

Ionic Behavior across Charged Membranes in Methanol–Water Solutions. 2. Ionic Mobility

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The permeability coefficients across cation- and anion-exchange membranes were measured for LiCl methanol–water solutions. The experimental data were analyzed on the basis of the Donnan equilibrium and the Nernst–Planck equation of ion flux considering the effect of the mean activity coefficient of an electrolyte in an external solution, and the theoretical predictions agreed well with the experimental data. The mobilities of ions in the membrane were determined by using the results of the effective membrane charge densities and the cation-to-anion mobility ratios obtained from the previous paper and a nonlinear regression method. The results showed that the mobility of ions in the membrane would decrease with an increase in the weight fraction of methanol. It is postulated that the counterions prefer to make ion pairs with the fixed charge groups in the mixed solvent system since the dielectric constant of methanol is smaller than water. Thus the ion pairs between the counterions and fixed charge groups will increase with the increase in methanol concentration, and the mobilities of the counterions will decrease.

1. Introduction

Theoretically, the transport phenomena of ions in a charged membrane–electrolyte aqueous solution system developed by Teorell, Meyer, and Sievers (TMS)^{1–3} can be treated using Donnan's equilibrium theory^{4,5} and the Nernst–Planck equation,^{6–9} if it is assumed that the fixed charge groups are homogeneously distributed in the membrane¹⁰ and the effect of the mean activity coefficient of the electrolyte in an external solution is negligible. The permeability coefficient across a charged membrane in an aqueous solution system has been studied by many authors.^{11–14} However, the studies and experimental data available for an electrolyte aqueous organic solution system are still limited.

The membrane potential of various weight fractions of LiCl methanol–water solution systems has been measured and fitted to the equation which is based on the TMS theory considering the effect of the mean activity coefficient of an electrolyte in an external solution for producing the effective membrane charge densities and the cation-to-anion mobility ratios.¹⁵ In order to completely understand the transport phenomena in such a system, the permeability coefficients are measured in the present paper. The mobilities of ions in the membrane can be obtained by using the results of the effective membrane charge densities and the cation-to-anion mobility ratios obtained in a previous paper¹⁵ and fitting the experimental data of the permeability coefficient to the equation which is based on the TMS theory by considering the effect of the mean activity coefficient of the electrolyte in the external solution. Finally, the ionic mobilities in the membrane are estimated as a function of the weight fraction of methanol, and the effects of methanol on them are discussed in this paper.

2. Theory

2.1. Permeability Coefficient. The ionic flux across the membrane, J_i , can be obtained by the Nernst–Planck equation which can be applied to the phase of the membrane without considering the associating effect of ions in the external solution

$$J_i = -\bar{\omega}_i RT \frac{d\bar{C}_i}{dx} - z_i F \bar{\omega}_i \bar{C}_i \frac{d\bar{\phi}}{dx} \quad i = +, - \quad (1)$$

where $\bar{\omega}_i$ and \bar{C}_i are the ionic mobility and the ion concentration of the ion i in the membrane, respectively, $\bar{\phi}$ is the electrical potential in the membrane, R is the gas constant, T is the absolute temperature, and F is Faraday's constant. The electroneutrality condition in a membrane requires that

$$\sum_{i=+,-} z_i \bar{C}_i + z_x C_x = 0 \quad (2)$$

and

$$J_+(x) = J_-(x) \quad (3)$$

where C_x is the fixed charge density, and z_i and z_x are the valences of ion i and fixed charge groups, respectively.

