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Ionic mobility in water-swollen poly(vinyl alcohol) membranes

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Abstract : Poly(vinyl alcohol) membranes having various kinds of water content were prepared. In a dialysis system consisting of one of the membranes and solutions of KCl, CaCl₂ and K₂SO₄ electrolytes, the membrane potential, the permeability coefficient and the partition coefficient were measured. The potential data indicate that in the membranes, the mobility of large ions decreases with decreasing water content more steeply than that of small ions. The ratio of the ionic mobility in the membranes to that in aqueous solution is in proportion to the square of membrane tortuosity as the prediction of Mackie and Meares' theory; however, the proportion coefficient is not unity for the ions. Hence, a modified equation of the theory was proposed in order to estimate the ionic mobility in the membranes.

1. Introduction

The diffusion of ions in swollen membranes has been applied to many industrial fields such as the purification of chemical products and the treatment of industrial waste water and also medical fields such as hemodialysis. The theoretical treatment of the diffusion in an aqueous solution was developed by Nernst [1] and Planck [2] who expressed flux of the *i*th ion, J_i , as the product of its mobility in an aqueous solution, ω_i , its concentration, C_i , and its driving forces:

$$J_i = -\omega_i C_i \left[\frac{RTd(\ln C_i)}{dx} + z_i F \frac{d\phi}{dx} \right] \quad (1)$$

where z_i is the valence of the ion; F , R and T are the Faraday constant, the gas constant and the absolute temperature, respectively; the terms, $RTd(\ln C_i)/dx$ and $z_i F d\phi/dx$ are the diffusion force and the electric force, respectively. This equation has been the basis of many studies [3,4] such as a theory for membrane potential by

Henderson [5] and by Goldman [6], and a theory for ionic permeation in a charged membrane by Teorell [7], Meyer, and Seivers [8]. However, the Nernst-Planck equation is insufficient for the diffusion in a swollen membrane because it does not take the effects of the membrane structure into account. To explain the diffusion in membranes, many authors have replaced the ionic mobility, ω_i , in eqn (1) with the apparent one, $\bar{\omega}_i$, which is a function of both ω_i and factors such as membrane geometry [9-26] and fixed charges in membranes [27-32]. The factors due to membrane geometry are related to the mobility ratio as [9,10]

$$\frac{\bar{\omega}_i}{\omega_i} = \frac{1}{\theta^2} \quad (2)$$

where θ is the tortuosity defined as a mean increase in path length due to the obstruction of membrane matrix. Mackie and Meares [11] derived stochastically the factor as a function of the water content, H , of a swollen membrane:

$$\theta = \frac{2-H}{H} \quad (3)$$

This study aims to analyze the relationship between the ionic mobility in water-swollen membranes and the water content. Hence, we measure the membrane potential, the permeability coefficient and the partition coefficient of KCl, CaCl₂ and K₂SO₄ using poly(vinyl alcohol) membranes having various kinds of the water content. The ionic mobility in the membranes obtained from the experiments is compared with the prediction of Mackie and Meares' theory.

2. Experiments

2.1 Samples

Membranes were cast from an aqueous solution of PVA [poly(vinyl alcohol), Wako Pure Chemical Industries Ltd., DP=2000]. The water content of the gel membranes was controlled by annealing at various temperatures for 20 minutes and by swelling in ion-exchanged water.

2.2. Measurement of membrane water content

Membrane water content, defined as the volume fraction of water in a swollen membrane, was estimated from the following equation:

$$H \equiv \frac{(W_s - W_d)/1.0}{(W_s - W_d)/1.0 + W_d/1.3} \quad (4)$$

where W_s and W_d are the weights of a membrane at the equilibrium swollen and dry states, respectively; and 1.0 and 1.3 are the densities of water and PVA, respectively. Table 1 shows the annealing temperature as well as the membrane thickness and the water content. The water content decreased with increasing annealing temperature.

2.3 Measurement of membrane potential

Membrane potential was measured in a diffusion dialysis system of KCl, CaCl₂ and K₂SO₄ electrolytes using the same apparatus as described elsewhere [33]

in order to obtain the mobility ratio of the cation and the anion of the electrolytes.

Table 1 Annealing temperature, T_a , and the water content, H , and the membrane thickness, d of sample membranes.

