Membrane Potential Across Charged Membranes in Organic Solutions

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The membrane potentials across cation- and anion-exchange membranes were measured for five LiBr−various-solvent systems. Water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol were used as the solvents in this work. The experimental data were analyzed on the basis of the Donnan equilibrium and the Nernst−Planck equation of ion flux considering the effect of ion pairing of the electrolyte in the external solution. The Fuoss formalism of ion pairing was adopted to estimate the effective ion concentration in the external solutions, and the theoretical predictions agreed well with the experimental data. The effective membrane charge densities and the cation-to-anion mobility ratios in the membrane were also determined in this work. The results showed that the effective membrane charge density will vary with the kind of solvent. We attempted to introduce the concept of ion pairing inside the membrane to clarify this phenomenon.

1. Introduction

The measure of the membrane potential is a significant method for characterizing the ion-transport phenomena across a charged membrane.[1,2] Theoretically, the membrane potential in a charged membrane−electrolyte aqueous solution system developed by Teorell, Meyer, and Sievers (TMS) can be treated by the Donnan equilibrium theory and the Nernst−Planck equation if it is assumed that the fixed charge groups are homogeneously distributed in the membrane[3] and the effect of the mean activity coefficient of the electrolyte in the external solution is negligible. The ion-transport phenomena across a charged membrane in an aqueous solution system have been studied by many authors.[4−11] However, the studies and experimental data available for the electrolyte−organic-solvent systems are limited,[12,13] thus the transport phenomena in these systems are not so clear.

In the present paper, the membrane potentials in five LiBr−various-solvent systems were measured and fitted to the equation which is based on the Donnan equilibrium and the Nernst−Planck equation considering the effect of ion pairing in the external solutions. Water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol were used as the solvents in this work. Because the studies and experimental data of the mean activity coefficient of the electrolyte in the organic solvent systems are limited, we adopted the Fuoss formalism of ion pairing to estimate the effective ion concentration in the external solutions. It is interesting to investigate whether those theoretical considerations cited above can be applied to electrolyte−organic-solvent systems. The experimental results are compared with the calculated ones in order to confirm that the extension of the TMS theory considering the effect of ion pairing in the external solutions can be applied well in such systems.

The effective membrane charge densities and the cation-to-anion mobility ratios in the membrane were also determined in order to examine whether the effective membrane charge density will vary with the kind of solvent. It is postulated that the counterions prefer to form ion pairs with the fixed-charge groups in the organic solvent systems because the dielectric constants of the organic solvents are smaller than that of water. Thus, the ion pairs between the counterions and fixed-charge groups will increase in the organic solvent systems to cause a decrease in the effective membrane charge density.

2. Theory

2.1. Membrane Potential. According to the studies of Teorell, Meyer, and Sievers, the potential difference across a membrane separating two baths which have different concentrations of aqueous solutions can be expressed by the sum of the Donnan potential between the membrane surface and the external solutions and the diffusion potential in the membrane. In a previous paper,[14] it was confirmed that their idea is also applicable to electrolyte−organic-solvent systems by a serious theoretical process.

The membrane potential, $\Delta\phi$, is the sum of the Donnan potential, $\Delta\phi_{\mathrm{Don}(1\rightarrow r)}$, and the membrane diffusion potential, $\Delta\phi_{\mathrm{diff}}$, given in a previous paper for the system of a salt whose cation has the same valence as the anion[14]

$$\Delta\phi = \Delta\phi_{\mathrm{Don}(1\rightarrow r)} + \Delta\phi_{\mathrm{diff}} \tag{1}$$

where

$$\Delta\phi_{\mathrm{Don}(1\rightarrow r)} = -\frac{RT}{z_+ F}\ln\left[\frac{\gamma_\pm'' C_s'' \bar{C}_+'}{\gamma_\pm' C_s' \bar{C}_+''}\right] \tag{2}$$

$$\Delta\phi_{\mathrm{diff}} = -\frac{RT}{z_+ F}\frac{r-1}{r+1}\ln\left[\frac{(r+1)\bar{C}_+'' + \frac{z_x}{z_+}C_x}{(r+1)\bar{C}_+' + \frac{z_x}{z_+}C_x}\right] \tag{3}$$

