

Ionic Transport Behavior across Charged Membranes with Low Water Content. I. Theoretical Aspect of Membrane Potentials in Membranes Having Inhomogeneously Distributed Fixed-Charge Groups

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This is our first report on the elucidation of the ionic transport phenomenon across charged membranes with low water content. In the present study, we proposed a new theoretical model of ionic transport across charged membranes with low water content, considering the effects of both an inhomogeneous fixed-charge distribution and the ion pairs in the membrane. We tried to analyze theoretically the properties of charged membranes (membrane potentials across charged membranes and the effective charge density of the charged membranes). Our theoretical prediction suggested that ion-pair formation was facilitated by the increase in the fixed-charge density of the membrane, the decrease in the dielectric constant of the membrane, and the increase in the valence of the counterion. It was also indicated that ion pairing depended on the center-to-center distance in an ion pair.

1. Introduction

Recently, the applications of charged (ion-exchange) membranes with low water content under severe conditions have become more attractive fields: the recovery of high concentrated acid/alkali, fuel cells, and high-temperature membrane processes for high efficiency. For these applications, the membranes require the following features: (i) high fixed-charge density, (ii) low volume flux generated by the osmotic pressure difference, and (iii) high thermal, mechanical, and chemical stability. The low-water-content charged membrane is a useful option.

The fixed-charge density of the membrane estimated by an ionic transport procedure (membrane potential method) is less than that determined by the equilibrium procedure (titration method).^{1–3} It has been considered that this phenomenon is attributed to the inhomogeneous fixed-charge distribution or ion pairing between the fixed-charge group and counterion.^{4–16} Recently, Mafé et al. have proposed a theoretical model considering an ion-pairing effect between fixed-charge groups and counterions in charged membranes.¹³ According to their paper, most of the fixed-charge groups in the membranes are neutralized by the counterions because of the formation of ion pairs. When the region in the charged membrane has a low dielectric constant (e.g., in the organic solvent system or for the low-water-content condition), the effectiveness of fixed-charge groups is decreased. Chou et al. studied the ion-pairing effect in an organic solvent system and showed that theoretical predictions of membrane properties, effective charge densities, and ionic mobilities in the membranes agreed well with experimental results from membrane potential and permeability measurements.^{14–16} In the low-water-content membrane system, however, the ion-pairing effect has not been verified both theoretically and experimentally. There have been also several

unclear points regarding the physicochemical properties of the low-water-content membranes. In such a system, the vicinity of a fixed-charge group in the charged membrane would have a low dielectric constant based on dielectric saturation.^{17,18} In addition, Tasaka et al. reported that a decrease in the water content of the membranes caused an increase in the dielectric constant of the charged membranes based on differential scanning calorimetry (DSC) measurements.¹⁹

The membrane potential measurement is a straightforward method for investigating ionic transport phenomena through charged membranes. The membrane potential is the potential difference that is generated between the electrolyte solutions of different concentrations separated by a charged membrane. Figure 1 shows the membrane transport system used in this study. According to Teorell, Meyer, and Sievers (TMS),²⁰ the membrane potentials in a charged membrane can, theoretically, be described by the Donnan equilibrium²¹ and the Nernst–Planck equation.²² In many previous studies, the classical TMS approach was used to analyze experimental membrane potentials in which the charged membrane was treated as having a homogeneous fixed-charge distribution. Charged membranes, however, have an inhomogeneous fixed-charge distribution under the concentration gradient across the membrane (e.g., membrane-potential measurement system and diffusion–dialysis system): the local concentration of counterions in the membrane varied from one surface to the other surface. Mafé et al. also suggested a theoretical model to analyze the transport phenomenon across membranes with an inhomogeneous fixed-charge distribution.¹¹ Here, we tried to expand the conventional theoretical model considering the ion-pairing effect in order to calculate the potential difference across the membrane with both homogeneous and inhomogeneous fixed-charge distributions. The theoretical model we present here is more versatile for a theoretical analysis of the ionic transport of charged membranes, particularly in the low-water-content membrane system and organic solvent system.

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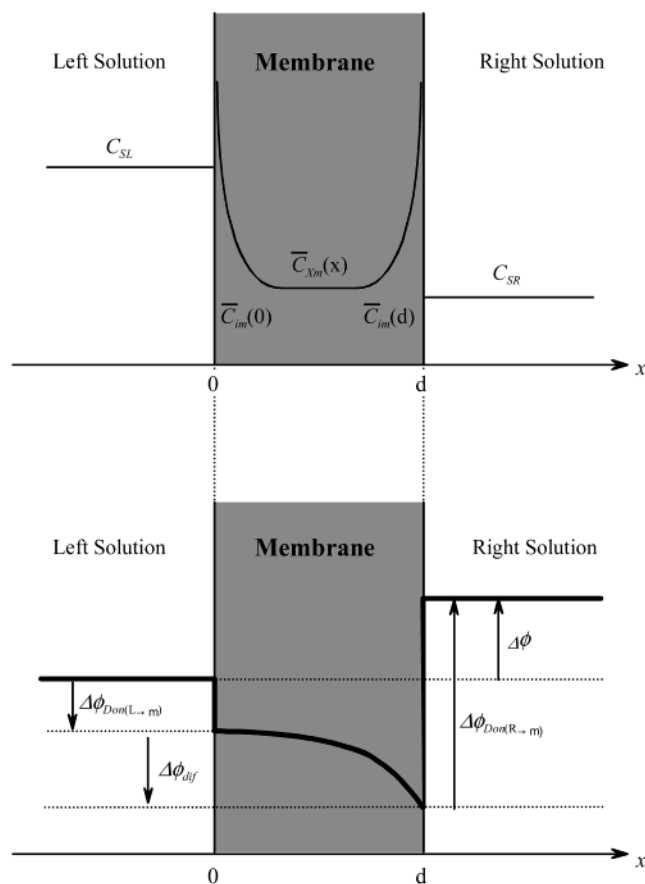


Figure 1. Schematic diagram of the membrane transport system. Ionic concentration profiles (top) and electric potential profiles (bottom) across a charged membrane.

