

Membrane Potentials and Permeation of NaCl in Poly(vinyl Alcohol-co-Itaconic Acid) Membranes

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Synopsis

The membrane potential and permeability of NaCl were measured for six crosslinked poly(vinyl alcohol-co-itaconic acid) membranes having various water contents [$0.25 \leq H \leq 0.83$ H₂O (g)/swollen membrane (g)] and interpreted by means of an equation derived from Schlögl's theory. Both results of the membrane potential and the permeability of the membranes having $H \geq 0.34$ could be satisfactorily interpreted by the theory. The permeability of NaCl in the membrane of $H=0.25$ gave, however, an increasing tendency with the decrease of the upstream concentration lower than 0.04 mol/L. It was considered that the concentration dependence reverse to what was caused by the Donnan exclusion might be due to the concentration dependence of the thermodynamic partition coefficient in nonfreezing water of the membrane. By the equations thus derived the membrane potential and the permeability of NaCl in the membrane of $H=0.25$ were explained qualitatively. The mobility ratios of Na⁺ and Cl⁻ and the effective charge density in the membranes were discussed.

INTRODUCTION

Transport phenomena such as permeation and membrane potential of synthetic membranes have received a great deal of attention to elucidate the permeability of ions through biological and synthetic membranes.

Several authors¹⁻⁵ investigated membrane potential and permeation of simple salts based on the theory of Teorell⁶ and Meyer and Sievers.⁷ Kobatake and co-workers⁸⁻¹¹ derived equations from membrane potentials and salt flux considering the effective charge density. They investigated the mobilities and activity coefficients of K⁺ and Cl⁻ in collodion-based polystyrene sulfonic acid membranes and found that the depression of mobility and activity coefficient of the counterions in the membranes could be represented by the empirical additivity rule known in polyelectrolyte solutions. Demisch and Pusch¹² calculated membrane potential and resistance for binary and ternary electrolyte solutions employing Schlögl's equations.¹³ The mobility ratios of the cations and the anions were estimated from membrane potential in weak and strong cation exchange membranes. Minoura and Nakagawa¹⁴ measured the membrane potential of poly(α -amino acid) membranes and found that the mobility ratios of Na⁺ and Li⁺ to K⁺ in the membranes were larger than those in aqueous solution. Kinoshita et al.¹⁵ studied ionic salt permeabilities and membrane potentials of charged polypeptide membranes. They applied free volume theory to the temperature dependence of ionic permeability and concluded that the magnitude of ionic permeability depends on the free volume of the membranes, the effective charge density of the membranes, and the critical ionic diffusant

size. Vink¹⁶ measured membrane potential and diffusion of NaCl in cellulosic membranes and interpreted the results using a modified Nernst-Planck equation employing the mean value theorem. Kimura et al.¹⁷ investigated membrane potential of carboxymethyl and carboxyethyl cellulose membranes having various degrees of substitution and found that the ionic mobility ratios of cation and anion gave the same dependence on the Stokes radius of the cations as those in the bulk aqueous solution. Koh and Silverman¹⁸ discussed the transport of hydroxide ions in Nafion membranes based on a heterogeneous membrane model carrying narrow capillaries. The results were compared with the ion flux obtained from a phenomenological model based on a cluster-network structure in the membranes.

In the present study, membrane potential and permeability of NaCl were measured for crosslinked poly(vinyl alcohol-co-itaconic acid) membranes with various water content [$0.25 \leq H \leq 0.83$ H₂O(g)/swollen membrane(g)] and interpreted by means of an equation derived from Schlögl's theory.^{12,14,17}

EXPERIMENTAL

Materials

Poly(vinyl alcohol-co-itaconic acid) (PVA-IA) used in this investigation was kindly supplied by Kuraray Co., Ltd. and was employed after Soxhlet extraction with methanol for 12 h. PVA-IA has 1.3 mol % of itaconic acid, its saponification value is 97.7 mol %, and its degree of polymerization is 1750, respectively. Distilled deionized water was used throughout the experiment. Membrane preparation and the method of crosslinking by acetalization of the membranes with glutaraldehyde was described in the previous paper.¹⁹ The water content of the membrane was controlled by the degree of crosslinking. The characteristics of the membranes are listed in Table I.

