

MEMBRANE CHARGE DISTRIBUTION OF CELLULOSE ACETATE MEMBRANE AROUND THE INTERFACE BETWEEN THE MEMBRANE AND BULK SOLUTION*

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Summary

To obtain an information on the membrane charge around the interface, we measured the membrane potential and ζ -potential of cellulose acetate in aqueous NaCl solution at 34°C. The ζ -potential was negative but nearly equal to zero. The Donnan potential obtained from the analysis of the membrane potential was also negative, but the absolute magnitude was much larger than ζ -potential. As the results of analysis, it was found that the cellulose acetate membrane itself had no fixed charge and the effective membrane charge was due to the Cl^- ions adsorbed by the membrane. The saturated adsorption amount expressed in surface density and the adsorption coefficient within the membrane were the same as those at the surface. It was, therefore, concluded that even if the surface density of adsorbed ions within the membrane is as small as at the membrane surface, the membrane charge strongly affects the Donnan potential. This is because the Donnan potential was affected not by the charge density expressed in surface density but by the charge density in volume density. Within the membrane, the charge density in volume density becomes very large since the pore radius is extremely small, even if the adsorbed amount in surface density was small.

1. Introduction

Cellulose acetate is one of the most important membrane materials for separation membranes, e. g., RO membranes. The separation efficiency of a membrane is significantly influenced not only by the sieving action but also by the membrane charge [1, 2]. The membrane charge interacts with ions electrically and affects the separation efficiency of ions through the partition of ions from the bulk solution into the membrane.

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Then, the charged state of the membrane around the interface is very important to consider the separation efficiency of a membrane. Figure 1 schematically shows the distribution of potential across the membrane. The membrane potential is the sum of the diffusion potential and the Donnan potentials. The Donnan potential is the potential at the inner position located just a little off the interface [3-5]. Therefore,

the membrane potential mainly reflects the charge within the membrane. On the other hand, the ζ -potential is the potential at the slipping plane and reflects the charge at the slipping plane. The slipping plane is at outer position just a little off the interface. Therefore, it is possible to obtain more precise information on the distribution of the membrane charge, especially at the interface, by comparing the Donnan potential with the ζ -potential [6].

In this paper we discuss the membrane charge around the interface between cellulose acetate membrane and bulk solution.

2. Experimental

2. 1. Membrane preparation

Cellulose acetate membranes of about 10 μm in thickness were formed by casting at room temperature. The casting solution was prepared by dissolving 17.0g of cellulose acetate (acetylation 55%), 68.0g of acetone and 1.5g of magnesium perchlorate into 13.5g of distilled water. The membranes formed were stocked in distilled water and swollen well.

2. 2. ζ -potential

The ζ -potential was determined by the streaming potential method. The rolled cellulose acetate membrane of 10 mm wide and about 6 m long was set in a Teflon cell. The electrolyte solution kept at 34°C in liquid reservoir was streamed through the cell by the pressure of nitrogen gas, and the potential difference generated between two Pt-electrodes was recorded as a function of the pressure. In this experiment, the NaCl aque-

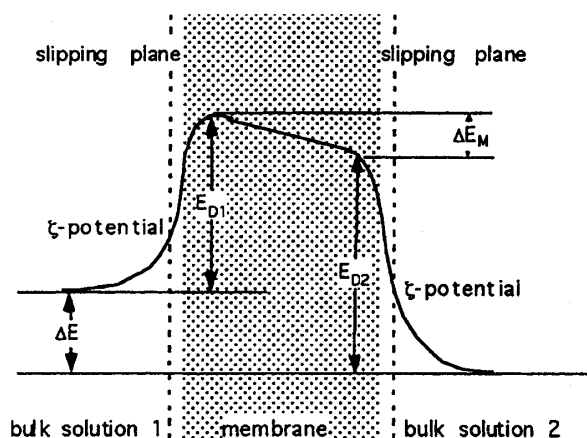


Fig. 1 Potential distribution across the membrane

ous solution of $0.1 \text{ mol} \cdot \text{m}^{-3}$ was used as the electrolyte solution. In this setting, the electrolyte solution flowed along the membrane surface. Therefore, we could measure the potential at outer position located just a little off the surface.

