

# Ion-Pairing Effects in Charged Membranes with Low Water Contents

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Recently, applications of charged membranes with low water contents in severe condition become more attractive fields: fuel cell, the recovery of high concentrated acid/alkali, and high-temperature membrane process. These applications require the membrane properties such as high charge density, low volume flux, and high stability (mechanical, chemical, and thermal). The low-water-content membrane is a promising alternative for these properties. Ionic transport phenomenon across the low-water-content charged membranes, however, has not verified both theoretically and experimentally. In the present study, we prepared charged membranes with low water contents by radical copolymerization and then analyzed their membrane potentials in order to elucidate ionic transport behavior across the membranes. The experimental results could be explained by the theoretical model considering the ion-pairing effect in the membranes (i.e., electrostatic interaction between the fixed-charged group and counterion in the membrane).

Key words: charged membrane, low water content, membrane potential, ion pair, fuel cell

## 1. INTRODUCTION

Recently, the applications of charged membranes with low water contents in severe condition become more attractive fields: fuel cell, the recovery of high concentrated acid/alkali, 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 membrane is a useful option.

Ionic transport phenomenon through charged membrane is strongly affected by the fixed-charge groups in the membrane. All of the fixed-charge groups in the membrane do not function perfectly. The fixed-charge density of the membrane estimated by the ionic transport procedure (membrane potential method) is less than that by the equilibrium procedure (titration method). It has been considered that this phenomenon is attributed to decrease of the activity of electrolytes in the membrane such as the ion pairing between the fixed-charge group and counterion in the membrane. Recently, Mafé et al. have proposed a theoretical model considering ion-pairing effect between the fixed-charge groups and counterions in the membrane [1]. According to their model, most of ion-pairing effect is more substantial in the low dielectric constant condition (e.g., nonaqueous solution system and low-water-content membrane system). Chou et al. studied the ion-pairing effect in the nonaqueous solution system, and revealed that theoretical predictions agreed well with the experimental results from the membrane potential and permeability measurements [2-5]. The ion-pairing effect in the low-water-content membrane system, on the other hand, has not verified experimentally.

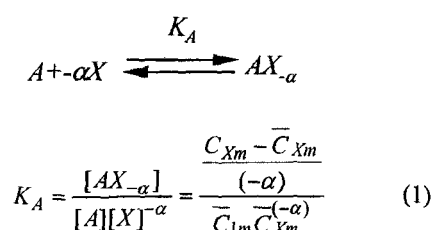
In the present study, we prepared low-water-content charged membranes by radical copolymerization and examined ion-pairing effect based on membrane potential measurements in order to elucidate ionic

transport behavior across the low-water-content charged membranes.

## 2. THEORY

### 2.1 Ion-pair formation in membrane

Here, we adapted a simple model based on the Fuoss approach to ion-pair formation in electrolyte solutions [6]. To apply the Fuoss formalism to the ion pair in a membrane, we consider the following association equilibrium.



where  $X$  and  $A$  represent fixed-charge groups and counterions, respectively,  $\alpha = z_1/z_X$  and  $z_i$  is the valence of  $i$ th species ( $i = 1$  for counterion,  $i = 2$  for coion, and  $i = X$  for fixed-charge group). The valence of the fixed-charge groups in the membrane is +1 or -1. The association constant between fixed-charge groups and counterions in a membrane is rewritten as

$$K_A = \frac{4\pi N_A a^3}{3 \times 10^{-3}} \exp(b) (-\alpha)^\alpha (\bar{C}_{1m})^{1+\alpha}$$

$$b = \frac{-z_1 z_X q^2}{4\pi \epsilon_v \epsilon_r a k_B T} \left( 1 - \frac{z_1 + z_X}{2z_X} \frac{\kappa a}{1 + \kappa a} \right) \quad (2)$$

where  $N_A$  is Avogadro's number,  $a$  is the center-to-center distance between ions,  $q$  is the

electronic charge,  $\epsilon_v$  and  $\epsilon_r$  are the dielectric constant of the vacuum and solvent, respectively,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\kappa$  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 used 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 membrane potential,  $\Delta\phi$ , is the sum of the Donnan potentials at the left and right interfaces and the diffusion potential in the membrane:

$$\Delta\phi = \Delta\phi_L + \Delta\phi_{df} + \Delta\phi_R \quad (3)$$

We can compute the membrane potential by calculating the diffusion potential across the membrane by the transport equations including ion-pairing effect (Details of calculation were described in Ref [7]).