Apparatus

The apparatus and procedure for measurements of membrane potential are exactly the same as those designed by Demisch and Pusch.¹² The concentration of aqueous NaCl solution was kept constant in one side of the cell, C'_s , at 1.0×10^{-3} mol/L and was changed in the other side of the cell, C''_s , from 1.0×10^{-4} to 1.0 mol/L.

TABLE I
Characteristics of Membranes

Membranes	H (g/g)	C_x^0 (eq/L)	L (μm)
VI-83	0.83	0.097	105
VI-73	0.73	0.16	103
VI-67	0.67	0.20	78
VI-47	0.47	0.33	55
VI-34	0.34	0.43	57
VI-25	0.25	0.51	55

The permeation cell is similar to that described elsewhere.^{16,20} It consists of two glass chambers separated by the membrane. The cell volume of upstream and downstream side is 245 and 68 mL, respectively. The effective membrane area is 7.28 cm². The solutions of each side were stirred effectively during the measurements to minimize the stagnant boundary layers on the surface of the membrane. The downstream concentration C_2 was monitored with electronic conductometer to determine the permeability coefficients of NaCl in the membranes. The permeation measurements were carried out within the limit of the concentration range of C_2 less than 1/100 of upstream side. The upstream concentration ($C_1=0.004-0.2$ mol/L) was, therefore, regarded as constant during the experiments. All measurements were performed at $25 \pm 0.05^\circ\text{C}$ in a thermostated water bath.

RESULTS

Membrane potentials $\Delta\phi$ of VI-83, 73, 67, 47, 34, and 25 membranes (water content of the membranes are 0.83, 0.73, 0.67, 0.47, 0.34, and 0.25, respectively) are shown in Figure 1. The maximum membrane potential $\Delta\phi_{\text{ex}}$ and $C''_{s-\text{ex}}$ obtained from Figure 1 are tabulated in Table II where $C''_{s-\text{ex}}$ is the concentration at $d\Delta\phi/dC''_s=0$ and $\Delta\phi_{\text{ex}}$ is the potential at $C''_{s-\text{ex}}$. It is found that $\Delta\phi_{\text{ex}}$ and $C''_{s-\text{ex}}$ increase with the decrease of water content of the membranes of $H \geq 0.34$. The increasing tendency of $\Delta\phi_{\text{ex}}$ and $C''_{s-\text{ex}}$ for the membranes of $H \geq 0.34$ is consistent with the values of the fixed charge concentration of the membranes, C_x^0 , shown in Table I, i.e., C_x^0 is found to increase with the decrease of the water content of the membranes. $\Delta\phi_{\text{ex}}$ of VI-25 is, however, observed to be lower than that of VI-34, although C_x^0 of VI-25 is higher than that of VI-34 (see Table I). The membrane potential data of VI-25 suggests that effective fixed charge of VI-25 may be lower than that of VI-34 or the conventional theory may not be appropriate to explain the potential in the case of low water content membranes such as VI-25.

Permeability coefficients P of the membranes are shown in Figures 2 and 3. P was found to decrease with decreasing water content of the membranes. This is caused by the increase of tortuosity and the decrease of the available area for solute permeation in the membranes with the decrease of the water content. It was also observed that P decreases with the decrease of C_1 in the membranes of $H \geq 0.34$ when C_1 is lower than 0.04 mol/L. This observation is similar to that found in other systems of charged membranes and explained by Donnan exclusion of solutes in the charged membranes.^{10,16} VI-25 shows, however, increasing tendency of P with the decrease of C_1 at $C_1 \leq 0.04$ mol/L. This results is the reverse tendency of those observed in the membranes of $H \geq 0.34$ and other charged membranes.^{9,15}

