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Bipolar Ion-Exchange Membranes Prepared from Blends of Graft Copolymers

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Bipolar ion-exchange membranes were prepared from graft copolymers of polyethylene (PE). Powders of styrene-grafted PE (I) and 4-vinylpyridine-grafted PE (II), or powders of ethyl acrylate-grafted PE (III) and II were blended in various proportions and melt-pressed to films. Ion-exchange groups were then introduced by the sulfonation (100%), alkaline hydrolysis (100%), or *N*-methylation (80—90%) of the blend polymer films. Although, in the titration curves of bipolar membranes, pH regions which apparently resemble the isoelectric point of polyampholytes appeared, no behavior based on the interaction between acidic and basic groups was indicated in the survey of their physico-chemical properties. The dependency of the concentration potential of the membranes (E_m), containing one kind of ionized group, on the mole fraction of the group (F_i) is not remarkable. On the other hand, the E_m of the membranes containing both positively- and negatively-charged groups is strongly dependent on F_i, because of the additive contribution of the oppositely-charged groups to the potential. The bi-ionic potential of the membrane, E_{K-Li}, was found to be a function of $E_m/|E_0|$ ($|E_0|$ is the absolute value of the concentration potential for ideal permselective membranes) in the cases of both I-II and II-III.

The behavior of polyampholites, which characterize many natural substances of biological importance, has long been an object of interest. Recently, some amphoteric ion-exchange membranes have been reported,[1-4] and interaction between acidic and basic groups in the membranes was observed in such phenomena as the membrane potential and the electric conductance.[3]

The gamma-ray-induced vapor-phase grafting of the ionogenic monomer onto polyethylene (PE) affords a convenient way for preparing homogeneous ion-exchange membranes.[4] In the present study, the preparation of bipolar membranes by blending monofunctional graft copolymers, and their physicochemical properties as a function of the membrane composition, were investigated.

Experimental

Materials. Commercial high-pressure PE powder of 200 mesh (mol wt of 23000) was used. The monomers used were styrene (St), 4-vinylpyridine (VP), and ethyl acrylate (EA), all of commercial grade. Deionized water was used throughout.

TABLE 1. GRAFT COPOLYMERS USED FOR THE PREPARATION OF BLEND FILMS

Code	Monomer	Dose 10^5 R	g %	C_g mmol/g	PMT °C
Ia(A)	ST	1.3	45.6	3.01	195
IIa(G)	VP	14.5	103	4.83	180
IIIa(H)	EA	2.2	58.5	3.69	185
IIb(N)	VP	3.1	43.5	2.89	181
IIIb	EA	2.2	65.0	3.94	185
IIc	VP	2.6	33.6	2.40	181

Preparation of Membranes. The procedures used in the preparation of membranes are shown in Scheme 1. The grafting onto PE powder was carried out by the irradiation of gamma rays in monomer vapor, as has been described in previous papers.[5,6]

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[1] Y. Onoue, *Denki Kagaku* (*J. Electrochem. Soc. Japan*, **30**, 225 (1962).

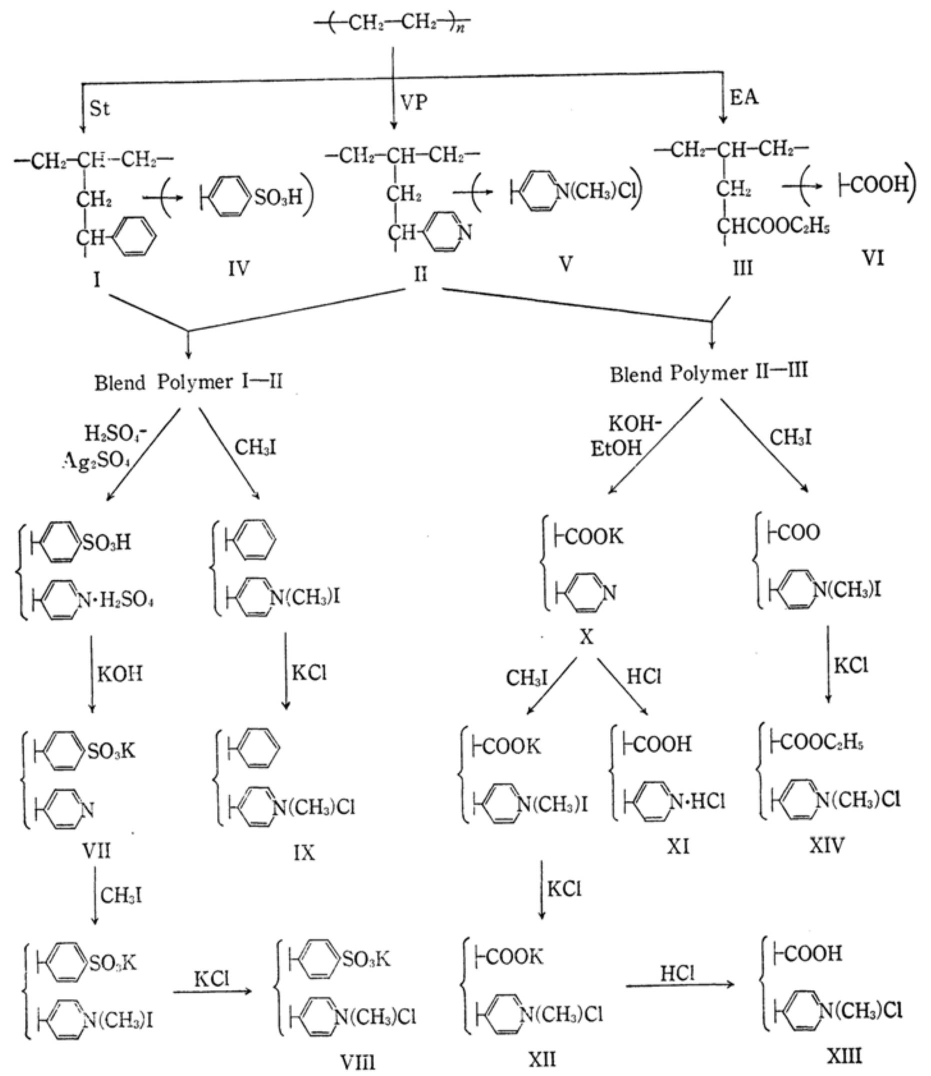
[2] P. E. Blatz, *J. Polymer Sci.*, **58**, 755 (1962).

