

# Interaction of Cation-Exchange Membrane with Polycation. II. Poly(*N*-Alkyl-4-Vinylpyridinium Halides)

NOBUHIKO OHMURA, YASUHIRO KAGIYAMA, and YUKIO  
MIZUTANI, *Tokuyama Soda Co. Ltd., Mikage-cho 1-1,  
Tokuyama City, 745, Japan*

## Synopsis

The effect of the hydrophile-lipophile balance (HLB) of poly(*N*-alkyl-4-vinylpyridinium halides) (PAVP) on the interaction between PAVP and the cation-exchange membrane was elucidated by using various alkyl groups: methyl, ethyl, octyl, and so on. In the electro-dialytic concentration of sea water by using the membrane on which PAVP has been adsorbed or ion-exchanged, the ratio of monovalent cations to total cations in the concentrated brine,  $\beta$  (Na + K), is almost same at the initial stage in species of PAVP. However, the deterioration ratio of  $\beta$ (Na + K) is smaller with decreasing HLB. In order to obtain the large value of  $\beta$ (Na + K), poly(*N*-methyl and dodecyl-4-vinylpyridinium chloride) (PMDVP), was investigated. PMDVP, of which the ratio of pyridinium groups quaternized with 1-bromododecane to total pyridinium groups (Qd) is about 40%, shows high initial value of  $\beta$ (Na + K) and its good durability.

## INTRODUCTION

Many investigators have studied on interactions between ion-exchange membranes and surface active agents or polyelectrolytes.<sup>1-14</sup> 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 polycations on the membrane surface, and it is industrially used to produce table salt by electro-dialytic concentration of sea water.<sup>7-9</sup> However, the detail of the relation between the preferential permselectivity for the monovalent cation and the structure of the polycation is still obscure.

In a previous paper, we reported on interaction between the cation-exchange membrane and poly(*N*-methyl-4-vinylpyridinium chloride) (PMVP).<sup>15</sup> To improve the ratio of monovalent cations to total cations in the brine,  $\beta$ (Na + K) and its durability, the formation of hydrophobic bonding interaction between the polycation and the cation-exchange membrane by introducing hydrophobic groups to the polycation would be one of the excellent approach. Here  $\beta$ (Na + K) also means the preferential permselectivity. In this paper, we investigated the effect of the hydrophile-lipophile balance (HLB)<sup>16-19</sup> of poly(*N*-alkyl-4-vinylpyridinium halides) (PAVP) onto the adsorbed or ion-exchanged amount, the preferential permselectivity, and its durability.

TABLE I  
Characteristics of Cation-Exchange Membrane<sup>a</sup>

Name	CM-1
Electric resistance <sup>b</sup> ( $\Omega \text{ cm}^2$ )	1.3
Transport number <sup>c</sup>	> 0.99
Water content <sup>d</sup> (g H <sub>2</sub> O/g Na <sup>+</sup> form dry membrane)	0.38
Ion exchange capacity (g H <sub>2</sub> O/g Na <sup>+</sup> form dry membrane)	2.3
Thickness (mm)	0.15

<sup>a</sup>Strongly acid cation-exchange membrane.

<sup>b</sup>Equilibrated with 0.5*N* NaCl solution at 25°C, measured at 1000 cycle A.C.

<sup>c</sup>Measured by electroalytic method at 25°C at 1.0 A/dm<sup>2</sup>.

<sup>d</sup>Equilibrated with 0.5*N* NaCl solution.

## EXPERIMENTAL

### Ion-Exchange Membrane

The cation-exchange membrane used was NEOCEPTA CM-1 prepared by the paste method (Tokuyama Soda Co. Ltd.)<sup>20-22</sup>; its characteristics are shown in Table I. Before the measurements, the membranes were soaked several times alternately 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<sub>3</sub>OK/CH<sub>3</sub>OH as an initiator.<sup>23</sup> Dimethyl sulfoxide and 4-vinylpyridine were distilled before use under reduced nitrogen atmosphere in the presence of calcium hydride. The molecular weight of poly(4-vinylpyridine) was calculated from that of poly(*N*-methyl-4-vinylpyridinium chloride) (PMVP). The molecular weight of PMVP was determined by using high performance liquid chromatography.

