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Theoretical Study on Asymmetric Membrane Potential

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It is well known that the asymmetry of membrane structure is closely related to the membrane function. We could obtain information on the asymmetry of membrane structure if we could analyze accurately the asymmetric membrane potential, since the asymmetry of membrane structure should affect the membrane potential. It is considered that the origin of the asymmetric membrane potential is the difference in properties between the two membrane surfaces. In this paper, the membrane is treated by dividing it into the two sublayer (surface layer) parts adjacent to each membrane surface and the inner membrane part. The asymmetric membrane potential is investigated theoretically on the base of this model. The results show that the effects of asymmetry with respect to the surface charge density on the surface potential and on the diffusion potential within the membrane compensate for each other. The membrane potential is, therefore, scarcely affected except in the case where the diffusion potential within the membrane is negligible. It is also pointed out that, in an asymmetric membrane system with respect to the surface charge density, diffusion potential within the membrane is generated even if the mobility of a cation is equal to that of an anion. When the diffusion potential within the membrane is not negligible, only the effect of the asymmetry with respect to the standard chemical potential at the membrane surfaces is measurable experimentally. Our theory was applied to the analysis of the membrane potential of a cellulose membrane, and gave good agreement with the experimental results. Various experimental methods to confirm whether the membrane is asymmetric or symmetric are discussed.

Keywords—membrane potential; asymmetric membrane; asymmetric membrane potential; surface charge density; standard chemical potential; cellulose membrane

Introduction

It is well known that the asymmetry of membrane structure is closely related to its function. As regards biomembranes, for example, the asymmetry of the localization of membrane carbohydrate was established by Nicolson and Singer.¹⁾ The carbohydrates are exposed only to the external milieu and are considered to be involved in surface-mediated functions.²⁾ Further, drug transport through the biomembrane is well known to be affected by the structure of the membrane surfaces.³⁾ When drug transport is investigated by using an artificial membrane, it is very important to have information regarding the asymmetry of membrane structure.

The asymmetry of membrane structure results from the difference in the packing fraction or the components of the membrane surface between internal and external surfaces. Therefore, the asymmetry of membrane structure results in a difference in the surface properties and should affect the membrane potential through the partition of ions between the bulk solution and the membrane surface. Thus, we should be able to obtain information about the asymmetry of membrane structure by analysis of the asymmetric membrane potential.

It is clear that the theoretical equations derived for a symmetric membrane are not applicable to analyze the asymmetric membrane potential. Ohki⁴⁾ derived theoretically an equation for the asymmetric membrane with respect to a fixed charge density, neglecting the

diffusion potential within the membrane. For most membranes, ion permeate to various degrees across the membrane, and a diffusion potential is set up within the membrane. In addition, one membrane surface may be different from the other surface with respect to the standard chemical potential for the same ion, since the differences in the properties between the membrane surfaces are due to the difference in the structure.

In this paper, we consider that the membrane potential can be represented as a sum of two surface potentials and the diffusion potential within the membrane. We derive equations for the standard chemical potential and the surface charge density of a membrane having different surfaces.

Membrane Potential

Membrane System and General Equation

The asymmetric membrane is treated by dividing it into two sublayer (surface layer) parts adjacent to each membrane surface and the inner membrane part. One sublayer will correspond to the carbohydrate layer for biomembranes and the modified layer for chemically modified membranes.

It is assumed that the Donnan equilibrium condition holds at the sublayer/bulk solution interface. Ions partitioned within the sublayer permeate through the membrane. The electric potential within the sublayer is considered to be equal to that at the membrane surface. The volume flow across the membrane is neglected.

Figure 1a shows a diagram of the membrane system. One sublayer is different from the other sublayer with respect to the fixed charge density and the standard chemical potential for the same ion.

The membrane potential, ΔE , is given by Eq. 1 with bulk solution 2 grounded as shown in Fig. 1b.

$$\Delta E = \Delta E_{D2} - \Delta E_{D1} + \Delta E_M = \Delta E_D + \Delta E_M \quad (1)$$

where ΔE_M is the diffusion potential within the membrane and ΔE_{D1} and ΔE_{D2} are the surface potentials at interfaces 1 and 2, respectively.

The surface potential is given by Eqs. 2 and 3 using the Donnan equilibrium condition,⁵⁾ where suffixes 1 and 2 denote the interfaces 1 and 2, respectively. S and B denote the sublayer and the bulk solution, respectively. k represents all ionic species including cations, i , and anions, a . z_k is the valence (algebraic) and $[k]$ is the molar concentration of the k -th ion.

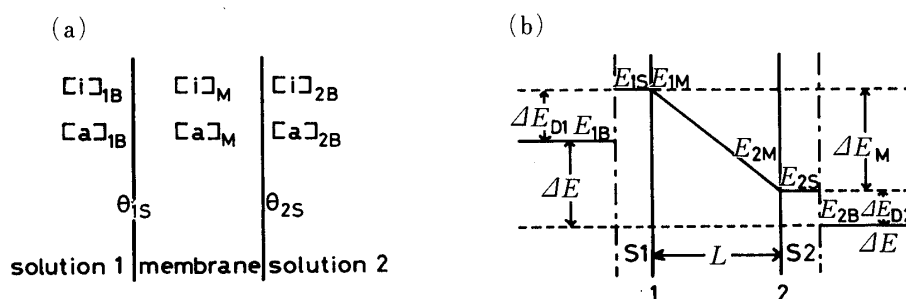


Fig. 1. (a) Diagram of an Asymmetric Membrane System

θ_{1S} , θ_{2S} : fixed charge density (mol/l) at sublayers 1 and 2, respectively.
 $i=1, \dots, n$ for cations and $a=1, \dots, m$ for anions.