[3] H. Jacobson, *J. Phys. Chem.*, **66**, 570 (1962).

[4] A. S. Michaels, *Ind. Eng. Chem.*, **57**, 32 (1965).

[5] M. Yanagita, H. Kawabe, K. Shinohara and T. Takamatsu, *Sci. Papers I.P.C.R.*, **57**, 10 (1963).

[6] M. Yanagita, H. Kawabe, K. Shinohara and T. Takamatsu, *ibid.*, **56**, 218 (1962).



Scheme 1. Preparation of Membranes.

TABLE 2. COMPOSITION OF BLEND POLYMER FILMS[a)]

Code		A	B	C	D	E	F	G
I-II	Ia	3.01	2.54	2.20	1.74	1.22	0.77	0
	IIa	0	0.75	1.29	2.05	2.86	3.59	4.83
Code		**H**	**I**	**J**	**K**	**L**	**M**	**N**
II-III	IIIa	3.60		2.23	1.61	1.04		0
	IIb	0		1.11	1.61	2.06		2.89
	IIIb		2.79				0.52	
	IIc		0.77				2.08	

a) The composition is expressed in the term of C_g (mmol/g) of both functional groups in the blends.

Three kinds of graft copolymers have been prepared: St-grafted PE (I), VP-grafted PE (II), and EA-grafted PE (III). The degree of grafting (g) (defined by the increase in the weight as $100\times[(W-W_0)/W_0]$), the content of the functional group in the graft copolymer (C_g in mmol/g), and the polymer-melt temperature (PMT) are shown in Table 1. Two kinds of copolymers, I and II or II and III, were well mixed in various ratios, and the blend powders were melt-pressed to film 0.15 mm thick under a pressure of 200 kg/cm^2 at 180°C for ten minutes. The compositions of the copolymers in the blend films are shown in Table 2.

Various kinds of membranes were prepared by the chemical treatments of the blend-polymer films shown in Scheme 1. The sulfonation of the phenyl group, the quaternization of the pyridine group, and the saponification of the ester group in the blend polymers were carried out according to previously-described procedures.[5,6]

Determination of Ion-exchange Capacity. Each group in the bipolar membranes was determined by a combination of the precipitation titration of the halogen ion with acid-base titration, as will be described below.

a) A membrane containing both a carboxylic acid group (a meq) and a pyridine group (b meq) was treated with a potassium hydroxide solution, washed thoroughly with water, and left immersed in 0.1 N HCl (x ml). After the membrane had then been removed, the solution was titrated with 0.1 N NaOH (y ml), and then with 0.1 N $AgNO_3$ (z ml) in the presence of nitric acid. The contents of the groups in membrane are:

$$a = 0.1 \times (z-y);\ b = 0.1 \times (x-y)$$

b) A membrane containing both a sulfonic acid group (a meq) and a pyridine group (b meq) was treated with a hydrochloric acid solution, washed with water, and left immersed in 0.1 N NaOH (x ml). The solution was titrated with 0.1 N HCl (y ml at the equivalent point, and with y' ml added), and then with 0.1 N $AgNO_3$ (z ml).

$$a = 0.1 \times [(x-y) - (z-y')];\ b = 0.1 \times (z-y')$$

c) A membrane containing both a carboxylic or sulfonic acid group (a meq) and a quaternary pyridinium group (b meq) was treated with a hydrochloric acid solution, washed with water, and left immersed in 0.1 N NaOH containing sodium nitrate in a 1 N concentration (x ml). The solution was titrated with 0.1 N HCl (y ml at the equivalent point, and with y' ml added), and then with 0.1 N $AgNO_3$ (z ml).

$$a = 0.1 \times (x-y);\ b = 0.1 \times (z-y')$$

The ion-exchange capacity was calculated for acidic and quaternary pyridinium groups on the basis of the dry weight of the membrane in the salt-form (C_d^{K} or C_d^{Cl} in meq/g), and also for both the groups on the basis of the wet weight (C_w in meq/g).

