Interaction of Cation-Exchange Membrane with Polycation
I. Poly(N-Methyl-4-Vinylpyridinium Chloride)

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Synopsis

We elucidated the effect of the molecular weight of poly(N-methyl-4-vinylpyridinium chloride) (PMVP) on its adsorbed or ion-exchanged amount on the cation-exchange membrane and the preferential permselectivity of the membrane for sodium ion to calcium ion. The amount of the adsorbed or ion-exchanged PMVP increases with time and then attains to a definite value at a definite concentration. Also, the ultimate value increases with increasing the concentration of PMVP. When the molecular weight of PMVP is 3090, the ratio of the pyridinium groups of PMVP ion-exchanged with the sulfonic acid groups on the membrane surface to the total pyridinium groups of the cohered PMVP is in the range of 70–80%. The relative transport number of calcium ions to sodium ions(P_{Na}^{Ca}) decreases with increasing the amount of adsorbed or ion-exchanged PMVP and the number of non-ion-exchanged pyridinium groups of PMVP on the membrane surface. The smaller the molecular weight of PMVP, the more the adsorbed or ion-exchanged amount and the more preferable the permselectivity for sodium ion.

INTRODUCTION

Many investigators have studied on interactions between ion-exchange membranes and surface-active agents or polyelectrolytes.[1-14]

It is known that the monovalent cations preferentially permeate through the cation-exchange membranes to the multivalent ones in the presence of the thin layer of the polycations on the membrane surface, and it is industrially used to produce table salt.[7-9]

However, the detail of the relation between the preferential permselectivity for the monovalent cation and the structure of the polycation is still obscure. In this paper, the interactions between the cation-exchange membranes and poly(N-methyl-4-vinylpyridinium chloride) (PMVP) were investigated in order to clarify the adsorption behavior of polycations to the cation-exchange membrane and the mechanism of the preferential permselectivity for sodium ion to calcium ion.

EXPERIMENTAL

Ion-Exchange Membrane

The cation-exchange membrane used was NEOSEPTA CM-1 prepared by the paste method (Tokuyama Soda Co. Ltd.),[15-17] its characteristics is shown in Table I.

TABLE I

Characteristics of Cation-Exchange Membrane[a]

Name	CM-1
Electric resistance[b]	1.3
(ohm-cm^2)[b]	
Transport number[c]	> 0.99
Water content[d]	0.38
(g H_2O/g Na^+ form dry membrane)	
Ion-exchange capacity	2.3
(meq./g Na^+ form dry membrane)	
Thickness (mm)	0.15

[a]Strongly acid cation-exchange membrane.
[b]Equilibrated with 0.5 N NaCl solution at 25°C, measured at 1000 cycle A.C.
[c]Measured by electrodialytic method at 25°C at 1.0 A/dm^2.
[d]Equilibrated with 0.5 N NaCl solution.

Before the measurements, the membranes were soaked several times alternatively in a 1 N hydrochloric acid solution and in a 0.5 N sodium chloride solution and then equilibrated in the salt solution which was used in the measurements.

Poly(4-Vinylpyridine)

Polymerization of 4-vinylpyridine was carried out by living anionic polymerization using dimethyl sulfoxide as a solvent and CH_3OK/CH_3OH as an initiator.[18] The molecular weight of PMVP used was 2640, 3090, 4310, 13,800, and 28,600.

Dimethyl sulfoxide and 4-vinylpyridine were distilled before use under reduced nitrogen atmosphere in the presence of calcium hydride.

Methyl iodide and nitroethane were distilled before use.

Poly(N-Methyl-4-Vinylpyridinium Chloride)

Methyl iodide (161 mmol) was added to a nitroethane solution of poly(4-vinylpyridine) (19 mmol in 100 mL) and the resultant solution was stirred at 30°C for 24 h. Then methyl iodide (161 mmol) was added to the solution, which was stirred at 30°C for 24 h.

After evaporation of the volatile components, the polycations of I^--form was converted into Cl^--form by treatment with anion-exchange resin, Amberlite IRA-410 of Cl^--form (Rohm & Haas Co. Ltd.).