(b) Schematic Diagram of Asymmetric Membrane Potential

Here, S indicates the sublayer at the membrane surface. ΔE_M , diffusion potential within the membrane; ΔE_{D1} , ΔE_{D2} , surface potential at interfaces 1 and 2, respectively; ΔE , membrane potential; L , thickness of membrane, $\Delta E_D = \Delta E_{D2} - \Delta E_{D1}$, $\Delta E = \Delta E_D + \Delta E_M$.

$$\Delta E_{D1} = -\frac{RT}{z_k F} \ln \left(g_{k1} \frac{[k]_{1S}}{[k]_{1B}} \right) \quad (2)$$

$$\Delta E_{D2} = -\frac{RT}{z_k F} \ln \left(g_{k2} \frac{[k]_{2S}}{[k]_{2B}} \right) \quad (3)$$

where g_{k1} and g_{k2} are the g_k values at interfaces 1 and 2, respectively, and are given by Eq. 4.

$$g_k = \gamma_{kS}/b_k \gamma_{kB} \quad (4)$$

γ_k is the activity coefficient, and

$$b_k = \exp(-\Delta\mu_k^\circ/RT) \quad (5)$$

where $\Delta\mu_k^\circ = \mu_{kS}^\circ - \mu_{kB}^\circ$ and μ_k° is the standard chemical potential of the k -th ion. R is the gas constant, T the absolute temperature and F the Faraday constant. From Eqs. 2 and 3, the surface potential difference ($\Delta E_{D2} - \Delta E_{D1}$) is

$$\Delta E_D = \frac{RT}{z_k F} \ln \left(\frac{g_{k1}}{g_{k2}} \frac{[k]_{1S}}{[k]_{2S}} \frac{[k]_{2B}}{[k]_{1B}} \right) \quad (6)$$

The diffusion potential, ΔE_M , is derived by integrating the potential gradient over the membrane thickness. It is assumed here that the membrane is homogeneous and that ions diffuse only along the x -axis which is normal to the membrane surface. The flux of each ion is regarded as proportional to its electrochemical potential gradient. The membrane system is assumed to be in a steady state in which no electric current flows across the membrane.

The distribution of the ionic concentration within the membrane is assumed to be given by Eq. 7.⁶⁾

$$[k]_M = (1 - \delta(x))[k]_{1S} + \delta(x)[k]_{2S} \quad (7)$$

where $\delta(x)$ is common to all kinds of ionic species.

Using Eq. 7, we can obtain Henderson's equation^{5,7)} as Eq. 8.

$$\Delta E_M = \frac{RT}{F} \frac{\sum_k z_k B_k ([k]_{1S} - [k]_{2S})}{\sum_k z_k^2 B_k ([k]_{1S} - [k]_{2S})} \ln \frac{\sum_k z_k^2 B_k [k]_{2S}}{\sum_k z_k^2 B_k [k]_{1S}} \quad (8)$$

where B_k is the mobility of the k -th ion within the membrane. From Eqs. 1, 6 and 8, the membrane potential, ΔE , is obtained as follows:

$$\begin{aligned} \Delta E &= \Delta E_D + \Delta E_M \\ &= \frac{RT}{z_k F} \ln \left(\frac{g_{k1}}{g_{k2}} \frac{[k]_{1S}}{[k]_{2S}} \frac{[k]_{2B}}{[k]_{1B}} \right) \\ &\quad + \frac{RT}{F} \frac{\sum_k z_k B_k ([k]_{1S} - [k]_{2S})}{\sum_k z_k^2 B_k ([k]_{1S} - [k]_{2S})} \ln \frac{\sum_k z_k^2 B_k [k]_{2S}}{\sum_k z_k^2 B_k [k]_{1S}} \end{aligned} \quad (9)$$

Partition of Ions between the Bulk Solution and the Sublayer

In order to use Eq. 9, we need to obtain the ionic concentration in the sublayer. These values are obtained from the electroneutrality condition and the Donnan equilibrium condition. For simplicity, we treat, hereinafter, the system which contains one kind of uni-univalent electrolyte (i^+ , a^-). The concentration of each ion is C_{1B} in bulk solution 1 and C_{2B} in bulk solution 2.

In this system, the electroneutrality condition is given by Eq. 10 and the Donnan

equilibrium condition by Eq. 11.

$$[i]_S - [a]_S + \theta_S = 0 \quad (10)$$

where θ_S is the fixed charge density in the sublayer.

$$\left(g_i \frac{[i]_S}{[i]_B} \right) = \left(g_a \frac{[a]_S}{[a]_B} \right)^{-1} \quad (11)$$

From Eqs. 10 and 11, we have

$$[i]_{1S} g_1 / C_{1B} = \sqrt{g_1^2 + 1} - g_{1S}, \quad [i]_{2S} g_2 / C_{2B} = \sqrt{g_2^2 + 1} - g_{2S} \quad (12)$$

and

$$[a]_{1S} g_1 / C_{1B} = \sqrt{g_1^2 + 1} + g_{1S}, \quad [a]_{2S} g_2 / C_{2B} = \sqrt{g_2^2 + 1} + g_{2S} \quad (13)$$

where $g_{1S} = \theta_{1S} g_1 / 2C_{1B}$, $g_{2S} = \theta_{2S} g_2 / 2C_{2B}$, $g_1^2 = g_{i1} \cdot g_{a1}$ and $g_2^2 = g_{i2} \cdot g_{a2}$. g_{i1} , g_{a1} , g_{i2} and g_{a2} are defined by Eq. 4.