DISCUSSION

The membrane potential and permeability coefficient of uni-univalent salt can be expressed by Nernst-Planck equation as eqs. (1) and (2) for homogeneous anionic charged membranes, supposing the following assumptions:

(i) The total membrane potential $\Delta\phi$ is given as the sum of the Donnan potential at the two interfaces between membrane and solution, and the

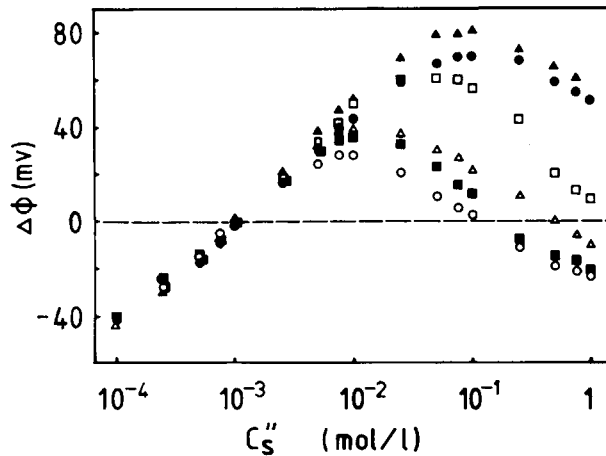


Fig. 1. Membrane potential $\Delta\phi$ vs. salt concentration C_s'' ; $C_s = 1 \times 10^{-3}$: (○) VI-83; (■) VI-73; (△) VI-67; (□) VI-47; (▲) VI-34; (●) VI-25.

diffusion potential in the membrane; the hydrodynamic permeability was neglected.

(ii) Electroneutrality holds in any part of the membrane.

(iii) The flux of anion and cation is equal in any part of the membrane:

$$\Delta\phi = -\frac{RT}{F} \left(\ln \frac{C_s' \sqrt{1+4y'^{1/2}} + 1}{C_s'' \sqrt{1+4y'^{1/2}} + 1} + U^* \ln \frac{\sqrt{1+4y'^{1/2}} + U}{\sqrt{1+4y'^{1/2}} + U} \right) \quad (1)$$

$$P = \frac{\omega_+ + \omega_- RT}{(\omega_+ + \omega_-)(C_1 - C_2)} \left\{ \left[1 + 4 \left(\frac{K_{\pm} C_1}{C_x} \right)^2 \right]^{1/2} - \left[1 + 4 \left(\frac{K_{\pm} C_2}{C_x} \right)^2 \right]^{1/2} - U^* \ln \frac{\sqrt{1+4(K_{\pm} C_1/C_x)^2} + U}{\sqrt{1+4(K_{\pm} C_2/C_x)^2} + U} \right\} \quad (2)$$

where ω_+ and ω_- are mobilities of cation and anion, C_x is the effective fixed charge concentration, K_{\pm} is the thermodynamic partition coefficient which is related to the standard chemical potential difference across the solution/membrane interface and the mean activity coefficients of the salt

TABLE II
 K_{\pm} , C_{s-ex}'' and $\Delta\phi_{ex}$ of NaCl

Membranes	K_{\pm}	C_{s-ex}'' (mol/L)	$\Delta\phi_{ex}$ (mV)
VI-83	0.90	0.0075	28
VI-73	0.78	0.010	36
VI-67	0.71	0.012	39
VI-47	0.54	0.040	61
VI-34	0.47	0.075	81
VI-25	0.42	0.10	70