Poly(N-methyl-4-vinylpyridinium chloride) (PMVP) was obtained and the yield was 95% (2.8 g). The molecular weight of PMVP was determined by using high performance liquid chromatography (gel permeation chromatography; GPC). GPC measurement was carried out at 25°C with the aid of a 655 liquid chromatography (Hitachi Co. Ltd.), using TSK-GEL PW type column (G 4000 PW) (Toyo Soda Co. Ltd.) in an aqueous solution of 1/10 M KCl–1/15 M H_3PO_4. The ultraviolet (UV) adsorption detector was used at the wave number of 265 nm. The standard polymers used for the calibration of the GPC column were standardized poly(ethylene oxide) (Toyo Soda Co. Ltd.). Figure 1 shows the GPC chart of PMVP. Table II shows the weight-average molecular weight (Mw), the number-average molecular weight (Mn)
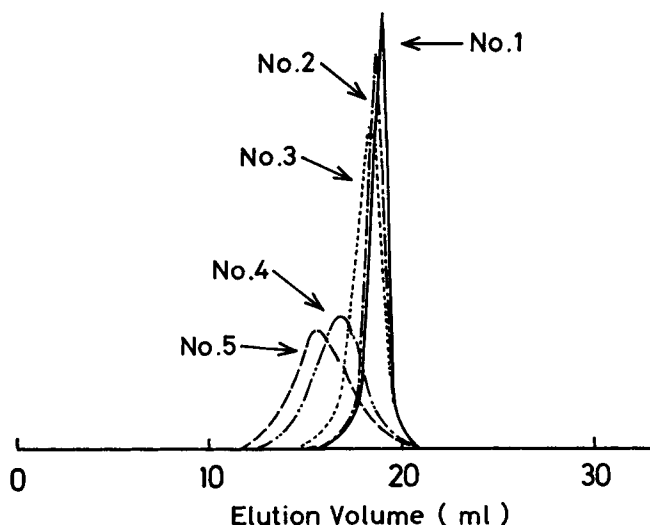
Fig. 1.   The GPC chart of poly-N-methyl-4-vinylpyridinium chloride.

TABLE II
Molecular Weight of PMVP Calculated with Computer from GPC Chart

No.	Mw	Mn	Mw/Mn
1	2640	2298	1.15
2	3090	2585	1.20
3	4312	3385	1.27
4	13819	6673	2.07
5	28583	10357	2.76

and Mw/Mn calculated with computer from GPC chart.[19, 20] The molecular weight distribution of the polymer is narrow.

Measurement

Determination of the Adsorbed or Ion-Exchanged Amount of PMVP on the Cation-Exchange Membrane

The cation-exchange membranes (7×12 cm^2) of H$^+$-form were immersed in an aqueous solution of PMVP, and allowed to stand with stirring at a definite temperature for a definite period. The adsorbed or ion-exchanged amount of PMVP on the membrane, Δm (eq/dm^2), was determined from its decrement in the solution. The concentration of PMVP in the solution was analyzed by the colloid titration,[21, 22] using a 1/400 N potassium poly(vinylsulfate) solution as a titrant and toluidine blue as an indicator.

Determination of the Proton Amount Delivered by Ion-Exchange of Polycation with the Membrane

The membrane of H$^+$-form, which was thoroughly washed with water in advance, was immersed in the solution of PMVP (pH 5.3–5.6). Then the

membrane was taken out and washed with water. The washing water was added to the solution of PMVP, and the resultant solution was titrated with a 0.01 N NaOH solution until the pH of the solution became to the same pH of the solution before the immersion of the membrane.

Thus, the proton amount liberated from the membrane, Δn (eq/dm^2), could be estimated.

Determination of P_{Na}^{Ca}

P_{Na}^{Ca} was determined as reported in the previous paper.[5] Electrodialysis was carried out in a mixed solution of 0.25 N sodium chloride and 0.25 N calcium chloride under the current density of 1.0 A/dm^2 for 90 min at 25°C with stirring. The relative transport number of calcium ion to sodium ion is defined as follows,

$$P_{Na}^{Ca} = \frac{(t_{Ca}/t_{Na})}{(C_{Ca}/C_{Na})}$$

where t_{Na} and t_{Ca} are the transport numbers of sodium ion and calcium ion in the membrane, respectively, and C_{Na} and C_{Ca} are the concentration of sodium and calcium ions before electrodialysis, respectively. Then, the values of C_{Na} and C_{Ca} are equal in this study.

RESULTS AND DISCUSSION

Adsorption Behavior of PMVP

Figure 2 shows the relationship between the adsorbed or ion-exchanged amount of PMVP onto the cation-exchange membranes of H$^+$-form and the immersion period. The amount is represented by the equivalent number of the pyridinium groups of PMVP adsorbed or ion-exchanged on the membrane. The amount of the adsorbed or ion-exchanged PMVP increases rapidly in the initial period, then it attains to an equilibrium. The more the concentration of PMVP, the longer the period to attain the equilibrium.

Figure 3 shows the relationship between the equilibrated amount of the adsorbed or ion-exchanged PMVP and the concentration of PMVP. The equilibrated amount of the adsorbed or ion-exchanged PMVP increases with increasing the concentration of PMVP and then levels off.

