

Dissociation Constant of a Weak Electrolyte in Charged Membrane

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In this study, the dissociation constant of acetic acid as a weak electrolyte in an ion-exchange membrane, \bar{K} , was estimated using the Donnan equilibrium theory, which has been applied to a strong polyelectrolyte membrane. The membrane charge density and the total concentration, which represents the sum of the dissociated proton concentration and carboxyl concentration of the undissociated electrolyte in the membrane, were determined by neutral titration; the charge effectiveness was determined from membrane potential measurements; and the proton concentration in the external solution phase was determined by Donnan equilibrium theory and used for the calculation of \bar{K} . The dissociation constants, \bar{K} , in the cation exchange membrane were on the order of 10^{-4} and were larger than that in water ($= 1.73 \times 10^{-5}$). The value of \bar{K} increased with an increase in the concentration in the external solution and decreased with the fixed charge density increase. It is suggested that the fixed charge group depresses the dissociation of the weak electrolyte.

1. Introduction

The transport phenomena of a weak electrolyte across a charged membrane has been the object of intensive membrane research in the areas of biology,¹ medicine, physiology,² pharmaceuticals, biotechnology,^{3–5} and environmental science.⁶ However, the precise mechanism of these phenomena has not been actively studied because of the complexity, especially, the effect of the hydrogen ion at the membrane surface and in the interior.⁷ In a previous paper, ionic mobilities of a weak electrolyte through charged membranes were discussed.⁸ The membrane potential across cation- and anion-exchange membranes was measured for acetic acid and glycine methyl ester hydrochloride aqueous solutions. Membrane potentials^{9–11} were correlated to the transport theory based on the Donnan equilibrium^{12,13} and the Nernst–Planck equation^{14–17} of the ion flux by introducing the dissociation constant of a weak electrolyte in aqueous solution to determine the ratios of the anion-to-cation mobilities in the ion-exchange membranes. In the case of acetic acid, they were estimated to be ~ 0.0001 – 0.001 times as small as those in water for an anion exchange membrane, and $\sim 10\,000$ times larger than those in water in a cation-exchange membrane. Therefore, it was suggested that the ion mobilities of weak electrolytes were significantly affected by the fixed charge groups in the membrane. In the case of the glycine methyl ester hydrochloride, the ratio was the same as in water, which meant that it behaved as a strong electrolyte. In a previous paper,⁸ these deviations were attributed to ionic mobility problems in the membrane. However, it was not considered that the dissociation constant in the membrane was different from that in the external aqueous solution. Determination of the dissociation constant will significantly contribute to the develop-

ment of transport phenomena studies of weak electrolytes in the charged membrane.

The dissociation constant is significantly affected by the physicochemical properties of the medium. In the external phase, the weak electrolyte is only surrounded by water molecules. On the other hand, in the membrane phase it is surrounded not only by the water molecules but also by polymer chains and charged groups. The polymer chain is hydrophobic and the charged group participates in the ordered structure formation of the water molecules. In the membrane phase, the charged group causes a change in the dielectric property of the medium, and the dissociation constant of a weak electrolyte is thereby influenced.¹⁸ There are two experimental procedures to examine the effects of a polymer and fixed charge group on the dissociation constant; one is to alter the polymer species by keeping a fixed charge concentration constant, and the other is to alter the fixed charge concentration in the same polymer matrix. The latter procedure is much easier than the former because it is realized only by changing the monomer concentration ratio of the matrix to the fixed charge group. If the dissociation constant in the membrane is measured as a function of the fixed charge concentration, we can provide insight into the analysis for the transport phenomena of a weak electrolyte across the charged membrane. The dissociation constant of a weak electrolyte in the electric field in the aqueous solution has been explained by Onsager,^{19,20} and the dissociation in a weak polyelectrolyte has also been discussed for a long time.²¹ However, there has been little discussion on weak electrolyte behavior in the charged membrane.²²