### Poly(*N*-Alkyl-4-Vinylpyridinium Halides)

Methyl iodide, 1-bromoethane, 1-bromobutane, benzylchloride, 1-bromooctane, 1-bromododecane, and nitroethane were distilled before use. Synthesis of PMVP is as follows: 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 further into the solution, which was stirred at 30°C for 24 h.

After evaporation of the volatile components, the polycations of I<sup>-</sup>-form was converted into Cl<sup>-</sup>-form by treatment with anion-exchange resin, Amberlite IRA-410 of Cl<sup>-</sup>-form (Rohm and Haas Co. Ltd.). 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<sub>3</sub>PO<sub>4</sub>.

The 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.).

### **Poly(*N*-Methyl and Dodecyl-4-Vinylpyridinium Chloride)**

An example of synthesis is shown as follows: In a 5-L four-necked flask equipped with a mechanical stirrer, a dropped funnel, a reflux condenser with a calcium chloride tube, and thermometer were placed 400 g of poly(4-vinylpyridine) (3.81 mol as 4-vinylpyridine) and 4 L of nitroethane. The flask was heated to 40°C, and 474 g (1.9 mol) of 1-bromododecane was dropwise added. Stirring was continued for 24 h. Thereafter, to a 5-L flask of the reaction mixture was added 541 g (3.8 mol) of methyl iodide, and stirring was further continued for 24 h at 30°C.

The solvent was evaporated at reduced pressure, and the residue washed twice with 700 mL of ethyl ether in order to remove unreacted 1-bromododecane. The white solid, which is polycation of Br<sup>-</sup> and I<sup>-</sup>-form, was converted into Cl<sup>-</sup>-form in methanol by treatment with anion-exchange resin, Amberlite IRA-410 of Cl<sup>-</sup>-form (Rohm and Haas Co. Ltd.). Poly(*N*-methyl and dodecyl-4-vinylpyridinium chloride) (PMDVP) was obtained and the yield was 95% [786 g, the ratio of pyridinium groups quaternized with 1-bromododecane to total pyridinium groups (Qd) is 40%].

Qd was determined as described below: Before adding methyl iodide, 10 mL of the reaction mixture were sampled, the solvent was evaporated at reduced pressure, and the residue was washed twice with 50 mL of ethyl ether. The Br/N ratio of the white solid was estimated by elemental analysis. Qd was determined from the Br/N ratio.

### **Measurement**

#### *Determination of the Amount of PAVP Adsorbed or Ion-Exchanged on the Cation-Exchange Membrane*

The cation-exchange membrane (7 × 12 cm<sup>2</sup>) of Na<sup>+</sup>-form were immersed in an aqueous solution of PAVP and allowed to stand with stirring for 120 h at 30°C. The amount of PAVP adsorbed or ion-exchanged on the membrane was determined from its decrement in the solution. The concentration of PAVP in the solution was analyzed by the colloid titration,<sup>24,25</sup> using a 1/400 N potassium polyvinylsulfate solution as a titrant and toluidine blue as an indicator.

#### *Determination of Relative Transport Number of Calcium Ion to Sodium Ion, $P_{Na}^{Ca}$*

$P_{Na}^{Ca}$  was determined by the same method apparatus as reported in the previous paper.<sup>5</sup> Electro dialysis was carried out in a mixed solution of 0.25N

sodium chloride and 0.25*N* calcium chloride under the current density of 1.0 A/dm<sup>2</sup> for 90 min at 25°C with stirring. The relative transport number of calcium ion to sodium ion is defined as follows:

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

where  $t_{\text{Na}}$  and  $t_{\text{Ca}}$  are the transport numbers of sodium ion and calcium ion in the membrane, respectively, and  $C_{\text{Na}}$  and  $C_{\text{Ca}}$  are the concentrations of sodium and calcium ions before electro dialysis, respectively.

#### *Determination of the Ratio of Monovalent Cations to Total Cations in the Brine*

Cation-exchange membrane, which had been treated with an aqueous PAVP solution, was installed into a electro dialyzer (effective membrane area 1.0 dm<sup>2</sup>) and flowing sea water. NEOSEPTA ACS was used as an anion-exchange membrane. Electro dialysis was carried out under the current density of 3.0 A/dm<sup>2</sup> at 30°C.