From Eqs. 12 and 13, we find that the asymmetry of membrane structure influences the partition of ions between the bulk solution and the sublayer through θ_{1S} , θ_{2S} , g_1 and g_2 , since generally $\theta_{1S} \neq \theta_{2S}$ and $g_1 \neq g_2$ for an asymmetric membrane.

Discussion

1 Asymmetry with Respect to the Standard Chemical Potential

1-1 Membrane Potential—In this section, we discuss the membrane system in which one sublayer is different from the other sublayer with respect to the standard chemical potential, but the fixed charge density is symmetric and $\theta_{1S} = \theta_{2S}$.

Generally, asymmetry of the standard chemical potential will be present in most membrane systems. However, the degree of the asymmetry is not enough to detect experimentally. The standard chemical potential for the same ion is affected by the components of the solution.⁸⁾ The asymmetry discussed here will, therefore, be realized by chemically modifying one surface of the membrane with a substance such as carbohydrate.

Here, we assume $g_{i1} = g_{a1} = g_{k1}$ and $g_{i2} = g_{a2} = g_{k2}$, and put the relation between g_{k1} and g_{k2} as follows:

$$g_{k1} = r_g g_{k2} \quad (14)$$

and therefore,

$$g_1 = r_g g_2 \quad (15)$$

since $g_1^2 = g_{i1} \cdot g_{a1} = g_{k1}^2$ and $g_2^2 = g_{i2} \cdot g_{a2} = g_{k2}^2$. From Eqs. 4, 5 and 14, we have

$$r_g = \frac{\gamma_{k1S}}{\gamma_{k1B}} \frac{\gamma_{k2B}}{\gamma_{k2S}} \exp \{ (\Delta\mu_{k1}^\circ - \Delta\mu_{k2}^\circ) / RT \} \quad (16)$$

where $\Delta\mu_{k1}^\circ = \mu_{k1S}^\circ - \mu_{k1B}^\circ$ and $\Delta\mu_{k2}^\circ = \mu_{k2S}^\circ - \mu_{k2B}^\circ$. In Eq. 16, the concentration dependence of the activity coefficient is negligibly small.⁹⁾ Therefore, r_g is a constant determined by the membrane and the ionic species, and shows the asymmetry of the standard chemical potential.

Substituting Eqs. 12, 13, 14 and 15 into Eq. 9, and rearranging, we have

$$\Delta E = \Delta E_D + \Delta E_M = \pm \frac{RT}{F} \left\{ \ln \left(\rho' \frac{\sqrt{g'^2 + 1} + |g'|}{\sqrt{g'^2 + \rho'^2 + |g'|}} \right) + \tau_0 \ln \left(\frac{\sqrt{g'^2 + 1} - \tau_0 |g'|}{\sqrt{g'^2 + \rho'^2} - \tau_0 |g'|} \right) \right\} \quad (17)$$

where $C_{1B} = rC_{2B}$, $\vartheta' = \vartheta'_{2S} = \rho' \vartheta'_{1S} = \theta_S g_2 / 2C_{2B}$, $\theta_S = \theta_{1S} = \theta_{2S}$ and

$$\rho' = r/r_g \quad (18)$$

$\tau_0 = (B_c - B_g)/(B_c + B_g)$ where suffix c denotes a co-ion and g denotes a counter-ion for the membrane charge. The double sign of the potential takes the same sign as the membrane charge.

From Eq. 17, it can be seen that the parameter r_g does not appear in this equation explicitly, but implicitly in ρ' ($=r/r_g$). This indicates that the asymmetry of the standard chemical potential modifies the C_{1B}/C_{2B} ratio, r , and replaces r with ρ' . In other words, the asymmetry of the standard chemical potential gives the membrane system the same effect as a change of C_{1B}/C_{2B} ratio. The asymmetric membrane potential is, therefore, strongly affected by r_g . For $r_g = 1$, Eq. 17 reduces to the equation for the symmetric membrane.⁵⁾

Figure 2a shows the magnitude of the membrane potential calculated by Eq. 17 as a function of $\log |\vartheta'|$ for constant r . The two components of the membrane potential are shown in Fig. 2b, ΔE_D by broken lines and ΔE_M by solid lines. Line b in Figs. 2a and 2b is for the symmetric membrane since $r_g = 1$.

From Fig. 2a, we find that the magnitude of the asymmetric membrane potential is greater than that of the symmetric membrane potential at $r_g < 1$ (line a), and is smaller at $r_g > 1$ (line d). This is because, in the asymmetric membrane system where r_g is not unity, r is modified to ρ' ($=r/r_g$) as mentioned above. The magnitude of the asymmetric membrane potential, therefore, decreases with increasing value of r_g . According to this concept, the magnitude of the asymmetric membrane potential becomes zero at $r_g = r$ (line c), and the sign of the potential reverses at $r_g > r$ compared with that at $r_g < r$.