Under the condition $z_+ = -z_-$, eq 4 can be obtained by differentiating eq 2

$$d\bar{C}_+/dx = d\bar{C}_-/dx \quad (4)$$

Inserting eqs 1 and 4 into eq 3, the term of $d\bar{\phi}/dx$ in eq 1 can be obtained by

$$\frac{d\bar{\phi}}{dx} = -\frac{RT}{z_+ F} \frac{\bar{\omega}_+ - \bar{\omega}_-}{\bar{\omega}_+ \bar{C}_+ + \bar{\omega}_- \bar{C}_-} \frac{d\bar{C}_+}{dx} \quad (5)$$

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Finally, the electrolyte flux across the membrane, J , can be estimated by inserting eq 5 into eq 1

$$J = J_+ = -\frac{\bar{\omega}_+ R T C_x}{(r+1)d} \left[\frac{2}{C_x} (\bar{C}_+'' - \bar{C}_+') + \frac{r-1}{r+1} \frac{z_x}{z_+} \ln \frac{(r+1)\bar{C}_+'' + (z_x/z_+)C_x}{(r+1)\bar{C}_+' + (z_x/z_+)C_x} \right] \quad (6)$$

where d is the thickness of the membrane, r is the cation-to-anion mobility ratio in the membrane defined by

$$r = \frac{\bar{\omega}_+}{\bar{\omega}_-} \quad (7)$$

and \bar{C}_+' and \bar{C}_+'' are the cation concentrations on the left- and right-hand sides of the charged membrane, respectively, which are given in a previous paper¹⁵

$$\bar{C}_+ = \sqrt{\left(\frac{z_x C_x}{2z_+} \right)^2 + \left(\frac{\gamma_{\pm} C_s}{Q} \right)^2} - \frac{z_x C_x}{2z_+} \quad (8)$$

where γ_{\pm} is the mean activity coefficient of the electrolyte in an external solution and can be calculated by some theories.^{16–18} The nonideality caused by the associating effect of ions in organic solution systems can be estimated by the mean activity coefficient of the electrolyte. The same method has been adopted to calculate the vapor pressure and the mean ionic activity coefficient in organic solution systems by some authors.^{19–21}

The permeability coefficient, P , can be easily obtained by the original definition

$$P = -\frac{J}{C_s'' - C_s'} \quad (9)$$

where C_s' and C_s'' are the concentrations of the solution on the left- and right-hand sides, respectively.

2.2. Mobility of an Ion in a Membrane. The theories of ion pairing have been studied by some authors.^{22,23} To explicitly evaluate the interaction of ion pairs between the counterion and fixed charge group in the membrane phase, we have used a very simple model that is based on the Fuoss approach to ion pairing in electrolyte solutions.^{23,24} The theoretical basis of the Fuoss approach to ion pairing is the linear Poisson–Boltzmann equation. Linearization of the Boltzmann factor might not be justified when the electrostatic potential energy is greater than kT . However, it is likely that the screened Coulomb potential may be used in this case over a range of concentrations greater than that for which the linearization of the Poisson–Boltzmann equation can be justified.²⁵ We have resorted to this approach because of its simplicity. Some of the assumptions introduced by Fuoss may also be questionable, since in our case, one of the ions in the ion pair is fixed.²⁶ The deviation which is caused by this problem can be compensated by the regressing process of two parameters in the new model.

Application of the Fuoss formalism to the ion pair in a membrane would lead to the association constant^{23,24}

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

$$b = \frac{e^2}{4\pi\epsilon_0\epsilon_s a kT} \quad (11)$$

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, T is the absolute temperature, and a is the contact distance.

If the interaction by which the immobilized reactant is formed proceeds very rapidly compared with the diffusion process, a local equilibrium can be assumed to exist between the free and immobilized components of the diffusing substance. As the first approximation, the concentration of immobilized substance, C_{im} , is directly proportional to the concentration of a substance free to diffuse, C_f , i.e.,

$$C_{im} = R C_f \quad (12)$$

According to the diffusion theory with chemical reaction, the relationship between the apparent diffusion constant, D_a , and the actual diffusion constant, D' , can be expressed in^{27–29}

$$D_a = \frac{1}{R+1} D' \quad (13)$$

where R has a similar physical meaning with the association constant K_A of ion pairing in the membrane phase if the reactant corresponds to the fixed charge group.^{30–36} Therefore, the following relationship can be obtained between R and K_A

$$R = \beta K_A \quad (14)$$

where β is a constant which indicates the effect of the association constant on the mobility of the counterion in the membrane. Taking into account eq 13, the relationship between the counterion mobility in the membrane, $\bar{\omega}_{counterion}$, and the association constant, K_A , is as follows