The ratio of monovalent cations to total cations in the brine,  $\beta(\text{Na} + \text{K})$  is defined as follows:

$$\beta(\text{Na} + \text{K})(\%) = \frac{C_{\text{Cl}} - C_{(\text{Ca} + \text{Mg})}}{C_{\text{Cl}}} \times 100$$

where  $C_{\text{Cl}}$  and  $C_{(\text{Ca} + \text{Mg})}$  are the concentrations of chloride ion and (calcium ion + magnesium ion) in the concentrated solution, respectively.

## RESULTS AND DISCUSSION

### Relation between HLB of PAVP and Adsorption Behavior

HLB,<sup>16-19</sup> which represents the balance of hydrophilic groups and hydrophobic groups of surface active agents, are correlated to such as their surface activity and solubility. The hydrophobic property increases with decreasing HLB.

The effect of HLB of PAVP on the adsorbed or ion-exchanged amount was investigated. HLB or PAVP is calculated by the following equation employed by Oda and Teramura<sup>18</sup>:

$$\text{HLB} = \text{inorganic factor}/\text{organic factor} \times k \quad (k = 10)$$

The value of the inorganic factor is shown in Table II. The value of the organic factor is 20 per carbon atom. In this article, we calculated HLB on the basis that the value of inorganic factor of ammonium groups is 400, and the pyridine ring and benzene ring are 15. HLB of PAVP is shown in Table III.

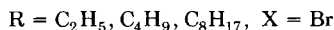
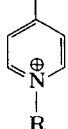
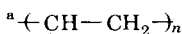
Figure 1 shows the relationship between HLB of PAVP and the adsorbed or ion-exchanged amount of PAVP. The adsorbed or ion-exchanged amount decreases abruptly with decreasing HLB. This should be attributed to the decrease of the penetration of PAVP into the inner part of the membrane with decreasing HLB because the molecules would get the spherical structure in the solution. This deduction is supported by the fact that the concentration

TABLE II  
The Value of Inorganic Factor

Factional group	Value of inorganic factor
Amine or ammonium salt	400
—SO <sub>3</sub> H	250
—COOH	150
—OH	100
Benzene ring	15
—C=C—	2

TABLE III  
HLB of PAVP<sup>a</sup> Used

R	HLB
CH <sub>3</sub>	25.9
C <sub>2</sub> H <sub>5</sub>	23.1
C <sub>4</sub> H <sub>9</sub>	18.9
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	15.4
C <sub>8</sub> H <sub>17</sub>	13.8



dependency of the adsorbed or ion-exchanged amount decreases with decreasing HLB of PAVP.

### Monovalent Cation Permselectivity and Its Durability

In a previous article, we reported that the preferential permselectivity for monovalent cation is obtained when the molecular weight is relatively smaller in the case of PMVP (HLB = 25.9).<sup>15</sup> PAVP, of which HLB is smaller than PMVP, was investigated in the similar manner as to that in the case of PMVP.

Figure 2 shows the effect of molecular weight of parent poly(4-vinylpyridine) on  $P_{\text{Na}}^{\text{Ca}}$  in the case of poly(*N*-benzyl-4-vinylpyridinium chloride) (PBVP) (HLB = 15.4) and poly(*N*-octyl-4-vinylpyridinium bromide) (POVP) (HLB = 13.8).

In the cases of both PBVP and POVP, the smaller the molecular weight, the more preferentially permselective to monovalent cations, which is similar to the behavior of PMVP. When HLB of PAVP is relatively smaller, the good preferential permselectivity for monovalent cations is obtained although the adsorbed or ion-exchanged amount is relatively less.

In order to evaluate the above-mentioned results, the electro-dialytic concentration of sea water was carried out continuously. Figure 3 shows the