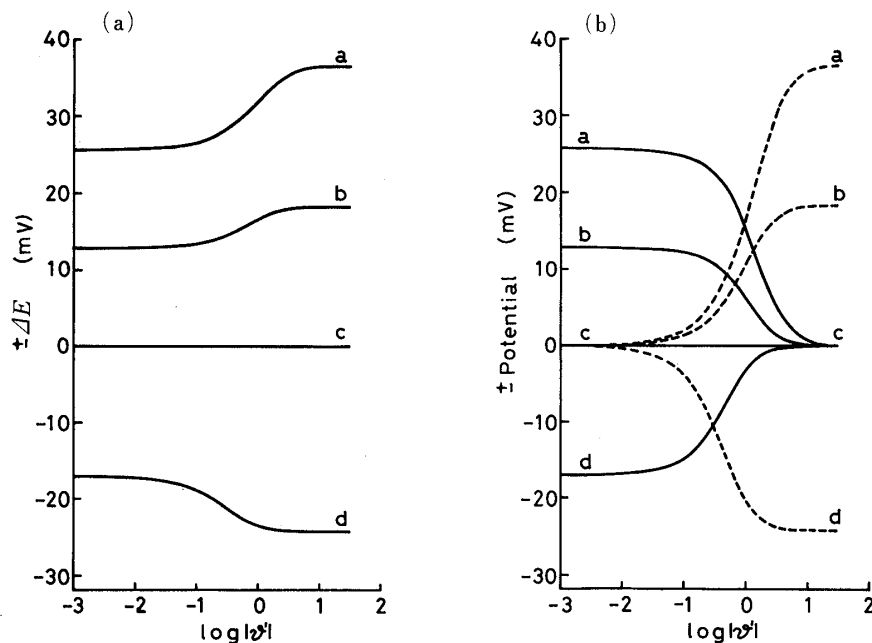


Fig. 2. (a) Membrane Potential of an Asymmetric Membrane with Respect to Standard Chemical Potential at $r=2$, $\tau_0 = -0.7$ and 34°C

The double sign of potential takes the same sign as the membrane charge.

$r_g = 0.5$ (a), 1(b), 2(c), 5(d).

(b) Two Components of the Asymmetric Membrane Potential Shown in Fig. 2a

Solid lines show the diffusion potential within the membrane and broken lines show the surface potential difference.

From Fig. 2b, it can be seen that the asymmetry of the standard chemical potential difference affects both ΔE_D and ΔE_M . In particular, when $r_g > r$ (line d), the sign of ΔE_M is opposite to that at $r_g < r$. This indicates that the reverse diffusion of ions across the membrane takes place under the condition of $r_g > r$.

1-2 Determination of the Values of Parameters—From Eq. 17, the limiting magnitude of the asymmetric membrane potential is given as follows:

$$C_{2B} \rightarrow \infty (|\mathcal{G}'| \rightarrow 0) \quad \Delta E = \pm \frac{RT}{F} \tau_0 \ln (1/\rho') \quad (19)$$

$$C_{2B} \rightarrow 0 (|\mathcal{G}'| \rightarrow \infty) \quad \Delta E = \pm \frac{RT}{F} \ln \rho' \quad (20)$$

From Eq. 20, the value of ρ' can be determined by using the value of the asymmetric potential measured at $C_{2B} \rightarrow 0 (|\mathcal{G}'| \rightarrow \infty)$. The determination of ρ' makes it possible to obtain the asymmetric parameter r_g , since $\rho' = r/r_g$ and r is known from the experimental conditions. If the value of ρ' is obtained, the value of τ_0 can be determined from Eq. 19. After the determination of ρ' and τ_0 , \mathcal{G}' is determined by Eq. 17 and $\theta_{sg_2} (= 2\mathcal{G}'C_{2B})$ is also determined.

2 Asymmetry with Respect to the Surface Charge Density

In this section, the membrane system of asymmetric charge density will be discussed, where $\theta_{1S} \neq \theta_{2S}$ but $g_{k1} = g_{k2} = g_k$. This membrane system can be realized by chemically modifying one surface of a membrane with a charged substance.

The ratio r_θ between θ_{1S} and θ_{2S} is written as

$$\theta_{1S} = r_\theta \theta_{2S} \quad (21)$$

Substituting Eqs. 12, 13 and 21 into Eq. 9, we have

$$\begin{aligned} \Delta E &= \Delta E_D + \Delta E_M \\ &= \pm \left\{ \frac{RT}{F} \ln \rho'' \frac{\sqrt{\mathcal{G}''^2 + 1} + |\mathcal{G}''|}{\sqrt{\mathcal{G}''^2 + \rho''^2} + |\mathcal{G}''|} + \frac{RT}{F} K'' \ln \left(\frac{1}{r_\theta} \frac{\sqrt{\mathcal{G}''^2 + 1} - \tau_0 |\mathcal{G}''|}{\sqrt{\mathcal{G}''^2 + \rho''^2} - \tau_0 |\mathcal{G}''|} \right) \right\} \end{aligned} \quad (22)$$

where

$$K'' = \frac{\tau_0(r_\theta \sqrt{\mathcal{G}''^2 + \rho''^2} - \sqrt{\mathcal{G}''^2 + 1}) - (r_\theta - 1) |\mathcal{G}''|}{r_\theta \sqrt{\mathcal{G}''^2 + \rho''^2} - \sqrt{\mathcal{G}''^2 + 1} - \tau_0(r_\theta - 1) |\mathcal{G}''|} \quad (23)$$

$$C_{1B} = rC_{2B}, \quad \mathcal{G}'' = \mathcal{G}_{2S}'' = \rho'' \mathcal{G}_{1S}'' = \theta_{2S} g / 2C_{2B}, \quad g^2 = g_1^2 = g_2^2 = g_i \cdot g_a = g_k^2 \quad \text{and}$$

$$\rho'' = r/r_\theta \quad (24)$$

Putting $r_\theta = 1$, Eq. 22 reduces to the equation for the symmetric membrane.