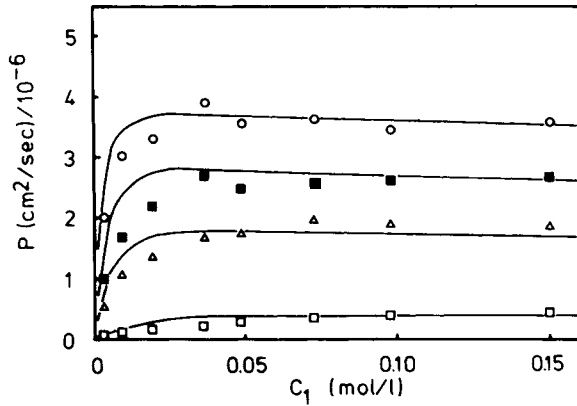


Fig. 2. Dependence of permeability coefficient of NaCl on the upstream concentration C_1 ; $C_2=C_1/100$: (○) VI-83; (■) VI-73; (△) VI-67; (□) VI-47. The solid lines are calculated by eq. (2) with constant K_{\pm} .

in the solution and membrane. $U=(\omega_+ - \omega_-)/(\omega_+ + \omega_-)$, $y=K_{\pm}C_s/C_x$, and R , T , and F are the conventional meanings. The derivation of eqs. (1) and (2) is described in other papers.^{12,14,17}

C_x is known to be given as eq. (3):^{12,14,17}

$$C_x = 2K_{\pm}C''_{s-ex}/\sqrt{(1-U^2)}/U^2 \tag{3}$$

It is possible to estimate U from the slope of $\Delta\phi$ as a function of C''_s at $C''_s > C''_{s-ex}$, although this is not available for the membranes with high C''_x such as VI-34 and VI-25 in this study. $\Delta\phi_{ex}$ can be given by the following equation derived from eqs. (1) and (3):

$$\Delta\phi_{ex} = -\frac{RT}{F} \left\{ \ln \frac{C''_{s-ex}U}{C'_s(1+U)} - 1 - \left(1 + \frac{C'^2_s(1-U^2)^{1/2}}{C''^2_{s-ex}U^2} \right) + U^* \ln \frac{U}{U^2-1} \left[U + \left(1 + \frac{C'^2_s(1-U^2)^{1/2}}{C''^2_{s-ex}U^2} \right)^{1/2} \right] \right\} \tag{4}$$

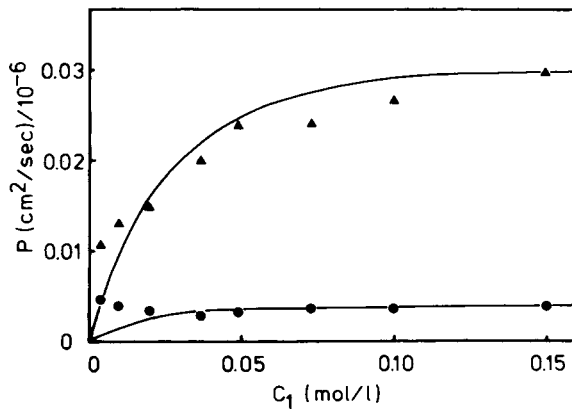


Fig. 3. Dependence of permeability coefficients of NaCl on the upstream concentration C_1 ; $C_2=C_1/100$: (▲) VI-34; (●) VI-25. The solid lines are calculated by eq. (2) with constant K_{\pm} .

Using the values of $\Delta\phi_{\text{ex}}$ and $C''_{s-\text{ex}}$, eq. (4) gives U , therefore ω_+/ω_- . Figure 4 shows the relation between U and $C''_{s-\text{ex}}/C'_s$ at $\Delta\phi_{\text{ex}} = 40\text{--}80$ mV obtained from eq. (4). It is found that $C''_{s-\text{ex}}/C'_s$ increases with the increase of $\Delta\phi_{\text{ex}}$ at a constant U value. U in the PVA-IA membranes is qualitatively expected not to depend on the water content significantly at $H \geq 0.34$, since $\Delta\phi_{\text{ex}}$ increases with the increase of $C''_{s-\text{ex}}$ at $H \geq 0.34$ (see Table II). The curve fitting job of the experimental $\Delta\phi$ to eq. (1) by adjusting C_x and U was performed by means of a nonlinear least square method. In the calculation, the initial values of U and C_x were estimated by eqs. (3) and (4). C_x and U thus obtained are summarized in Table III.