In this study, the concentration and the dissociation constant of a weak electrolyte in the membrane are estimated using the Donnan equilibrium theory. The concentration and dissociation constant are examined as a function of the total concentration,

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TABLE 1: Apparent Dissociation Constant \bar{K} in Cation-Exchange Membrane Equilibrated with 0.1 mol/L CH_3COOH

parameter	cation-exchange membrane					anion-exchange membrane	
	TK11	TK12	TK13	TK15	K101	TA13	A201
\bar{K} (mol/L)	6.0×10^{-4}	3.3×10^{-4}	2.2×10^{-4}	1.5×10^{-4}	2.4×10^{-4}	5.6×10^{-5}	9.1×10^{-5}

TABLE 2: Physicochemical Properties of Ion-Exchange Membrane

parameter	cation-exchange parameter					anion-exchange membrane	
	TK11	TK12	TK13	TK15	K101	TA13	A201
QC_x (mol/L)	1.09	1.08	1.14	1.03	0.684	0.981	0.570
C_x (mol/L)	4.02	5.41	5.67	6.34	5.53	6.17	3.14
Q	0.271	0.200	0.201	0.162	0.124	0.159	0.181
water content (%)	18.3	19.8	26.6	31.6	24.4	32.2	27.8
thickness (μm)	100	105	110	122	220	109	230

C_0 , in the external solution and membrane fixed charge density to discuss the effect of the charge group on the dissociation constant.

2. Theory^{22,23}

2.1. Ternary Ionic System. CH_3COOH as a weak electrolyte is dissociated into cations (H^+) and anions (CH_3COO^-) in the membrane. If the counterion has already been replaced by Cl^- , as in the case of an anion-exchange membrane, or by K^+ , as in the case of a cation-exchange membrane, the CH_3COOH -membrane system is called a ternary ionic system. Each species is in equilibrium between the charged membrane phase and the aqueous solution phase. The volume and the total concentration of solution are V_e (mL) and C_0 (mol/L), respectively. For the following discussion, only the anion-exchange membrane is treated. Concentrations of CH_3COOH , H^+ , CH_3COO^- , and Cl^- are represented by C_i (where $i = \text{S}, 1, 2, \text{ and } 3$, respectively) in the external solution phase and by \bar{C}_i (where $i = \text{S}, 1, 2, \text{ and } 3$, respectively) in the membrane phase. Assuming a Donnan equilibrium between the membrane phase and the external solution phase, the following equation of the fifth degree for C_1 is obtained by taking into account the electroneutrality, the dissociation equilibrium, and the mass balance:

$$C_1^5(V_m^2 - V_e^2Q^2) + C_1^4\{V_eQ^2V_mC_X + 2K(V_m^2 - V_e^2Q^2)\} + C_1^3K(K - 2C_0)(V_m^2 - V_e^2Q^2) + C_1^2K\{Q^2V_mC_X(V_mC_X - KV_e) - 2KC_0(V_m^2 - V_e^2Q^2)\} + C_1K\{C_0Q^2V_mC_X(2V_eK - V_mC_X) + KC_0^2(V_m^2 - V_e^2Q^2)\} - V_eQ^2V_mC_XK^2C_0^2 = 0 \quad (1)$$

where V_m is the water volume in the membrane, K is the dissociation equilibrium constant in the external solution ($\text{p}K = 4.76$ at 25.0°C for acetic acid), $C_0 (= C_S + C_1)$ is the total concentration of the external solution, C_X is the membrane charge density (concentration), and Q is the parameter that shows the charge effectiveness, and from the Donnan equilibrium is defined as:

$$Q_2 = C_1C_2/\bar{C}_1\bar{C}_2 = C_1C_3/\bar{C}_1\bar{C}_3 \quad (2)$$

The membrane charge density, C_X , and the total acetic acid concentration in the membrane, $\bar{C}_0 (= \bar{C}_S + \bar{C}_1)$, are determined from titration measurements. The parameter Q is calculated from the effective membrane charge density, QC_X , which is determined from membrane potential measurements as shown in Table 1, and C_XC_1 is determined by solving eq 1 using Newton's method. Using C_1 , the other concentrations, C_S , C_2 ,