The limiting magnitudes of Eq. 22 are

$$C_{2B} \rightarrow \infty (|\mathcal{G}''| \rightarrow 0) \quad \Delta E = \pm \frac{RT}{F} \tau_0 \ln \frac{1}{r} \quad (25)$$

and

$$C_{2B} \rightarrow 0 (|\mathcal{G}''| \rightarrow \infty) \quad \Delta E = \pm \left(\frac{RT}{F} \ln \rho'' - \frac{RT}{F} \ln \frac{1}{r_\theta} \right) = \pm \frac{RT}{F} \ln r \quad (26)$$

From Eqs. 25 and 26, it is found that the limiting magnitudes of the membrane potential in this case are independent of the asymmetry of membrane structure. Equations 25 and 26 are the same as the limiting magnitudes of the symmetric membrane potential.⁵⁾

Next, we consider the bulk concentration dependence of Eq. 22. For the calculation, the

average membrane charge density over the membrane volume, θ_{av} , is kept constant. θ_{av} is assumed to be given by $(\theta_{1S} + \theta_{2S})/2$. θ_{1S} and θ_{2S} , therefore, satisfy the following relations:

$$\theta_{1S} = r_\theta \theta_{2S}, \quad \theta_{1S} + \theta_{2S} = 2\theta_{av} \quad (27)$$

In the cases where $\tau_0 = 1$ and -1 , Eq. 22 can be rewritten as follows: at $\tau_0 = 1$,

$$\Delta E = \pm \left\{ \frac{RT}{F} \ln \rho'' \frac{\sqrt{g''^2 + 1} + |g''|}{\sqrt{g''^2 + \rho''^2 + |g''|}} + \frac{RT}{F} \ln \left(\frac{1}{r_\theta} \frac{\sqrt{g''^2 + 1} - \tau_0 |g''|}{\sqrt{g''^2 + \rho''^2} - \tau_0 |g''|} \right) \right\} \quad (28)$$

$$= \pm \frac{RT}{F} \ln \frac{1}{r} \quad (29)$$

and at $\tau_0 = -1$,

$$\Delta E = \pm \left\{ \frac{RT}{F} \ln \rho'' \frac{\sqrt{g''^2 + 1} + |g''|}{\sqrt{g''^2 + \rho''^2 + |g''|}} - \frac{RT}{F} \ln \left(\frac{1}{r_\theta} \frac{\sqrt{g''^2 + 1} - \tau_0 |g''|}{\sqrt{g''^2 + \rho''^2} - \tau_0 |g''|} \right) \right\} \quad (30)$$

$$= \pm \frac{RT}{F} \ln r \quad (31)$$

From Eqs. 29 and 31, the magnitudes of membrane potential at $\tau_0 = \pm 1$ are the same as the magnitudes of the symmetric membrane potential at $\tau_0 = \pm 1$.⁵⁾ In addition, from Eqs. 28 and 30, it is found that the asymmetry of surface charge density affects both ΔE_D and ΔE_M . However, these effects on ΔE_D and ΔE_M compensate for each other and do not influence the membrane potential.

At $\tau_0 = 0$, Eq. 22 can be rewritten as follows:

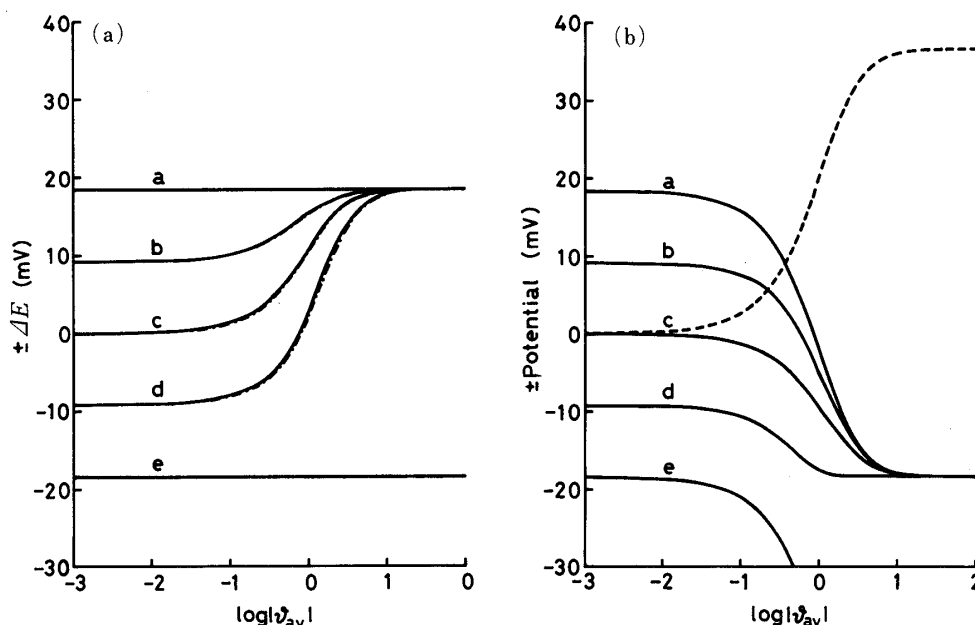


Fig. 3. (a) Membrane Potential of an Asymmetric Membrane with Respect to the Surface Charge Density at $r=2$, $r_\theta=0.5$ and 34°C

$g_{av} = \theta_{av}g/2C_{2B}$ and $\theta_{av} = (\theta_{1S} + \theta_{2S})/2$. The double sign of the potential takes the same sign as the membrane charge. Broken lines show the symmetric membrane potential under the same conditions except that $r_\theta=1$. $\tau_0 = -1$ (a), -0.5 (b), 0 (c), 0.5 (d), 1 (e).