Samples	T_a [°C]	H [-]	d [μm]
M-1	-	0.83	207
M-2	110	0.70	125
M-3	140	0.64	117
M-4	160	0.54	145
M-5	170	0.44	91
M-6	185	0.37	85
M-7	195	0.29	105

2.4 Measurement of partition coefficient

Partition coefficient of KCl, CaCl₂ and K₂SO₄ electrolytes was measured by the following steps: A membrane, weighted in the dry state, was immersed in the ion-exchanged water for 5 days. The swollen membrane was equilibrated in C_e ($= 1.0 \times 10^{-2}$ mol dm⁻³) of the electrolyte solutions for 24h. After the weight was measured, the membrane was immersed in V_1 ($= 0.5$ dm³) of ion-exchanged water for 24h. The concentration of the electrolyte in this solution, C_e^a , was measured by a conductivity meter [TOA CM-15A]. The partition coefficient of the electrolyte is given as

$$K_e \equiv \frac{\bar{C}_e}{C_e} = \frac{V_1 C_e^a}{(w_w - w_d)/d_s} \frac{1}{C_e} \quad (5)$$

where w_d and w_w are the weight of the membrane in the dry and in the wet states, respectively, and d_s is the density of membrane-immersed solution.

2.5 Measurement of permeation coefficient

Permeability coefficient of KCl, CaCl₂ and K₂SO₄ electrolytes through the membranes was measured in a dialysis system of the electrolyte solutions using the same apparatus as described elsewhere [33]. The initial concentration of the side L and the side R cells of the dialysis system are 0.01 and 0.001 mol dm⁻³, respectively. The permeability coefficient, P_e , was

evaluated from the initial slope of the time-versus-concentration curve, $\Delta C_e / \Delta t$, using the following equation:

$$P_e = -\frac{V_R d}{(C_e^L - C_e^R) S'} \frac{\Delta C_e}{\Delta t} \quad (6)$$

where V_R is the volume of the side R; d is the membrane thickness. S' ($=S \cdot H$) is the effective membrane area; S is the cross-sectional area of the membrane.

3. Results and Discussion

3.1 The relationship between the mobility ratio of the cation to the anion and the water content

As mentioned in the Appendix, eqn. (1) gives membrane potential, $\Delta\phi$, in a diffusion dialysis system consisting of electrolyte solutions and a non-charged membrane:

$$\Delta\phi = -\frac{RT}{F} \frac{r_m - 1}{z_c r_m - z_a} \ln(r) \quad (7)$$

where $r = C_i^L / C_i^R$. The mobility ratio of the cation to the anion in the membrane is defined as

$$r_m = \frac{\bar{\omega}_c}{\bar{\omega}_a} \quad (8)$$

Eqn. (7) indicates that the mobility ratio, r_m , is estimated from the membrane potential data. In order to analyze the relationship between r_m and membrane water content, the membrane potential was measured using the PVA membranes having various kinds of water content. The mobility of K^+ , Ca^{2+} , Cl^- and SO_4^{2-} ions in an aqueous solution are $7.9 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, $3.2 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, $8.2 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$ and $4.3 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, respectively [34]. Hence, r_m of $CaCl_2$, KCl and K_2SO_4 electrolytes in an aqueous solution ($H=1$) are 0.39, 0.96 and 1.84, respectively. The membrane potential calculated from the r_m ($H=1$) are -13.9mV , -0.83mV and 8.9mV , respectively.

Fig. 1 shows the experiments of the membrane potential as well as the calculations when $H=1$ as a

Fig.1 The membrane potential in a dialysis system of KCl , $CaCl_2$ and K_2SO_4 as a function of the water content, H .

function of the water content, H . The membrane potential of K_2SO_4 has positive values and increases with decreasing H while that of $CaCl_2$ has negative values and decreases with decreasing H . The potential of KCl is almost zero and is independent of H . Since the Stokes law indicates that the value of solute mobility is in inverse proportion to its hydration radius, the hydration radius of Ca^{2+} ions is larger than that of Cl^- ions; the radius of SO_4^{2-} ions is larger than that of K^+ ions. K^+ ions have almost the same hydration radius as Cl^- ions.