A number of theoretical treatments of the physical state of polymers adsorbed from solutions have been reported so far.[23-27] Equation (1) is reported concerning the adsorption of a solute in a solution to a solid surface,[28]

$$\Delta m = \frac{aC}{(1 + bC)} \tag{1}$$

where Δm is the adherent amount on the solid surface, C is the concentration of solute in the solution, a and b are constants inherent in the solid, the solute, and the solvent. Equation (1) can be modified as follows,

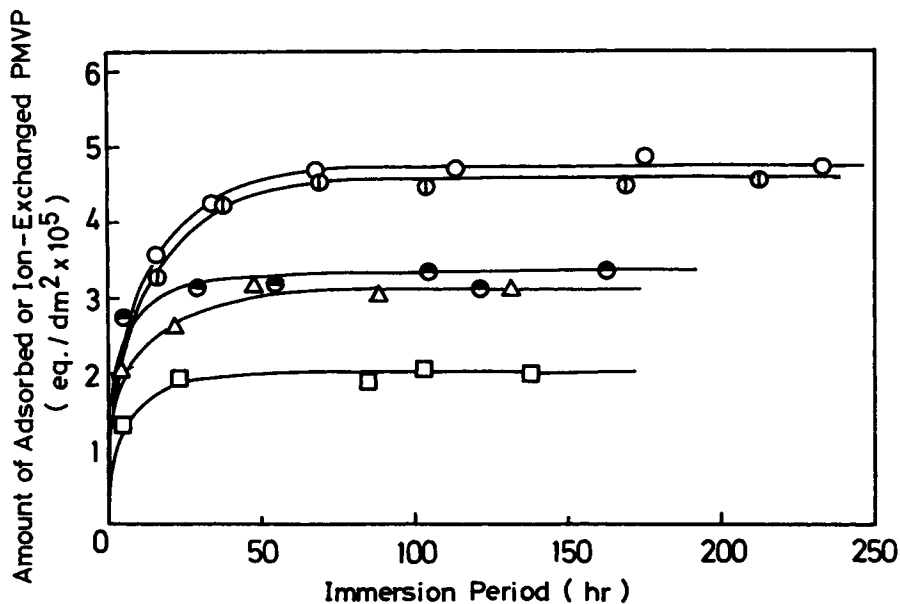$$\Delta \frac{C}{m} = \frac{1}{a} + \frac{b}{a}C \tag{2}$$

Fig. 2.   The relationship between the adsorbed or ion-exchanged amount of PMVP and the immersion period at 30°C. The concentration of PMVP: (□) 21.5 (eq/1 × 10^5), (△) 51.5 (eq/1 × 10^5), (◗) 101.5 (eq/1 × 10^5), (Φ) 212.0 (eq/1 × 10^5), (○) 316.5 (eq/1 × 10^5). The molecular weight of PMVP: 3090.
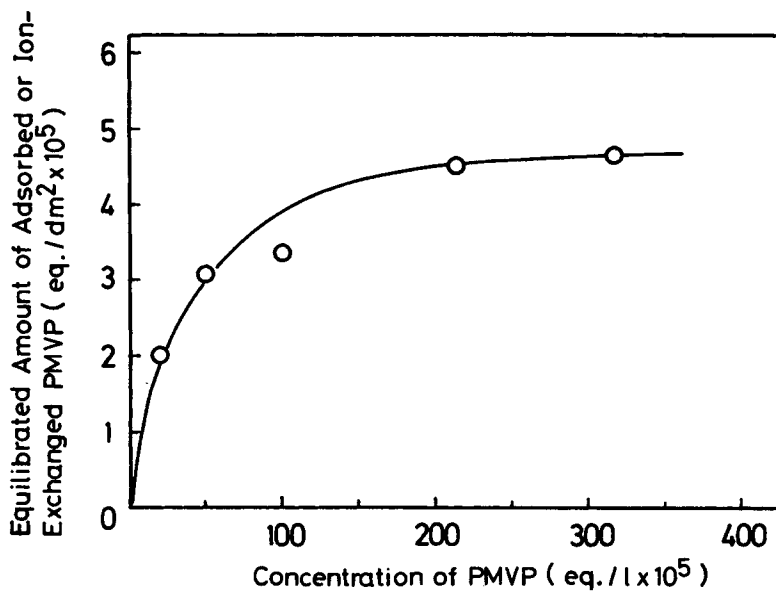