Examples of the plots of $\Delta\phi$ against C''_s calculated by eq. (1) with C_x and U in Table III are shown in Figures 5 and 6. It is found that in the case of VI-83 Donnan potential, the first term in eq. (1) is nearly constant at $C''_s > 10^{-2}$, and the slope is almost the same as that of diffusion potential [the second term in eq. (1)]. The membrane potential of VI-83 can be thus reproduced well by eq. (1). The same level of the agreement is also found for $H \geq 0.34$. It is, therefore, concluded that eq. (1) can explain the experimental results of the membrane potentials of PVA-IA membranes at $H \geq 0.34$. However, the equation cannot satisfactorily explicate the membrane potential of VI-25 at $C''_s > 0.25$ mol/L. This comes from the fact that $\Delta\phi_{\text{ex}}$ of VI-25 is lower than that of VI-34 while C''_s and $C''_{s-\text{ex}}$ of VI-25 are higher than those of VI-34. Higher $C''_{s-\text{ex}}$ and lower $\Delta\phi_{\text{ex}}$ lead to the greater value of U for VI-25 than VI-34 (see Fig. 4). This gives a gentle slope of $\Delta\phi$ against C'_s at $C''_s > C''_{s-\text{ex}}$ and results in the deviation from eq. (1) at $C''_s > C''_{s-\text{ex}}$ as found in Figure 6.

In Figures 2, 3, and 7 the calculated curves of the permeability by eq. (2) with C_x and U in Table III are illustrated by a solid line. ω_+ , an available parameter, was estimated to give the best fit of eq. (2) with the experimental results and is also shown in Table III. Satisfactory agreement was found between the solid lines and the experimental results for the membranes of $H \geq 0.34$. The discrepancy in VI-25 at $C_1 \leq 0.04$ mol/L, however, could not be explained by eq. (2).

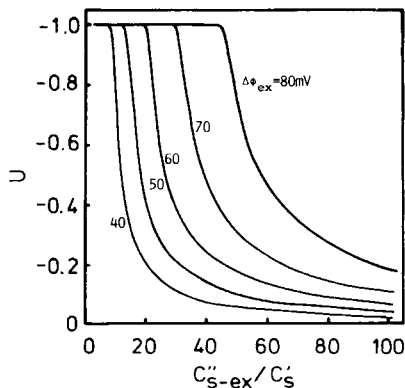


Fig. 4. Theoretical calculation of U as a function of $C''_{s-\text{ex}}/C'_s$ at $\Delta\phi_{\text{ex}} = 40, 50, 60, 70,$ and 80 mV.

TABLE III
Parameters of Membrane Potential and Permeation of NaCl obtained by Eqs. (1) and (2)

Membranes	U	ω_+/ω_-	$\omega_+/10^{-10}$ (cm ² /s V)	$C_x/10^{-2}$ (eq/L)	C_x^0/C_x
VI-83	-0.60	0.25	9.3	1.0	0.103
VI-73	-0.67	0.20	7.2	1.0	0.103
VI-67	-0.64	0.22	5.2	1.5	0.078
VI-47	-0.69	0.18	1.3	3.2	0.097
VI-34	-0.35	0.48	0.17	2.6	0.059
VI-25	-0.18	0.70	0.032	1.1	0.023

Both membrane potential and permeability of VI-25 could not be explained by eqs. (1) and (2), which are widely used to explain the transport phenomena in charged membranes.^{12,14,17}

In this context we have tried to modify eqs. (2) and (3). Toyoshima et al.⁹ proposed equations of membrane potentials and flux considering the concentration dependence of mobility and activity coefficients of ions in the membrane. Curve fitting of eq. (11) in Ref. 9 to the permeability of NaCl in VI-25 with arbitrarily chosen α , β , μ_+^0 , and ϕX , however, failed in reproducing the tendency found in Figure 7.