The objectives of this investigation are (i) to propose a new ionic transport model across charged membranes with low water

content, considering the both effects of an inhomogeneous fixed-charge distribution and the ion pairs in the membrane, and (ii) to estimate theoretically the membrane potentials across charged membranes and the effective charge density of the charged membranes.

2. Theory

2.1. Concept of Ion Pairs in the Membrane. There are many studies on the theories of ion pairs in electrolyte solutions.^{23–31} To estimate the electrostatic interaction between fixed-charge groups and counterions in a membrane, we take a very simple model based on the Fuoss approach to ion-pair formation in electrolyte solutions.²³ In the membrane, the fixed-charge groups pair with the counterions (Figure 2). To apply the Fuoss formalism to the ion pair in a membrane, we consider the following association equilibrium.

$$A + -\alpha X \xrightleftharpoons{K_A} AX_{-\alpha}$$

$$K_A = \frac{[AX_{-\alpha}]}{[A][X]^{-\alpha}} = \frac{C_{Xm} - \bar{C}_{Xm}}{\bar{C}_{lm} \bar{C}_{Xm}^{(-\alpha)}} \quad (1)$$

X and A represent fixed-charge groups and counterions, respectively, $\alpha = z_1/z_X$, and z_i is the valence of the i th species ($i = 1$ for counterions, 2 for co-ions, and X for fixed-charge groups). We consider, without the loss of generality, that the valence of the fixed-charge groups in the membrane is ± 1 . The association constant between fixed-charge groups and counterions in a membrane is rewritten as

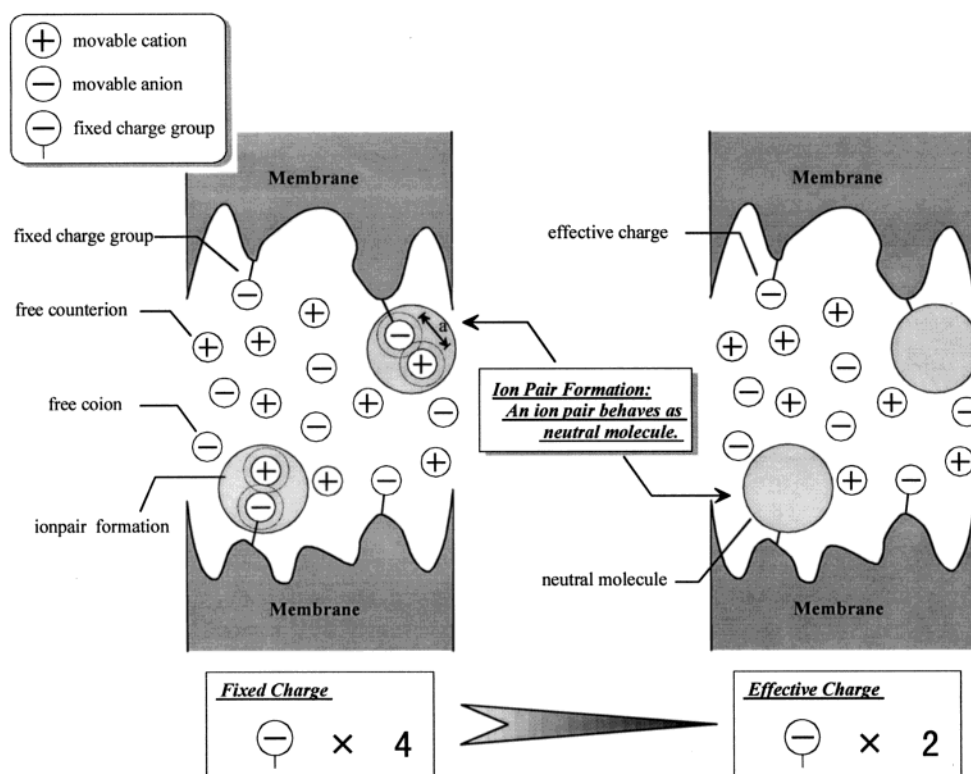


Figure 2. Simplified view of the ion-pair phenomena in a negatively charged membrane.

$$K_A = \frac{4\pi N_A a^3}{3 \times 10^{-3}} \exp \left[\frac{-z_1 z_X q^2}{4\pi \epsilon_v \epsilon_r a k_B T} \left(1 - \frac{z_1 + z_X}{2z_X} \frac{\kappa a}{1 + \kappa a} \right) \right] (-\alpha)^a (\bar{C}_{1m})^{1+a} \quad (2)$$

where N_A is Avogadro's number, a is the center-to-center distance between ions, q is the electronic charge, ϵ_v and ϵ_r are the dielectric constant of the vacuum and solvent, respectively, k_B is Boltzmann's constant, T is the absolute temperature, κ is the reciprocal of the Debye–Hückel length, and \bar{C}_{1m} is the concentration of counterions in the membrane.

2.2. Membrane Potential. The membrane transport system in this study is shown in Figure 1. The charged membrane, whose thickness is d , separates two solutions of the same electrolyte. $\bar{C}_{im}(x)$ represents the concentration of the i th species at coordinate x within the membrane. C_{iL} and C_{iR} denote the concentrations of the i th species in the bulk electrolyte solutions for the left-side cell and right-side cell, respectively. The basic assumptions of our theory are as follows:

(A-1) In the external electrolyte solutions, all electrolytes dissolve perfectly, and the activity coefficient of all ions is equal to unity.

(A-2) The osmotic pressure of the hydrostatic flow of water is negligible.

(A-3) The effect of the diffusion boundary layer at membrane–solution interfaces is negligible

2.2.1. Donnan Potential at the Membrane–Solution Interface. If a charged membrane is placed into an electrolyte solution, then there are considerable concentration differences between the membrane phase and the electrolyte solution phase. Then, the potential difference at the interface between the two phases, called the Donnan potential, is generated.