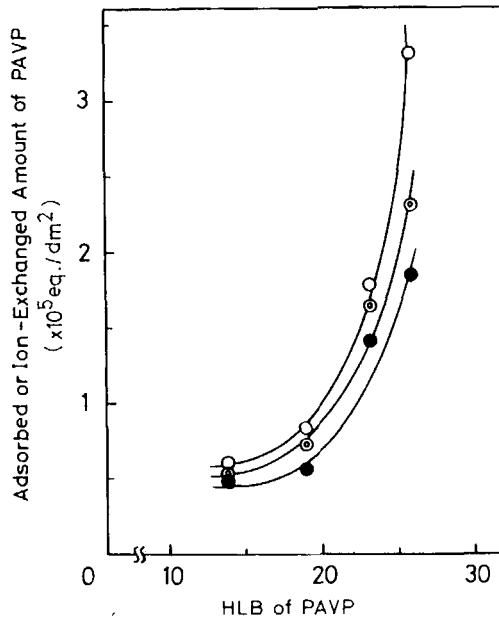


Fig. 1. The relationship between HLB of PAVP and the adsorbed or ion-exchanged amount of PAVP on the cation-exchange membrane at 30°C. The concentration of PAVP (mg/L): (●) 50; (⊙) 100; (○) 150. The molecular weight of parent poly(4-vinylpyridine), 2200.

relationship between the ratio of monovalent cations to total cations in the brine,  $\beta(\text{Na} + \text{K})$ , and electro dialysis period in the cases of PMVP and PBVP. The durability of  $\beta(\text{Na} + \text{K})$  in the case of PBVP is better than that in the case of PMVP. Though durability is improved by using PAVP, which has smaller HLB,  $\beta(\text{Na} + \text{K})$ , is about 87%. This value is still inefficient, and this should be attributed to the scantiness of the adsorbed or ion-exchanged

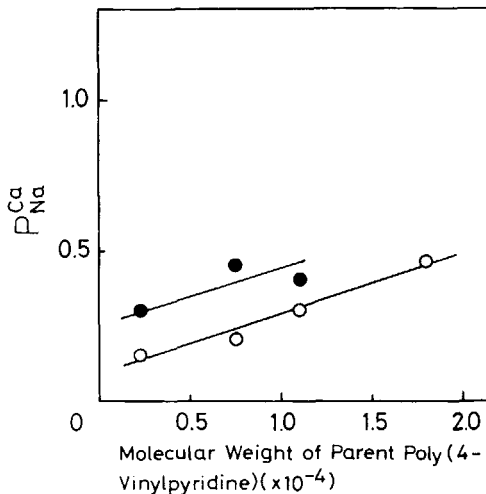


Fig. 2. The effect of molecular weight of parent poly(4-vinylpyridine) on  $P_{\text{Na}}^{\text{Ca}}$  in the case of poly(*N*-benzyl-4-vinylpyridinium chloride) (PBVP) and poly(*N*-octyl-4-vinylpyridinium bromide) (POVP): (○) PBVP, (●) POVP. The concentration, 50 mg/L.

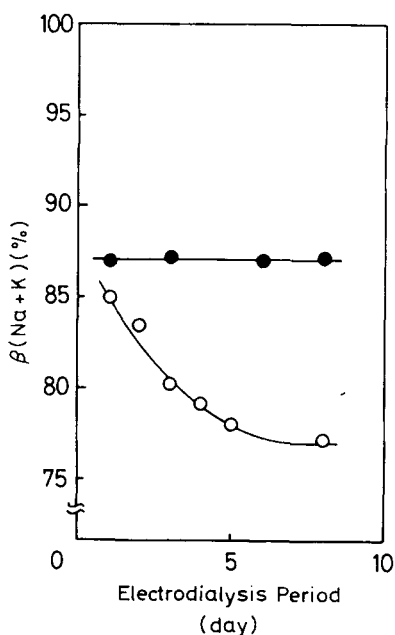
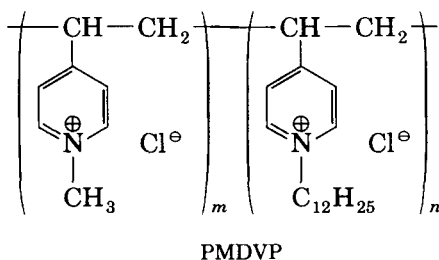


Fig. 3. The relationship between the ratio of monovalent cations to total cations in the brine,  $\beta(\text{Na} + \text{K})$ , and electrodiolysis period in the case of PMVP and PBVP at 30°C: (○) PMVP; (●) PBVP. The concentrations of PMVP, 1500 mg/L, and PBVP, 150 mg/L. The molecular weight of parent poly(4-vinylpyridine) of PMVP and PBVP, 2200.

amount. If the adsorbed or ion-exchanged amount could increase, it is possible to attain a high value of  $\beta(\text{Na} + \text{K})$  with good durability.