Fig. 3.   The relationship between the equilibrated amount of the adsorbed or ion-exchanged PMVP and the concentration of PMVP at 30°C.
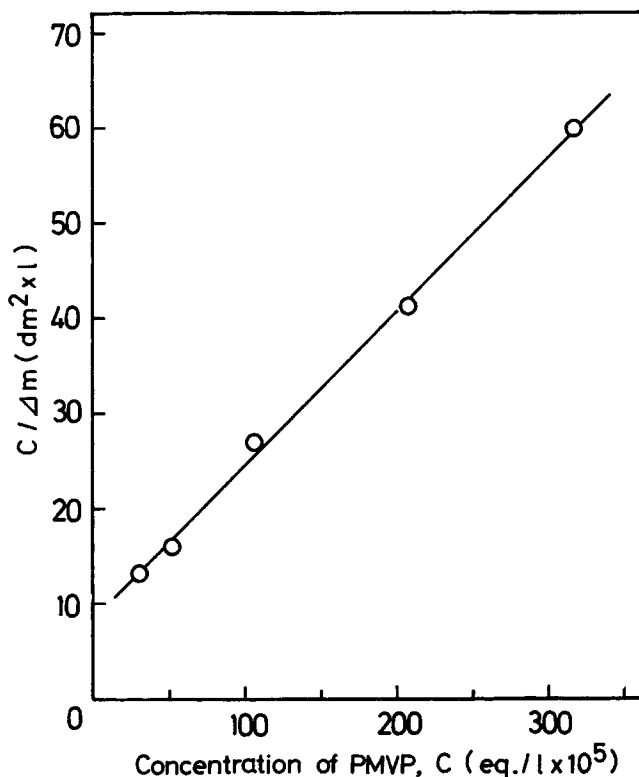
Fig. 4. Langmuir plot of $C/\Delta m$ against C at 30°C.

By using the data in Figure 3, the plot of C against $C/\Delta m$ is shown in Figure 4. The linear relation can be observed and, therefore, it means that the adsorption in this system is of Langmuir's type.

Figure 5 shows the relationship between the equilibrated amount of the adsorbed or ion-exchanged PMVP and the temperature. The equilibrated amount of the adsorbed or ion-exchanged PMVP increases with elevating temperature. Presumably, PMVP penetrates into the inner part of the membrane because of the increase in the mobility of PMVP chains in the solution and the swelling of the membrane.

The ratio of the cationic groups ion-exchanged with sulfonic acid groups on the cation-exchange membrane to the total cationic groups of polyelectrolyte cohered on the cation-exchange membrane has been little investigated in detail so far. Sata reported that most of the imino groups of poly(ethylene-imine) which adsorbed or ion-exchanged with the membrane surface did not ion-exchange with the sulfonic acid groups on the membrane.[2] Here, it should be noted that poly(ethyleneimine) has usually a crosslinked structure. However, no studies on any linear polycation have been reported yet.

Therefore, we determined the value of (the amount of the liberated H^+)/(the amount of the adsorbed or ion-exchanged PMVP), $(\Delta n/\Delta m)$. The amount of the adsorbed or ion-exchanged PMVP is correspondent to the total amount of the pyridinium groups of PMVP cohered on the membrane surface, and the
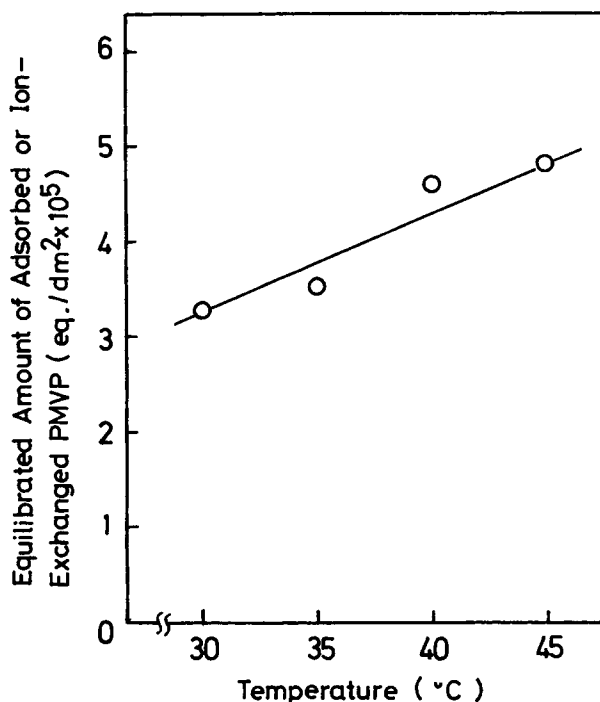
Fig. 5.   The relationship between the equilibrated amount of the adsorbed or ion-exchanged PMVP and temperature of the PMVP solution. The concentration of PMVP: 126.5 (eq/1 $\times$ 10^5), immersion period: 120 h.

amount of the liberated H^+ is equivalent to the amount of the pyridinium groups of PMVP bonding with the sulfonic acid groups on the membrane surface. Thus, we can calculate the ratio of the pyridinium groups of PMVP ion-exchanged with the sulfonic acid groups on the membrane surface to the total pyridinium groups of PMVP cohered on the membrane surface.