C_3 , \bar{C}_S , \bar{C}_1 , \bar{C}_2 , and \bar{C}_3 are successively determined. Finally, the apparent dissociation equilibrium constant in the membrane, \bar{K} , is obtained from the following equation:

$$\bar{K} = \bar{C}_1\bar{C}_2/\bar{C}_S \quad (3)$$

2.2. Binary Ionic System. If the counterion has already been replaced by CH_3COO^- in the case of an anion-exchange membrane or by H^+ in the case of a cation-exchange membrane instead of Cl^- or K^+ , it is called a binary ionic system. Concentrations of CH_3COOH , H^+ , and CH_3COO^- are represented by C_i (where $i = \text{S}, 1, \text{ and } 2$, respectively) in the aqueous solution phase and by \bar{C}_i (where $i = \text{S}, 1, \text{ and } 2$, respectively) in the membrane phase. Assuming that the Donnan equilibrium is also applicable between the membrane phase and the external solution, the apparent dissociation equilibrium constant in the membrane, \bar{K} , is obtained as follows:

$$\bar{K} = \bar{C}_1\bar{C}_2/\bar{C}_S = (K^2 + 2KC_0 - K\sqrt{K^2 + 4KC_0})/2Q^2(\bar{C}_0 + Z_XC_X/2 - K\sqrt{(Z_XC_X/2)^2 + (C_1/Q)^2}) \quad (4)$$

where Z_X is the ionic valence of the fixed charge group.

3. Experimental Section

3.1. Materials. Anion-exchange membranes (A201 and TA13; Asahi Chemical), which are composed of quaternized ammonium groups, and cation-exchange membranes (K101, TK11, TK12, TK13, and TK15; Asahi Chemical), which are composed of sulfonic acid groups in polymer matrixes, were used for the measurements. The effective charge density, QC_X ; charge density, C_X ; charge effectiveness, Q ; water content; and membrane thickness are shown in Table 2. Prior to the measurement, the anion-exchange membranes were immersed in 1 mol/L HCl for 1 day, and the cation-exchange membranes were immersed in 2 mol/L KCl for 2 days to exchange the counterions into the same species. After both membranes were sufficiently washed with ion-exchanged water, they were immersed in the ion-exchanged water for 1 day to remove the excess ions in the membrane matrix.

3.2. Measurement of Membrane Water Content. After soaking the samples in deionized water for >24 h, the samples were wiped with filter paper and then quickly weighed. The water content was determined according to the following relationship and is listed in Table 2²⁴: water content (%) = $100(m_w - m_d)/m_d$ where m_w and m_d are the weights of the swollen and dried membranes, respectively. The dried membrane weight was measured after evacuation for 5 h at 80°C .

3.3. Measurement of Effective Charge Density, QC_X . Effective charge densities of the membranes were determined

by the membrane potential measurements as shown in a previous paper and are listed in Table 2⁸.

3.4. Measurement of Charge Density, C_X .⁸ Anion-exchange membranes were immersed in 1 mol/L KOH, and the cation-exchange membranes were immersed in 1 mol/L HCl for >24 h to exchange all the counterions into OH^- and H^+ , respectively. After both membranes were sufficiently washed with deionized water, they were immersed in deionized water to remove the excess KOH and HCl in the membrane matrix, and the deionized water was exchanged every hour. This procedure was repeated before the water became neutral. Thus, the obtained samples were immersed in 100 mL of 2 mol/L KCl aqueous solution, and the neutralization titration was performed by adding 0.1 mol/L HCl or 0.2 mol/L KOH in a stepwise manner under flowing N_2 gas at 25.0 ± 0.1 °C to determine the amount of the counterion. The pH values were measured with a complex electrode (GST-5211C; TOA Electric) and a pH meter (IMS-40S; TOA Electric). The fixed charge density, C_X , was calculated by dividing the amount of the counterion by the water content ($m_w - m_d$) and is listed in Table 2.