The electrochemical potentials of the i th species in an external electrolyte solution and in a membrane are given by μ_{iL} and $\bar{\mu}_{im}$, respectively.

$$\mu_{iL} = \mu_{iL}^0 + RT \ln C_{iL} + z_i F \phi_L \quad (3)$$

$$\bar{\mu}_{im} = \bar{\mu}_{im}^0 + RT \ln \bar{\gamma}_{im} \bar{C}_{im} + z_i F \bar{\phi}_m \quad (4)$$

μ_{iL}^0 and $\bar{\mu}_{im}^0$ are the standard electrochemical potentials of the i th species, C_{iL} is the concentration of the i th species, R is the gas constant, F is Faraday's constant, $\bar{\gamma}_{im}$ is the activity coefficient, and ϕ_L and $\bar{\phi}_m$ are the local electric potentials. Subscripts L and m denote the values in the external electrolyte solution for the left-side cell and the membrane, respectively.

In a state of Donnan equilibrium, that is, the electrolyte solution phase equilibrates with the membrane phase, μ_{iL} is always equal to $\bar{\mu}_{im}$.

$$\mu_{iL} = \bar{\mu}_{im} \quad (5)$$

The Donnan potential at the left interface, $\Delta\phi_{\text{Don}(L \rightarrow m)}$, is given from eqs 3–5 by

$$\Delta\phi_{\text{Don}(L \rightarrow m)} = \bar{\phi}_m - \phi_L = -\frac{RT}{z_i F} \ln \frac{\bar{\gamma}_{im} \bar{C}_{im}(0)}{k_i C_{iL}} \quad (6)$$

Here, k_i is the partition coefficient of the i th species.

$$\bar{\mu}_{im}^0 - \mu_{iL}^0 = -RT \ln k_i \quad (7)$$

Similarly, the Donnan potential at the right interface, $\Delta\phi_{\text{Don}(R \rightarrow m)}$, is expressed by

$$\Delta\phi_{\text{Don}(R \rightarrow m)} = \bar{\phi}_m - \phi_R = -\frac{RT}{z_i F} \ln \frac{\bar{\gamma}_{im} \bar{C}_{im}(d)}{k_i C_{iR}} \quad (8)$$

The total Donnan potential is then obtained by

$$\Delta\phi_{\text{Don}} = \Delta\phi_{\text{Don}(L \rightarrow m)} + \Delta\phi_{\text{Don}(m \rightarrow R)} = -\frac{RT}{F} \ln \frac{C_{iR} \bar{C}_{im}(0)}{C_{iL} \bar{C}_{im}(d)} \quad (9)$$

The condition of electroneutrality in the membrane and in the bulk electrolyte solutions requires that and

$$z_1 \bar{C}_{1m} + z_2 \bar{C}_{2m} + z_X \bar{C}_{Xm} = 0 \quad (10)$$

$$z_1 C_{1j} = -z_2 C_{2j} = z_1 z_2 C_{sj} \quad j = L, R \quad (11)$$

where C_{sj} is the salt concentration in the bulk electrolyte solutions.

According to eqs 6, 8, 10, and 11, the concentrations of cations and anions in the membrane at the left and right interfaces obey the following equations.

$$\bar{C}_{1m}(j)^{-z_2} \left\{ \bar{C}_{1m}(j) + \frac{z_X}{z_1} \bar{C}_{Xm}(j) \right\}^{z_1} - \left(\frac{\bar{\gamma}_{1m}}{k_1} \right)^{z_2} \left(\frac{\bar{\gamma}_{2m}}{k_2} \right)^{-z_1} (z_2 C_{sj})^{z_1 - z_2} = 0 \quad j = L, R \quad (12)$$

$$\bar{C}_{2m}(j)^{z_1} \left\{ \bar{C}_{2m}(j) + \frac{z_X}{z_2} \bar{C}_{Xm}(j) \right\}^{-z_2} - \left(\frac{\bar{\gamma}_{1m}}{k_1} \right)^{z_2} \left(\frac{\bar{\gamma}_{2m}}{k_2} \right)^{-z_1} (z_1 C_{sj})^{z_1 - z_2} = 0 \quad j = L, R \quad (13)$$

2.2.2. Diffusion Potential in the Membrane. If there is a concentration gradient of ions in a charged membrane, then the ions diffuse in the direction of that gradient. The polarization of the charge then tends to be generated because of the difference in ionic mobility between ions. However, to preserve local electroneutrality, the electric field (diffusion potential) is set up.

The basic equation describing the ionic transport through the charged membrane is the Nernst–Planck equation.

$$J_i = -\bar{D}_{im} \left(\frac{d\bar{C}_{im}}{dx} + z_i \bar{C}_{im} \frac{F}{RT} \frac{d\bar{\phi}_m}{dx} \right) \quad (14)$$

where J_i and \bar{D}_{im} are the ionic flux and the diffusion coefficient of the i th species in the membrane. In this study, we estimate the diffusion coefficient in the membrane to be that in the electrolyte solution for simplicity. (We confirmed that the influence of the diffusion coefficient in the membrane on the calculated results was not substantial.) By reordering eqs 2, 10, and 14, the following expressions are derived (Appendix A.1):

$$\frac{d\bar{\phi}_m}{dx} = \frac{\left(1 - \frac{z_2}{z_1} \right) \frac{d\bar{C}_{2m}}{dx} - \frac{z_X}{z_1} \frac{d\bar{C}_{Xm}}{dx} + \frac{J_1}{\bar{D}_{1m}} + \frac{J_2}{\bar{D}_{2m}}}{\frac{F}{RT} z_X \bar{C}_{Xm}} \quad (15)$$

$$\frac{d\bar{C}_{2m}}{dx} = \frac{J \frac{dC_{Xm}}{dx} + K}{1 - JH} \quad (16)$$

