

# Polyethylenimine–Polyepichlorohydrin Interpolymer for Chelating Ion-Exchange Membrane

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## Synopsis

Polyethylenimine membranes consisting of linear polyethylenimine (PEI) and polyepichlorohydrin (PECH) were prepared by casting and heating an *N,N*-dimethylformamide solution of the two polymers under nitrogen at 100°C for 60 min. The membrane was also prepared by a heat-press method in a conventional manner. The cast membrane obtained was transparent. The membrane has a crosslinked structure due to the reaction between the secondary amino groups in PEI and the chloromethyl groups in PECH. Although a larger feed ratio of PEI/PECH gave membranes with a larger adsorption capacity for  $\text{Cu}^{2+}$  ions, the optimum ratio was 40/100 with respect to mechanical properties. A belt conveyor system using the PEI membrane was able to transport  $\text{Cu}^{2+}$  ions from one bath to another. In a diffusion dialysis against 1*N* HCl, the PEI membrane crosslinked rather tightly showed a specific ion-selective transfer character. For example, in  $\text{Cu}^{2+}$ – $\text{Ca}^{2+}$  system the permeability ratio  $P_{\text{Cu}}/P_{\text{Ca}}$  was about 3.8. The selectivity arises from the difference between affinities (extractabilities) of PEI toward metal ions. The selectivity was changed depending on the pH value.

## INTRODUCTION

Polyethylenimine (PEI) is a good complexing agent for heavy metal ions.<sup>1</sup> Recently we have reported the preparation of a chelating resin containing linear PEI, i.e., poly(styrene-*g*-ethylenimine).<sup>2</sup> The resin was quite effective for the adsorption of metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$ . The findings prompted us to prepare elastic chelating ion-exchange materials consisting of PEI. Elastic ion-exchange materials are expected to exhibit desired properties in several purposes of applications, e.g., an ion-exchange membrane. The preparation of the elastic materials can be performed by the following two methods: 1. graft polymerization onto an elastomer, and 2. blending PEI with an elastomer followed by crosslinking the two polymers with each other. Graft polymerization of 2-methyl-2-oxazoline onto poly(1,3-butadiene-*co*-1-chloro-1,3-butadiene) was carried out as an example of method 1.<sup>3</sup> The present paper describes an example of method 2, in which polyepichlorohydrin (PECH) was used as an elastomer. Since PECH possesses moderately active chloromethyl groups, the method seems to be convenient to prepare anion-exchange materials by reacting this group with amines such as PEI.

When the elastic ion-exchange materials containing PEI is used as a membrane, specific ion-selective transfer characteristics might be expected for the PEI membrane. The chemical species extracted more readily by a carrier permeated more rapidly through a liquid membrane of the carrier.<sup>4</sup> The gel-type

PEI membrane will show a similar phenomenon under suitable conditions. The PEI membrane is known to adsorb heavy metal ions, e.g.,  $\text{Cu}^{2+}$ . The adsorbed  $\text{Cu}^{2+}$  has low mobility in the membrane and is not permeable through the membrane because of the high stability of PEI- $\text{Cu}^{2+}$  complex. If the complex stability is lowered with a change of pH, the complexed  $\text{Cu}^{2+}$  will have a proper mobility in the membrane and will become permeable. In this paper the selective transfer is also described.

## EXPERIMENTAL

### Materials

Commercial PECH, Herclor H [Hercules Inc. Ltd., Moony viscosity (ML, 100°C) = 40] was dissolved in benzene. The benzene solution was filtered and poured into a large amount of methanol to reprecipitate the polymer. The reprecipitated polymer was dried at 30°C at 1 mm Hg and used for the preparation of casting solutions. For the heat-press procedure, Herclor H or Herclor C [poly(epichlorohydrin-co-ethylene oxide), Hercules Inc. Ltd., Moony viscosity (ML, 100°C) = 55] was used without further purification.

Anal. of Herclor H Calcd for  $(\text{C}_3\text{H}_5\text{OCl})_n$ : C, 38.94; H, 5.45; Cl, 38.32. Found: C, 38.74; H, 5.56; Cl, 38.10. Anal. of Herclor C Found: C, 42.29; H, 6.30; Cl, 27.77. The elemental analysis of Cl gave 55.6 mol% of epichlorohydrin unit for Herclor C.