#### The Effect of Ratio of Pyridinium Groups Quaternized with 1-Bromododecane to Total Pyridinium Groups

It is necessary to develop the suitable polyelectrolyte which results in proper adsorbed or ion-exchanged amount and have proper lipophilicity. The former contributes high permselectivity for monovalent cations and the latter contributes the durability of the permselectivity. Then poly(*N*-methyl and dodecyl-4-vinyl pyridinium chloride) (PMDVP) was investigated. The structure of PMDVP is shown as follows:



This is based on the idea that dodecyl groups of quaternary pyridinium groups act as supplement of the permselectivity.

The ratio of pyridinium groups quaternized with 1-bromododecane to total pyridinium groups (Qd) of PMDVP was studied. PMDVP, of which Qd is in

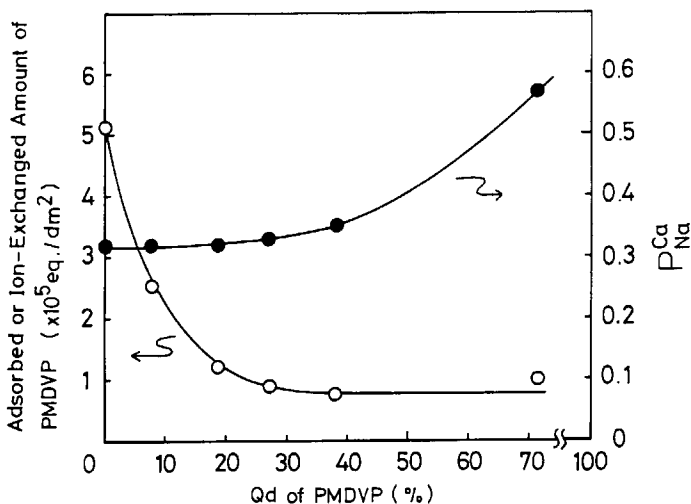


Fig. 4. The effect of the ratio of pyridinium groups quaternized with 1-bromododecane to total pyridinium groups (Qd) of PMDVP on the adsorbed or ion-exchanged amount and  $P_{Na}^{Ca}$  at 30°C. The adsorbed or ion-exchanged amount of (O) PMDVP; (●)  $P_{Na}^{Ca}$ . The concentration of PMDVP, 600 mg/L. The molecular weight of parent poly(4-vinylpyridine), 2200.

the range of 0–40%, is soluble in water. However, PMDVP, of which Qd is 71%, is insoluble in water and, therefore, a water–methanol mixed solution (1 : 1 in weight) was used.

Figure 4 shows the effect of Qd of PMDVP on the adsorbed or ion-exchanged amount and  $P_{Na}^{Ca}$ . The adsorbed or ion-exchanged amount decreases rapidly with increasing Qd. The adsorbed or ion-exchanged amount of PMDVP, of which Qd is 40%, is about 1/7 in comparison with PMDVP treated without 1-bromododecane. This should be attributed to decrease of the penetration of PMDVP in the membrane's pore with increasing Qd because the electrolyte would get spherical structure; on the other hand, the formation of ion-bonding between pyridinium groups and sulfonic acid groups on the membrane surface would be difficult because of bulkiness of dodecyl pyridinium groups.

In spite of difference of the adsorbed or ion-exchanged amount, the remarkable change of  $P_{Na}^{Ca}$  is not observed in the range of 0–40%. Presumably, the ratio of the pyridinium groups non-ion-exchanged with the sulfonic acid groups on the membrane to the total pyridinium groups would increase with increasing *N*-dodecyl pyridinium groups in the polymer.

The electro dialytic concentration of sea water was carried out by using the cation-exchange membrane on which the polyelectrolyte had been adsorbed or ion-exchanged and the result is shown in Figure 5. Figure 6 shows the effect of Qd of PMDVP on the initial value of  $\beta(\text{Na} + \text{K})$  and the deterioration ratio of  $\beta(\text{Na} + \text{K})$ ;  $\Delta\beta$  was calculated from the data in Figure 5 as follows:

$$\Delta\beta (\%/day) = \frac{(\text{first day}) - (\text{eighth day})}{7}$$

When Qd of PMDVP is in the range of 5–40%, the initial value of  $\beta(\text{Na} + \text{K})$  is larger. However, in the case of 0 and 71%,  $\beta(\text{Na} + \text{K})$  is smaller.