$$\bar{\omega}_{counterion} = \frac{1}{\beta K_A + 1} \frac{\omega_{counterion}}{q^2} \quad (15)$$

where q is the tortuosity factor^{37,38} and $\omega_{counterion}$ is the mobility of a counterion in an external solution. Clearly the effect of the ion pairing is to slow down the mobility of the counterion. In the limited case, K_A will tend to infinity if the ion-pair strongly associates together, and then $\bar{\omega}_{counterion}$ will become zero. On the other hand, K_A will tend to zero if the interaction of the ion-pair is very weak, and $\bar{\omega}_{counterion}$ will become $\omega_{counterion}/q^2$ as the behavior appearing in the charged gel membrane.³⁹

If it is assumed that $\omega_{counterion}$ in a mixed solvent linearly changes with the consistency of the pure solvent, then the mobility of the counterion in an external solution can be estimated by

$$\omega_{counterion} = \omega_{counterion,1} x_1 + \omega_{counterion,2} x_2 \quad (16)$$

where x_1 and x_2 are the salt-free mole fractions of solvents 1 and 2, respectively.

The dielectric constant of a mixed solvent can be estimated from Oster's mixing rule⁴⁰

$$\epsilon_s = \epsilon_1 + [(\epsilon_2 - 1)(2\epsilon_2 + 1)/2\epsilon_2 - (\epsilon_1 - 1)]x_2 V_2/V \quad (17)$$

where ϵ_1 and ϵ_2 are the dielectric constants of solvents 1 and 2, respectively, and V is the partial molar volume of a mixed solvent which can be simply estimated by

$$V = x_1 V_1 + x_2 V_2 \quad (18)$$

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

membrane	thickness (mm)	water content (wt %)	ion-exchange capacity (meq/g)
K-171	0.11–0.13	20–23	1.5–1.6
A-201	0.22–0.24	26–27	1.4–1.6

where V_1 and V_2 are the partial molar volume of solvent 1 and 2, respectively.

Inserting eqs 10, 11, and 16 into eq 15 and applying the relationships of eqs 17 and 18, we can obtain the theoretical formalism for estimating $\bar{\omega}_{\text{counterion}}$ as follows

$$\bar{\omega}_{\text{counterion}} = \frac{(\omega_{\text{counterion},1}x_1 + \omega_{\text{counterion},2}x_2)/q^2}{\frac{4\pi N_A}{3 \times 10^{-3}} \beta a^3 \exp\left\{\frac{e^2}{4\pi\epsilon_0 akT\{\epsilon_1 + \Delta\epsilon x_2 V_2/V\}}\right\} + 1} \quad (19)$$

where

$$\Delta\epsilon = (\epsilon_2 - 1)(2\epsilon_2 + 1)/2\epsilon_2 - (\epsilon_1 - 1) \quad (20)$$

The mobility of co-ion in a membrane, $\omega_{\text{co-ion}}$, can then be obtained from eq 7.

3. Experimental Section

3.1. Materials. A cation-exchange membrane (K-171: Asahi Chemicals), which is composed of poly(divinylbenzene-*co*-styrene) containing sulfonic acid groups, and an anion-exchange membrane (A-201: Asahi Chemicals), which is composed of poly(butadiene-*co*-styrene) containing quaternized ammonium groups in a polymer matrix, were used for the measurements. The thickness, water content, and ion-exchange capacity of these membranes are listed in Table 1. Before any measurements were carried out, both membranes were immersed in 3 mol/L LiCl for three 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 matrix.⁴¹

3.2. Measurement of the Modified Degree of Hydration. The modified degree of hydration, H , similarly defined as the degree of hydration presented by other authors,^{12,38} was the volume fraction of the mixed solvent in a wet membrane. It could be estimated from the following equation

$$H = \frac{(W_w - W_d)/\rho_s}{(W_w - W_d)/\rho_s + W_d/\rho_m} \quad (21)$$

where W_w and W_d are the weights of a membrane at the equilibrium wet and dry states, respectively, and ρ_s and ρ_m are the densities of the mixed solvent and membrane, respectively. For simplicity, the density of the mixed solvent was calculated using the following empirical equation

$$\rho_s = \frac{1}{\sum_n x'_n/\rho_n} \quad (22)$$

where x'_n and ρ_n are the salt-free weight fraction and density of solvent n , respectively.