As shown in Figure 6(A), if $\Delta n/\Delta m = 1$, all the pyridinium groups of PMVP ion-exchange with the sulfonic acid groups on the membrane surface. If $\Delta n/\Delta m = 0.2$, it means that only 20% of the pyridinium groups of PMVP ion-exchange with the sulfonic acid groups on the membrane surface as shown in Figure 6(B).

Figure 7 shows the relationship between the amount of the adsorbed or ion-exchanged PMVP and $\Delta n/\Delta m$. The value of $\Delta n/\Delta m$ is in the range of 0.7–0.8, the remarkable change is not observed in spite of the increase in the amount of the adsorbed or ion-exchanged PMVP. This means that the ratio of the pyridinium groups of PMVP non-ion-exchanged with the sulfonic acid groups on the membrane surface to the total pyridinium groups of PMVP cohered on the membrane is in the range of 20–30%.

Therefore, we consider that the cation-exchange membrane and PMVP partially form polysalts. Many papers reported that a 1 : 1-polysalt is formed when a polycation and a polyanion are mixed in the solution.[29-31] However the 1 : 1-polysalt cannot be formed in this study because the membrane is

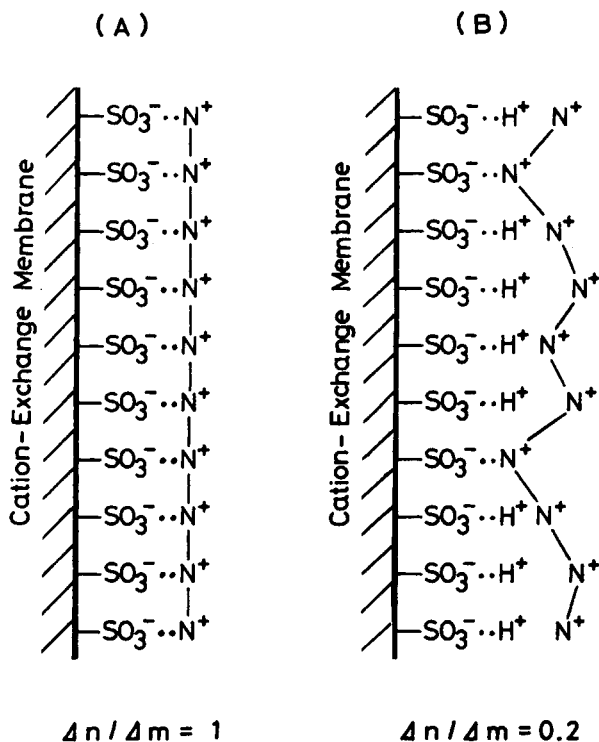$$\Delta n / \Delta m = 1 \qquad \Delta n / \Delta m = 0.2$$

Fig. 6.　Schematic example of the interaction of PMVP with the sulfonic acid groups on the surface of the cation-exchange membrane.
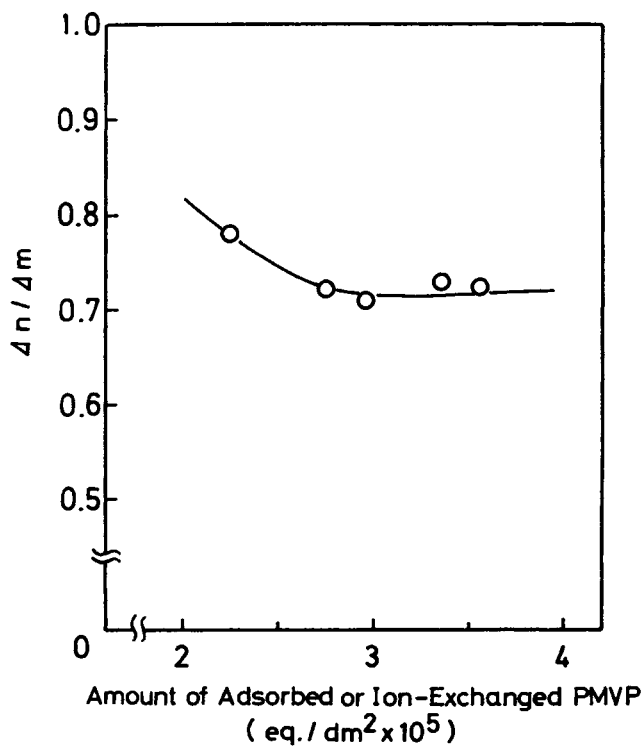
Fig. 7.　The relationship between the amount of the adsorbed or ion-exchanged PMVP and $\Delta n/\Delta m$ at 30°C. The concentration of PMVP: 116.3 (eq/1 $\times$ 10⁵).