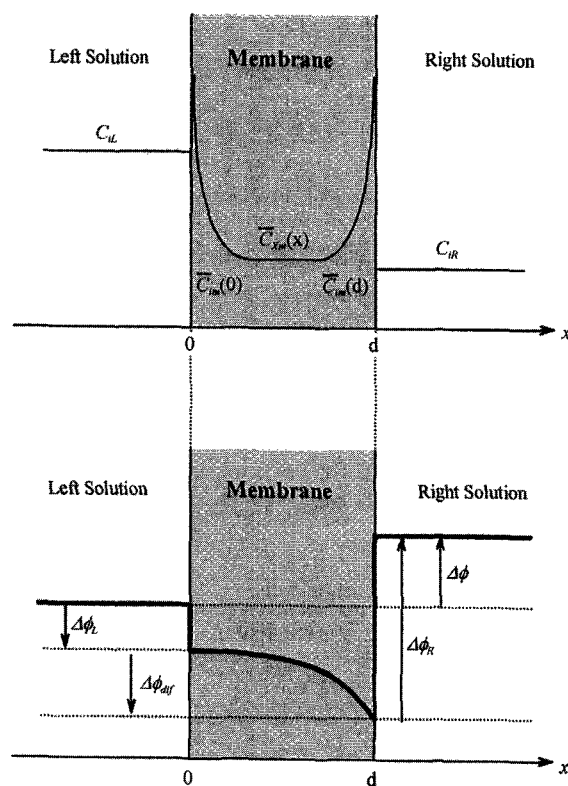


Fig.1 Schematic diagram of the membrane transport system.

## 3. EXPERIMENTAL SECTION

### 3.1 Membrane preparation

Cation-exchange membranes (CEMs), composed of poly(styrene-co-divinylbenzene) containing sulfonic acid groups, and anion-exchange membranes (AEMs), composed of poly(styrene-co-4-vinylpyridine-co-divinylbenzene) containing quaternary pyridinium groups were prepared by radical copolymerization [8, 9].

### 3.2 Membrane potential

A membrane was installed at the center of the measuring cell, which had two acrylic containers, one on either side of the membrane. Both containers were filled with the electrolyte solutions of different concentration: the concentration of right container was kept constant at 1 mmol/l and that of left one was varied from 1 mmol/l to 3.0 mol/l. KCl, NaCl, LiCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> were used to measure the membrane potentials of CEMs. NaCl, NaBr, NaI, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> were used to measure the membrane potentials of AEMs. All measurements were carried out at 25 ± 0.1°C.

## 4. RESULTS AND DISCUSSION

The physicochemical properties of the prepared membranes are summarized in Table 1. We succeed in preparing the low-water-content charged membranes, whose water contents are less than 10%, by radical copolymerization. The calculated results of membrane potential based on the theoretical model considering the ion-pairing effect agreed well with the experimental ones. Figure 2 shows dielectric constant in the membranes as a function of the water content from our theoretical analysis. Figure 3 shows the charge effectiveness of the membranes as a function of the water content. The charge effectiveness ( $Q$ ) of the membrane is defined as follows.

$$Q = \frac{\frac{1}{d} \int_0^d \bar{C}_{xm}(x) dx}{C_{xm}} \quad (4)$$

Table I. Physicochemical properties of prepared membranes

Membrane	Water Content* (w/w%)	Exchange Capacity (meq./g-dry memb.)	Fixed Charge Density (mol/l)	Thickness (μm)
CEM-1	6.7	0.62	8.6	50
CEM-2	15	1.5	8.5	50
CEM-3	40	2.9	4.2	50
Aciplex K-501**	30	1.5	5.5	170
AEM-1	9.0	0.58	5.9	50
AEM-2	11	0.71	5.6	50
AEM-3	22	0.77	2.7	50
Aciplex A-501**	26	1.4	5.4	140

\*water content =  $(w_{wet} - w_{dry})/w_{wet}$ , where  $w_{wet}$  = the membrane weight in the equilibrium swollen state and  $w_{dry}$  = the membrane weight in the dry state.

\*\* commercial hydrocarbon-type ion-exchange membranes from Asahi Kasei Corporation.

The estimated dielectric constant ( $\epsilon_r$ ) in the membrane is smaller than that in the bulk water; and the charge effectiveness ( $Q$ ) of the membrane was small ( $< 0.3$ ). These results suggested that fixed-charge groups in the membrane were neutralized by associated counterions. This is attributed to the dielectric saturation in the membrane. The charge effectiveness ( $Q$ ) of the membrane in divalent counterion system ( $MgCl_2$  and  $CaCl_2$  for CEMs;  $Na_2SO_4$  for AEMs) is much lower than that in monovalent counterion system. This phenomenon can be also explained by ion-pairing effect: the electrostatic interaction between fixed-charge group and counterion depends on the valence of ions.