3.5. Neutralization Titration in Ternary Ionic System.^{24,25} The anion- and cation-exchange membranes were immersed in 2 mol/L KCl aqueous solution for >24 h to exchange all the counterions to Cl^- and K^+ , respectively. After the membranes were sufficiently washed with deionized water, which was confirmed by the conductivity in water, they were immersed in 400 mL of acetic acid aqueous solution of concentration C_0 for >24 h; the C_0 values were 0.001, 0.003, 0.01, 0.03, 0.1, 0.2, 0.5, and 1 mol/L. After the equilibrium was attained between the membrane and external solution, the membrane was removed from the solution, and the surface was carefully wiped with a wiping paper and again immersed in 100 mL of 2 mol/L KCl aqueous solution to perform the neutralization titration with KOH. The concentration of KOH ranged from 0.01 to 0.2 mol/L depending on the acetic acid concentration. In the case of a low concentration, the blank titration was performed using 100 mL KCl aqueous solution to correct the titration value. Thus, \bar{C}_0 in eq 7 was determined. The measurement was performed at 23 °C with circulating N_2 gas.

3.6. Neutralization Titration in Binary Ionic System. The anion- and cation-exchange membranes were immersed in 1 mol/L CH_3COOK and HCl aqueous solutions for >24 h to exchange all the counterions to CH_3COO^- and H^+ , respectively. After the membranes were sufficiently washed with deionized water, they were immersed in 400 mL of acetic acid aqueous solution of concentration C_0 for >24 h, as shown in section 3.5. After the equilibrium was attained, the neutralization titration was performed with 0.1 or 0.2 mol/L KOH at 23 °C in circulating N_2 gas. The concentration of KOH ranged from 0.01 to 0.2 mol/L depending on the acetic acid concentration. Thus, \bar{C}_0 was determined.

3.7. Determination of Apparent Dissociation Constant in the Membrane. The apparent dissociation constant of acetic acid in the membrane, \bar{K} , was calculated using C_1 , \bar{C}_0 , Q , and C_X . In the case of the ternary ionic system, C_1 is determined from eq 1 and the ion concentrations, \bar{C}_1 , \bar{C}_2 , and \bar{C}_8 in the membrane were obtained using C_1 . The parameter \bar{K} is calculated from eq 3, but the activity coefficient is assumed to be 1; therefore, it is an apparent one and not the real one (this assumption will be discussed later). In the case of the binary ionic system, \bar{K} is determined using eq 4.

4. Results and Discussion

4.1. Ionic Concentration in the Membrane and Apparent Dissociation Constant of Weak Electrolyte.

The total acetic

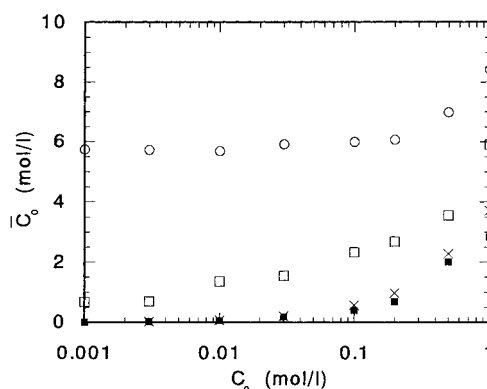


Figure 1. The total concentrations of dissociated and undissociated acetic acid ($\bar{C}_0 = \bar{C}_1 + \bar{C}_8$) in the charged exchange membrane determined by titration are plotted as a function of the total concentration in the external solution (C_0). Key: (□) K101 in ternary ionic system; (■) A201 in ternary ionic system; (○) K101 in binary ionic system; (×) A201 in binary ionic system.