R is the gas constant, T is the absolute temperature, F is the Faraday constant, z_+ is the valence of the cation, z_x is the valence of the fixed charge groups, C_x is the fixed charge density, C_s is the electrolyte concentration in the external solution, $\gamma_\pm$ is the mean activity coefficient of the electrolyte in the external

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solution, r is the cation mobility, $\bar{\omega}_+$, to the anion mobility, $\bar{\omega}_-$, ratio in the membrane phase defined by

$$r = \frac{\bar{\omega}_+}{\bar{\omega}_-} \tag{4}$$

and $\bar{C}_+$ is the cation concentration in the charged membrane given by

$$\bar{C}_+ = \sqrt{\left(\frac{z_x C_x}{2z_+}\right)^2 + \left(\frac{\gamma_\pm C_s}{Q}\right)^2} - \frac{z_x C_x}{2z_+} \tag{5}$$

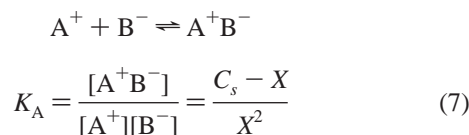where

$$Q = \left(\frac{\bar{\gamma}_+ \bar{\gamma}_-}{k_+ k_-}\right)^{1/2} \tag{6}$$

$\bar{\gamma}_+$ and $\bar{\gamma}_-$ are the cation and anion activity coefficients, respectively, and k_+ and k_- are the distribution coefficients of the cation and anion, respectively. The superscripts $'$ and $''$ indicate the left and right sides of the system, respectively.

2.2. Effect of Ion Pairing in the External Solutions. In eqs 2 and 5, the mean activity coefficient of the electrolyte, is multiplied by the electrolyte concentration, C_s, in the external solutions. The effect of the mean activity coefficient of the electrolyte is usually neglected in aqueous solutions, but it cannot be neglected in organic solutions because of the low dielectric constant of the organic solvent. Unfortunately, the studies and experimental data on the mean activity coefficient of the electrolyte in the organic solutions are limited.[15−18] In this work, we attempt to adopt the concept of ion pairing to estimate the nonideality caused by the associating effect of ions in the external solutions.

At somewhat higher concentrations, the mutual distances between cations and anions decrease sufficiently for the ion−ion interactions to become significant. The effect causes the association of the cation and anion and forms the ion pair in the solution

$$A^+ + B^- \rightleftharpoons A^+B^-$$

$$K_A = \frac{[A^+B^-]}{[A^+][B^-]} = \frac{C_s - X}{X^2} \tag{7}$$

where K_A is the association constant, $[A^+B^-]$, $[A^+]$, and $[B^-]$ are the ion pair and cation and anion concentrations in the solution, respectively, and X is the effective ion concentration.

Application of the Fuoss formalism for the association constant of the ion pair is expressed by[19−22]

$$K_A = \frac{4\pi N_A}{3 \times 10^{-3}} a^3 \exp(b) \tag{8}$$

$$b = \frac{e^2}{4\pi\epsilon_0\epsilon_s akT} \tag{9}$$

where N_A is Avogadro's number, e is the electronic charge, ϵ_s is the dielectric constant of the solvent, ϵ_0 is the vacuum permittivity, k is the Boltzmann constant, and a is the contact distance.
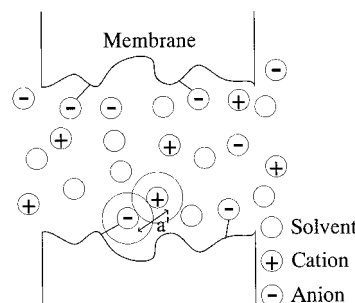

Figure 1. Simplified view of the membrane and the external solutions. The ion pairing phenomena between the free counterion and the fixed-charge group in the membrane phase are schematically shown.

By substituting the calculation result of K_A in eq 8 into eq 7, the effective ion concentration in the external solution can be obtained.

2.3. Effective Membrane Charge Density. To explicitly evaluate the interaction of ion pairs between the counterion and the fixed-charge group in the membrane phase, we have presented a very simple model that is based on the Fuoss approach to ion pairing in electrolyte solutions in the previous papers.[14,23,24] Figure 1 schematically shows the ion pairing phenomena. A membrane region with a low dielectric constant solvent including the membrane charge groups, the counterions, and some sorbed electrolyte in equilibrium with the external electrolyte solution is schematically represented.