Linear PEI was prepared as follows. 2-Methyl-2-oxazoline (50 g) was polymerized in 200 ml acetonitrile with an initiator of ethyl trifluoromethanesulfonate (0.4 ml) at 80°C for 8 hr under nitrogen atmosphere. The product polymer, poly(*N*-acetylenimine), 45 g, was dissolved in 200 ml of water containing 50 g NaOH. The mixture was stirred at 100°C for 20 hr under nitrogen. When the solution was cooled to room temperature, a white solid precipitated. The precipitate was well washed with water until the washings became neutral and recrystallized from water, followed by vacuum drying at room temperature for 48 hr. The product PEI shows water of crystallization.<sup>5</sup> To remove the water of crystallization the polymer was dried at 70°C *in vacuo* (0.1 mm Hg) until water was no longer distilled. (It normally took 4–7 days.) The waxlike dry PEI was dissolved in dry benzene at 60°C, and the solution was lyophilized at room temperature to give a powdery, dry linear PEI, 20 g ( $[\eta] = 0.25$  in methanol at 30°C).

### Preparation of Membrane

**Heat-Press Procedure.** Herclor H or Herclor C was masticated at 50–60°C on an open roll, and the required amounts of compounding ingredients were added. The mixture was well milled, calendered, and cured under heat-press at 160 or 120°C and 120 kg/cm<sup>2</sup> for a definite time. The compounding recipes are shown in Table I.

**Casting Procedure.** A typical example was as follows. Herclor H, 10 g, was dissolved in 50 ml *N,N*-dimethylformamide (DMF). Then 4 g PEI was added to the solution, and the mixture was vigorously stirred at 60°C. After defoaming the homogeneous casting solution was cast on Petri dishes or glass plates and

TABLE I  
Compounding Recipes for Curing<sup>a</sup>

	I	II	III	IV	V	VI
PECH <sup>b</sup>	100	100	100	100	100	100
Linear PEI	5	—	5	—	40	40
Stearic acid	—	1	—	0.75	—	—
Pb <sub>3</sub> O <sub>4</sub>	—	5	—	5	—	—
2-Mercaptoimidazoline	—	1.5	—	1.5	—	—
Curing temperature (°C)	160	160	160	160	120	120

<sup>a</sup> Parts given by weight.

<sup>b</sup> Herclor H for I, II, and V; Herclor C for III, IV, and VI.

placed in an oven at 100°C for 60 min under 560 mm Hg nitrogen atmosphere. The membrane was immersed in water, stripped off from the glass plates, and extracted with methanol at room temperature to remove DMF and nongrafted PEI, followed by drying *in vacuo* at 30°C to a constant weight.

The nature of these membranes was greatly dependent on the conditions of the drying and crosslinking operation. Additional studies have shown that very rapid evaporation of DMF leads to a brittle film.

**Mechanical Measurement and Swelling Test.** The stress-strain curves were recorded on an automatic tensile tester at room temperature using 3–4 ring shape specimens (1 × 1 mm, ring circle: 40 mm) on all samples. Tensile strength at break  $T_B$ , elongation at break  $E_B$ , and modulus at 50% elongation  $M_{50}$  were read in the stress-strain curves and the data averaged.

The swelling test was carried out by soaking circular samples (1 mm thick × 12 mm in diameter) in benzene, methanol, or distilled water at 30°C for 72 hr. The degree of swelling ( $1/v_r$ ), water content ( $w$  %), and sol fraction (sol %) were calculated by the following equations\* measuring  $W_0$ ,  $W_1$ ,  $W_2$ , and  $W_3$ :

$$1/v_r = \frac{V_S}{V_0} = \frac{W_2 - W_1}{W_3 - W_1} \quad (1)$$

$$w = \frac{W_2 - W_3}{W_2} \times 100 \quad (2)$$

$$\text{sol} = \frac{W_0 - W_3}{W_0} \times 100 \quad (3)$$

where  $v_r$  is the gel fraction of swollen sample,  $V_S$  is the volume of swollen sample,  $V_0$  is the volume of the gel fraction,  $W_0$  is the weight of the sample before soaking,  $W_1$  is the weight of the swollen sample in the solvent,  $W_2$  is the weight of the swollen sample in air, and  $W_3$  is the weight of the gel fraction of sample which was obtained after it was soaked, dried, and reached constant weight.