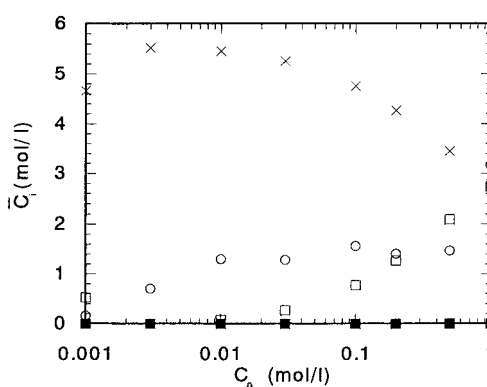


Figure 2. Concentrations of H^+ , CH_3COO^- , K^+ , and CH_3COOH in cation-exchange membrane (\bar{C}_i) are plotted as a function of the total concentration in the external solution (C_0) for K101-ternary ionic system. Key: (□) corresponds to H^+ ; (■) CH_3COO^- ; (○) CH_3COOH ; (×) K^+ .

acid concentration, \bar{C}_0 , which denotes the sum of the dissociated proton concentration and carboxyl group concentration of the undissociated acetic acid in the membrane, was determined by neutral titration to use it for the calculation. In Figure 1, \bar{C}_0 is plotted as a function of C_0 . The white and black squares indicate the results of K101 and A201, respectively, in the ternary system, and the white circle and cross are those in the binary system. According to a previous paper,⁸ the concentrations of proton, acetic acid anion, acetic acid, and potassium ion in the membrane were estimated and shown in Figures 2–5 as a function of C_0 . Figures 4 and 5 show the K101- and A201-binary ionic systems, respectively. The concentrations of CH_3COO^- in K101 and H^+ in A201 are very low because of the Donnan exclusion for co-ions. In the ternary ionic system, we can estimate the amount of exchanged counterions from Figures 2 and 3; that is, K^+ to H^+ in K101 and Cl^- to CH_3COO^- in A201. In the case of a strong electrolyte, almost all of the counterions can be exchanged with the other one at 1.0 mol/L. On the other hand, in the case of a weak electrolyte, only half of the counterions can be exchanged with the other one at 1.0 mol/L because of the low concentration of dissociated ions.

Substituting \bar{C}_i in Figure 2 into eq 3 and those in Figure 3 into eq 4, the apparent dissociation constants in the membranes, \bar{K} , were calculated and plotted in Figure 6 as a function of C_0 . At the same time, the equilibrium dissociation constant of acetic

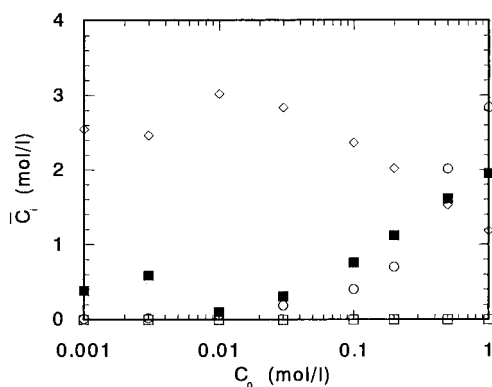


Figure 3. Concentrations of H^+ , CH_3COO^- , Cl^- , and CH_3COOH in anion-exchange membrane (\bar{C}_i) are plotted as a function of the total concentration in the external solution (C_0) for A201-ternary ionic system. Key: (\square) H^+ ; (\blacksquare) CH_3COO^- ; (\circ) CH_3COOH ; (\diamond) Cl^- .