Titration Curves of Membranes. The titration curves of monopolar membranes in the presence of sodium chloride were determined in the usual ways reported previously.[7,8] In the case of bipolar membranes, each sample was titrated with a 1 N HCl solution, washed thoroughly, and left immersed in 40 ml of the solution, containing various amounts of sodium hydroxide or hydrogen chloride but no salt, for seven days. The pH of the solution was then measured, and the portions were titrated with 0.1 N HCl or 0.1 N NaOH and with 0.1 N $AgNO_3$. The initial content of chloride ions in the membrane sample was determined separately. The amounts of both sodium and chloride ions in membrane and in solution at each equilibrium were calculated in a way similar to that described in the previous section.

Other Properties of Membranes. The thickness, water content (w in wt%), molality of the ionized group ($\bar{m}$), concentration potential (E_m in mV), and electric conductivity ($\bar{k}$ in $\Omega^{-1}cm^{-1}$) of membranes were measured in the ways described in a previous paper.[6] The bi-ionic potential was measured, in a way similar to the E_m measurement, by using the cell: |0.1 N KCl| membrane|0.1 N LiCl|. The density of the wet membrane (d) was determined by the use of a pycnometer.

Results and Discussion

Preparation of the Membranes. The blend polymer films, I-II (B–F), containing both phenyl and pyridine groups, were quantitatively sulfonated in a concentrated sulfuric acid containing 1% silver sulfate. The sulfonation of the sample, D, was followed by the capacity measurement and found to be almost completed within an hour at 50°C. The monofunctional film I (A), containing a phenyl group, was sulfonated under the same conditions and found to reach a constant capacity value in five hours. The higher reaction rate of the sulfonation of I-II than of I may be attributed to the swelling effect of ionized pyridine groups in sulfuric acid. The film II (G), containing only pyridine groups, was not sulfonated under the above conditions. The II-III (I-M) films, containing both ester and pyridine groups, were treated with a 1 N KOH - 80% ethanol solution at 75°C for three hours and found to be hydrolysed almost quantitatively. After sulfonation or saponification, the films were treated with methyl iodide - acetone (1 : 1 volume ratio) at 30°C for 5—24 hr; the degree of the quaternization of pyridine groups were found to be 80—90%.

Titration Curves of the Membranes. The titration curves of monopolar membranes were

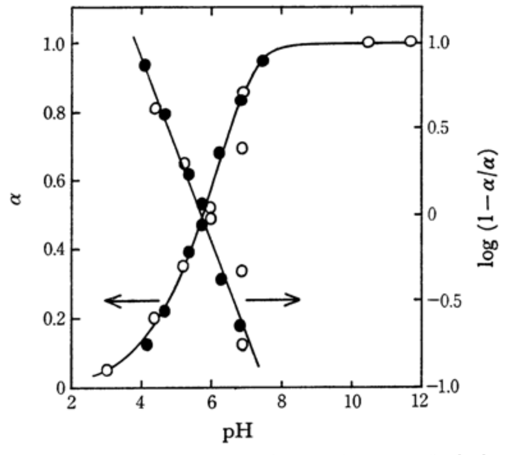


Fig. 1. Titration curves of membrane VI (○) and saponified EA-DVB resin (●) in the presence of 0.1 N NaCl.

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[7] H. Kawabe, S. Sugimoto and M. Yanagita, *Reports Sci. Res. Inst.* (in Japanese), **30**, 257 (1954).

[8] H. Kawabe and M. Yanagita, *J. Sci. Res. Inst.*, **50**, 199 (1959).

first examined. The titration curve of IV (A), containing only sulfonic acid groups, in the presence of 0.1 N NaCl was shown to be typical for strong acid at pH's lower than 7, where the ion-exchange capacity of a dry membrane in the H-form was 2.10 meq/g. The elementary analysis of the membrane showed 7.03% S, which agrees with the value calculated from the capacity at pH 7.

The titration curve of VI (H), containing only carboxylic acid groups, in the presence of 0.1 N NaCl, and that of the saponified EA-divinylbenzene (DVB) copolymer[9,10] containing 5% DVB, are shown in Fig. 1, where α is the degree of ionization. The plots for both the exchangers are, coincidentally, on the same curve. In the figure, the Henderson-Hasselbach-Kathchalsky relation,[11] $\mathrm{pH}=\mathrm{p}K_a-n'\log[(1-\alpha)/\alpha]$, is also shown, where $\mathrm{p}K_a$ and n' are 5.8 and 1.9 respectively. Gregor and Frederic[12] reported that the values of $\mathrm{p}K_a$ and n' for the titration of polyacrylic acid with sodium hydroxide were 5.29 and 1.95 in the presence of 0.1 N NaCl, and 6.79 and 2.13 in the absence of any added salt.