**Dialysis with Membrane.** Transport selectivity through membranes was measured in the cell (Fig. 1) with a circular piece of Cl-form membrane, which was immersed in 0.1N HCl for 48 hr and allowed to reach equilibration in distilled

\* When the density of the solvent is  $\rho$ ,

$$W_2 - W_1 = [W_3 + (V_S - V_0)\rho] - (W_3 - V_0\rho) = V_S\rho$$

$$W_3 - W_1 = W_3 - (W_3 - V_0\rho) = V_0\rho$$

From these equations, we then have eq. (1).

water for 48 hr. Metal ion solutions containing two kinds of divalent metal cations (each 0.05 mol/l.) (60 ml) and 1*N* HCl (60 ml) were placed in cells A and B, respectively. These solutions were stirred with Teflon bars at room temperature (ca. 20°C). After a fixed period of time, each cation concentration in cell B was determined by chelatometry using masking agents.<sup>6</sup>

**Adsorption of Cu<sup>2+</sup> with PEI Membranes.** A dry membrane (0.25 g) and Cu<sup>2+</sup> aqueous solution (0.025 mol/l., 50 ml) were placed in a 100-ml Erlenmeyer flask. The mixture was allowed to stand at 30°C with occasional shaking. After a fixed period of the time, the Cu<sup>2+</sup> concentration of the supernatant solution was determined by chelatometry with EDTA. The quantity of Cu<sup>2+</sup> adsorbed was calculated from the difference of the ion concentration before and after adsorption. The cupric ion solution was prepared by dissolving a commercial reagent of CuCl<sub>2</sub>·2H<sub>2</sub>O in Clark Lubs' buffer solution (potassium hydrogen phthalate/sodium hydroxide, pH 4). The quantity of Cu<sup>2+</sup> adsorbed increased with time, as shown in Figure 2. When it ceased changing, the adsorption value was taken as the adsorption capacity of membrane.

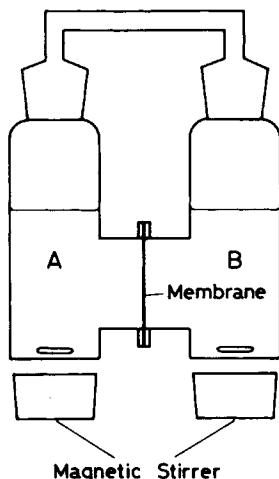


Fig. 1. Apparatus for the dialysis experiments.

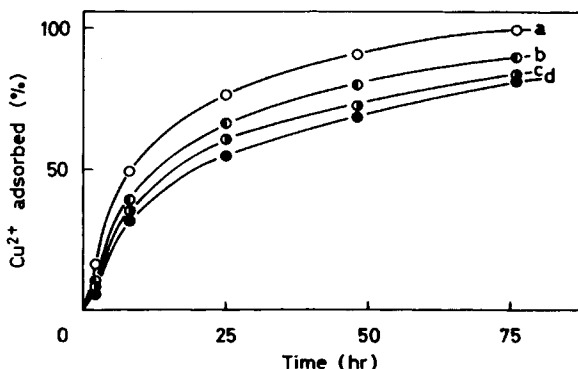


Fig. 2. Adsorption rate of Cu<sup>2+</sup> at pH 4 (30°C). Membrane 4 (0.25 g) in 50-ml Cu<sup>2+</sup> (0.025 mol/l) solution: 0.15 (a), 0.50 (b), 1.03 (c), and 2.45 mm thick (d) (dry state).

## RESULTS AND DISCUSSION

## Carrier Polymer for Membrane

It is important that the PEI and carrier polymer be very compatible with each other in order to achieve interpolymer membranes having a polymer network. Several elastomers containing halogen atoms, e.g., polychloroprene, 1-chloro-1,3-butadiene copolymer,<sup>7</sup> chlorinated polyethylene, chlorosulfonated polyethylene, and polyepichlorohydrin were examined as carriers by comparing the vulcanizates cured with ordinary vulcanizing agents with those cured with PEI. PECH samples (Herclor H and C) gave better results. As shown in Table II, Herclor H and C were crosslinked with PEI. The benzene-soluble fraction (sol %) mainly came from noncrosslinked free Herclor H or C. The vulcanizates cured with PEI showed higher modulus, lower tensile strength, and lower elongation than those cured with 2-mercaptoimidazoline. Herclor H cured with PEI showed a higher modulus than Herclor C cured with PEI, which means that the cured Herclor H had a higher network density due to its higher chlorine content.