The theoretical formalism for estimating effective membrane charge density, QC_x, can be expressed[14]

$$QC_x = \frac{C_x}{\dfrac{4\pi N_A}{3 \times 10^{-3}} k'(a')^3 \exp\left(\dfrac{e^2}{4\pi\epsilon_0 a'kT\epsilon_s}\right) + 1} \tag{10}$$

where a' is the contact distance between the counterion and the fixed-charge group in the membrane phase and k' is a constant indicating the effect of the association constant on the membrane charge density.

Some of the assumptions introduced when the Fuoss formalism is applied to the membrane phase may also be questionable because, in this case, one of the ions in the ion pair is fixed. The entropy term for ion-pairing formation is neglected in the Fuoss approach because the resulting ion pairing can move freely in the solution, which is not the case here (see Figure 1). The deviation caused by this problem can be compensated by the regressing process of two parameters a' and k' in the present model.

3. Experimental Section

3.1. Materials. A cation-exchange membrane (K-101, Asahi Chemicals), which is composed of poly(divinylbenzene-*co*-styrene) containing sulfonic acid groups in a polymer matrix, and an anion-exchange membrane (A-201, Asahi Chemicals), which is composed of poly(butadiene-*co*-styrene) containing quaternary amine groups in a polymer matrix, were used for the measurements. The thickness, water content, and ion-exchange capacity of both membranes that were measured and provided by the manufacturer are given in Table 1. Before the measurements were carried out, both membranes were immersed in a 3 mol/L LiBr aqueous solution for 3 days to ensure that the counterions were exchanged for the same species. After both membranes were thoroughly washed with ion-exchanged water, they were immersed in ion-exchanged water for 3 days to remove the excess ions in the membrane matrixes. Finally,

TABLE 1: Physicochemical Properties of the Studied Ion-Exchange Membranes

membrane	thickness (mm)	water content (wt %)	ion-exchange capacity (meq/g)
K-101	0.22	27	1.9
A-201	0.23	26	1.5

both membranes were immersed in ion-exchanged water [H_2O], dimethyl sulfoxide [$(CH_3)_2SO$], ethylene glycol [$HOCH_2CH_2$-OH], methanol [CH_3OH], and *n*-propanol [$CH_3CH_2CH_2OH$] for 1 week to ensure that the solvents were sorbed in the membrane phase.

3.2. Measurement of Equilibrium Swelling Degree. The equilibrium swelling degree of both membranes, S, was decided by determining the weight difference between the solvent-swollen membrane and the membrane vacuum-dried at 110 °C. The membrane was swollen by soaking it in the solvent at 20 °C for 1 week and carefully removing the surface solvent with filter paper. The equilibrium swelling degree was defined by[25]

$$S = \frac{W_w - W_d}{W_d} \tag{11}$$

where W_w and W_d are the weights of the membrane in the equilibrium wet and dry states, respectively.

The fixed charge density, C_x, of the membrane could be calculated by

$$C_x = \frac{d}{S} C_{capacity} \tag{12}$$

where $C_{capacity}$ is the ion-exchange capacity of the membrane in meq/g of dry membrane and d is the density of the solvent in g/cm^3.

3.3. Measurement of Membrane Potential. The membrane potentials of both membranes used in this work were measured to obtain the effective membrane charge densities and the cation-to-anion mobility ratios in the membrane with the various solvents at 20.0 ± 0.5 °C. A charged membrane was installed at the center of the measuring cell, which had two glass containers, one on either side of the membrane. The volume of each container was 200 cm^3, and the membrane area was 7.55 cm^2. Electrolyte solutions of different concentrations were poured into these containers; the concentration in the left container was varied from 0.001 to 2.0 mol/L, and that in the right was kept constant at 0.001 mol/L. The solvents used in this work were water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol. An electrometer (TOA HM-20E) connected to glass electrodes (TOA HS-205C) was used for the measurement of the electrical potential. Two glass electrodes were placed in saturated KCl solutions which were connected to the containers by salt bridges. LiBr was used as a strong electrolyte to measure the membrane potential. The solutions in both containers were stirred by magnetic stirrers to minimize the effect of the boundary layers on the membrane potential.

4. Results and Discussion

The measured results for the equilibrium swelling degree, S, and the fixed-charge density, C_x, of both membranes in the various solvents are listed in Table 2. Both membranes are cross-linked; therefore, they are not swelled so much by the organic solvents, so that the values of S are similar in the various solvents.