(b) Two Components of the Asymmetric Membrane Potential Shown in Fig. 3a

Solid lines show the diffusion potential within the membrane and the broken line the surface potential difference. $\tau_0 = -1$ (a), -0.5 (b), 0 (c), 0.5 (d), 1 (e).

$$\Delta E = \Delta E_D + \Delta E_M = \pm \left\{ \frac{RT}{F} \ln \rho'' \frac{\sqrt{g''^2 + 1} + |g''|}{\sqrt{g''^2 + \rho''^2} + |g''|} - \frac{RT}{F} \frac{(r_\theta - 1) |g''|}{r_\theta \sqrt{g''^2 + \rho''^2} - \sqrt{g''^2 + 1}} \ln \frac{1}{r_\theta} \frac{\sqrt{g''^2 + 1}}{\sqrt{g''^2 + \rho''^2}} \right\} \quad (32)$$

From Eq. 32, it is found that even if $\tau_0 = 0$, a diffusion potential is generated within the membrane. This is one of the characteristic properties arising from the asymmetry of surface charge density. Equation 32 is, of course, not the same as the equation for the symmetric membrane.

Figure 3a shows the bulk concentration dependence of Eq. 22 as a function of $\log |\vartheta_{av}|$ for various values of τ_0 , where $\vartheta_{av} = \theta_{av} g / 2C_{2B}$. In Fig. 3a, r_θ and r have been kept constant. Broken lines show the symmetric membrane potential under the same conditions as for the other lines except that $r_\theta = 1$. From Fig. 3a, it is found that the membrane potential is scarcely affected by the asymmetry of surface charge density, even when $\tau_0 \neq \pm 1$ or $\vartheta_{av} \neq 0$ or ∞ . The two components of the asymmetric membrane potential are shown in Fig. 3b, ΔE_D by a broken line and ΔE_M by solid lines. In Fig. 3b, ΔE_D is the same for all lines since r_θ and r are kept constant, but ΔE_M varies with the value of τ_0 . Line c in Fig. 3b is the diffusion potential at $\tau_0 = 0$, and it is found that ΔE_M is not zero even if $\tau_0 = 0$.

In order to study the effect of asymmetric charge distribution further, we will consider the bulk concentration dependence of Eq. 22 for various values of r_θ keeping τ_0 and r constant.

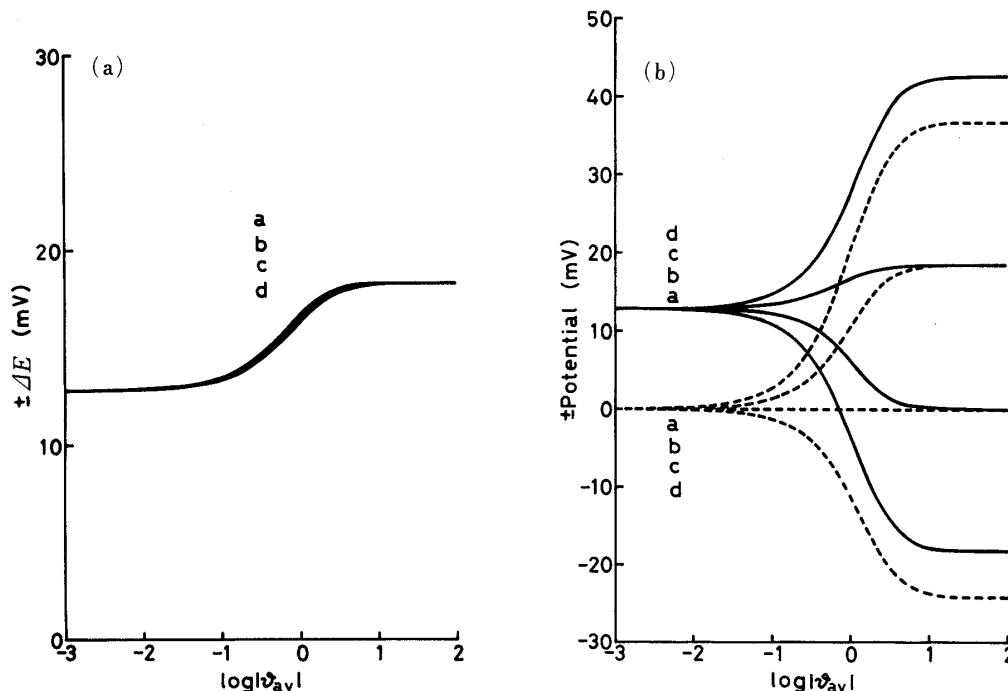


Fig. 4. (a) Membrane Potential of an Asymmetric Membrane with Respect to the Surface Charge Density at $r = 2$, $\tau_0 = -0.7$ and 34°C

The double sign of the potential takes the same sign as the membrane charge. $r_\theta = 0.5$ (a), 1(b), 2(c), 5(d).