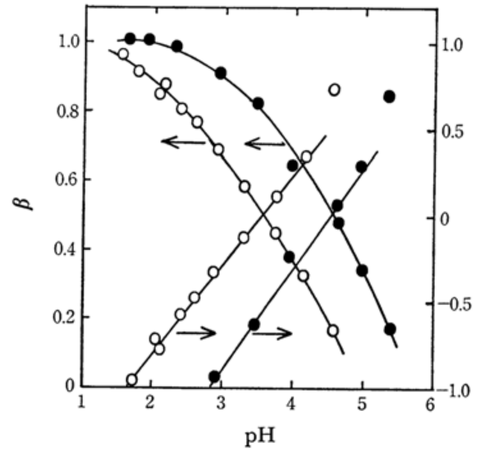

Fig. 2. Titration curves of VP grafted PE film (II) in the presence of 0.1 N NaCl (○) and 1 N NaCl (●).

The titration curves of II, containing only pyridine groups, are shown in Fig. 2, where β is the degree of ionization. From the plots for the $\mathrm{pH}=\mathrm{p}K_a+n'\log[(1-\beta)/\beta]$ relation, also shown in the figure, the values of $\mathrm{p}K_a$ and n' are 3.5 and 1.9 in 0.1 N NaCl, and 4.5 and 1.7 in 1 N NaCl. As may be seen in Fig. 2, the increase in the concentration of added salt (C_s) by $\Delta\log C_s=1$ results in the increase of $\mathrm{p}K_a$ by about unity. A similar effect of added salt has been observed in the titration curve of the cross-linked polyacrylic acid resin, though the value of $\mathrm{p}K_a$ decreases upon the addition of salt.[10] Since the internal pH of an ion-exchange membrane or resin is different from that of an external solution, it is noticeable that the Henderson-Hasselbach-Katchalsky relation is established for these exchangers. This titration behavior of weak electrolyte-type exchangers may be understood when it is considered that the concentration of salt in the exchangers is quite low as a result of Donnan exclusion and that α or β is directly dependent on the internal pH ($\overline{\mathrm{pH}}$), which is a simple function of the external pH, as may be estimated by ($\mathrm{pH}+\log a_{\mathrm{Na}}$) in the case of cation exchangers and by ($\mathrm{pH}-\log a_{\mathrm{Cl}}$) in the case of anion exchangers, where a is the activity of the ion in solution.*1

When Figs. 1 and 2 are compared, it may be seen that if both II and VI exist in 0.1 N NaCl, both the groups will ionize at the pH region of 3—5.

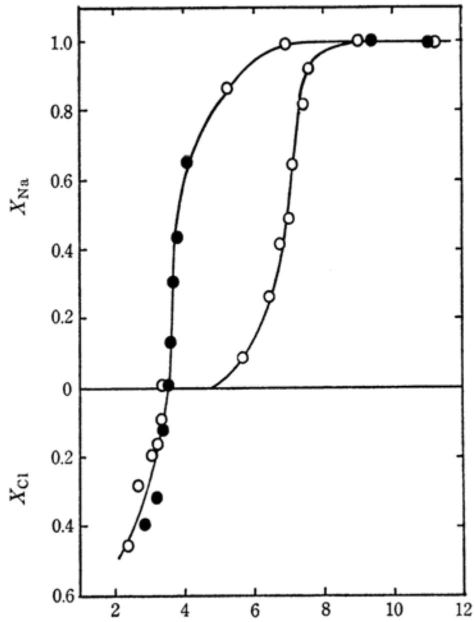

Fig. 3. Titration curves of membranes VII(●) and X (○) in the absence of added salt.

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9) H. Kawabe and M. Yanagita, *J. Sci. Res. Inst.*, **53**, 98 (1959).

10) H. Kawabe and M. Yanagita, *ibid.*, **53**, 227 (1959).

11) A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polymer Sci.*, **13**, 69 (1954).

12) H. P. Gregor and M. Frederic, *ibid.*, **23**, 451 (1957).

*1 The relation between the internal pH value and the external pH value of ion-exchange resins has been discussed by Kawabe and Yanagita[8] and by Nagasawa, Ishitani and Kagawa,[13] and quantitatively expressed by Eq. (15) and Eq. (5) of the respective papers.

13) M. Nagasawa, H. Ishitani and I. Kagawa, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **61**, 806 (1958).

Such a region will become narrow as the concentration of salt in the solution decreases, because the titration curves of II and VI transfer to lower and higher pH values respectively. It can, then, be predicted that if there is no interaction between acidic and basic groups in the bipolar membrane X (or XI), each group will be separately determined in the titration curve of the membrane at lower salt concentrations, probably lower than 0.01 N. Under such conditions, a pH region which apparently resembles the isoelectric point of polyampholytes may be observed in the titration curve of X, though neither group is ionized in the region in this case. Figure 3 shows the titration curve of X in the absence of any added salt;[*2] here the above-mentioned region is observed at pH 3.5—5, where neither group is ionized. The titration curve of the membrane VII, containing both sulfonic acid and pyridine groups, is also shown in Fig. 3. The fact that each titration curve separated by the line, $\overline{X}=0$, is quite similar to that of the corresponding monopolar membrane seems to justify the assumption that there is no interaction between acidic and basic groups in VII and X.