Here,

$$A = -\frac{1}{\beta} \left[1 + \frac{1}{K_A} \bar{C}_{Xm}^{(\alpha-1)} \{ (1 + \alpha) \bar{C}_{Xm} - \alpha C_{Xm} \} \right] \quad \left(\beta = \frac{z_2}{z_X} \right) \quad (17)$$

$$B = \frac{1}{K_A^2} \frac{1}{\beta} \bar{C}_{Xm}^\alpha [\bar{C}_{Xm} - C_{Xm}] \quad (18)$$

$$C = \frac{1}{K_A} \frac{1}{\beta} \bar{C}_{Xm}^\alpha \quad (19)$$

$$D = \frac{1}{2\kappa} \frac{1000N_A}{\epsilon_v \epsilon_r k_B T} \left[(z_2 q)^2 - \frac{z_2}{z_1} (z_1 q)^2 \right] \quad (20)$$

$$E = -\frac{1}{2\kappa} \frac{1000N_A}{\epsilon_v \epsilon_r k_B T} \frac{1}{\alpha} (z_1 q)^2 \quad (21)$$

$$F = K_A \left[\bar{C}_{lm} \frac{z_X + z_1}{2z_X} \frac{a}{(1 + \kappa a)^2} \frac{z_1 z_X q^2}{4\pi \epsilon_v \epsilon_r a k_B T} D - z_2 \bar{C}_{lm}^{-1} \left(\frac{1}{z_1} + \frac{1}{z_X} \right) \right] \quad (22)$$

$$G = K_A \left[\frac{z_X + z_1}{2z_X} \frac{a}{(1 + \kappa a)^2} \frac{z_1 z_X q^2}{4\pi \epsilon_v \epsilon_r a k_B T} E - \bar{C}_{lm}^{-1} \left(1 + \frac{1}{\alpha} \right) \right] \quad (23)$$

$$H = \frac{1 - BF}{A + BG} \quad (24)$$

$$I = \frac{-C}{A + BG} \quad (25)$$

$$J = \frac{\frac{z_2}{\alpha} \bar{C}_{2m}}{z_2 \bar{C}_{2m} \left(1 - \frac{z_2}{z_1} \right) + z_X \bar{C}_{Xm}} \quad (26)$$

$$K = \frac{-z_2 \bar{C}_{2m} \left(\frac{J_1}{D_1} + \frac{J_2}{D_2} \right) - z_X \bar{C}_{Xm} \frac{J_2}{D_2}}{z_2 \bar{C}_{2m} \left(1 - \frac{z_2}{z_1} \right) + z_X \bar{C}_{Xm}} \quad (27)$$

To obtain the ionic concentration and the electric potential profile in the membrane, eqs 15 and 16 must be solved using eqs 12 and 13 as boundary conditions. We have employed the following iterative procedure:

(1) We assume an arbitrary value for the flux of counterions, J_1 . The flux of co-ions, J_2 , can be calculated as $J_2 = -z_1 J_1 / z_2$, considering that the systems have no electric current.

(2) Equation 16 is solved using the modified Euler method with the boundary conditions at the left interface.

(3) We check the boundary conditions at the right interface. The initial value of the flux of counterions is changed and the numerical calculation is repeated until the solution satisfies the boundary conditions at the right interface.

We can then obtain the electric potential profile within the membrane to integrate eq 15. The diffusion potential ($\Delta\phi_{\text{dif}}$) in

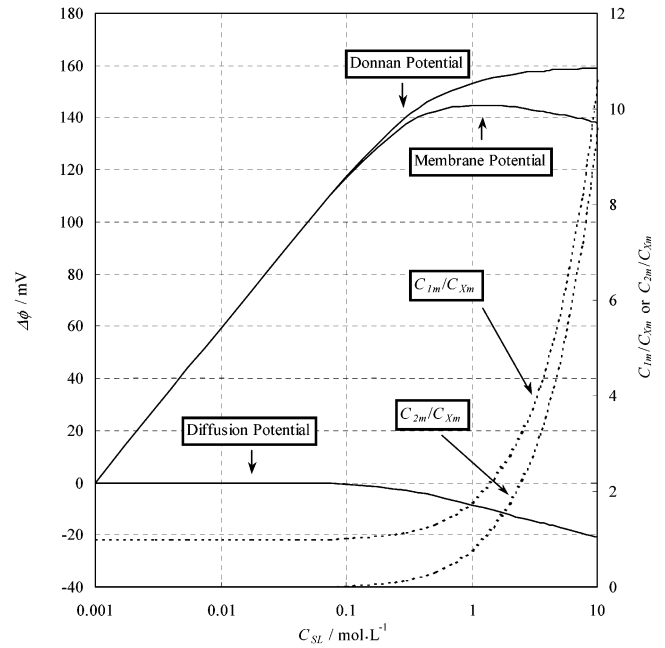


Figure 3. Potential profiles (membrane potentials, Donnan potentials, and diffusion potentials) and the ionic concentration (counterion and co-ion concentrations) in the membrane as a function of the salt concentration in the bulk electrolyte solutions for the left-side cell.

the membrane is calculated as

$$\Delta\phi_{\text{dif}} = \bar{\phi}(R) - \bar{\phi}(L) \quad (28)$$

The membrane potential, $\Delta\phi$, is the sum of the Donnan potentials and the diffusion potential.

$$\Delta\phi = \Delta\phi_{\text{Don}} + \Delta\phi_{\text{dif}} \quad (29)$$

It is noteworthy that by calculating the diffusion potential in the membrane numerically we can compute the membrane potential of the membrane with an inhomogeneous fixed-charge distribution.

3. Theoretical Calculation of Membrane Potential

3.1. Relationship between Membrane Potential and Permselectivity of the Charged Membrane. Figure 3 shows the potential profiles (membrane potentials, Donnan potentials, and diffusion potentials) and the ionic concentration (the counterion concentration and the co-ion concentration) in the membrane as a function of the salt concentration in the bulk electrolyte solutions for the left-side cell. The membrane potential goes through a maximum as the salt concentration increases. In the region where the membrane potential decreases with an increase in the salt concentration, the concentration of the co-ions in the membrane is steeply increased; the permselectivity of the charged membrane is decreased.