The magnitude of ζ -potential was determined using the Helmholtz-Smoluchowsky's equation, eq.(1).

$$\zeta = (\eta\kappa/\varepsilon)(H/P) \quad (1)$$

Here, η ($\text{N} \cdot \text{s} \cdot \text{m}^{-2}$) is the viscosity coefficient of electrolyte solution, κ ($\text{S} \cdot \text{m}^{-1}$) the electric conductivity, ε ($\text{F} \cdot \text{m}^{-1}$) the permittivity, H (mV) the streaming potential and P ($\text{N} \cdot \text{m}^{-2}$) the pressure.

2. 3. Membrane potential

The membrane was clamped tightly between two cells. The cells were filled with electrolyte solution and plugged up to prevent the volume flow. The membrane potential was measured using NaCl at 34°C and for $r = C_{1B} / C_{2B} = 2$, where C_{1B} and C_{2B} were the NaCl concentration in bulk solution 1 and 2, respectively. The potential difference, ΔE_{ob} , was measured by inserting Ag-AgCl electrode directly into the bulk solutions [7, 8]. The electrode inserted into the bulk solution 2 was grounded. Then, the membrane potential was given by eq. (2).

$$\Delta E = \Delta E_{\text{ob}} - \frac{RT}{F_A} \ln \frac{a_2}{a_1} \quad (2)$$

where a_1 and a_2 are the activity of Cl^- ion [9] in bulk solution 1 and 2, respectively.

3. Theoretical

Figure 2 shows the membrane model used for the analysis of membrane potential [10, 11]. The membrane itself is assumed to be homogeneous, with both surfaces having the same properties.

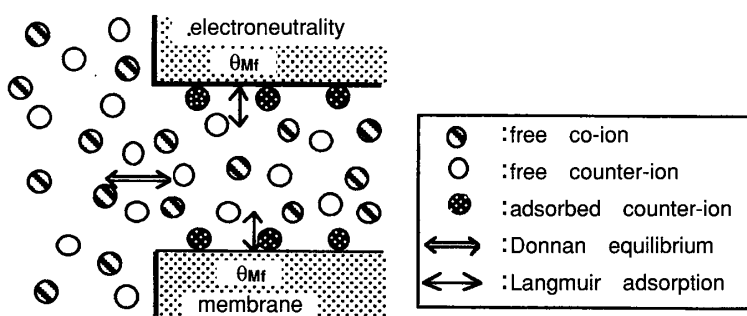


Fig. 2 Selective ion adsorption model

In this model, ions are partitioned from the bulk solution into the membrane pore under the influence of the Donnan potential. Among partitioned ions in the membrane pore, either cations or anions are adsorbed selectively by the pore wall according to the Lang-

muir model. The adsorbed ions bound at the pore wall give the electric charge to the membrane and affect the Donnan equilibrium. In the steady state, the Donnan equilibrium condition is set up between free ions in the bulk solution and at the pore end. The adsorbed ions are in equilibrium with free ions in the pore. No electric current flows through the membrane in the steady state. Electroneutrality condition is satisfied at everywhere within the system.

In this paper, we treat the membrane system that contains one kind of uni-univalent electrolyte, cation, i , and anion, a . We assume that the system is in the steady state and is of no volume flow through the membrane. If anions are adsorbed selectively and the ionic valence of adsorbed ion Z_{ad} is -1 , the concentration of each ion partitioned to membrane surface and the effective membrane charge density at the membrane surface are obtained by solving the following equations simultaneously.

$$[i]_M - [a]_M + \theta_M = 0 \quad (3)$$

$$\theta_M - \theta_{Mf} = -[n_0] \kappa_0 [a]_M / (1 + \kappa_0 [a]_M) \quad (4)$$

$$[i]_M / [i]_B = [a]_B / [a]_M \quad (5)$$

Here, subscripts M and B indicate membrane and bulk solution, respectively. Square brackets indicate concentrations ($\text{mol} \cdot \text{m}^{-3}$), with subscripts M and B indicating concentrations of free ions in the membrane and in the bulk solution, respectively. θ_M ($\text{mol} \cdot \text{m}^{-3}$) is the effective membrane charge density and θ_{Mf} ($\text{mol} \cdot \text{m}^{-3}$) the fixed membrane charge density. θ_M and θ_{Mf} are algebraic and may be positive or negative. κ_0 ($\text{m}^3 \cdot \text{mol}^{-1}$) is the adsorption coefficient and $[n_0]$ ($\text{mol} \cdot \text{m}^{-3}$) the saturated amount of adsorbed ion. In this system, the membrane potential is given by eq. (6).