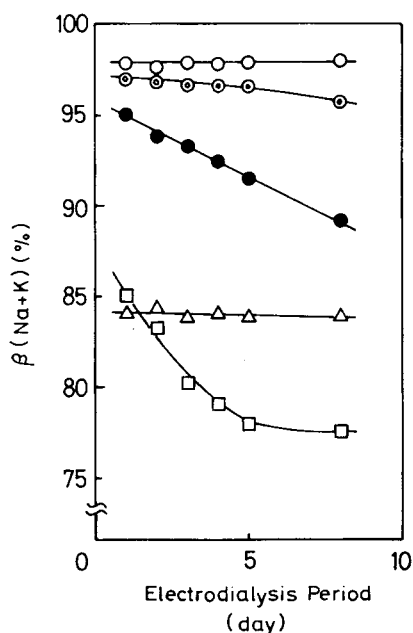


Fig. 5. The relationship between  $\beta(\text{Na} + \text{K})$  and electro dialysis period in the case of PMDVP at 30°C. Qd of PMDVP (%): (□) 0; (●) 4.8; (⊙) 18.3; (⊙) 37.9; (△) 71.1. The concentration of PMDVP, 1500 mg/L. The molecular weight of parent poly(4-vinylpyridine), 2200.

Probably, the smaller initial value in the case of PMDVP without dodecyl groups should be attributed to the remarkable deterioration of  $\beta(\text{Na} + \text{K})$  for 24 h before measurement.

The good durability of  $\beta(\text{Na} + \text{K})$  is obtained with increasing the content of dodecyl groups in the polyelectrolyte. When Qd of PMDVP is 40%, the initial value of  $\beta(\text{Na} + \text{K})$  becomes larger and durability is improved. There-

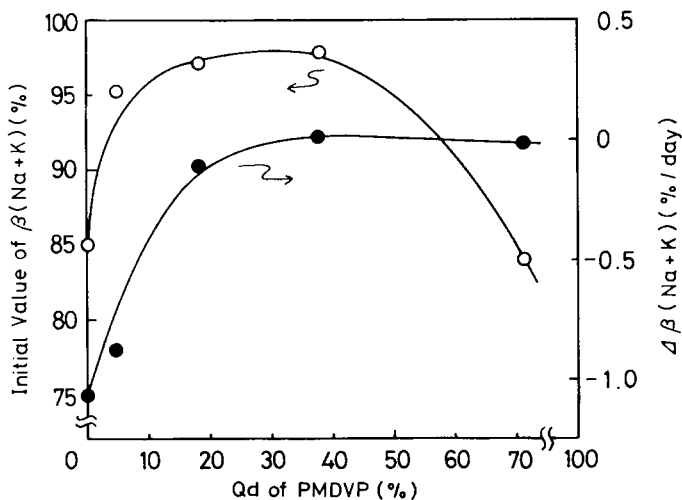


Fig. 6. The effect of Qd of PMDVP on the initial value of  $\beta(\text{Na} + \text{K})$  and  $\Delta\beta(\text{Na} + \text{K})$  at 30°C. The initial value of: (○)  $\beta(\text{Na} + \text{K})$ ; (●)  $\Delta\beta(\text{Na} + \text{K})$ . The concentration of PMDVP, 1500 mg/L. The molecular weight of parent poly(4-vinylpyridine), 2200.