3.2. Influence of Ion Pairs on a Membrane Potential Profile. Figure 4 shows the distribution of the effective charge density (\bar{C}_{Xm}) inside the membrane along the direction of membrane thickness calculated by using eqs 9, 15, and 16. The effective charge density increased from the interface adjoining the left-side cell, which is filled with the high-concentration electrolyte solution, to that adjoining the right-side cell with the low-concentration electrolyte solution, although the fixed-charge density is constant at any point in the membrane. From this result, if there are ion pairs between the fixed-charge groups and counterions in the membrane, then the distribution of the effective charge is inhomogeneous even in a membrane with a homogeneous fixed-charge distribution. Therefore, the mem-

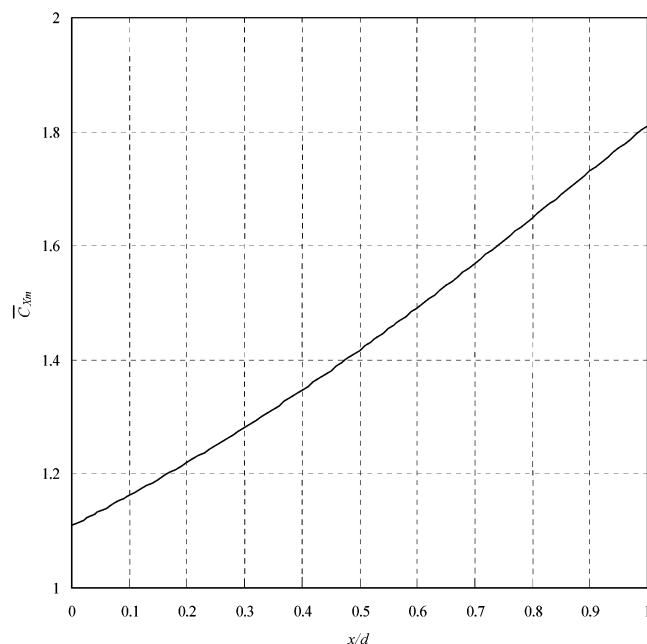


Figure 4. Theoretical prediction of the effective charge density (\bar{C}_{Xm}) as a function of distance inside the membrane along the direction of membrane thickness. In this case, $C_{Xm}(x) = 5.0$ M, $\epsilon_r = 78$, $a = 4$ Å, the salt is NaCl, and the salt concentration in the bulk electrolyte solutions for the left-side cell is 3.0 M.

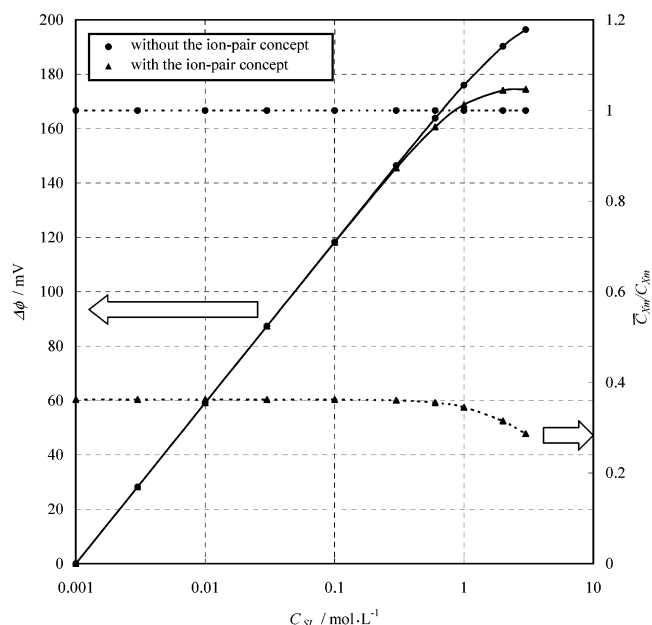


Figure 5. Theoretical prediction of membrane potentials (—) and charge effectiveness (···) as a function of salt concentration in the bulk electrolyte solutions for the left-side cell with (●) or without (▲) the ion-pair concept. In this case, $C_{Xm}(x) = 5.0$ M, $\epsilon_r = 78$, $a = 4$ Å, and the salt is NaCl.

brane must be treated as a membrane with an inhomogeneous fixed-charge distribution.

Figure 5 shows theoretical calculations of membrane potentials and the charge effectiveness (\bar{C}_{Xm}/C_{Xm}) as a function of the salt concentration in the bulk electrolyte solutions for the left-side cell with or without the ion-pair concept. From this Figure, if there are no ion pairs in the membrane, then the membrane potential is linearly increased with the external salt concentration because of adequate Donnan exclusion. However, fixed-charge groups pair with the counterions, the effective charge density of the membrane is decreased in the high external

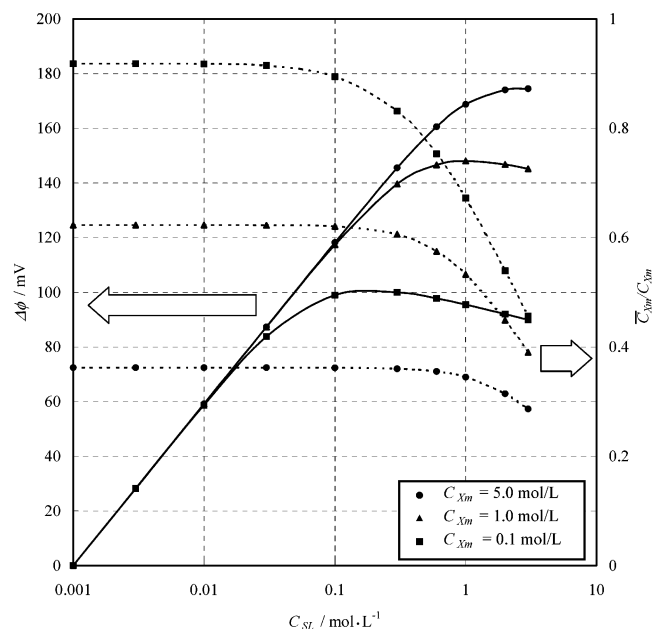


Figure 6. Theoretical prediction of membrane potentials (—) and charge effectiveness (···) as a function of salt concentration in the bulk electrolyte solutions for the left-side cell with fixed-charge densities of $C_{Xm}(x) = 5.0$ (●), 1.0 (▲), and 0.1 M (■). In this case, $\epsilon_r = 78$, $a = 4$ Å, and the salt is NaCl.