3.3. Measurement of the Permeability Coefficient. The permeability coefficients of both membranes used in this work were measured to obtain the mobilities of ions in the membrane

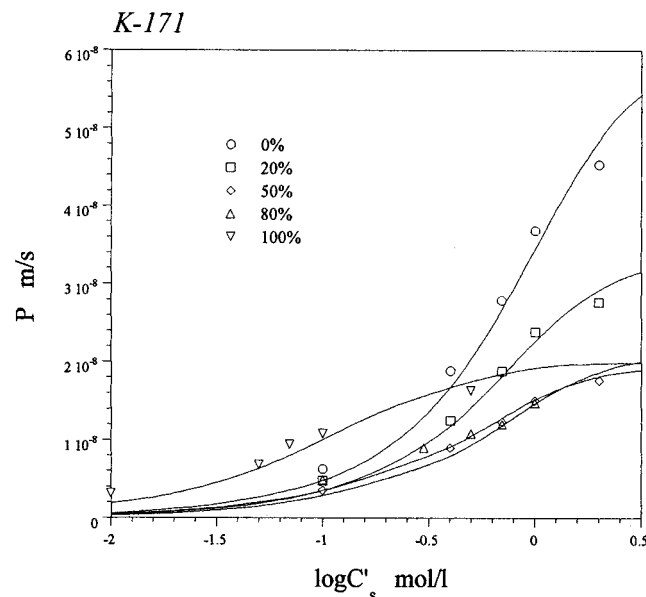


Figure 1. Permeability coefficient of cation-exchange membrane for the various weight fractions of methanol from 0% to 100%. Solid lines are the theoretical results obtained by fitting the experimental data to eqs 6 and 9.

as a function of the weight fraction of methanol. 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 cm³, and the membrane area was 7.55 cm². Electrolyte solutions of different concentrations were poured into these containers; the concentration in the left container was varied from 0.01 to 2.0 mol/L, and the container on the right side was filled with the mixed solvent without containing electrolyte. The weight fractions of methanol in the mixed solvents were 0, 20, 50, 80, and 100%. The data were measured by using a digital conductivity meter (TOA CM-20E) connected to a conductivity cell (TOA CG-511B). The relationship between the conductivity and concentration was obtained before measurement, and LiCl was used as a strong electrolyte to measure the permeability. The solutions in both containers were stirred by magnetic stirrers to minimize the effect of the boundary layers on the flux of ions. The permeability coefficient, P , was estimated from the ion concentration change with time in the right side using the following equation

$$P = -\frac{V\Delta C'_s}{(C''_s - C'_s)SH\Delta t} \quad (23)$$

where V is the volume of the right container, $\Delta C'_s$ is the ion concentration change on the right side at time interval Δt , and S is the membrane area. If the value of C'_s was kept smaller than 0.01 C''_s at time interval Δt , then the value of $C''_s - C'_s$ can be adopted as C''_s without leading to any obvious errors.

4. Results and Discussion

The results for the permeability coefficients of K-171 and A-201 are shown in Figures 1 and 2, respectively. In Figures 1 and 2, the theoretical results for the LiCl methanol–water solutions calculated by eqs 6 and 9 are shown as lines, and the experimental data was in good agreement with the calculated results. In both membranes, the permeability coefficient slightly increases with the concentration on the left side in the low-