$$\Delta n / \Delta m = 1 \qquad \Delta n / \Delta m = 0.2$$

Fig. 6.　Schematic example of the interaction of PMVP with the sulfonic acid groups on the surface of the cation-exchange membrane.

Fig. 7.　The relationship between the amount of the adsorbed or ion-exchanged PMVP and $\Delta n/\Delta m$ at 30°C. The concentration of PMVP: 116.3 (eq/1×10^5).

rigid. Therefore, the free pyridinium groups which cannot be ion-exchanged with the sulfonic acid groups remains in the range of 20–30%.

Permselectivity

Figure 8 shows the relationship between the amount of the adsorbed or ion-exchanged PMVP and P_{Na}^{Ca}. The more the amount of the adsorbed or ion-exchanged PMVP, the less the P_{Na}^{Ca}. The amount of the adsorbed or ion-exchanged PMVP varies with the concentration of PMVP and the immersion period, and the amount of the adsorbed or ion-exchanged PMVP is directly correlated to P_{Na}^{Ca}.

Figure 9 shows the relationship between $(\Delta m - \Delta n)$ and P_{Na}^{Ca}. P_{Na}^{Ca} decreases with increasing the number of the free pyridinium groups of PMVP on the membrane surface $(\Delta m - \Delta n)$, although some plots deviate to some extent.

Permselectivity of monovalent cations due to presence of the thin layer of polycations, on the cation-exchange membrane surface has been reported in the previous paper.[1-14] When the polycation layer is formed on the cation-exchange membrane surface, the free cationic groups exist on the membrane surface as shown in Figure 10. Therefore, the electrostatic repulsion to calcium
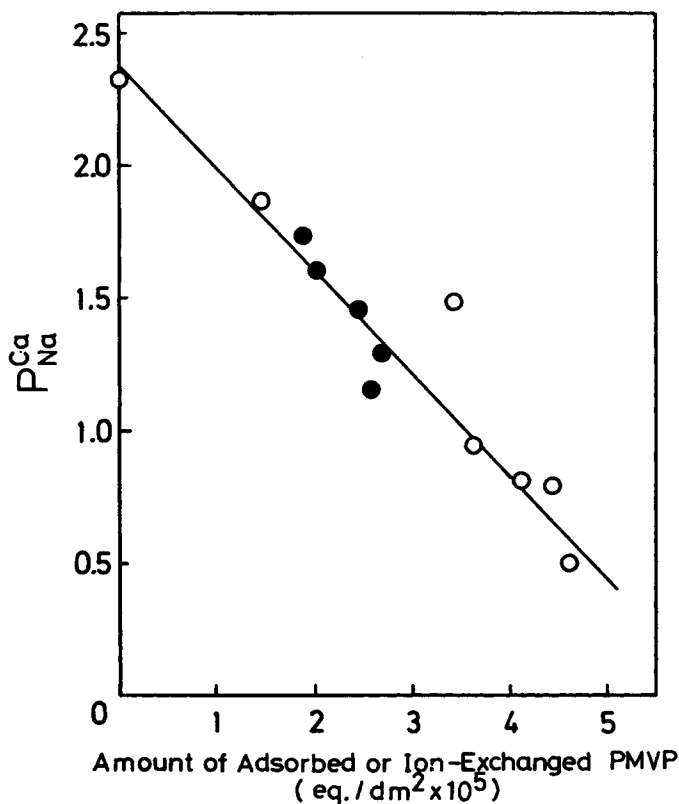