salt concentration region, and the membrane potential is lower than that of the membrane with no ion pairs. These results show that the ion pairs between the fixed-charge groups and counterions in the membrane cause the charged membrane to have a lower effective charge density and make the permselectivity of the charged membrane lower as the result.

3.3. Dependence of the Fixed-Charge Density in the Membrane on a Membrane Potential Profile. We exhibit calculation results of membrane potentials and the charge effectiveness at different fixed-charge densities in Figure 6. When the external electrolyte concentration is low compared to the fixed-charge density, the counterion concentration and the fixed-charge density in the membrane are almost the same. As a result, the membrane with a higher fixed-charge density has a lower value of the charge effectiveness because the ion association is enhanced if the concentration of counterions in the membrane is high (eq 1). When the external electrolyte concentration is higher than the fixed-charge density, a number of counterions go into the membrane as a consequence of the ineffectualness of Donnan exclusion. Therefore, the charge effectiveness is decreased steeply under that condition. From membrane-potential profiles, the permselectivity of the membrane with a higher fixed-charge density is, however, higher than that of the membrane with a lower fixed-charge density, contrary to the order of the charge effectiveness.

3.4. Dependence of Dielectric Constant on a Membrane Potential Profile. The dependence of membrane potentials and the charge effectiveness on the dielectric constant is shown in Figure 7. The permselectivity and charge effectiveness of the membrane are decreased with the decrease in the dielectric constant because the electrostatic interaction in the lower-dielectric-constant medium is stronger than that in the higher-dielectric-constant medium. The fixed-charge groups are then more likely to pair with the counterions in the membrane.

3.5. Dependence of Center-to-Center Distance in an Ion Pair on a Membrane Potential Profile. Figure 8 shows the

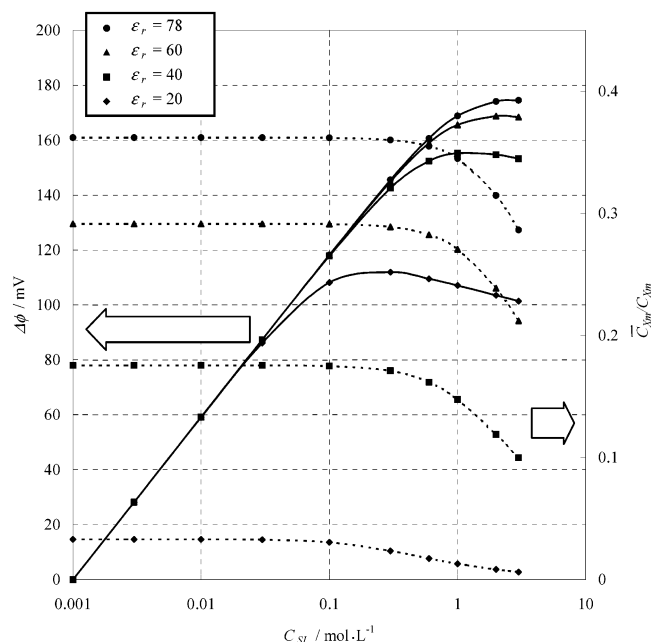


Figure 7. Theoretical prediction of membrane potentials (—) and charge effectiveness (···) as a function of salt concentration in the bulk electrolyte solutions for the left-side cell with dielectric constants of $\epsilon_r = 78$ (●), 60 (▲), 40 (■), and 20 (◆). In this case, $C_{Xm}(x) = 5.0$ M, $a = 4$ Å, and the salt is NaCl

dependence of membrane potentials and the charge effectiveness on the center-to-center distance in an ion pair. The permselectivity and charge effectiveness of the membrane are decreased with an increment of center-to-center distance when $\epsilon_r = 78$ and increased when $\epsilon_r = 20$. The Fuoss formalism applied to the association constant is composed of two factors. The term $(4\pi N_A a^3)/(3 \times 10^{-3})$ is a factor that expresses the increase in the probability of the collision of two ions by increasing the volume occupied by the ions. However, the exponential term stands for a shielding factor owing to the ion charges. From Figure 8, for a monovalent counterion, the former is dominant if the dielectric constant is high, and the latter is dominant for a low dielectric constant.

3.6. Dependence of the Valence of a Counterion on a Membrane Potential Profile. In Figure 9, we describe the calculation results of membrane potentials and the charge effectiveness for different kinds of counterion valences. As the discussion of dielectric constant dependence, the electrostatic interaction between the fixed-charge groups and divalent counterions is stronger than that between the fixed-charge groups and monovalent counterions. Therefore, the permselectivity of the membrane and the charge effectiveness are decreased with the increase in the valency of counterions.