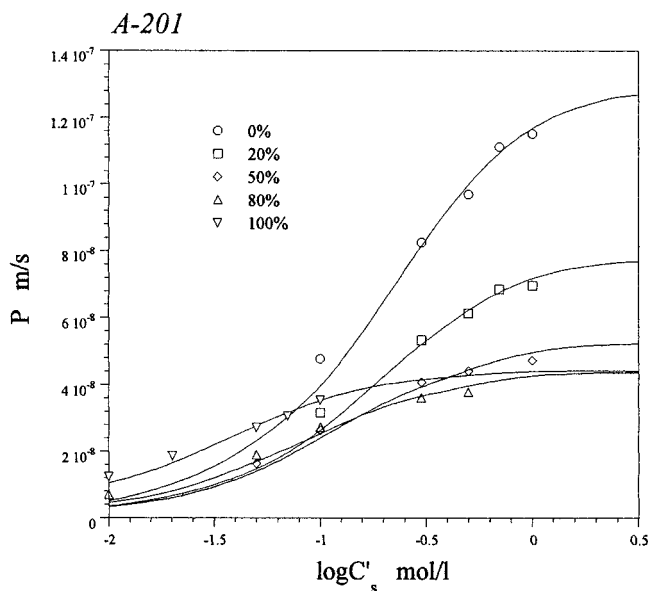


Figure 2. Permeability coefficient of anion-exchange membrane for the various weight fractions of methanol from 0% to 100%. Solid lines are the theoretical results obtained by fitting the experimental data to eqs 6 and 9.

TABLE 2: Values of the Effective Membrane Charge Densities and the Cation-to-Anion Mobility Ratios in a Membrane for the Various Weight Fractions of Methanol from 0 to 100%

weight fractions of methanol (%)	cation-exchange membrane		anion-exchange membrane	
	QC_x (mol/L)	r	QC_x (mol/L)	r
0	-1.638	0.393	0.351	1.900
20	-1.135	0.405	0.282	1.922
50	-0.855	0.415	0.195	1.958
80	-0.530	0.424	0.116	1.985
100	-0.139	0.434	0.049	2.024

concentration range. When the concentration on the left side is around the effective membrane charge density, a sharp increase in the permeability coefficient appears. After that, with the increase in concentration on the left side, the increasing rate of the permeability coefficient slows down again and finally reaches a maximum. From Figures 1 and 2, it can be found that the maximum of the permeability coefficient will decrease as the weight fraction of methanol increases.

The mobility of a cation in a membrane, \bar{w}_+ , can be estimated by fitting the experimental data of the permeability coefficient to eqs 6 and 9. A nonlinear parameter estimation program UNCMIN⁴² is used to fit the experimental data. In the estimation process, C_s and C'_s are the experimental results, while the effective membrane charge density and the cation-to-anion mobility ratio are obtained from a previous paper¹⁵ which are listed in Table 2, and \bar{w}_+ is the unknown parameter. The mobility of the anion in a membrane, \bar{w}_- , can be calculated by eq 7. The calculated results of \bar{w}_+ and \bar{w}_- in various weight fractions of methanol are shown in Figure 3. The solid lines in Figure 3 are the theoretical results obtained by fitting the mobilities of the counterion in a membrane to eq 19 using the nonlinear parameter estimation program UNCMIN.⁴² This can well describe the variation tendency of mobility of a counterion in a membrane with the weight fraction of methanol. According to the definition of Mackie and Meares,³⁸ the tortuosity factor, q , can be expressed by

$$q = (2 - H)/H \quad (24)$$

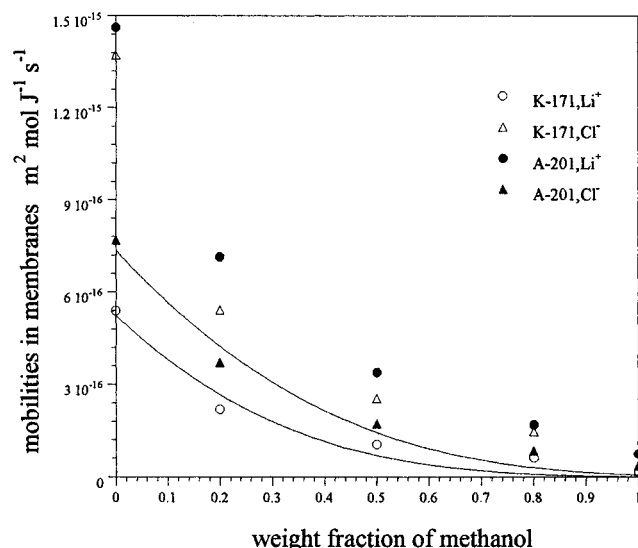


Figure 3. Mobility of ions in cation-exchange membrane and anion-exchange membrane with the various weight fractions of methanol. Solid lines are the theoretical results obtained by fitting the data to eq 19.

