	Transport ratio (%)
1	0.1 mol dm^{-3} HCl, 0.1 mol dm^{-3} NaCl	0.1 mol dm^{-3} NaOH	13.6
2	0.05 mol dm^{-3} HCl, 0.1 mol dm^{-3} NaCl	0.1 mol dm^{-3} NaOH	8.6
3	0.01 mol dm^{-3} HCl, 0.1 mol dm^{-3} NaCl	0.1 mol dm^{-3} NaOH	6.3

experimental conditions. However, the investigation of that is little studied in the field of macromolecules.

Macromolecular Complex Membrane

The 1-A membrane in Table I was not damaged in either 0.1 mol dm^{-3} NaOH or 0.1 mol dm^{-3} hydrochloric acid solution, even after 2 days. This membrane was used in the study of the transport of alkali metal ions. The aluminum, sulfur and nitrogen contents in the MC used to prepare the membrane were 0.78, 8.53, and 2.92%, respectively. The active transport experimental was carried out at 30°C. The concentration of the Na^+ ion on both the left and right sides of the cell was kept identical initially. In the left side, the cell contained HCl, while the right side cell contained NaOH.

Experimental conditions of the active transport of Na^+ and transport ratio were shown in Table IV. Figure 5 shows concentration changes for Na^+, Cl^-, and pH with reaction time in both the side chambers containing 0.1 mol dm^{-3} HCl. Despite the fact that both 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

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

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 Table IV. The transport ratio corresponds to the $[H^+]$, and it becomes higher with increasing of $[H^+]$. 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.

Selective transport from the right side cell to the left side cell through the membrane was observed under 0.05 mol dm^{-3} concentration of both NaOH and KOH solutions in the right side cell and at 0.1 mol dm^{-3} HCl solution in the left side cell at 30°C. The ratios of transported ions selectivity[4-7] were

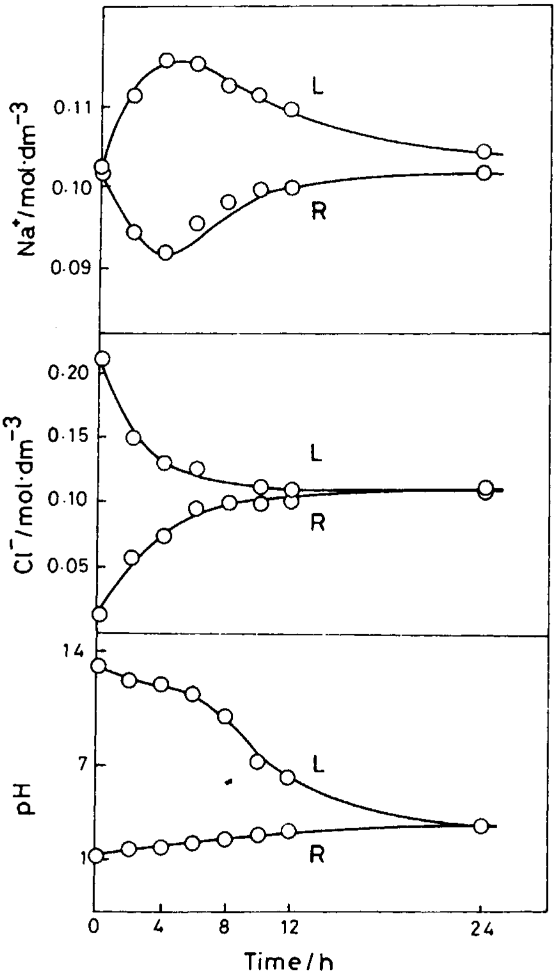

Fig. 5. Time–transport curves of Na^+, Cl^-, and pH of the active transport at 30°C.

calculated from the following equation:

$$\text{Selectivity} = [K^+]_{L,t}/[K^+]_{R,0} \Big/ [Na^+]_{L,t}/[Na^+]_{R,0}$$

The selectivity of the transport with reaction time is shown in Table V. The concentration change of alkali metal ions with the time of transport in both side cells at pH 1.0 is shown in Figure 6. The ratio of the permeated K^+ to the permeated Na^+ changed with reaction time.

Figure 7 indicates that the membrane potential difference becomes greater as the concentration of HCl in the left side is increased, and this tendency is consistent with result in Table IV. The membrane potential difference, however, decreases with reaction time. This decrease in the potential difference is not only due to the transport of Na^+ from the right to left side, but also due to the permeation of Cl^- from the left to right side. Therefore, on the basis of the results described above, we speculate that the transport of Na^+ will be effected in the following manner. The MC membrane is considered to be a sort

