Ionic behavior across ion-exchange membranes in organic solutions

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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 counter-ions 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 counter-ions 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, $\Delta\phi_{\mathrm{Don(l\rightarrow r)}}$, 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]

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

where

$$\Delta\phi_{\text{Don(l}\to\text{r)}} = -\frac{RT}{z_+F}\ln\left[\frac{\gamma''_\pm C''_s \overline{C}'_+}{\gamma'_\pm C'_s \overline{C}''_+}\right] \quad (2) \qquad \Delta\phi_{\text{diff}} = -\frac{RT}{z_+F}\frac{r-1}{r+1}\ln\left[\frac{(r+1)\overline{C}''_+ + \frac{z_x}{z_+}C_x}{(r+1)\overline{C}'_+ + \frac{z_x}{z_+}C_x}\right] \quad (3)$$

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

$r = \frac{\overline{\omega}_+}{\overline{\omega}_-}$ (4), and $\overline{C}_+$ is the cation concentration in the charged membrane given by

$$\overline{C}_+ = \sqrt{\left(\frac{z_xC_x}{2z_+}\right)^2 + \left(\frac{\gamma_\pm C_s}{Q}\right)^2} - \frac{z_xC_x}{2z_+} \quad (5), \qquad \text{where} \quad Q = \left(\frac{\overline{\gamma}_+\overline{\gamma}_-}{k_+k_-}\right)^{1/2} \quad (6)$$

$\overline{\gamma}_+$ and $\overline{\gamma}_-$ are the cation and anion activity coefficients, respectively, and k_+ and k_- are the distribution coefficients of 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 eqns. (2) and (5), the mean activity coefficient of the electrolyte, $\gamma_\pm$, 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

$$A^+ + B^- \rightleftharpoons A^+B^- \qquad K_A = \frac{[A^+B^-]}{[A^+][B^-]} = \frac{C_s - X}{X^2} \quad (7)$$

where K_A is the association constant, $[A^+B^-]$, $[A^+]$ and $[B^-]$ are the ion pair, 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]

$$K_A = \frac{4\pi N_A}{3\times10^{-3}}a^3\exp(b) \quad (8) \qquad b = \frac{e^2}{4\pi\varepsilon_0\varepsilon_s akT} \quad (9)$$

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.

By substituting the calculation result of K_A in eqn. (8) into eqn. (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 counter-ion 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 shows schematically the ion pairing phenomena. A membrane region with low dielectric constant solvent including the membrane charge groups, the counter-ions 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 in[14]

$$QC_x = \frac{C_x}{\frac{4\pi N_A}{3\times 10^{-3}} k'(a')^3 \exp\left(\frac{e^2}{4\pi\varepsilon_0 a' kT\varepsilon_s}\right) + 1} \quad (10)$$

where a' is the contact distance between the counter-ion 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 presented model.

3. Experimental

3.1. Material

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 which were measured and offered by the manufacturer are given in Table 1. Before the measurements were carried out, both membranes were immersed in 3 mol/l LiBr aqueous solution for three days to ensure that the counter-ions were exchanged for the same species. After both membranes were thoroughly washed with ion-exchanged water, they were immersed in ion-exchanged water for three days to remove the excess ions in the membrane matrices. Finally, both membranes were immersed in ion-exchanged water [H_2O], dimethyl sulfoxide [$(CH_3)_2SO$], ethylene glycol [$HOCH_2CH_2OH$], methanol [CH_3OH] and *n*-propanol [$CH_3CH_2CH_2OH$] for a 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 $110\,^{\circ}\mathrm{C}$. The membrane was swollen by soaking it in the solvent at $20\,^{\circ}\mathrm{C}$ for a week and carefully removing the surface solvent with filter paper. The equilibrium swelling degree was defined by[25]

$$S = \frac{W_w - W_d}{W_d} \quad (11),$$

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

$$C_x = \frac{d}{S} C_{capacity} \quad (12)$$

where $C_{capacity}$ is the ion-exchange capacity of the membrane in meq/g-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 $20.0\pm0.5\,^{\circ}\mathrm{C}$. 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.

The results for the membrane potentials of K-101 and A-201 are shown in Figs. 2 and 3, respectively. In Figs. 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 eqn. (1) are shown as lines. From Figs. 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 ions, this will cause some errors which occurred. The structure inhomogeneities of the membranes may be another factor that cause the deviations. But based on the experimental results that the deviations increase with the decreases of the electric constants, we intend to explained the deviations 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 contents, the assumption of neglecting the effect of the inhomogeneity in this work would become quite reasonable.[26]

The effective membrane charge density, QC_x, and the cation-to-anion mobility ratio in the membrane, r, are estimated by applying eqn. (1) to the corrected experimental data, considering the effect of ion pairing in the external solutions with a nonlinear regressing 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 Fig. 4 as a function of the specific dielectric constant. Q is also calculated using eqn. (10) and is plotted in Fig. 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 difference 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 counter-ion 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 can see that the values of 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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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

Table 2 The experimental results of the equilibrium swelling degree, *S*, and the fixed charge density, C_x, in the various solvents

solvent	K-101		A-201	
	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

Table 3 The values of the effective membrane charge density, QC_x, and the cation-to-anion mobility ratio in membrane, *r*, in the various solvents

solvent	K-101		A-201	
	QC_x mol/l	$r = \overline{\omega}_+ / \overline{\omega}_-$	QC_x mol/l	$r = \overline{\omega}_+ / \overline{\omega}_-$
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