TABLE 3: Parameters a and β , Obtained by Fitting to Eq 19

	$a \times 10^{10}$ m	β
cation-exchange membrane	2.61	15.1
anion-exchange membrane	3.49	17.6

In the case of a commercial ion-exchange membrane, the modified degree of hydration, H , is about 0.2–0.4, which corresponds to a q of 9–4. For simplicity, we fixed the tortuosity factor at $q = 5$ for the general charged membranes without causing any obvious errors, and the parameters a and β obtained by fitting to eq 19 are listed in Table 3.

From Figure 3, it can be found that the mobilities of a counterion in a membrane are smaller than those of a co-ion in a membrane, and the mobilities of a counterion in a membrane are smaller than their corresponding values in a mixed solvent. It is assumed that most of the counterions are adsorbed by the fixed charge groups, and the entrapped counterions have difficulty in moving to the adjoining sites. This is one of the reasons why the mobilities of counterions are very low.

Mafé et al.²⁶ suggested that the mobility of a co-ion in a membrane is the same as that in pure solvent, and the mobility of a counterion in a membrane is a function of the fixed charge groups in the membrane for a very low water content membrane system. The equations by Mafé et al. are modified and adapted to the systems in this study as follows

$$\frac{\bar{w}_{\text{co-ion}}}{w_{\text{co-ion}}} = \alpha \quad (25)$$

$$\frac{\bar{w}_{\text{counterion}}}{w_{\text{counterion}}} = \alpha \frac{\bar{C}_{\text{co-ion}} + \phi C_x}{\bar{C}_{\text{co-ion}} + C_x} \quad (26)$$

where α is a parameter for reducing the effect that occurs from the difference of the structure, and ϕ is a parameter that is a function of the ion concentration.

The ratios of ionic mobility for both membranes, which is the in membrane-to-in pure solvent ratio, \bar{w}_i/w_i , are shown in Table 4. Based on the reason that $\phi < 1$ in all regions of the ion concentration, the ratio of \bar{w}_i/w_i for the co-ion will be larger

TABLE 4: Ratios of Ionic Mobility Denoted as $\bar{\omega}_i/\omega_i$ in Membrane-to-in Pure Solvent, $\bar{\omega}_i/\omega_i$, for Both Membranes

solvent	cation-exchange membrane		anion-exchange membrane	
	$\bar{\omega}_+/\omega_+ \times 10^3$	$\bar{\omega}_-/\omega_- \times 10^3$	$\bar{\omega}_+/\omega_+ \times 10^3$	$\bar{\omega}_-/\omega_- \times 10^3$
water ^a	1.299	1.675	3.519	0.938
methanol ^b	0.040	0.069	0.174	0.065

^a In water: $\omega_{\text{Li}^+} = 4.154 \times 10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$ and $\omega_{\text{Cl}^-} = 8.201 \times 10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$. ^b In methanol: $\omega_{\text{Li}^+} = 4.254 \times 10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$ and $\omega_{\text{Cl}^-} = 5.618 \times 10^{-13} \text{ m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$.

than that for the counterion. The results in Table 4 agreed with this conclusion.

From Table 4, it can also be found that the ratio of $\bar{\omega}_i/\omega_i$ in methanol is much smaller than that in water in both membranes of K-171 and A-201. One of the reasons is that the counterions prefer to make ion pairs with the fixed charge groups in a mixed solvent system since the dielectric constant of methanol is smaller than water. Thus the ion pairs between counterions and fixed charge groups will increase with the increase in methanol concentration, and the mobilities of the counterion will decrease.

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