The stocks of Herclor H and C compounded with 40 parts of PEI were heat-pressed to prepare PEI membranes. Their physical properties are shown in Table III.

The major components of the benzene- and methanol-soluble fractions at 30°C were PECH and PEI, respectively. Both the benzene- and methanol-soluble fractions (sol %) of cured Herclor C stock (sample VI) were larger than those of cured Herclor H stock (sample V). This is probably due to the low chlorine content of Herclor C. Cured Herclor H stock had a higher tensile strength  $T_B$  than that of Herclor C. These data show that Herclor H is superior to Herclor C in the preparation of PEI membranes.

TABLE II  
Physical Properties of the Vulcanizates<sup>a</sup> Cured with PEI (I and III) or 2-Mercaptoimidazoline (II and IV)

Sample <sup>b</sup>	Curing Time (min)	$M_{50}$ (kg/cm <sup>2</sup> )	$T_B$ (kg/cm <sup>2</sup> )	$E_B$ (%)	$1/\nu_r$ (benzene)	Sol % (benzene)
I	15	10.0	12.6	63	3.08	3.0
	30	10.5	12.6	60	3.03	3.3
	60	10.2	12.9	66	3.20	3.4
II	15	4.1	14.8	267	5.11	3.7
	30	4.5	14.0	222	4.75	3.5
	60	4.8	10.5	157	5.29	9.6
III	15	6.5	13.3	134	4.72	8.8
	30	9.0	14.7	83	3.69	7.1
	60	6.5	15.7	142	4.38	7.6
IV	15	5.5	15.1	260	5.39	7.4
	30	5.8	14.1	208	5.12	6.9
	60	6.0	13.2	181	4.97	7.1

<sup>a</sup> Herclor H (I and II) or Herclor C (III and IV).

<sup>b</sup> See Table I.



apparent grafting efficiency, which was calculated from the nitrogen content,\* was hardly influenced by the PEI loading, i.e., 65–71% in the range of the experiments. Membranes having a higher nitrogen content showed a larger adsorption capacity for  $\text{Cu}^{2+}$  ions (Table IV). The tensile strength at break  $T_B$  was highest when the PEI/Herclor H feed ratio was 40/100 (Table V). With an increase in the PEI feed ratio,  $M_{50}$  increased,  $E_B$  decreased,  $1/v_r$  decreased in benzene and increased in methanol, and hardly changed in water. This is probably due to the crystallinity of linear PEI. Linear PEI is not soluble in water at 30°C, and therefore the membrane swells slightly in water at this temperature.

TABLE IV  
Preparation of Membranes by Casting Method<sup>a</sup>

No.	Linear PEI (g)	N Content <sup>b</sup> (mmol/g)	Apparent Grafting Efficiency (%)	$\text{Cu}^{2+}$ Capacity (mmol/g) <sup>b</sup>
1	1.04	1.48	67	0.19
2	1.97	2.52	66	0.47
3	3.04	3.53	65	0.84
4	4.03	4.62	69	1.27
5	5.02	5.54	71	1.51

<sup>a</sup> Herclor H 10.0 g, DMF 50 ml, 100°C, 60 min.

<sup>b</sup> Per dry membrane at pH 4.

TABLE V  
Physical Properties of Membranes Prepared by Casting Method

No.	$M_{50}$ (kg/cm <sup>2</sup> )	$T_B$ (kg/cm <sup>2</sup> )	$E_B$ (%)	$1/v_r$			Water Content <sup>b</sup> (%)
				Benzene	Methanol	Water	
1	11.0	26.1	330	5.13	2.20	1.16	10.2
2	15.1	28.0	202	3.42	2.68	1.30	17.8
3	16.8	29.2	152	2.87	3.29	1.35	18.9
4	18.0	30.0	119	2.41	3.95	1.38	19.8
4B <sup>b</sup>	—	18.5	25	1.72	1.67	1.37	19.7
5	18.6	28.7	105	2.24	4.66	1.40	20.8

<sup>a</sup> Per wet membrane.

<sup>b</sup> The membrane was prepared by heating membrane 4 at 100°C for 30 min *in vacuo*.