Partition coefficients K_{obs} of NaCl in VI-25 determined by desorption method¹⁷ is shown in Figure 8 as a function of the equilibrium salt concentration C_0 , where K_{obs} is defined as \bar{C}/C_0 and \bar{C} is the sorbed concentration by the membranes. As found in the figure, K_{obs} of VI-25 shows a minimum at $C_0=0.04$ mol/L and increases with the decrease of C_0 . This suggests that the thermodynamic partition coefficient K_{\pm} probably depends on the concentration, while K_{\pm} in eqs. (1) and (2) is assumed to be independent of the concentration. Since exactly the same tendency was found between P and K_{obs} as a function of the concentration (cf. Fig. 7), deviation of $\Delta\phi$ and P in VI-25 from eqs. (1) and (2) is probably due to the above inadequate assumption for K_{\pm} in VI-25. As we have found that the permeability coefficients of CO₂ and C₄H₆ in the water-swollen PVA-IA mem-

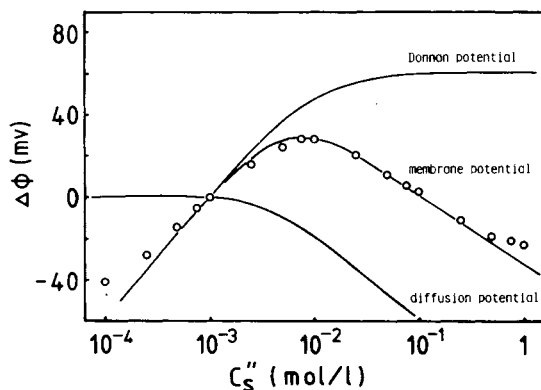


Fig. 5. Membrane potential $\Delta\phi$ of VI-83 vs. salt concentration C_s'' ; $C_s'=1 \times 10^{-3}$ mol/L. The solid lines are calculated by eq. (1) with constant K_{\pm} .

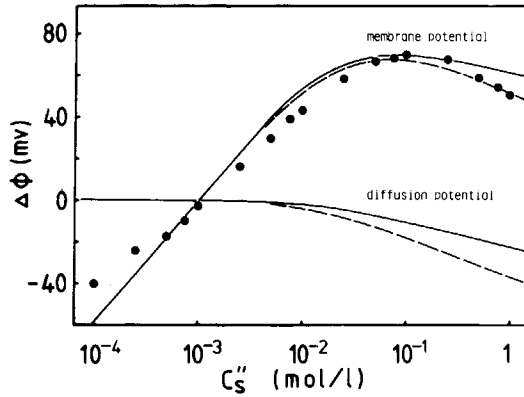


Fig. 6. Membrane potential $\Delta\phi$ of VI-25 vs. salt concentration C_s'' ; $C_s' = 1 \times 10^{-3}$ mol/L. The solid lines are calculated by eq. (1) with constant K_{\pm} . The broken lines are calculated by eq. (1) with K_{\pm} by eq. (5).

branes also showed an increasing tendency with decreasing pressure which was due to the pressure dependence of the solubility.²¹ Increase of permeability and partition coefficients with the decrease of concentration is usually explained by the dual permeation model²²⁻²⁷ assuming the sorption mechanism consisting of Henry-plus Langmuir-type modes.