$$\Delta E = E_{1B} - E_{2B} = \Delta E_D + \Delta E_M = \frac{RT}{F_A} \ln \left(\frac{[a]_{2M} [a]_{1B}}{[a]_{2B} [a]_{1M}} \right) + \Delta E_M \quad (6)$$

Here, subscripts 1 and 2 denote membrane surface 1 and 2 which contacts with bulk solution 1 and 2, respectively. E_{1B} and E_{2B} denote the potential in the bulk solution 1 and 2, respectively. ΔE_D denotes the difference of the Donnan potential at the both surfaces and ΔE_M the diffusion potential within the membrane. R is the gas constant, T the absolute temperature and F_A the Faraday constant. ΔE_M is obtained by integrating eq. (7) over free ion concentration within the membrane where B_i and B_a are the mobility of cation and anion, respectively [11, 12].

$$\Delta E_M = -\frac{RT}{F_A} \int \left(\frac{B_i d[i]_M - B_a d[a]_M}{B_i [i]_M + B_a [a]_M} \right)$$

$$= -\frac{RT}{F_A} \int \frac{(B_i - B_a)(1 + \kappa_0[a]_M)^2 + B_i[n_0]\kappa_0}{\{(B_i + B_a)(1 + \kappa_0[a]_M)^2 + B_i[n_0]\kappa_0(1 + \kappa_0[a]_M)\}[a]_M - B_i(1 + \kappa_0[a]_M)^2\theta_{Mf}} d[a]_M \quad (7)$$

4. Results and Discussion

Figure 3 shows the experimental results of the membrane potential as a function of $\log C_{2B}$, where C_{2B} is the concentration of lower side bulk solution. In Fig. 3, the solid line shows the theoretical curve calculated with the values of parameters shown in Table 1. From Table 1, it was found that the membrane itself has no fixed membrane charge. The effective membrane charge is due to the Cl^- ions adsorbed selectively.

Table 2 shows the magnitude of ζ -potential and the charge density (surface density), Γ , determined from the ζ -potential. Table 2 also shows the magnitude of Donnan potential, E_D , and the charge density (volume density) at the position of the Donnan potential, θ_{MD} determined from the analysis of membrane potential. From Table 2, it is seen that the sign of the Donnan potential is the same as that of the ζ -potential. However, the absolute magnitude of the Donnan potential is much higher than that of the ζ -potential. This means that the effective membrane charge density within the membrane is higher than that at the membrane interface. Because, the Donnan potential reflects the effective charge at the inner position located just a little off the interface, while the ζ -potential reflects the charge at outer position just a little off the interface. Assuming the ζ -potential is the surface potential, for the bulk solution of $0.1 \text{ mol} \cdot \text{m}^{-3}$, the concentration of Cl^- ion at the surface is calculated from the Boltzman distribution to be $9.85 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$. Assuming the Langmuir adsorption

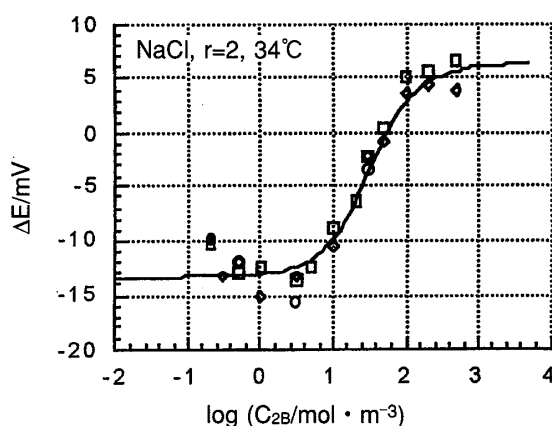


Fig. 3 Membrane potential measured for NaCl at 34°C. Solid line shows theoretical curve.

Table 1 Values of parameters of cellulose acetate

| τ | $\theta_{Mi}/\text{mol} \cdot \text{m}^{-3}$ | $[n_0]/\text{mol} \cdot \text{m}^{-3}$ | $\kappa_0/\text{m}^3 \cdot \text{mol}^{-1}$ |
|--------|--|--|---|
| -0.35 | 0.0 | 61.8 | 0.2 |

$\tau = (B_{Na} - B_{Cl})/(B_{Na} + B_{Cl})$, Cl^- ions are adsorbed.