TABLE 3. GENERAL PROPERTIES OF MEMBRANES

Code		C_d^{K} meq/g	C_d^{Cl} meq/g	C_w meq/g	w %	$\overline{m}$	d
VII	A	2.10		1.09	48.2	2.25	1.078
	B	1.94		1.18	39.2	3.01	1.062
	C	1.80		1.08	40.1	2.69	1.074
	D	1.61		0.98	39.0	2.52	1.053
	E	1.16		0.67	42.1	1.60	1.064
	F	0.99		0.63	36.8	1.70	1.066
VIII	B	2.10	0.48	1.55	40.0	3.88	1.081
	C	1.69	0.77	1.21	50.7	2.39	1.050
	D	1.37	1.30	1.44	45.8	3.14	1.089
	E	1.04	1.80	1.30	54.2	2.40	1.028
	F	0.76	1.30	1.60	53.6	2.99	1.039
IX	B		0.54	0.51	4.6	11.0	1.014
	C		0.98	0.87	11.7	7.36	1.046
	D		1.66	1.26	23.8	5.31	1.048
	E		2.20	1.48	32.7	4.54	1.079
	F		2.71	1.65	39.1	4.21	1.046
	G		1.60	1.63	2.99	3.06	
X	H	2.23		1.93	40.0	4.64	
	I	2.47		1.28	48.3	2.64	1.046
	J	2.06		1.11	46.1	2.41	1.040
	K	1.45		0.88	39.6	2.21	1.020
	L	1.02		0.69	32.6	2.12	1.008
	M	0.51		0.43	13.8	3.14	0.986
XII	I	3.35	0.49	1.52	46.8	3.23	1.024
	J	2.00	0.79	1.53	44.9	3.41	1.033
	K	1.37	1.18	1.65	35.2	4.70	1.002
	L	0.91	1.46	1.76	26.0	6.74	0.984
	M	0.48	1.25	1.49	14.7	8.64	0.984
XIII	I		0.43	0.34	21.9	1.53	1.023
	J		0.75	0.53	29.5	1.78	1.021
	K		1.26	0.88	30.4	2.88	1.024
	L		1.57	1.09	30.8	3.54	1.015
	M		1.10	0.92	16.6	5.52	1.009
XIV	I		0.54	0.50	7.3	6.82	1.000
	J		1.13	0.95	16.0	5.91	1.000
	K		1.30	0.96	26.2	3.64	0.986
	L		1.46	1.11	24.5	4.49	0.996
	M		1.58	1.30	17.2	7.61	0.989
	N		2.11	1.43	32.0	4.42	

General Properties of the Membranes. The properties of the membranes are summarized in Table 3. In the membranes containing oppositely-charged groups (VIII and XII) the properties appear to be attributable to the additive contribution of the two groups and no abnormal behavior based on the interaction between the two groups is indicated.

Electrochemical Properties of the Membranes. The relation between the conductivity of a membrane ($\overline{k}$ in $\Omega^{-1}\,\mathrm{cm}^{-1}$) in a 1-1-type electrolyte solution and the concentration of the ion ($\overline{C}_i$ in eq/l) in the membrane may be expressed by:

$$\overline{k} = 10^{-3} \sum \overline{\lambda}_i \overline{C}_i \tag{1}$$

where $\overline{\lambda}_i$ is the equivalent conductivity of the ionic species i. When a membrane is in a dilute solution of electrolytes, since the concentration of sorbed salt in the membrane will be negligible compared with that of exchanged ions, $\overline{\lambda}_i$ may be related to the limiting equivalent conductivity of the species, $\lambda_i{}^0$, by the equation:[14]

$$\overline{\lambda}_i = \lambda_i{}^0 \phi h A_i F_i{}' F_i \tag{2}$$

where ϕ is the pore volume fraction; h, the tortuosity factor, and $F_i{}'$ and F_i, Ferry and Faxen's drag factors, and where A_i is related to the activation energy for diffusion. Thus, $\overline{k}$ will be strongly dependent on the structural factors of the membrane and on the interactions between the mobile species and its surroundings.

The linear relation between $\overline{k}$ and $\overline{C}$ has been reported for an anion-exchange membrane prepared from ethyleneimine and epichlorohydrin.[15] As is shown in Figs. 4 and 5, in the case of graft copolymer membranes containing one kind of ionized group, the plots of $\overline{k}$ against $\overline{C}$ can be substancially expressed by:

$$\log \overline{k} = a + b\,\overline{C} \tag{3}$$

where a and b are the experimental constants. This means, in turn, that $\overline{\lambda}_i$ decreases greatly as

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[*2] In Fig. 3, $\overline{X}_{\mathrm{Na}}$ and $\overline{X}_{\mathrm{Cl}}$ are the mole fractions of exchanged sodium and chloride ions in the bipolar membranes, respectively as defined by $\overline{X}_{\mathrm{Na}}=\overline{n}_{\mathrm{RNa}}/(\overline{n}_{\mathrm{RH}}+\overline{n}_{\mathrm{RNa}})$ and $\overline{X}_{\mathrm{Cl}}=\overline{n}_{\mathrm{RNHCl}}/(\overline{n}_{\mathrm{RN}}+\overline{n}_{\mathrm{RNHCl}})$, where $\overline{n}_i$ is the number of moles of the species i in the membrane and where RH and RN represent free acidic and basic groups respectively.