TABLE VI  
Ion Concentration in Conveyor System<sup>a</sup>

Time (hr)	Bath 1 (in H <sub>2</sub> O)			Bath 2 (H <sub>2</sub> O)			Bath 3 (1N HCl)		
	$\text{Cu}^{2+}$	$\text{Ca}^{2+}$	Cu/Ca	$\text{Cu}^{2+}$	$\text{Ca}^{2+}$	Cu/Ca	$\text{Cu}^{2+}$	$\text{Ca}^{2+}$	Cu/Ca
0	83.6	82.4	1.01	0	0	—	0	0	—
3	—	—	—	—	—	—	1.74	0.53	3.28
6	67.0	68.0	0.99	12.0	12.0	1.00	3.44	1.54	2.23

<sup>a</sup> Concentration in mol/m<sup>3</sup>. See Figure 3 for schematic of system.

\* Apparent grafting efficiency (%)

$$\begin{aligned}
 &= \frac{\text{Nonextracted PEI (g)}}{\text{Feed PEI (g)}} \times 100 \\
 &= \frac{\text{Nitrogen content of extracted sample}}{\text{Nitrogen content of the sample before extraction}} \times 100
 \end{aligned}$$

The membrane, however, swells in acidic water. The degree of this swelling is approximately the same as that in methanol.

The above data show that sample 4 seems to be the best. Therefore, membrane 4 was used for the adsorption experiment. Figure 2 shows the adsorption of  $\text{Cu}^{2+}$  with membranes of varying thickness. In these experiments dry membranes were used. The induction period shown in Figure 2 is due to the time required for swelling of the membrane in order to adsorb  $\text{Cu}^{2+}$  ion. Since the membrane was of the gel type, it took about 75 hr to reach adsorption equilibrium, even when its thickness was 0.15 mm. In the case of a macroporous bead resin, it took about 48 hr.<sup>2</sup>

### Transport of $\text{Cu}^{2+}$ with a Conveyor System

A simple device used for this experiment is shown in Figure 3. A belt of membrane sample 4 in the wet state was not strong enough to rotate for a long time. Therefore, strips of the membrane (8 mm wide and 1 mm thick, wet state) were stuck onto the surface of a polyvinylchloride belt with adhesive and bound with a fine nylon string. The metal ion solution (300 ml) containing equimolar amounts of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$ , 300 ml distilled water, and 300 ml 1*N* HCl were placed in baths 1, 2, and 3, respectively. The belt was allowed to run in the direction shown by an arrow at a speed of 4 cm/min, and the  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  concentrations in the baths were followed by titration with EDTA standard solution using thioglycolic acid as a masking agent for  $\text{Cu}^{2+}$ . The results are shown in Table VI. The very pale yellow belt turned to blue in bath 1 and was decolorized completely in bath 3.  $\text{Cu}^{2+}$  ions were selectively adsorbed in bath 1 by a chelation with PEI and transported to bath 3, where the  $\text{Cu}^{2+}$  was desorbed with HCl and PEI was converted to HCl salt form. The HCl salt of PEI was returned to bath 1, in which HCl was liberated and PEI complexed the  $\text{Cu}^{2+}$  ions again. Since the pH in bath 1 decreased with the liberation of HCl, NaOH was added into the solution to keep pH  $\sim$ 4.5. The metal ions were transported not only by chelation with PEI, but also by water solution remaining on the belt surface. The metal ions in bath 2 were transported in this way. In fact, the Cu/Ca ratio found in this bath equaled unity, which was the same as that in bath 1. In bath 3 the Cu/Ca ratio is greater than unity. This means that  $\text{Cu}^{2+}$  ions were transported more readily than  $\text{Ca}^{2+}$  by PEI chelation. The ratio, however, decreased with the progress of time. This is attributed to the fact that the amount transported by simply drenching the surface is fairly large, as shown in bath 2.

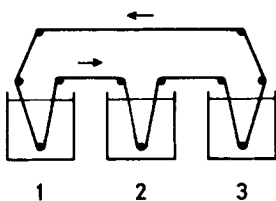


Fig. 3. The conveyor system: belt, 8 mm wide; 1 mm thick (wet state); volume, 300 ml each.