Table 2 Potential and charge density

| E_D/mV | $\theta_{MD}/\text{mol} \cdot \text{m}^{-3}$ | ζ/mV | $\Gamma/\text{mol} \cdot \text{m}^{-2}$ |
|-----------------|--|-------------------|---|
| -34.24 | -0.34 | -0.4 | -9.4×10^{-11} |

at $0.1 \text{ mol}/\text{m}^3$ NaCl aq. soln.

and using the values of $[n_0]$ and κ_0 shown in Table 1 and $9.85 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$, the concentration of adsorbed chloride ion at the surface is calculated to be $1.19 \text{ mol} \cdot \text{m}^{-3}$. This value, $1.19 \text{ mol} \cdot \text{m}^{-3}$, is larger than $|\theta_{MD}|$ and does not consistent with the relation of E_D and ζ -potential.

At the interface, ions are adsorbed at the surface. Even within the membrane, ions are adsorbed at the pore wall. Therefore, it is natural to discuss about the effective membrane charge density with the dimension of surface density ($\text{mol} \cdot \text{m}^{-2}$). Since ions are adsorbed at the surface both at the interface and within the membrane, the value of adsorption coefficient at the interface is very likely the same as that within the membrane. If so, the saturated amount of adsorbed ion in volume density, $[n_0]$, is related with the saturated amount of adsorbed ion in surface density, Γ_s , by eq.(8) [12]

$$[n_0] = \Gamma_s S/V = 2\Gamma_s \pi r_p l / \pi r_p^2 l = 2\Gamma_s / r_p \quad (8)$$

where S denotes the inner surface area of the pore wall, V the volume of the pore, r_p the pore radius and l the unit length of the pore. For the bulk solution of $0.1 \text{ mol} \cdot \text{m}^{-3}$, the concentration of Cl^- ion at the surface is $9.85 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$ as mentioned above. At that time, the surface charge density, Γ , is $-9.4 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2}$ and the adsorption coefficient, κ_0 , is $0.2 \text{ m}^3 \cdot \text{mol}^{-1}$. Then, the saturated adsorption amount expressed in surface density, Γ_s , is calculated from the Langmuir isotherm equation to be $(\Gamma_s = 9.4 \times 10^{-11} (1 + 0.2 \times 9.85 \times 10^{-2}) / (0.2 \times 9.85 \times 10^{-2})) = 4.9 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2}$. From eq. (8), using the values of $[n_0]$ and Γ_s , the pore radius, r_p , is obtained to be about 2 \AA . This value is just a reasonable value for cellulose acetate membrane [13]. Therefore, it is concluded that the saturated amount of adsorbed ion in surface density is the same at the membrane surface and within the pore.

In the case where the membrane contacts with the bulk solution of $0.1 \text{ mol} \cdot \text{m}^{-3}$, the concentration of Cl^- ion partitioned to the pore end is $2.75 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$. Therefore, the effective membrane charge density in surface density at the pore end is $-2.71 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2}$ and about one thirds of the effective charge density at the surface, $-9.4 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2}$. Nevertheless, the magnitude of the Donnan potential is about 90 times as high as the magnitude of the ζ -potential. This is because the Donnan potential is affected by the charge density expressed in volume density. Within the membrane, the charge density in volume density becomes high and affects the partition of ions strongly and generates a large Donnan potential since the pore radius is extremely small, even if the charge density in surface density is very small.

5. Conclusion

We discussed the membrane charge of the cellulose acetate membrane around the interface by comparing the Donnan potential and the ζ -potential. The Donnan potential was obtained from the analysis of the membrane potential. The ζ -potential was determined from the streaming potential. As the results, it was made clear that the effective membrane charge in aqueous NaCl solution was due to the Cl^- ions adsorbed by the membrane and the membrane itself has no fixed membrane charge. Expressing the concentration of adsorbed ion by the surface density, $\text{mol}\cdot\text{m}^{-2}$, the adsorption isotherm within the membrane was the same as at the membrane surface. Nevertheless, the Donnan potential was more strongly affected by the adsorbed chloride ions than the ζ -potential, even if the adsorption amount of ion within the membrane was as small as at the surface. This is because that the Donnan potential was affected not by the charge density expressed in surface density but by the charge density in volume density. Within the membrane, the charge density in volume density becomes very high since the pore radius is extremely small, even if the amount of adsorbed ion in surface density was small.

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