(b) Two Components of the Asymmetric Membrane Potential Shown in Fig. 4a

Solid lines show the diffusion potential within the membrane and broken lines the surface potential difference.

Figure 4a shows the bulk concentration dependence of Eq. 22 as a function of $\log |\vartheta_{av}|$ for constant r . The two components of the membrane potential are shown in Fig. 4b, ΔE_D by broken lines and ΔE_M by solid lines. In Figs. 4a and 4b, line b is for the symmetric membrane, since $r_\theta = 1$.

From Fig. 4b, both ΔE_D and ΔE_M are strongly dependent on the asymmetry of the surface charge density. The asymmetry affects the partition of electrolyte between the bulk solution and the sublayer and, therefore, affects not only the surface potential but also the diffusion potential within the membrane.

The membrane potential is nevertheless only a little affected. The increase of the value of r_θ shifts the line a little to the left (to lower bulk concentration) in a parallel manner as shown in Fig. 4a. This is because the increase of the value of r_θ increases the charge density in sublayer 1, but decreases that in sublayer 2. If the surface charge is positive, ΔE_{D1} changes toward more positive and ΔE_{D2} changes toward more negative. Therefore, ΔE_D ($= \Delta E_{D2} - \Delta E_{D1}$) changes toward more negative as shown in Fig. 4b. The anion concentration in sublayer 1 increases, while the cation concentration decreases. On the other hand, the anion concentration in sublayer 2 decreases, while the cation concentration increases. Thus, the concentration gradient-dependent part of the anion flux from interface 1 to 2 across the membrane increases, while that of the cation flux decreases. The diffusion potential within the membrane, ΔE_M ($= E_{1M} - E_{2M}$), changes toward more positive in order to decrease the anion flux and to increase the cation flux as shown in Fig. 4b, because the system is in the steady state in which no electric current flows across the membrane. In this manner, the variations of ΔE_D and ΔE_M compensate for each other. The membrane potential is, therefore, a little affected by r_θ .

In addition, the limiting magnitudes of the membrane potential are equal to those of the symmetric membrane as shown by Eqs. 25 and 26. This indicates that the effect of the asymmetry of surface charge on the asymmetric membrane potential is not easy to detect.

If we know the surface charge density at one surface of the membrane, we can find the value of r_θ from the position of the line in Fig. 4a. However, the surface charge density is one of the parameters which is determined by the membrane potential measurement, and is not known before the experiment. The only case in which the membrane potential of the asymmetric membrane due to the surface charge can be analyzed is the case in which either ΔE_D or ΔE_M is negligibly small.

From Eq. 22, ΔE_D is negligible under the condition of $\rho'' = 1$, that is $r_\theta = r$, or $|\vartheta''| = 0$. The membrane potential under the condition of $\rho'' = 1$ is shown by line c in Fig. 4a. From Fig. 4a, it is clear that it is impossible to distinguish the asymmetric membrane potential from the symmetric membrane potential. When $|\vartheta''| = 0$, the membrane potential is given by Eq. 25. It is again clear that it is impossible to distinguish this from the symmetric membrane potential.

When the diffusion potential within the membrane is negligible, that is $B_i = B_a = 0$, the membrane potential is, from Eq. 22,

$$\Delta E = \pm \frac{RT}{F} \ln \left(\rho'' \frac{\sqrt{\vartheta''^2 + 1 + |\vartheta''|}}{\sqrt{\vartheta''^2 + \rho''^2 + |\vartheta''|}} \right) \quad (33)$$

The limiting magnitudes of Eq. 33 are

$$C_{2B} \rightarrow \infty (|\vartheta''| \rightarrow 0) \quad \Delta E = 0 \quad (34)$$

and

$$C_{2B} \rightarrow 0 (|\vartheta''| \rightarrow \infty) \quad \Delta E = \pm \frac{RT}{F} \ln \rho'' \quad (35)$$

From Eqs. 33 and 35, the value of the parameters ρ'' and ϑ'' are determined.

Namely, the effect of the asymmetry of surface charge density on the membrane potential is not measurable except in a membrane system in which the diffusion potential within the membrane is negligible. Kamo and Kobatake¹⁰⁾ measured the membrane potentials of several membranes in which one membrane surface is different from the other surface of the membrane with respect to the surface charge. They concluded experimentally that the necessary condition for the appearance of the steady asymmetric membrane potentials is no permeation of ions across the membrane. In their experiments, this condition was realized for collodion membranes which contain less than 8.7% water.

3 Asymmetry with Respect to Both the Standard Chemical Potential and the Surface Charge Density

The last type of asymmetric membrane to be discussed is a membrane in which both the standard chemical potential and the surface charge density are different at the two membrane surfaces ($g_{k1} = r_g g_{k2}$, $\theta_{1s} = r_\theta \theta_{2s}$). The membrane potential is given by replacing ρ'' ($=r/r_\theta$) with ρ ($=r/r_g r_\theta$) in Eq. 22 as follows:

$$\Delta E = \pm \left\{ \frac{RT}{F} \ln \rho \frac{\sqrt{\vartheta^2 + 1} + |\vartheta|}{\sqrt{\vartheta^2 + \rho^2} + |\vartheta|} + \frac{RT}{F} K \ln \left(\frac{1}{r_\theta} \frac{\sqrt{\vartheta^2 + 1} - \tau_0 |\vartheta|}{\sqrt{\vartheta^2 + \rho^2} - \tau_0 |\vartheta|} \right) \right\} \quad (36)$$

where

$$K = \frac{\tau_0(r_\theta \sqrt{\vartheta^2 + \rho^2} - \sqrt{\vartheta^2 + 1}) - (r_\theta - 1)|\vartheta|}{r_\theta \sqrt{\vartheta^2 + \rho^2} - \sqrt{\vartheta^2 + 1} - \tau_0(r_\theta - 1)|\vartheta|} \quad (37)$$

$$\rho = r/r_g r_\theta \text{ and } \vartheta = \vartheta_{2s} = \theta_{2s} g_2 / 2C_{2B} = \rho \vartheta_{1s}.$$