TABLE VII  
 Selective Transport by Competitive Experiments<sup>a</sup>

No.	Divalent Ion		Time (hr)	Concentration (mol/m <sup>3</sup> )		Selectivity (M <sub>1</sub> /M <sub>2</sub> )
	M <sub>1</sub>	M <sub>2</sub>		M <sub>1</sub>	M <sub>2</sub>	
1	Cu	Ca	48	0.210	0.062	3.4
2	Cu	Ca	96	0.792	0.233	3.4
3 <sup>b</sup>	Cu	Ca	240	~0	0.220	~0
4	Cu	Mg	96	0.774	0.151	5.1
5	Cu	Mg	120	1.145	0.212	5.4
6	Cu	Ni	48	0.285	0.071	4.0
7	Cu	Ni	96	0.715	0.193	3.7
8	Cu	Ni	400	3.324	0.870	3.8
9	Ni	Ca	96	0.247	0.224	1.1
10	Ni	Ca	120	0.362	0.306	1.2
11 <sup>c</sup>	Ni	Ca	96	0.138	0.084	1.6
12 <sup>c</sup>	Ni	Ca	120	0.168	0.102	1.6
13	Ca	Mg	96	0.269	0.199	1.4
14	Ca	Mg	120	0.388	0.252	1.5

<sup>a</sup> Metal ion solution (M<sub>1</sub> = M<sub>2</sub> = 0.05 mol/l.): 60 ml was dialyzed against 60 ml 1N HCl. Membrane: No. 4B, 7.1 cm<sup>2</sup>, 0.42 mm thick (wet).

<sup>b</sup> Dialyzed against distilled water (pH ~ 4.5).

<sup>c</sup> Dialyzed against 0.1N HCl + 0.05M KCl (pH ~ 1).

### Selective Transport by Dialysis

First, membrane 4 was used for dialysis. A solution containing Cu<sup>2+</sup> and Ca<sup>2+</sup> ([Cu<sup>2+</sup>]<sub>0</sub> = [Ca<sup>2+</sup>]<sub>0</sub> = 0.05 mol/l) in cell A (Fig. 1) was dialyzed against 1N HCl in cell B through membrane 4. The concentrations of Cu<sup>2+</sup> and Ca<sup>2+</sup> in cell B after 24 hr were 7.58 and 7.4 mol/m<sup>3</sup>, respectively. The ratio of [Cu]/[Ca] was 1.02, indicating little selectivity. It was assumed that additional crosslinking was necessary to obtain a membrane capable of selective transport. Therefore, membrane 4B was prepared by heating membrane 4 at 100°C for 30 min *in vacuo*.

A similar dialysis experiment was carried out using membrane 4B. The concentration of each ion in cell B is plotted as a function of time in Figure 4. The ratio of permeability,  $P_{Cu}/P_{Ca}$ , is nearly equal to the concentration ratio in

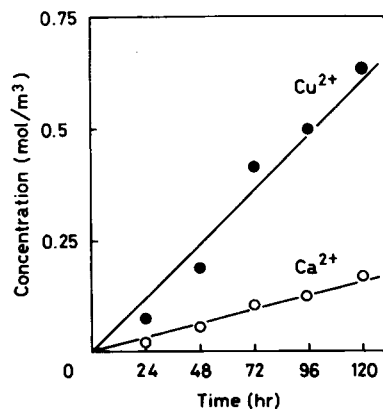


Fig. 4. Dialysis with membrane 4B (section, 7.1 cm<sup>2</sup>; thickness, 0.69 mm in wet state) against aqueous 1N HCl. Dialyzed solution (cell A): [Cu<sup>2+</sup>]<sub>0</sub> = [Ca<sup>2+</sup>]<sub>0</sub> = 0.05 mol/l.

cell B,  $[Cu]/[Ca]$ , when the ion concentration is low.\* Since  $[Cu]/[Ca] \approx 3.8$ , the membrane showed a selectivity, which was due to the higher extractability of PEI for  $Cu^{2+}$ .

In the case of using cellophane as a membrane, the concentrations of  $Cu^{2+}$  and  $Ca^{2+}$  in cell B after 8 hr were 0.0137 and 0.0139 mol/l, respectively. The ratio  $[Cu]/[Ca]$  was 0.99, indicating that cellophane has no selectivity.