14) H. Kawabe, H. Jacobson, I. F. Miller and H. P. Gregor, *J. Colloid Interface Sci.*, **21**, 79 (1966).

15) G. Manecke and K. F. Bohnoeffer, *Z. Electrochem.*, **55**, 475 (1951).

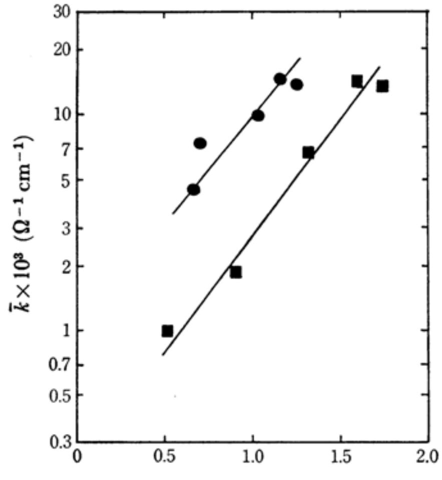

Fig. 4. Dependence of conductivity of membranes VII (●) and IX (■) on concentration of counter ion in membranes.

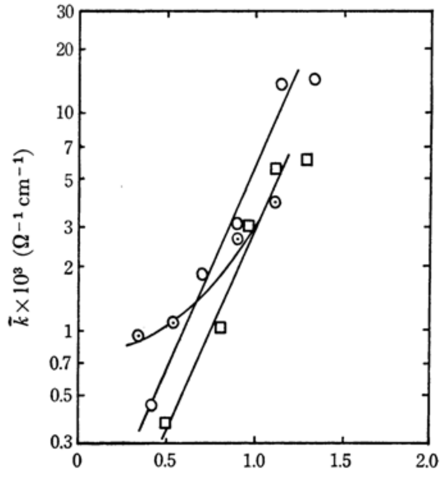

Fig. 5. Dependence of conductivity of membranes X (○), XIII (⊙) and XIV (□) on concentration of counter ion in membranes.

TABLE 4. EQUIVALENT CONDUCTANCE OF MEMBRANES

Code		$\bar{C}$ eq/l	$\bar{\lambda}$ Ω^{-1}cm^{2}eq^{-1}	$100(\bar{\lambda}/w)$
VII	B	1.25	11	28
	C	1.16	13	31
	D	1.03	9.4	24
	E	0.71	11	26
	F	0.67	6.7	18
IX	B	0.52	1.9	41
	C	0.91	2.0	17
	D	1.32	5.0	21
	E	1.60	8.9	27
	F	1.73	8.0	20
X	I	1.34	26	54
	J	1.15	12	26
	K	0.90	3.4	8
	L	0.70	2.6	8
	M	0.42	1.1	8
XIII	I	0.35	2.7	12
	J	0.54	2.0	7
	K	0.90	2.9	10
	L	1.11	3.5	11
	M	0.93	1.6	10
XIV	I	0.50	0.74	10
	J	0.80	1.3	8
	K	0.95	3.2	12
	L	1.11	5.1	21
	M	1.29	4.7	27

the capacity of the membrane decreases. The exceptionally higher values of $\bar{k}$ of XIII at lower $\bar{C}$ values may be ascribed to the contribution of a carboxylic acid group. In graft copolymer membranes, polar groups are not homogeneously distributed but are concentrated on graft chain; here the exchange-diffusion of ions may take place mainly through the internal polyelectrolyte region, which is composed of ionized groups. Therefore, the lower $\bar{\lambda}$ values at lower $\bar{C}$(or C_w) values, shown in Table 4, are probably attributable mainly to the lower pore-volume fraction and partly to the lower tortuosity factor. In fact, the calculated values of $100\times(\bar{\lambda}/w)$ listed in the table seem to be almost independent of $\bar{C}$. In the case of membranes containing oppositely-charged groups (VIII and XII), large values of $\bar{k}$ (around $2\times10^{-2}\Omega^{-1}\cdot$cm^{-1}) are observed almost independently of the membrane composition.

The concentration potential of a membrane is given by:

$$E_m = -\frac{\boldsymbol{RT}}{\boldsymbol{F}}\left[\bar{t}_{\mathrm{K}}\ln\frac{a_{\mathrm{K}}''}{a_{\mathrm{K}}'}-\bar{t}_{\mathrm{Cl}}\ln\frac{a_{\mathrm{Cl}}''}{a_{\mathrm{Cl}}'}\right] \quad (4)$$

where a_i is the activity of the species i in solution ($a'>a''$) and where $\bar{t}_i$ is the transference number of ions in the membrane. The concentration potentials of various membranes placed between 0.1 N KCl and 0.05 N KCl are shown in Fig. 6, in which F_{K} and F_{Cl} are the mole fractions of ionized acidic and basic groups[*3] respectively, and in which $|E_0|$ is the absolute value of the ideal concentration potential as given by the Nernst equation. The absolute values of the concentration potential of VII and XIII increase, and those of IX, X, and XIV, decrease with an in-