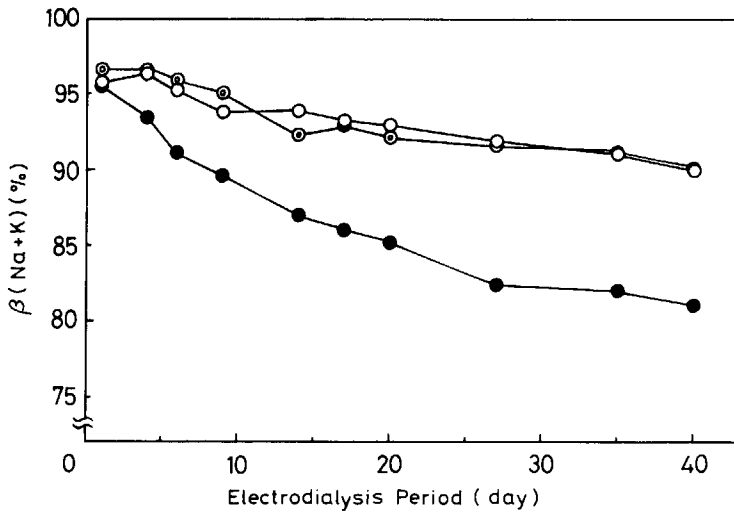


Fig. 7. The relationship between the molecular weight of parent poly(4-vinylpyridine) and  $\beta(\text{Na} + \text{K})$  used by PMDVP, of which Qd is about 40%. The molecular weight of parent poly(4-vinylpyridine): (○) 1200; (⊙) 2600; (●) 16,000. Qd of PMDVP (%): (○) 46.2; (⊙) 38.3; (●) 43.5. The concentration of PMDVP, 500 mg/L.

fore, PMDVP, of which Qd is 40%, is a good polyelectrolyte to get good preferential permselectivity for monovalent cation because the adsorbed or ion-exchanged amount, which contributes the initial value of  $\beta(\text{Na} + \text{K})$ , and the quantity of dodecyl groups, which contributes the durability, balance successfully.

Figure 7 shows the relationship between the molecular weight of parent poly(4-vinylpyridine) and  $\beta(\text{Na} + \text{K})$  used by PMDVP, of which Qd is about

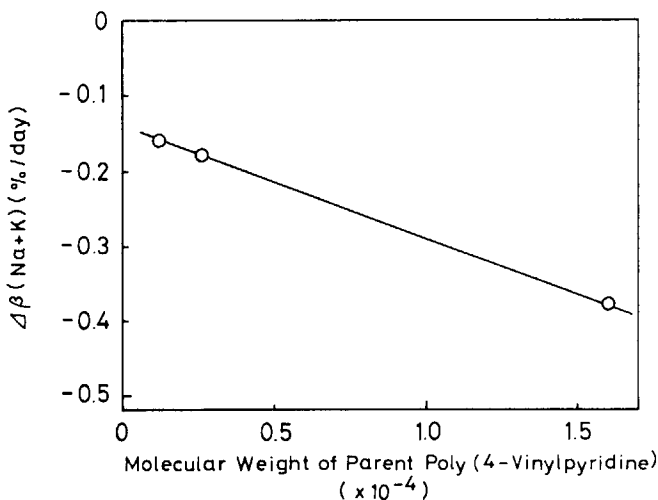


Fig. 8. The relationship between the molecular weight of parent poly(4-vinylpyridine) and  $\Delta\beta(\text{Na} + \text{K})$ .

40%. The initial value of  $\beta(\text{Na} + \text{K})$  is high in every case. However, when the molecular weight is larger, the deterioration of  $\beta(\text{Na} + \text{K})$  is larger.

Figure 8 shows the relationship between the molecular weight of parent poly(4-vinylpyridine) and  $\Delta\beta(\text{Na} + \text{K})$ , which was calculated from the data in Figure 7. When the molecular weight is smaller, the durability of  $\beta(\text{Na} + \text{K})$  is more improved. This should be attributed to the difficult removal of PMDVP from the membrane because it penetrates into the inner part of the membrane.

The adequate molecular weight of parent poly(4-vinylpyridine) is in the range of 1000–3000. Such poly(4-vinylpyridine) is easily synthesized by living anion polymerization using  $\text{CH}_3\text{OK}/\text{CH}_3\text{OH}$  as an initiator.

### CONCLUSIONS

We investigated the effect of HLB of PAVP on the interaction between PAVP and cation-exchange membrane.

1. The adsorbed or ion-exchanged amount of PAVP decreases with decreasing HLB.
2. When HLB of PAVP is smaller, the durability of  $\beta(\text{Na} + \text{K})$  is improved, but the initial value of  $\beta(\text{Na} + \text{K})$  is low.
3. PMDVP, of which Qd is about 40%, is most appropriate polyelectrolyte for this purpose. When the molecular weight of parent poly(4-vinylpyridine) is in the range of 1000–3000, the high initial value of  $\beta(\text{Na} + \text{K})$  and the high durability are obtained.

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