TABLE 2: Experimental Results of the Equilibrium Swelling Degree, S, and Fixed Charge Density, C_x, in Various Solvents

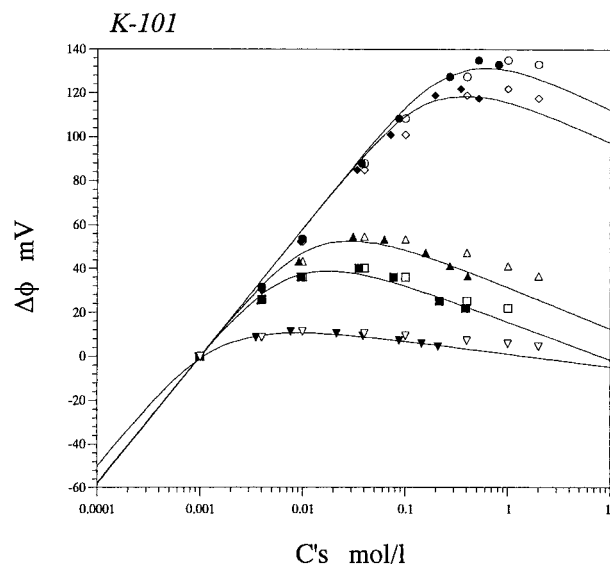|	K-101		A-201	
solvent	S	C_x (mol/L)	S	C_x (mol/L)
water	0.39	−4.9	0.37	4.1
dimethyl sulfoxide	0.41	−5.1	0.45	3.7
ethylene glycol	0.43	−4.9	0.42	4.0
methanol	0.37	−4.0	0.39	3.0
n-propanol	0.41	−3.7	0.45	2.7

Figure 2. Membrane potentials of the cation-exchange membrane for the various solvents. ●, ■, ◆, ▲, and ▼, respectively, indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol, considering the effect of ion pairing in the external solutions. ○, □, ◇, △, and ▽, respectively, indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol, neglecting the effect of ion pairing in the external solutions. Solid lines are the theoretical results obtained by fitting the experimental data to eq 1.

The results for the membrane potentials of K-101 and A-201 are shown in Figures 2 and 3, respectively. In Figures 2 and 3, the experimental data obtained by considering and neglecting the effect of ion pairing in the external solutions are shown by black and hollow marks, respectively, and the theoretical results for the LiBr solutions calculated by eq 1 are shown as lines. From Figures 2 and 3, it can be found that the theoretical lines agree well with the experimental data corrected by considering the effect of ion pairing in the external solutions, and some deviations exist between the theoretical lines and the uncorrected experimental data. One of the reasons is that the mean activity coefficients of the electrolyte do not equal unity, especially in the regions of low dielectric constant and high concentration, so that the amount of the ion pairs in the external solutions will increase to above 90%. If we neglect the nonideality caused by the associating effect of the ions, this will cause some errors to occur. The structure inhomogeneities of the membranes may be another factor that causes the deviations. But based on the experimental results that the deviations increase with the decreases of the electric constants, we explain the deviations as being caused by the effect of ion pairing in the external solutions rather than the effect of the structure inhomogeneities of the membranes. In fact, because both membranes used in this work have somewhat large fixed-charge densities and low water content, the assumption of neglecting the effect of the inhomogeneity in this work would be quite reasonable.[26]
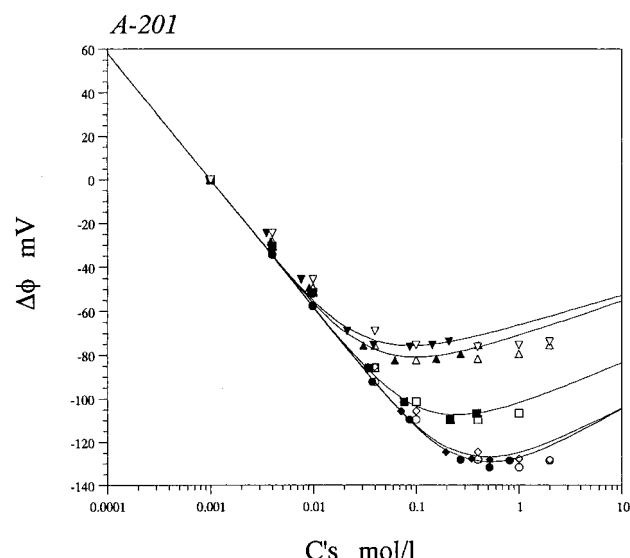
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Figure 3. Membrane potential of the anion-exchange membrane for the various solvents. ●, ■, ◆, ▲, and ▼, respectively, indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol, considering the effect of ion pairing in the external solutions. ○, □, ◇, △, and ▽, respectively, indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol, neglecting the effect of ion pairing in the external solutions. Solid lines are the theoretical results obtained by fitting the experimental data to eq 1.