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[*3] The mole fractions F_{K} and F_{Cl} are defined as follows: $F_{\mathrm{K}}=\bar{n}_{\mathrm{RK}}/(\bar{n}_{\mathrm{RK}}+\bar{n}_{\mathrm{RN}})$ for VII and X; $F_{\mathrm{K}}=\bar{n}_{\mathrm{RK}}/(\bar{n}_{\mathrm{RK}}+\bar{n}_{\mathrm{RNCl}})$ for VIII and XII; $F_{\mathrm{Cl}}=\bar{n}_{\mathrm{RNCl}}/(\bar{n}_{\mathrm{RK}}+\bar{n}_{\mathrm{RNCl}})$ for VIII and XII; $F_{\mathrm{Cl}}=\bar{n}_{\mathrm{RNCl}}/(\bar{n}_{\mathrm{RH}}+\bar{n}_{\mathrm{RNCl}})$ for IX and XIV, and $F_{\mathrm{Cl}}=\bar{n}_{\mathrm{RNCl}}/(\bar{n}_{\mathrm{RH}}+\bar{n}_{\mathrm{RNCl}})$ for XIII, where $\bar{n}_{\mathrm{R}}$ represents the number of moles of an inactive group, such as phenyl and the ester, and where $\bar{n}_{\mathrm{RNCl}}$ is that of the quaternary pyridinium group.

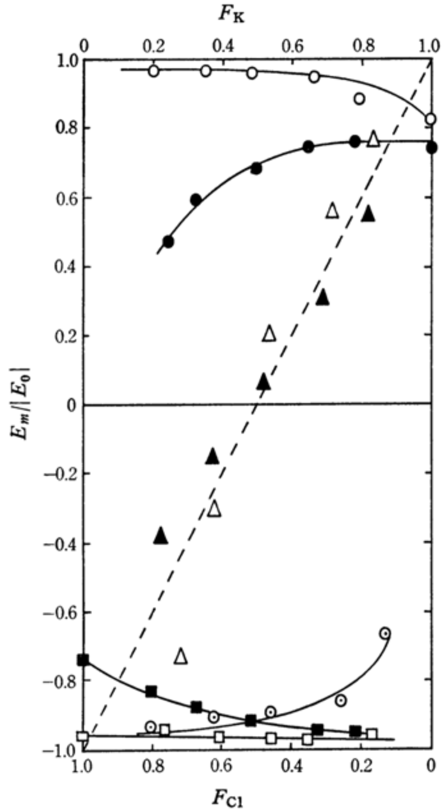

Fig. 6. Dependence of permselectivity of membranes VII (●), VIII (▲), IX (■), X (○), XII (△), XIII (⊙) and XIV (□) on mole fraction of membrane components.

crease in the mole fraction of each ionized group. This is in accordance with the behavior of each membrane except X with respect to the molality of the ionized group described in the previous section. As the Donnan exclusion of salt becomes less effective upon the decrease in $\bar{m}$, the salt content in membrane will increase and the potential will decrease. The sign of the E_m of the membrane XI, containing a carboxylic acid group and a partially-ionized pyridine group, is negative under acidic conditions, but it becomes positive upon repeated washings of the membrane, probably because of the very weak basicity of the pyridine group and the high mobility of the hydrogen ions. Thus, the behavior of X and XI is similar to that of an amphoteric membrane, in which the potential varies from negative to positive depending upon the pH of the solution.[3)]

The plots for VIII and XII, which contain oppositely-charged groups, are on the broken line in Fig. 6. Since E_m is expressed by Eq. (4) and since $\bar{t}_i$ is given by $(\bar{\lambda}_i\bar{C}_i)/(\sum\bar{\lambda}_i\bar{C}_i)$, the potential of VIII and XII will be a linear function of $F_i(=\bar{C}_i/\sum\bar{C}_i)$ provided that there is no interaction between the two groups and provided the mobilities of K and Cl ions are equal in a membrane.

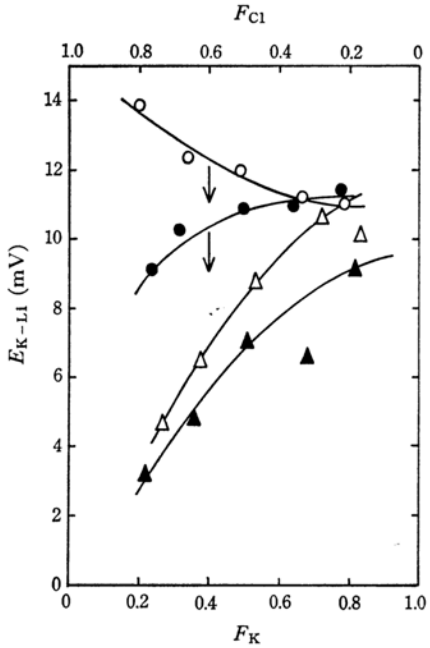

Fig. 7. Dependence of bi-ionic potential of membranes VII (●), VIII (▲), X (○), and XII (△) on mole fraction of membrane components.