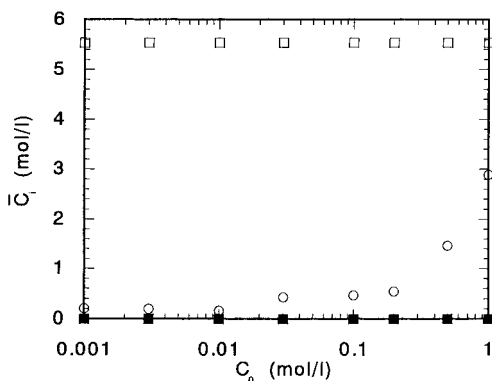


Figure 4. Concentrations of H^+ , CH_3COO^- , and CH_3COOH in cation-exchange membrane (\bar{C}_i) are plotted as a function of the total concentration in the external solution (C_0) for K101-binary ionic system. Key: (\square) H^+ ; (\blacksquare) CH_3COO^- ; (\circ) CH_3COOH .

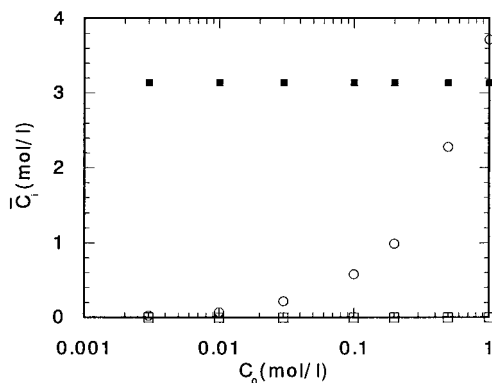


Figure 5. Concentrations of H^+ , CH_3COO^- , and CH_3COOH in anion-exchange membrane (\bar{C}_i) are plotted as a function of the total concentration in the external solution (C_0) for A201-binary ionic system. Key: (\square) H^+ ; (\blacksquare) CH_3COO^- ; (\circ) CH_3COOH .

acid in water at 25 °C ($=1.73 \times 10^{-5}$) is also shown as the solid line. \bar{K} is larger than that in water. In this case, the effect of the activity coefficients is ignored. Usually the activity coefficient is <1 in this concentration range. Therefore, \bar{K} in the membrane might be smaller than that in water. However, we should consider the effects of the physical and chemical structures of the membrane on the activity coefficients. Taking into account the cation-exchange membrane K101 in Figure 4, the activity coefficient of the counterion is supposed to be constant because the concentration is nearly constant in the membrane even if C_0 is increased. Also, as the co-ion

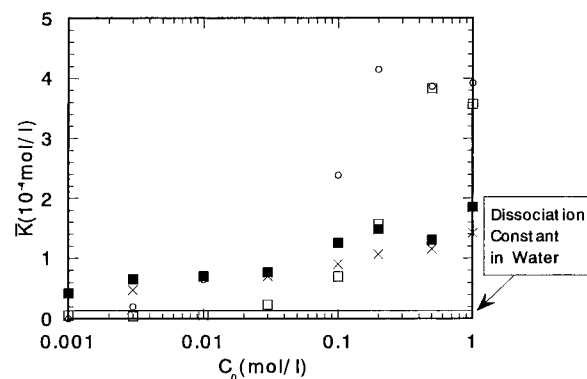


Figure 6. Apparent dissociation constants in charged membrane (\bar{K}) are plotted as a function of the total concentration in the external solution (C_0). Key: (\square) K101 in the ternary ionic system; (\blacksquare) A201 in the ternary ionic system; (\circ) K101 in the binary ionic system; (\times) A201 in the binary ionic system.