4. Conclusions

We studied the theoretical aspects of ionic transport phenomena across charged membranes with low water content. The classical Fuoss approach to ion-pair formation was applied to calculate the association constant of ion pairs. To evaluate the membrane potentials across the membranes, we presented a new theoretical model considering the effects of both the inhomogeneities of the fixed-charge distribution and the ion pairs in the membrane. Our theoretical prediction suggested that the distribution of the effective charge is not uniform in a membrane even with a membrane with a homogeneous fixed-charge distribution if there are ion pairs between fixed-charge groups and counterions in the membrane. Therefore, the membrane

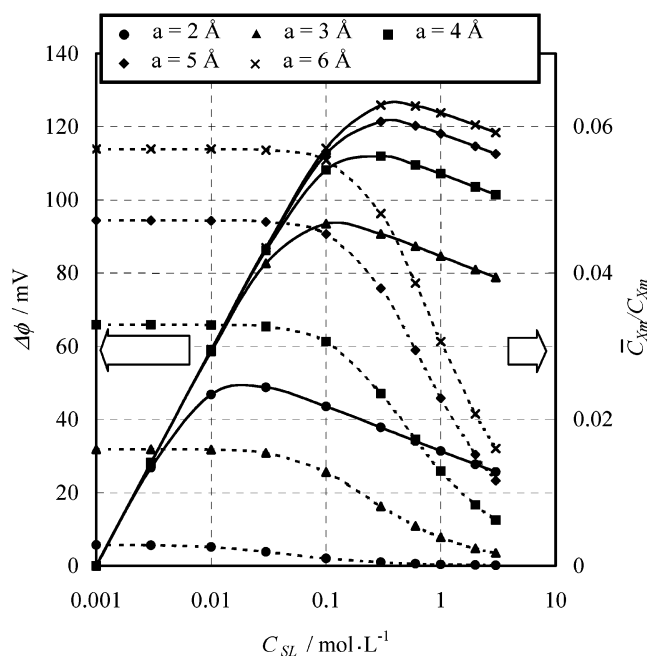
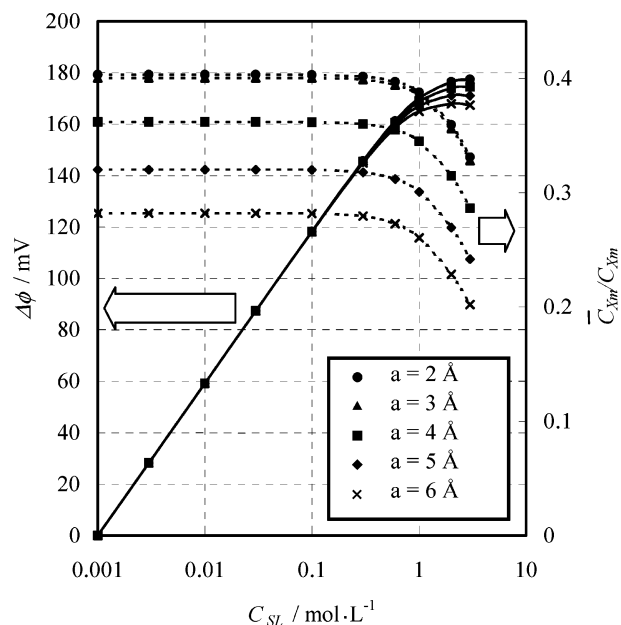


Figure 8. Theoretical prediction of membrane potentials (—) and charge effectiveness (···) as a function of salt concentration in the bulk electrolyte solutions for the left-side cell with center-to-center distances in an ion pair of $a = 2$ Å (●), 3 Å (▲), 4 Å (■), 5 Å (◆), and 6 Å (×). In this case, $C_{Xm}(x) = 5.0$ M, $\epsilon_r = 78$ (top) and 20 (bottom), and the salt is NaCl.

must be regarded as a membrane with an inhomogeneous fixed-charge distribution. The membrane potentials and effective charge density estimated by the theoretical model considering ion-pair formation are less than that determined by classical TMS theory; the larger the association constant of ion pairs, the smaller the membrane potentials and effective charge density. The association constant is increased with a dielectric constant decrease and with an increase in the valency of counterions. In addition, the dependence of the association constant on the center-to-center distance in an ion pair is determined by the competitive effect of two factors. One is the probability factor of the collision of two ions based on the volume occupied by the ions. The other is a shielding factor owing to the ionic charges.

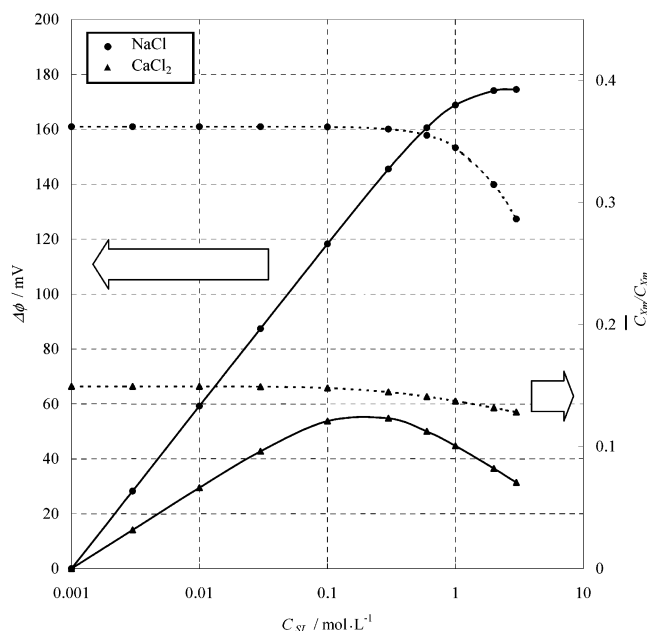
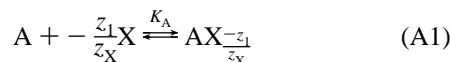


Figure 9. Theoretical prediction of membrane potentials (—) and charge effectiveness (···) as a function of salt concentration in the bulk electrolyte solutions for the left-side cell with counterion valences of $z_1 = 1$ (NaCl (●)) and 2 (CaCl₂ (▲)). In this case, $C_{xm}(x) = 5.0$ M, $\epsilon_r = 78$, and $a = 4$ Å.

Our theoretical model indicates that membranes with high fixed-charge density and high dielectric constant would be the ones with high effective charge density and high permselectivity. If a membrane has low water content, then the fixed-charge density of the membrane is high. Therefore, the permselectivity of the membranes with low water content is kept high. The charge effectiveness, however, decreased with the water-content decrease cited above. Experimental studies are now in progress to examine unclear effects, such as the dielectric constant of the membrane and the center-to-center distance in an ion pair, on the ionic transport behavior across charged membranes with low water content.