Fig. 8.   The relationship between the amount of the adsorbed or ion-exchanged PMVP on the cation-exchange membrane of H^+-form and P_{Na}^{Ca} at 30°C. The concentration of PMVP: (●) 25.5 (eq/1 × 10^5), (○) 255.0 (eq/1 × 10^5). The molecular weight of PMVP: 3090.
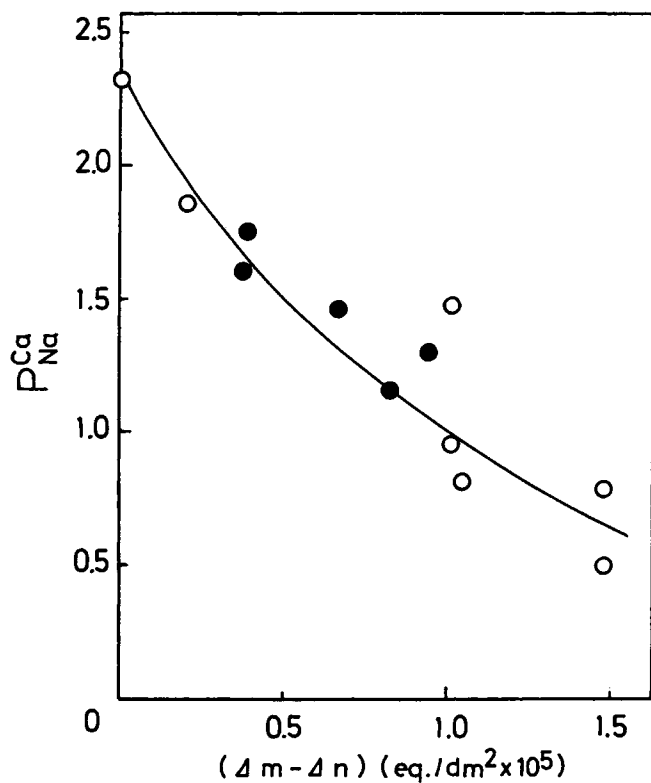
Fig. 9. The relationship between $(\Delta m - \Delta n)$ and P_{Na}^{Ca} at 30°C. The concentration of PMVP: (●) 25.5 $(eq/1 \times 10^5)$, (○) 255.0 $(eq/1 \times 10^5)$.
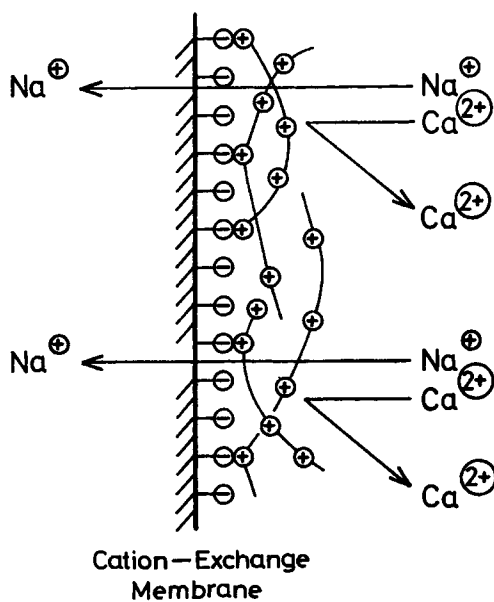

Cation—Exchange
Membrane

Fig. 10. Mechanism of monovalent cation permselectivity.

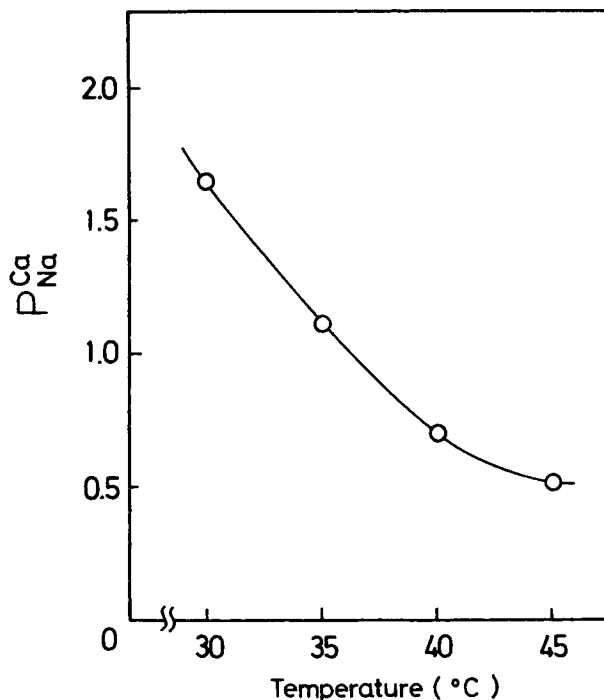Fig. 11.   The relationship between the temperature of PMVP solution and P_{Na}^{Ca}. The concentration of PMVP: 126.5 (eq/1 $\times$ 10^5), immersion period: 120 h.

ions are stronger than that to sodium ions. Consequently, monovalent cations preferentially permeate through the membrane to the multivalent ones. This is supported by the result shown in Figure 9.