K_{\pm} was assumed to be expressed by eq. (5) to interpret the results of $\Delta\phi$ and P in VI-25:

$$K_{\pm} = K_P + K_L S_L / (1 + K_L C_0) \quad (5)$$

where K_P is the Henry's law constant and S_L and K_L are the Langmuir-type capacity constant and affinity constant, respectively. Dependence of K_{\pm} on the concentration may be ascribed to the activity coefficients of NaCl in the membranes with low water content such as VI-25. In an interpretation of the pressure dependence of the permeability of CO_2 and C_4H_6 in the previous paper,²¹ the Langmuir site was assigned to the nonfreezing

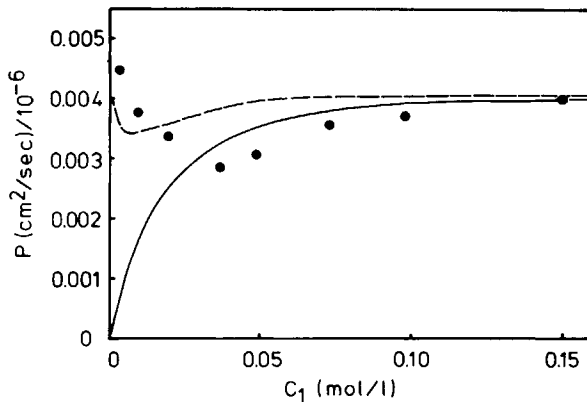


Fig. 7. Dependence of permeability coefficients of NaCl in VI-25 on the upstream concentration C_1 ; $C_2 = C_1/100$. The solid line is calculated by eq. (2) with constant K_{\pm} . The broken line is calculated by eq. (2) with K_{\pm} by eq. (5).

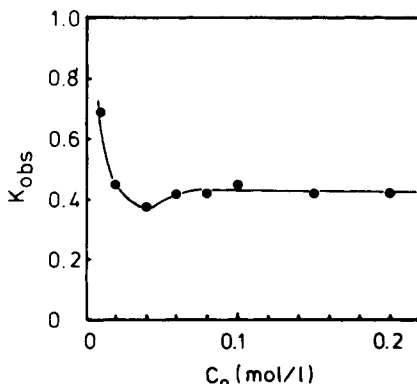


Fig. 8. Plots of K_{obs} of against C_0 of NaCl for VI-25.

water phase. The state of water in VI-25 is known to one state of nonfreezing water, due to the low water content.¹⁹ It is well known that interfacial water like the nonfreezing water has some different properties to compare with the bulk water, e.g., the heat capacity,^{19,28} the viscosity,^{28,29} and the ion selectivities.^{28,30} The Langmuir mode in VI-25 may be caused by the specific properties of nonfreezing water.

An example of the calculated curves of $\Delta\phi$ by eq. (1) using K_{\pm} of eq. (5) for VI-25 is given by the broken lines in Figure 6, where K_P , K_L , S_L , C_x , and U are 0.445, 2000 L/mol, 0.0027 mol/L, 0.0145 eq/L water in membrane, and -0.315 , respectively. It is found that the curve with eq. (5) can better explain the membrane potential of VI-25 than with constant K_{\pm} at $C'_s > 0.25$ mol/L. The calculated curve of P by eq. (2) with eq. (5) for the same membrane is shown as the broken line in Figure 7. K_P , K_L , S_L , and C_x used in the calculation are the same as those in Figure 6. Although an exact reproduction of the experimental results of P was not observed, the minimum of the permeability and the increasing tendency with decreasing the concentration were found in Figure 7.

The above consideration suggests that the assumption of the concentration dependent K_{\pm} can explain $\Delta\phi$ and P of NaCl in VI-25 membrane.

In Table III it is found that ω_+/ω_- at $H \geq 0.34$ is lower than 0.63 in bulk solution.¹⁴ This is probably due to an electrostatic trapping of the counterions to the fixed charge.¹⁶ It is also found that C_x/C_x^0 in the membranes is lower than 0.11. This is due to the partial dissociation of carboxyl groups in the membranes as discussed by some investigators,^{12,17} and the charge of carboxyl groups may be embedded in the polymer matrix in some extent. C_x/C_x^0 decreases with decreasing water content of the membranes. This is probably due to the decrease of dielectric constant of the membranes which leads to the lower dissociation constant of the carboxyl groups in the membranes.

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