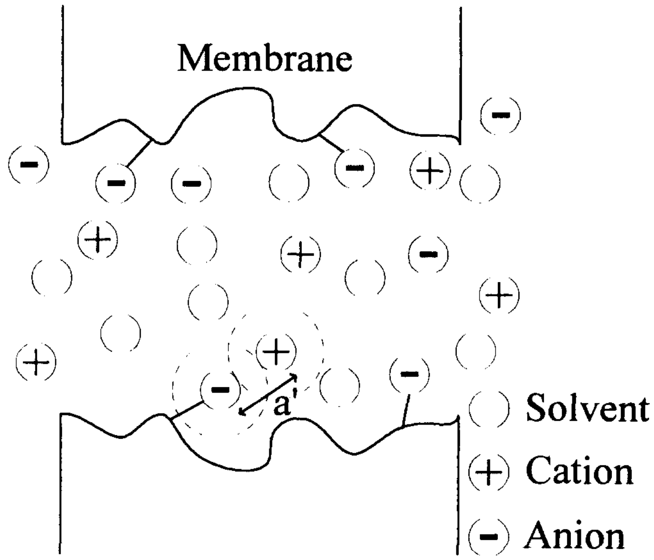

Fig. 1 Simplified view of the membrane and the external solutions. The ion pairing phenomena between the free counter-ion and the fixed charge group in the membrane phase are schematically shown.

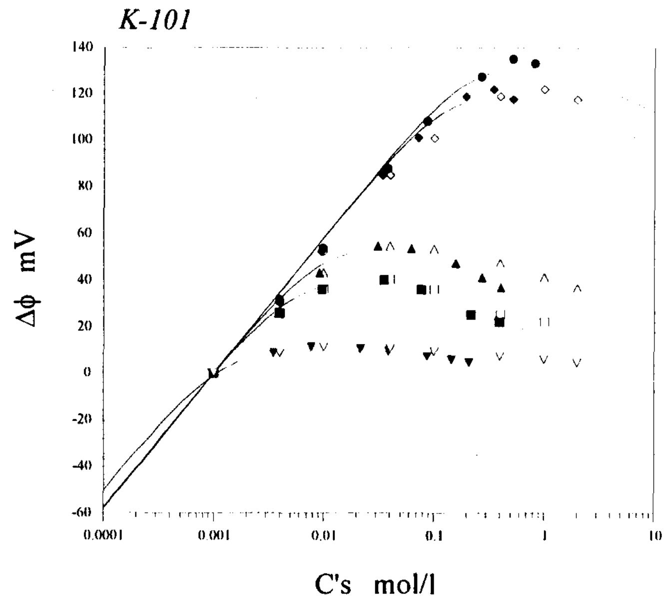

Fig. 2 Membrane potentials of cation-exchange membrane for the various solvents. ●, ■, ◆, ▲ and ▼ respectively indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol and *n*-propanol, considering the effect of ion pairing in the external solutions. ○, □, ◇, ∧ and ∨ respectively 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 eqn. (1).

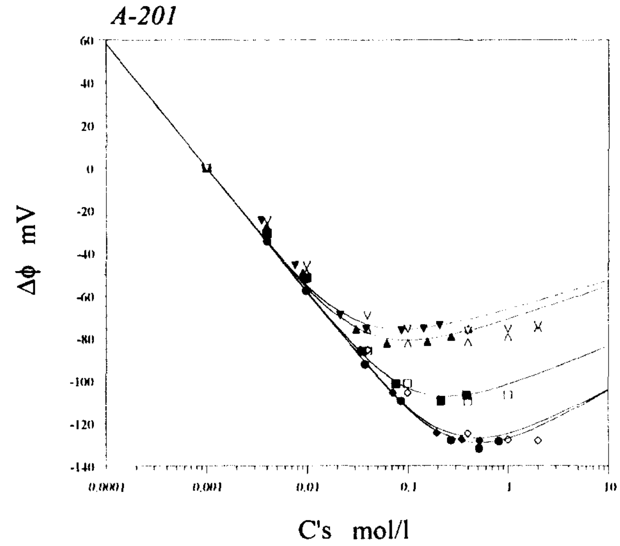

Fig. 3 Membrane potential of anion-exchange membrane for the various solvents. ●, ■, ◆, ▲ and ▼ respectively indicate the experimental data for water, dimethyl sulfoxide, ethylene glycol, methanol and *n*-propanol, considering the effect of ion pairing in the external solutions. ○, □, ◇, ∧ and ∨ respectively 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 eqn. (1).

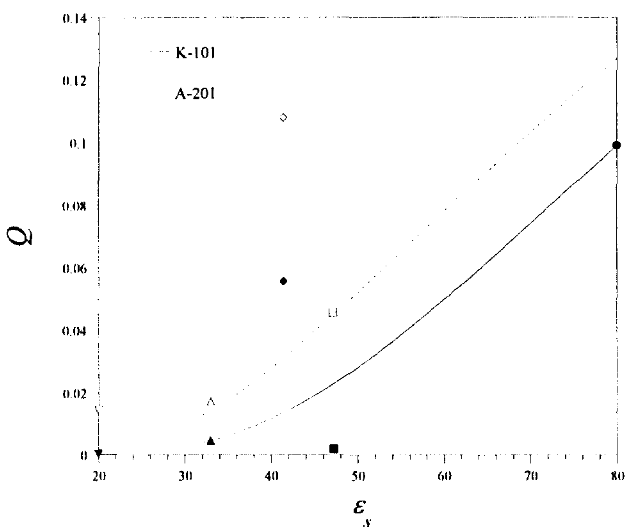

Fig. 4 The values of Q in cation- and anion-exchange membranes with the various dielectric constants of the solvents. ●, ■, ◆, ▲ and ▼ respectively indicate the calculated results for membrane K-101 in water, dimethyl sulfoxide, ethylene glycol, methanol. ○, □, ◇, ∧ and ∨ respectively indicate the calculated 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 eqn. (10).