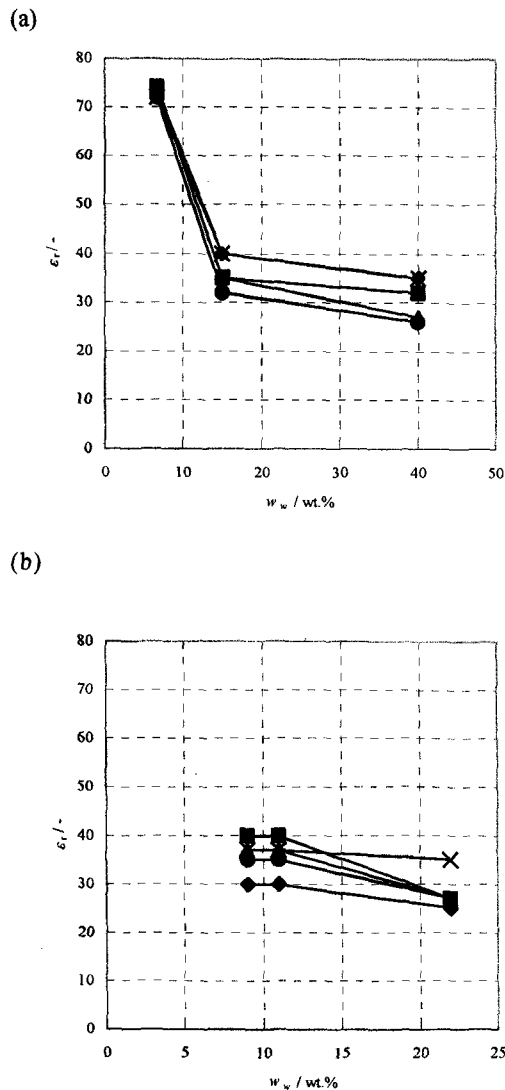


Fig.2. Dielectric constant ( $\epsilon_r$ ) of charged membranes as a function of the water content from theoretical analysis: (a) for CEMs. ●, ▲, ■, ◆, and × represent KCl, NaCl, LiCl,  $CaCl_2$ , and  $MgCl_2$  for respectively; (b) for AEMs. ●, ▲, ■, ◆, and × represent NaCl, NaBr, NaI,  $NaNO_3$ , and  $Na_2SO_4$ , respectively.

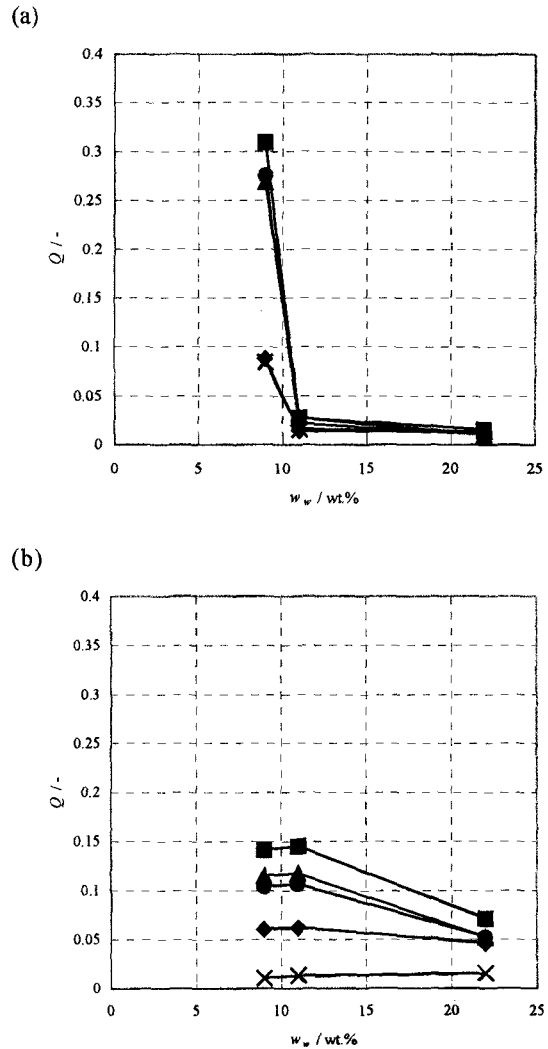


Fig.3. Charge effectiveness ( $Q$ ) of charged membranes as a function of the water content: (a) for CEMs. ●, ▲, ■, ◆, and × represent KCl, NaCl, LiCl,  $CaCl_2$ , and  $MgCl_2$  for respectively; (b) for AEMs. ●, ▲, ■, ◆, and × represent NaCl, NaBr, NaI,  $NaNO_3$ , and  $Na_2SO_4$ , respectively.

### 5. CONCLUSIONS

In the present study, we examined the ion-pairing effect in the low-water-content charged membranes. The membrane potential measurements supported that the ion-pairing effect was substantial in the low-water-content membrane system. Our theoretical analysis also demonstrated the followings: (i) Dielectric constants in the membranes were smaller than the values in bulk water. (ii) The water-content dependence of the charge effectiveness ( $Q$ ) of the membranes obeyed that of the dielectric constants in the membranes. The charge effectiveness of membranes increased with the decrease of water content in the membranes, especially for CEMs. This result indicates that charged membranes with low water contents would be ones with high charge effectiveness and permselectivity.

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