TABLE 3: Values of Effective Membrane Charge Density, QC_x, and the Cation:Anion Mobility Ratio in Membrane, *r*, in Various Solvents

| | K-101 | | A-201 | |
solvent	QC_x (mol/L)	$r = \bar{\omega}_+/\bar{\omega}_-$	QC_x (mol/L)	$r = \bar{\omega}_+/\bar{\omega}_-$
water	−0.48	0.43	0.51	2.9
dimethyl sulfoxide	−0.010	0.46	0.17	2.1
ethylene glycol	−0.27	0.36	0.43	2.5
methanol	−0.018	0.51	0.052	1.8
n-propanol	−0.0016	0.68	0.039	1.6

The effective membrane charge density, QC_x, and the cation-to-anion mobility ratio in the membrane, *r*, are estimated by applying eq 1 to the corrected experimental data, considering the effect of ion pairing in the external solutions with a nonlinear regression process. In the process of estimation, C_s' and C_s'' are the experimental results and QC_x and *r* are the unknown parameters. The values of QC_x and *r* in the various solvents are given in Table 3.

Applying the values of C_x in Table 2 and the values of QC_x in Table 3, the values of *Q* can be calculated and are shown in Figure 4 as a function of the specific dielectric constant. *Q* is also calculated using eq 10 and is plotted in Figure 4 as a solid line for the cation-exchange membrane (K-101) and a dotted line for the anion-exchange membrane (A-201). They roughly describe the variation tendency of the effective membrane charge density with the dielectric constant of the solvents. The failed data points from the theoretical prediction can be caused by the complexity of the organic molecular structure contacting with the polymer inside the membrane phase. Especially in dimethyl sulfoxide and ethylene glycol, the ion solvation effects of the former show large differences between a cation and an anion,[27] and the latter has two hydroxyl groups.

It is generally known that charged groups in the membrane have more influence on the counterion than on the co-ion.[3] The ion mobility ratios of LiBr in pure water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol are 0.495, 0.495, 0.367, 0.700, and 0.685, respectively.[28−30] From Table 3, we
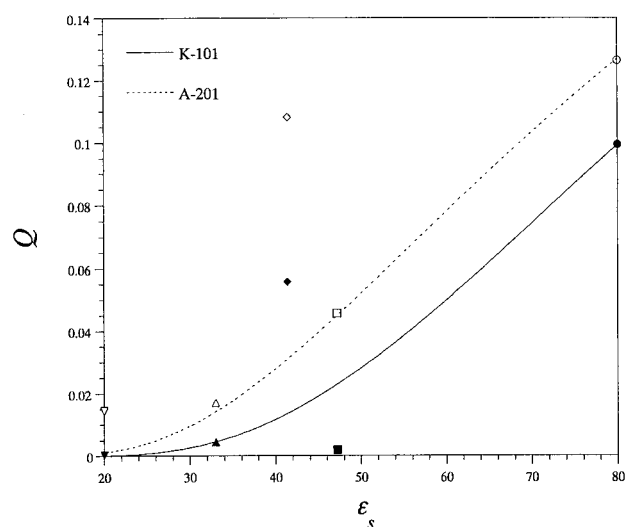

Figure 4. Values of *Q* in cation- and anion-exchange membranes with the various dielectric constants of the solvents. ●, ■, ◆, ▲, and ▼, respectively, indicate the calculated results for membrane K-101 in water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol. ○, □, ◇, △, and ▽, respectively, indicate the calculated results for membrane A-201 in water, dimethyl sulfoxide, ethylene glycol, methanol, and *n*-propanol. Solid and dotted lines are the theoretical results obtained by fitting the calculated data to eq 10.

can see that the values of the ion mobility ratio in the cation-exchange membrane are smaller than those in pure solvents and are larger in the anion-exchange membrane. The results agree well with the conclusion cited above.

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