TABLE V
Change of Selectivity with Reaction Time

Time (h)	Selectivity
2	1.1
4	1.1
6	1.2
8	1.2
10	1.2
12	1.1
24	1.1

of charged membrane for which the functional group of $-OSO_3^-$ in PVSK is responsible. The membrane was then immersed in basic or acidic solution for about 3 h. The IR spectrum of the membrane immersed in an acidic solution exhibited the medium absorption at 800–900 cm^{-1} assigned to the $-OSO_3H$ group, but that immersed in basic solution exhibited only a weak absorption. In addition, that immersed in basic solution exhibited the medium absorption at 900–940 cm^{-1}, assigned to the $-OSO_3^-$ group. On the acidic side, this characteristic absorption band almost disappeared. Therefore, it was concluded that the MC moiety was opened on the alkaline side and closed 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. The permeation phenomenon in the case where a charged membrane is used is explained in terms of the Donnan membrane equilibrium. It is difficult to analyze much 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, the membrane potential $\Delta\phi$ can be regarded as the sum of the Donnan potential $\Delta\phi_{\mathrm{Don},\,L}$ and $\Delta\phi_{\mathrm{Don},\,R}$ at the two solution–membrane interfaces and the

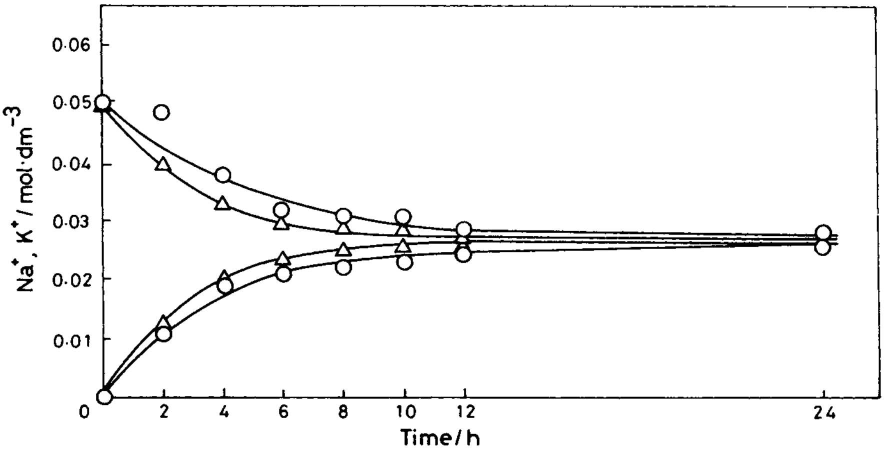

Fig. 6. Changes in the concentration of Na^+ and K^+ at the selective transport: (○) Na^+; (△) K^+.

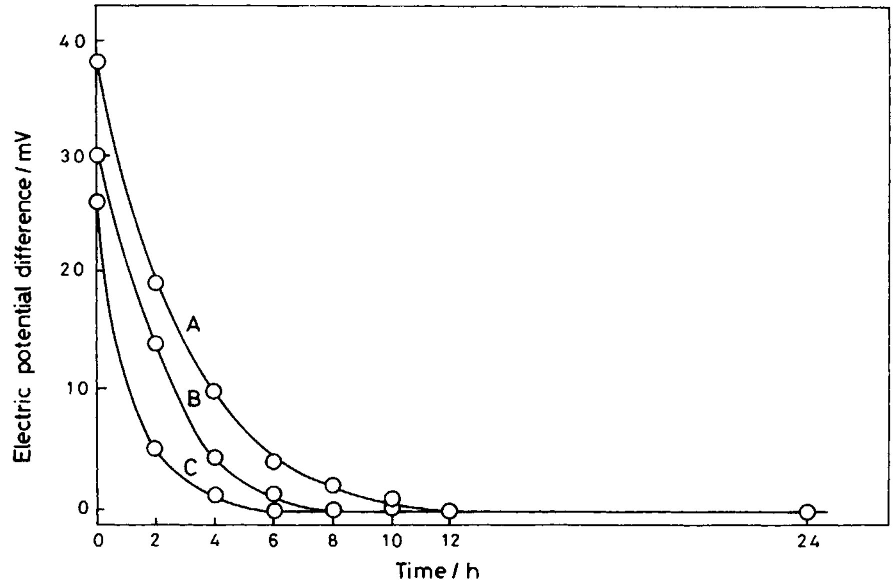

Fig. 7. Changes in the electric potential difference with the time: (A) no. 1, (B) no. 2, (C) no. 3 in Table IV.

diffusion potential $\Delta\phi_{Dif}$ in the membrane.[18] In this system, the membrane surface potential is low because MC 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 the $-OSO_3^-$ group in the membrane serve as carriers for Na^+.[19] However, the Donnan exclusion for Cl^- is small due to the small cation-exchange capacity (OSO_3K about 0.15%), and there are $-N^+$ groups in the membrane capable of attracting Cl^-, as 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 conclusion, we consider that the driving force of the active transport of alkali ions is a gradient of the hydrogen ion concentration, which the binding of the alkali metal ions to surface group is attributable to the degree of the ring opening of the MC membrane with hydrogen bonding, which affect the selectivity.[20,21]

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

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