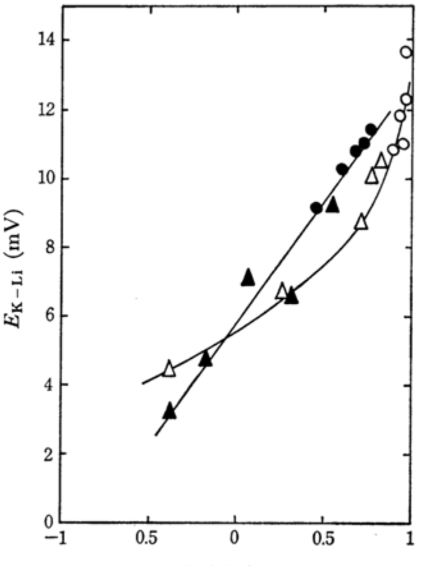

Fig. 8. Dependence of bi-ionic potential of membranes VII (●), VIII (▲), X (○) and XII (△) on permselectivity of the membranes.

The bi-ionic potential of the bipolar membranes for 0.1 N KCl - 0.1 N LiCl, E_{K-Li}, is shown as a function of F_i in Fig. 7. When E_{K-Li} is plotted against $E_m/|E_0|$, a simple relationship is indicated, as is shown in Fig. 8. The fact that E_{K-Li} decreases simply with the decrease in $E_m/|E_0|$

may be understood by considering that chloride ions in a membrane tend to transfer in a direction so as to reduce the bi-ionic potential, which is given for ideal permselective membranes[16] by:

$$E_{\mathrm{K-Li}}=\frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{\overline{D}_{\mathrm{K}}aK'\overline{f}_{\mathrm{Li}}}{\overline{D}_{\mathrm{Li}}a_{\mathrm{Li}}''\overline{f}_{\mathrm{K}}} \tag{5}$$

where $\overline{D}$ represents the diffusion coefficient of the ions in a membrane; a, the activity of ions in solution, and $\overline{f}$, the activity coefficient of the ions in a membrane. The fact that the $E_{\mathrm{K-Li}}$ of the membrane is positive may be qualitatively explained by Eq. (5). Provided that the ion-exchange selectivity coefficient, $K_{\mathrm{Li}}^{\mathrm{K}}$, is expressed by the activity coefficient ratio, $\overline{f}_{\mathrm{Li}}/\overline{f}_{\mathrm{K}}$, and that the diffusion coefficient is related to the conductivity through the Nernst-Einstein equation, $D=\boldsymbol{R}T\lambda/\boldsymbol{F}^2$, the following equation is established:

$$E_{\mathrm{K-Li}}=\frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\left[\frac{\overline{k}_{\mathrm{K}}}{\overline{k}_{\mathrm{Li}}}K_{\mathrm{Li}}^{\mathrm{K}}\right] \tag{6}$$

In the membranes containing a sulfonic acid group (VII and VIII), the selectivity coefficient term seems to be more important, because $\overline{k}_{\mathrm{K}}/\overline{k}_{\mathrm{Li}}$ for the membrane VII is less than unity in some regions in Fig. 9. It is known that $K_{\mathrm{Li}}^{\mathrm{K}}$ is greater than unity for sulfonic acid-type resins. On the other hand, since the $K_{\mathrm{Li}}^{\mathrm{K}}$ of a carboxylic acid-type resin is known to be less than unity, it may be predicted from Eq. (6) that $\overline{k}_{\mathrm{K}}$ will be much higher than $\overline{k}_{\mathrm{Li}}$ for the membranes containing a carboxylic-acid group (X and XII). It may be seen in Fig. 9 that $\overline{k}_{\mathrm{K}}/\overline{k}_{\mathrm{Li}}$ is greater than 3 for the membrane X.[*4]

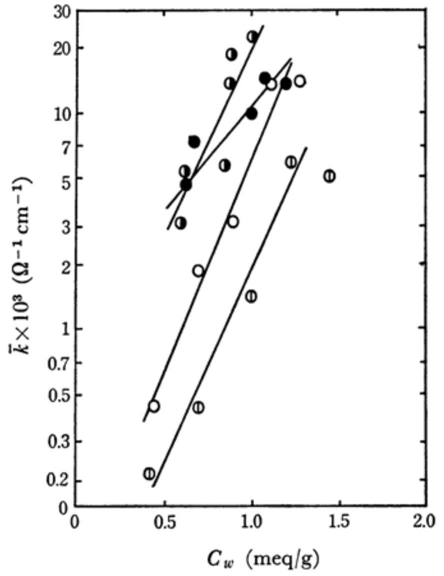

Fig. 9. Conductivities of membrane VII and X.
●: VII in K-form ◑: VII in Li-form
○: X in K-form ⦶: X in Li-form

In reviewing the properties of the membranes prepared from blends of monofunctional graft copolymers, no interaction between acidic and basic groups is indicated, and the concentration potentials of the membranes containing oppositely-charged groups are shown to be additive contributions of the two terms in Eq. (4) in relation to both the groups. This suggests that most of the functional groups of both copolymers in a blend are not brought into contact by the melt-pressed procedure.

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[*4] A large difference between sulfonic acid-type membranes and carboxylic acid-type membranes in regard to the conductance of alkali-metal ions was previously observed for monofunctional graft copolymer membranes.[5]

16) F. Helfferich, "Ion Exchange," McGraw-Hill, Inc., New York (1962), p. 380.