Appendix

A.1. Calculation of the Diffusion Potential across the Charged Membrane by Using the Transport Equations Including the Ion Pair Effect. To apply the Fuoss formalism to the ion pair in a membrane, we consider the following association equilibrium.



The association constant between fixed-charge groups and counterions in a membrane is rewritten as

$$K_A = \frac{4\pi N_A a^3}{3 \times 10^{-3}} \exp \left[\frac{-z_1 z_X q^2}{4\pi \epsilon_r \epsilon_0 a k_B T} \left(1 - \frac{z_1 + z_X}{2z_X} \frac{ka}{1 + ka} \right) \right] (-\alpha)^\alpha (\bar{C}_{1m})^{1+\alpha} \quad (A2)$$

The association equilibrium is shown as eq A1; then, that

equilibrium has the following association constant K_A .

$$K_A = \frac{[AX_{-\alpha}]}{[A][X]^{-\alpha}} = \frac{C_{xm} - \bar{C}_{xm}}{-\alpha} \frac{1}{\bar{C}_{1m} \bar{C}_{xm}^{-\alpha}} \quad (A3)$$

$$-\alpha K_A \bar{C}_{1m} \bar{C}_{xm}^{-\alpha} + \bar{C}_{xm} - C_{xm} = 0 \quad (A4)$$

The condition of electroneutrality in the membrane requires that

$$z_1 \bar{C}_{1m} + z_2 \bar{C}_{2m} + z_X \bar{C}_{xm} = 0 \quad (A5)$$

The bar denotes the values considered for the ion-pair concept. From eqs A4 and A5, we can obtain the following equation.

$$\bar{C}_{2m} = -\frac{1}{\beta} \bar{C}_{xm} \left[1 + \frac{1}{K_A} \bar{C}_{xm}^{\alpha-1} (\bar{C}_{xm} - C_{xm}) \right] \quad (A6)$$

Equation A6 is differentiated with respect to x , which is the coordinate along the direction of membrane thickness.

$$\frac{d\bar{C}_{2m}}{dx} = A \frac{d\bar{C}_{xm}}{dx} + B \frac{dK_A}{dx} + C \frac{dC_{xm}}{dx} \quad (A7)$$

Before we differentiate eq A2, the derivative dK/dx is calculated.

$$\kappa = \sqrt{\frac{1000 N_A \{ (z_1 q)^2 \bar{C}_{1m} + (z_2 q)^2 \bar{C}_{2m} \}}{\epsilon_r \epsilon_0 k_B T}} \quad (A8)$$

$$\frac{d\kappa}{dx} = D \frac{d\bar{C}_{2m}}{dx} + E \frac{d\bar{C}_{xm}}{dx} \quad (A9)$$

We can then get the derivative dK_A/dx by using eq A9 as follows:

$$\frac{dK_A}{dx} = F \frac{d\bar{C}_{2m}}{dx} + G \frac{d\bar{C}_{xm}}{dx} \quad (A10)$$

From eqs A7 and A10, we obtain the following differential equation.

$$\frac{d\bar{C}_{xm}}{dx} = \frac{(1 - BF) \frac{d\bar{C}_{2m}}{dx} - C \frac{dC_{xm}}{dx}}{A + BG} \equiv H \frac{d\bar{C}_{2m}}{dx} + I \frac{dC_{xm}}{dx} \quad (A11)$$

The basic equation describing the ionic transport through a charged membrane is the Nernst–Planck equation (eq 14).

By reordering eqs A4 and 14, the following expressions are derived:

$$\frac{d\bar{C}_{2m}}{dx} = J \frac{d\bar{C}_{xm}}{dx} + K \quad (A12)$$

Finally, by using eqs A11 and A12, the derivative $d\bar{C}_{2m}/dx$ is expressed as follows:

$$\frac{d\bar{C}_{2m}}{dx} = \frac{JI \frac{dC_{xm}}{dx} + K}{1 - JH} \quad (A13)$$

List of Symbols

a : center-to-center distance in an ion pair

C_{im} : concentration of the i th species in the membrane

C_{iL} , C_{iR} : concentrations of the i th species in bulk electrolyte solutions for left-side and right-side cells, respectively

C_{sL} , C_{sR} : salt concentrations in bulk electrolyte solutions for left-side and right-side cells, respectively

D_{im} : diffusion coefficient of the i th species in the membrane

F : Faraday's constant

J_i : ionic flux of the i th species in the membrane

K_A : association constant between fixed-charge groups and counterions in a membrane

k_B : Boltzmann's constant

N_A : Avogadro's number

q : electronic charge

R : gas constant

T : absolute temperature

z_i : valence of the i th species

α : z_1/z_X

β : z_2/z_X

$\Delta\phi$: membrane potential

$\Delta\phi_{\text{dif}}$: diffusion potential in the membrane

$\Delta\phi_{\text{Don}}$: Donnan potential across the membrane

$\Delta\phi_{\text{Don(L-m)}}$: Donnan potential at the left interface

ϵ_v , ϵ_r : dielectric constants of the vacuum and solvent, respectively

$\phi(L)$, $\phi(R)$: diffusion potentials at the left and right interfaces, respectively

ϕ_L , ϕ_R , ϕ_m : local electric potentials

γ_{im} : activity coefficient of the i th species in the membrane

κ : reciprocal of the Debye–Hückel length

μ_{iL} , μ_{iL}^0 : electrochemical potential and the standard electrochemical potential of the i th species in the external electrolyte solution for the left-side cell, respectively

μ_{im} , μ_{im}^0 : electrochemical potential and the standard electrochemical potential of the i th species in the membrane, respectively

subscript i : 1 for counterions, 2 for co-ions, and X for fixed-charge groups

References and Notes

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