In order to confirm PEI membrane selectivity, competitive experiments between several metal ions were carried out. The results are shown in Table VII. The selectivity is attributable to the affinity (extractability) of PEI for an ion and the size of hydrated ion. The metal ions used in these experiments were all divalent. Therefore, the order of the size of hydrated ion is evaluated by the order of mobility of the ion in aqueous solution. The mobility at the experimental temperature is in the following order:  $Ca^{2+} > Cu^{2+} \approx Mg^{2+} \approx Ni^{2+}$ .<sup>9</sup> In the case of Ca-Mg, the selectivity mainly depends on the mobility, because these ions have no affinity for PEI. For ions having affinity for PEI, however, the mobility is a minor factor. Cupric ions, having smaller mobility, are more permeable than  $Ca^{2+}$ . The selectivity ratio of Cu/Ca is 3.4 in Table VII, whereas it is 3.8 in Figure 4. The difference is probably dependent on the difference in membrane thickness. When the dialysis was carried out against distilled water,  $Cu^{2+}$  was hardly permeable, and the membrane turned to blue. The cupric ion extracted by the membrane cannot diffuse because of the high stability of the PEI complex.

The permeability of  $Cu^{2+}$  was higher in the cases of Cu-Mg and Cu-Ni combinations. This results from the higher extractability of the PEI membrane for  $Cu^{2+}$ . In the Ni-Ca combination, poor selectivity of Ni/Ca (= 1.2) was observed. However, since  $Ni^{2+}$  has a lower mobility and is more permeable, it is assumed that PEI has a higher affinity for  $Ni^{2+}$  under these conditions. The poor selectivity can be improved if the affinity becomes greater. This was realized in experiments Nos. 11 and 12, i.e., in dialysis against 0.1N HCl (pH  $\approx$  1).

It is also important to control the degree of crosslinking of the membrane, as we assumed. Membrane 4B was obviously crosslinked to a higher degree than membrane 4. Although more highly crosslinked structure makes the membrane brittle (Table V), it is an important factor in giving greater selectivity to the membrane. The degree of hydration of the membrane is decreased by higher crosslinking. The lower hydration depressed the diffusion of  $Ca^{2+}$ . The selectivity, therefore, was enhanced.

\* Noguchi and Satake<sup>8</sup> derived the following equation from Fick's law:

$$2AP/V_B \Delta x = -t^{-1} \ln(1 - 2C_B/C_0)$$

where  $A$ ,  $P$ ,  $V_B$ ,  $\Delta x$ ,  $C_B$ ,  $C_0$ , and  $t$  are membrane section, permeability, volume of the solution in cell B, membrane thickness, solute concentration in cell B, initial concentration in cell A, and time, respectively. If  $C_B \ll C_0$ , the above equation is simplified to:

$$C_B = KPt$$

$$K = (A/\Delta x)(C_0/V_0) = \text{const}$$

Therefore,

$$[Cu]/[Ca] = P_{Cu}/P_{Ca}$$

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### References

1. E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, **1957**, 86; H. Thiele and K. H. Gronau, *Makromol. Chem.*, **59**, 207 (1963).
2. T. Saegusa, S. Kobayashi, and A. Yamada, *Macromolecules*, **8**, 390 (1975).
3. T. Saegusa, A. Yamada, and S. Kobayashi, *Polym. J.*, **11**, 53 (1979).
4. C. F. Reusch and E. L. Cussler, *AIChE J.*, **19**, 736 (1973); D. K. Schiffer, A. Hochhauser, D. F. Evans, and E. L. Cussler, *Nature*, **250**, 484 (1974); E. M. Choy, D. F. Evans, and E. L. Cussler, *J. Am. Chem. Soc.*, **96**, 7085 (1974); R. P. Cahn and N. N. Li, *J. Membr. Sci.*, **1**, 129 (1976).
5. T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 108 (1972).
6. K. Ueno, *Kireito Tekitei Ho*, 15th ed., Nankodo, Tokyo, 1974, pp. 183, 491.
7. S. Yamashita, S. Atomori, S. Kohjiya, and T. Miyagawa, *J. Appl. Polym. Sci.*, **17**, 3049 (1973); S. Yamashita, S. Kohjiya, S. Atomori, and A. Yamada, *Angew. Makromol. Chem.* **56**, 65 (1976).
8. H. Noguchi and I. Satake, *Polym. Prep. Jpn.*, **25**, 1665 (1976).
9. Kagakubinran Kisoheh (Handbook of Chemical Constants), 2nd ed., Maruzen, Tokyo, 1975, p. 1190. (Cited from R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1959, and *Landolt-Börnstein-Tabellen* Band II, Teil 7, Elektrisch Eigenschaften II, Springer-Verlag, Berlin, 1960, p. 257.)

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