Fig 2(a) shows r_m of $CaCl_2$ electrolyte obtained from the potential data as a function of H . As mentioned above, r_m of $CaCl_2$ is 0.39 in the case of $H=1$ and decreases with decreasing H . This means that the mobility of Ca^{2+} ions in the membranes decreases with decreasing H more steeply than Cl^- ions does. Fig. 2(b) shows r_m of KCl and K_2SO_4 electrolytes. The mobility ratio of K_2SO_4 increases with decreasing H . This means that the mobility of SO_4^{2-} ions in the membranes decreases with decreasing H more steeply than K^+ ions does. The mobility ratio of KCl is almost equal to unity when $H=1$, and is independent of H . The dependence of the

mobility ratio on the water content indicates that in water-swollen membranes, the mobility of large ions

Fig. 2 The mobility ratio of the cation to the anion, r_m , as a function of the water content, H .
(a) the data for CaCl_2 , (b) the data for KCl and K_2SO_4 .

decreases with decreasing water content more steeply than that of small ions.

3.2 The experiments of the partition coefficient and the permeability coefficient

Fig. 3 shows the partition coefficient of KCl , CaCl_2 and K_2SO_4 electrolytes in the membranes. The partition coefficients of all the electrolytes decrease with decreasing H . The decrease of K_2SO_4 is steeper than that of KCl and CaCl_2 .

Fig. 3 The partition coefficient of KCl , CaCl_2 and K_2SO_4 as a function of the water content, H .

Fig. 4 The permeability coefficient of KCl , CaCl_2 and K_2SO_4 as a function of the square of the tortuosity, $[H/(2-H)]^2$.

Fig. 4 shows the permeability coefficient of the electrolytes as a function of the square of the tortuosity, $[H/(2-H)]^2$. The permeability coefficients decrease with decreasing $[H/(2-H)]^2$.

Fig. 5 The diffusion coefficient of KCl , CaCl_2 and K_2SO_4 as a function of the square of the tortuosity, $[H/(2-H)]^2$.

The permeability coefficient is given as the product of the partition coefficient and the diffusion coefficient. Fig. 5 shows the diffusion coefficient, D_e , of the electrolytes in the membranes obtained from the experiments of the partition coefficient and the permeability coefficients. The diffusion coefficients of all the electrolytes decrease with decreasing the tortuosity factor and are in proportion

to the factor. The slope of KCl is larger than that of K_2SO_4 and $CaCl_2$.

3.3 Comparison of the experiments with Mackie and Meayers' theory

As mentioned in the Appendix, Eqn. (1) gives the diffusion coefficient of an electrolyte as

$$D_e = \frac{(z_c - z_a)\omega_c RT}{z_c r_m - z_a} \quad (9)$$

The mobility ratio, m_r , is defined as

$$m_r = \frac{\bar{\omega}_i}{\omega_i} \quad (10)$$

where $\bar{\omega}_i$ is the ionic mobility in the membranes obtained from the experiments; ω_i is the ionic mobility in aqueous solution [34]. In order to compare the experiments with the prediction of Mackie and Meares' theory, m_r is obtained in terms of eqns (7) and (9) from the data of the potential and the diffusion coefficient.

Fig. 6 The ratio of ionic mobility in the membranes to that in aqueous solution as a function of the square of the tortuosity, $[H/(2-H)]^2$. (a) the

data for the cations, (b) the data for the anions.

Figs.6(a) and 6(b) show m_r of the cations and the anions, respectively, as a function of the square of tortuosity factor, $[H/(2-H)]^2$. The m_r of K^+ ions for KCl is almost the same as that for K_2SO_4 . The m_r of Cl^- ions for KCl is also almost the same as that for $CaCl_2$. These results confirm that Kohlrausch's law of the independent migration of ions is held in the swollen PVA membranes.

Mackie and Meares' theory predicts that m_r is in proportion to the square of tortuosity factor, $[H/(2-H)]^2$, and the proportion coefficient is unity for all electrolytes. The experiments of the m_r are in proportion to the square of the factor; however, the proportion coefficients are not unity and have different values from each other. In order to estimate ionic mobility in a swollen membrane, we give a modified equation of the theory as:

$$\frac{\bar{\omega}_i}{\omega_i} = \alpha_i \frac{1}{\theta^2} \quad (11)$$

The proportion coefficient, α_i , for the ions was obtained from the experiments and listed in Table 2.

Table 2 The proportion coefficient, α_i , of the ions for the electrolytes.

Ion	electrolyte	α_i
K^+	KCl	0.94
K^+	K_2SO_4	0.94
Ca^{2+}	$CaCl_2$	0.60
Cl^-	KCl	0.68
Cl^-	$CaCl_2$	0.68
SO_4^{2-}	K_2SO_4	0.56

The α_i of K^+ ions is almost equal to unity, which means that Mackie and Meares' theory can predicts the mobility of K^+ ions in a swollen membrane. However, the α_i of ions with large hydration radius such as Ca^{2+} ions and SO_4^{2-} ions is much smaller than unity. A physical meaning of α_i is considered to be that: Mackie and Meares considered

a simple lattice model for homogeneous matrix.