concentration is very low in the membrane, the activity coefficient is assumed to be 1. Kobatake et al.^{26,27} applied the additivity rule of the ionic activity coefficients in a polyelectrolyte dilute solution to the charged membrane, in which the counterion and co-ion activity coefficients, γ_{counter} and γ_{co} , respectively, are expressed as follows:

$$\gamma_{\text{counter}} = \gamma_{\text{counter}} \frac{\bar{C}_{\text{co}} + \phi C_X}{\bar{C}_{\text{co}} + C_X} \quad (5)$$

$$\gamma_{\text{co}} = \gamma_{\text{co}} \quad (6)$$

where γ_{counter} and γ_{co} are the activity coefficients in water, \bar{C}_{co} is the concentration of the co-ion in the membrane, and ϕ is a constant <1 (usually ~ 0.2 in the case of an artificial membrane). From eqs 5 and 6, the activity coefficients of the cation and anion in the membrane can be estimated, where \bar{C}_{co} is calculated from eq 1 and can be found as a constant in the external ionic concentration range 0.001–1.0 mol/L. As shown in Figure 4, the concentration of undissociated acetic acid in the membrane abruptly increased from 0.1 mol/L C_0 , corresponding to the point where \bar{K} abruptly increased. It is suggested that the concentration dependence of \bar{K} is influenced by the activity coefficient change of undissociated acetic acid. In A201, \bar{K} is one-half that in K101, which implies the effect of charge density because the charge density of the former membrane is one-half that of the latter one.

4.2. Real Dissociation Constant of Weak Electrolyte in the Charged Membrane. Taking into account the activity coefficient of each species in the external solution, the following relationship is obtained from the Donnan equilibrium theory in the 1 valent cation and 1 valent anion system:

$$\gamma_+ C_+ / k_+ \gamma_+ C_+ = k_- \gamma_- C_- / \gamma_- C_- \quad (7)$$

or

$$\gamma_+ C_+ \gamma_- C_- = k_+ k_- \gamma_+ C_+ \gamma_- C_- \quad (8)$$

where $\bar{\gamma}_i$ is the activity coefficient of the i species in the membrane, γ_i is that of the external solution, and k_i is the partition coefficient of the i species between the external solution and the membrane in which $i = +$; for proton, $-$; for acetic acid anion. On the other hand, because undissociated weak electrolytes are in equilibrium between the external solution and

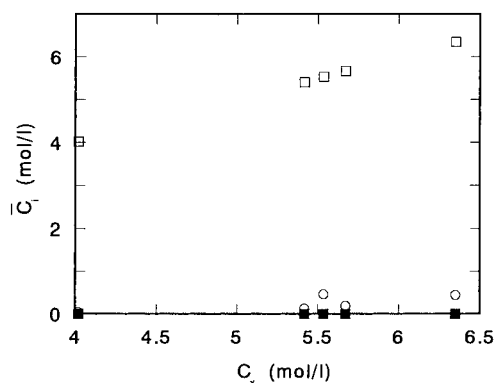


Figure 7. Concentrations of H^+ , CH_3COO^- , and CH_3COOH in cation-exchange membrane (\bar{C}_i) equilibrated with 0.1 mol/L acetic acid solution are plotted as a function of the fixed charge density (C_x). Key: (\square) H^+ , (\blacksquare) CH_3COO^- ; (\circ) CH_3COOH .

the membrane, the following relationship is introduced:

$$\bar{\gamma}_s \bar{C}_s = k_s \gamma_s C_s \quad (9)$$

where the subscript s indicates the undissociated solute. The real dissociation constant of the weak electrolyte in the membrane, \bar{K}_{th} , is rearranged using eqs 8 and 9 as follows:

$$\begin{aligned} \bar{K}_{\text{th}} &= \frac{\bar{a}_+ \bar{a}_-}{\bar{a}_s} = \frac{\bar{\gamma}_+ \bar{C}_+ \bar{\gamma}_- \bar{C}_-}{\bar{\gamma}_s \bar{C}_s} = \\ &= \frac{k_+ k_- \gamma_+ C_+ \gamma_- C_-}{k_s \gamma_s C_s} = (k_+ k_- / k_s) (a_+ a_- / a_s) = \\ &= (k_+ k_- / k_s) K_{\text{th}} \quad (10) \end{aligned}$$

where K_{th} is the real dissociation constant of the weak electrolyte in the external aqueous solution. Equation 10 tells us that the dissociation constant in the membrane depends only on the partition coefficients, which are already defined as a measure of the standard chemical potential difference of each species between the external solution and the membrane as shown in eq 11:

$$\bar{\mu}_i^0 - \mu_i^0 = -RT \ln k_i \quad (11)$$

where the standard chemical potential, μ_i^0 , is defined from the electrochemical potential of an ion in the medium as follows:

$$\mu_i = \mu_i^0 + RT \ln \gamma_i C_i + z_i F \varphi \quad (12)$$

where φ is the electric potential. The standard chemical potential of the electrolyte in the membrane depends on the ionic size and physicochemical properties of the solvent. Introduction of charge groups into the polymer chain induces the physicochemical property change of the solvent in the membrane. According to this procedure, the partition coefficients are affected by the fixed charge groups on the polymer chains. Therefore, \bar{K}_{th} is expected to be a function of the fixed charge density.

4.3. Dissociation Constant in the Membrane as a Function of Charge Density. The apparent dissociation constants of acetic acid in the cation-exchange membrane were determined as a function of the fixed charge density for a 0.1 mol/L external solution in the binary system. The concentrations of ions and undissociated neutral molecules in the membranes are shown in Figure 7 and the apparent dissociation constants, \bar{K} , are shown in Figure 8 as a function of the fixed charge density. The \bar{K} values are also listed in Table 1 with the results of the anion-exchange membrane. Prior to the discussion on the relationship between the fixed charge groups and dissociation constants, the

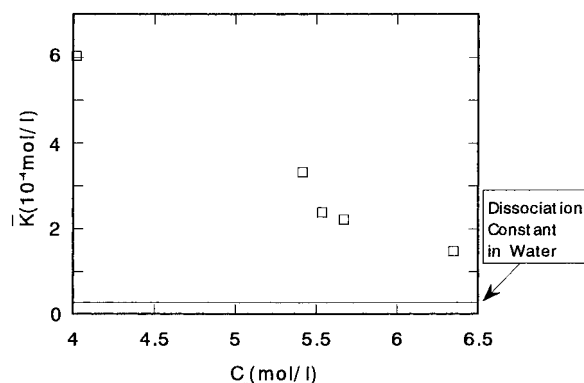


Figure 8. Apparent dissociation constants in charged membrane (\bar{K}) equilibrated with 0.1 mol/L acetic acid solution are plotted as a function of the fixed charge density (C_x).

activity coefficients are considered. In Figure 7, the counterion concentration in the membrane increases with an increase in the fixed charge densities whereas that of the co-ion remains constant. Using eqs 5 and 6, $\bar{\gamma}_+$ and $\bar{\gamma}_-$ were calculated and found to be constant and not dependent on the fixed charge density. On the other hand, the concentration of undissociated acetic acid increased from 0.03 mol/L (TK11) to 0.43 mol/L (TK15). However, the neutral molecule concentration, which affects the dissociation constant, is >0.47 mol/L ($C_0 = 0.1$ mol/L) for the cation-exchange membrane, as seen in Figure 6. Therefore, the activity coefficient of the neutral molecule is supposed to be constant for this concentration range in this system.

From the results just cited, the tendency in Figure 8 cannot be altered even if the effect of the activity coefficient is considered. Figure 8 and Table 1 show that \bar{K} in the cation-exchange membrane is on the order of 10^{-4} larger than those in an anion-exchange membrane ($=5.6 \times 10^{-5}$ for TA13 and 9.1×10^{-5} for A201) and also much larger than that in water ($=1.73 \times 10^{-5}$). The larger dissociation constant in the membrane than in water reminds us of the interaction between the solutes and the membrane other than that between the electric field and solute because the dissociation constant decreases with an increase in the fixed charge density. Therefore, it is concluded that the fixed charge groups have the effect of depressing the dissociation of a weak electrolyte. The fixed charge groups may influence the water structure in the membrane to induce the dielectric property change in the water region.

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