Figure 11 shows the relationship between the temperature of the PMVP solution and P_{Na}^{Ca}. The higher the temperature, the better the permselectivity. This can be explained as follows: the amount of the adsorbed or ion-exchanged PMVP increases with increasing the temperature of the PMVP solution as shown in Figure 5 and then the free pyridinium groups increases.

Effect of Molecular Weight of PMVP

Figure 12 shows the effect of molecular weight on the equilibrated amount of the adsorbed or ion-exchanged PMVP and P_{Na}^{Ca}. The immersion period was 120 h, because we preliminarily confirmed that it is enough to get the equilibrated value of the amount of the adsorbed or ion-exchanged PMVP. The equilibrated amount of the adsorbed or ion-exchanged PMVP increases with decreasing the molecular weight. Especially, the equilibrated amount of the adsorbed or ion-exchanged PMVP sharply changes in the range of the molecular weight of 2500–5000. For example, the amount of the adsorbed or ion-exchanged PMVP of molecular weight of 3090 is five times as much as that of PMVP of 28,600. Probably, the difference of five times in the amount of the adsorbed or ion-exchanged PMVP should be attributed to the penetration of PMVP with smaller molecular weight into the inner part of the membrane.
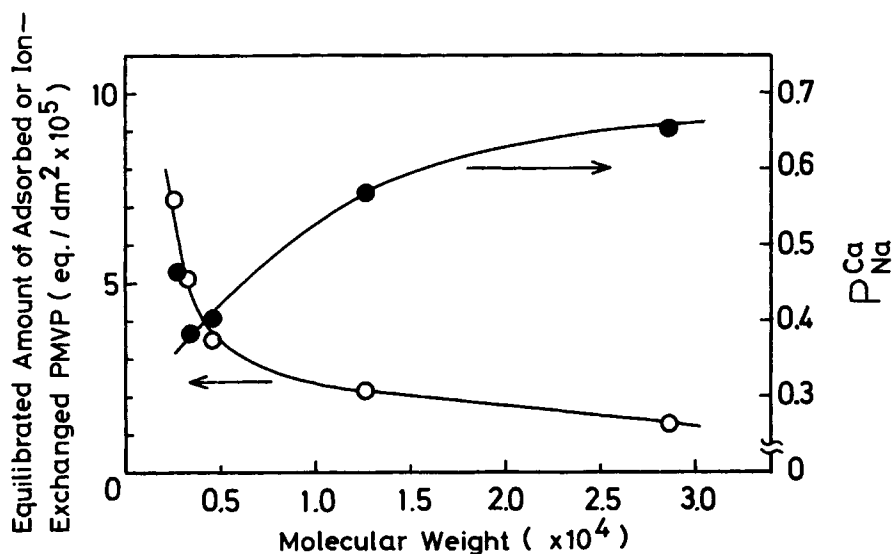
Fig. 12. The effect of molecular weight on the equilibrated amount of adsorbed or ion-exchanged PMVP and P_{Na}^{Ca} at 30°C. (○): equilibrated amount of adsorbed or ion-exchanged PMVP, (●): P_{Na}^{Ca}. The concentration of PMVP: 350.0 (eq/1 × 10^5), immersion period: 120 h.

When the molecular weight is smaller, the high permselectivity for monovalent cations is obtained. For example, P_{Na}^{Ca} in the case of the molecular weight of 3090 is 0.39 and, on the other hand, P_{Na}^{Ca} is 0.64 in the case of the molecular weight of 28,600. It is understandable as follows: the amount of the adsorbed or ion-exchanged PMVP of molecular weight of 28,600 is less than that of 3090, and therefore, the free pyridinium groups of PMVP of molecular weight of 28,600 is less than that of 3090.

CONCLUSIONS

We investigated the interaction between the cation-exchange membrane and PMVP.

1. The amount of the adsorbed or ion-exchanged PMVP increases with increasing the concentration of PMVP and then levels off over a definite concentration.
2. The adsorption of PMVP onto the cation-exchange membrane surface is of the Langmuir's type.
3. In the measurement by using PMVP of which the molecular weight is 3090, the ratio of the free pyridinium groups of PMVP non-ion-exchanged with the sulfonic acid groups on the membrane surface to the total pyridinium groups of PMVP is in the range of 20–30%.
4. The free polycations on the membrane surface endow the cation-exchange membrane the preferential permselectivity for the monovalent cations to the divalent cations.
5. The smaller the molecular weight, the more the equilibrated amount of the adsorbed or ion-exchanged PMVP. When the molecular weight is 2500–5000, the high permselectivity for monovalent cations can be obtained.

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