Fig. 7 Schematic diagram of ionic diffusion in a swollen membrane.

They also assumed that all ions have the same radius. However, in an apparent system, membrane matrix is heterogeneous, and the radius of ions differs from each other. Hence, as shown in Fig. 7, the number of the paths where large ions can go through will be smaller than that where small ions can. This means that the effective membrane area, S' , for the large ions is smaller than that for the small ions. Moreover, the average length of the paths where large ions can go through will be larger than that where small ions can. This means that the effective tortuosity of large ions is larger than that of small ions. For large ions, the effective area decreases and the effective tortuosity increases with decreasing water content more steeply than for small ions. Therefore, the proportion coefficients, α_i , of large ions such as Ca^{2+} ions is smaller than that of small ions such as K^+ ions. The α_i of Cl^- ions is much smaller than unity though the mobility of Cl^- ions in aqueous solution is almost equal to that of K^+ ions. The difference of α_i between the two ions may be due that the hydration structure of Cl^- ions differs from that of K^+ ions.

4. Conclusions

In order to analyze the relationship between the ionic mobility in water-swollen membranes and the water content, we measured the membrane potential, the permeability coefficient and the partition coefficient of KCl , CaCl_2 and K_2SO_4 using PVA membranes having various kinds of the water content.

The potential data indicates that in water-swollen membranes, the mobility of large ions decreases with decreasing water content more steeply than that of small ions. The ionic mobilities in the membranes obtained from the experiments are in proportion to the square of the tortuosity as the prediction of Mackie and Meares' theory; however, the proportion coefficient is not unity for the ions. Hence, a modified equation of the theory was proposed in order to estimate the ionic mobility in the membranes. We think that the deviation between the experiments and the prediction of Mackie and Meares' theory occurs because for the large ions, the effective membrane area is smaller, and the effective tortuosity is larger than that for the small ions as the water content decreases.

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Appendix

From eqn. (1), the ion flux in a membrane is given as

$$J_i = -\bar{\omega}_i \bar{C}_i \left[\frac{RTd(\ln \bar{C}_i)}{dx} + z_i F \frac{d\phi}{dx} \right] \quad (\text{A-1})$$

In a diffusion dialysis system consisting of a membrane

and solutions of an electrolyte, the electric current across the membrane should be equal to zero:

$$I = FS \sum z_i J_i = FS(z_c J_c + z_a J_a) = 0 \quad (\text{A-2})$$

where the subscripts "c" and "a" indicate the cation and the anion of the electrolyte, respectively. The electroneutrality condition in the membrane requires that

$$\sum z_i \bar{C}_i = 0 \quad (\text{A-3})$$

$d\phi/dx$ in the system is obtained from eqns. (A-1), (A-2) and (A-3) as

$$\frac{d\phi}{dx} = -\frac{RT}{F} \frac{(\omega_c - \omega_a)}{(z_c \omega_c - z_a \omega_a) \bar{C}_i} \frac{d\bar{C}_i}{dx} \quad (I = c \text{ or } a) \quad (\text{A-4})$$

Thus, $\Delta\phi$ is given by integrating eqn. (A-4) as

$$\Delta\phi = -\frac{RT}{F} \frac{r_m - 1}{z_c r_m - z_a} \ln \left(\frac{\bar{C}_i^R}{\bar{C}_i^L} \right) \quad (\text{A-5})$$

where $\bar{C}_i^R$ and $\bar{C}_i^L$ are the ionic concentration in the membrane surface at cell R and cell L, respectively. Eqn. (5) indicates $\bar{C}_i = C_i \cdot K_i$. The electroneutrality condition in the membrane gives $K_c = K_a = K_e$. Hence, Eqn. (A-5) gives Eqn. (7). The ionic flux is given from eqn. (A-4) into (A-1) and (A-2) as

$$J_i = -\frac{RT}{d} \frac{(\omega_c - \omega_a)}{(z_c \omega_c - z_a \omega_a)} K_i \cdot \Delta C_i \quad (\text{A-6})$$

The diffusion coefficient is given from eqn. (A-6) as

$$D_e = -\frac{J_i d}{\Delta C_e K_e} = \frac{(z_c - z_a) \omega_c RT}{z_c r_m - z_a} \quad (\text{A-7})$$

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