As already discussed in section 1, the asymmetry of the standard chemical potential modifies r to ρ' ($=r/r_g$). It is pointed out in section 2 that the effect of the asymmetric distribution of the membrane charge is not measurable except for a membrane system in which the diffusion potential is negligible. The arguments mentioned above are valid for the membrane treated in this section. In other words, for example, the asymmetric membrane potential at $r=2$, $r_g=0.5$ and $r_\theta=2$ is equivalent to that at $r=4$ and $r_\theta=2$.

If the diffusion potential within the membrane is negligible, the membrane potential is given by Eq. 38, from Eq. 36.

$$\Delta E = \pm \frac{RT}{F} \ln \left(\rho \frac{\sqrt{\vartheta^2 + 1} + |\vartheta|}{\sqrt{\vartheta^2 + \rho^2} + |\vartheta|} \right) \quad (38)$$

4 Application to a Cellulose Membrane

Here, we try to apply our theory to the membrane potential of a cellulose membrane, as investigated by Nakagaki and Miyata¹¹⁾ using NaCl under conditions of 34 °C and $r=2$. The experimental results are shown in Fig. 5a by open circles.

The limiting magnitudes of the membrane potential at $C_{2B} \rightarrow \infty$ and $C_{2B} \rightarrow 0$ are determined by extrapolating the smoothed line drawn through the experimental data. If the cellulose membrane is asymmetric with respect to the surface charge density and the diffusion potential within the membrane is negligible, the limiting magnitude of the potential at $C_{2B} \rightarrow \infty$ should be zero from Eq. 34. However, the limiting magnitude at $C_{2B} \rightarrow \infty$ is not zero. Therefore, we may treat the cellulose membrane as an asymmetric membrane with respect to the standard chemical potential and apply Eq. 17.

From the limiting magnitude of the potential, we determined the values of τ_0 and ρ' using Eqs. 19 and 20 to be $\tau_0=0.18$ and $\rho'=1.68$. From Eq. 18, the value of r_g is determined to be 1.19. The solid line in Fig. 5a shows the theoretical curve calculated by the use of Eq. 17 with these values. The two components of this membrane potential are shown in Fig. 5b by solid

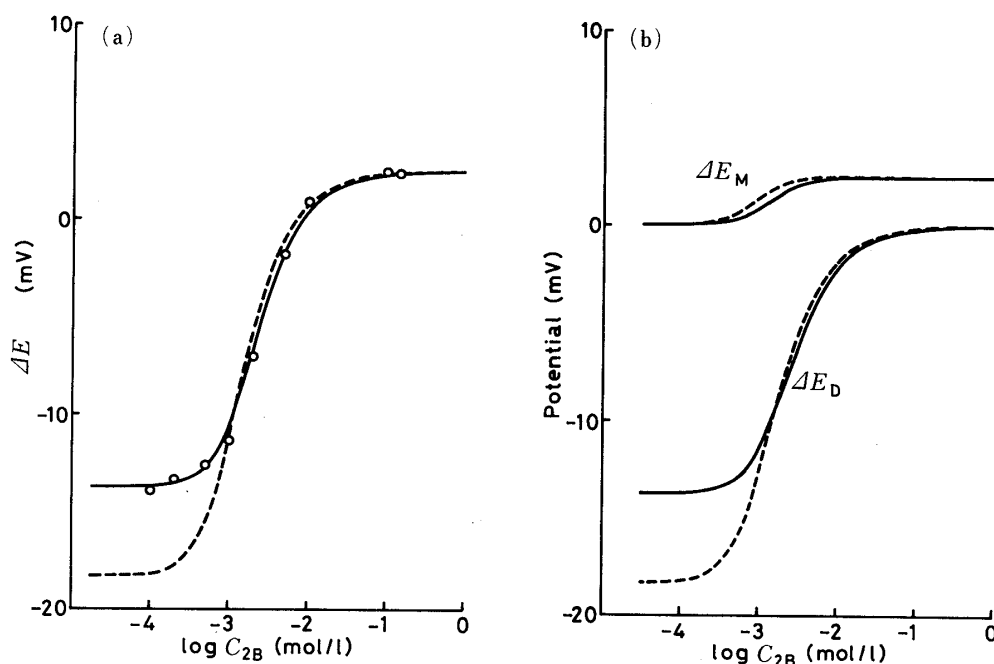


Fig. 5. (a) Membrane Potential of a Cellulose Membrane at $r=2$ and 34°C

Open circles show the experimental data.¹⁰⁾ The solid line shows the theoretical curve calculated using Eq. 18 with $\theta_s g_2 = -4.0 \times 10^{-3}$ (mol/l), $\tau_0 = 0.18$ and $\rho' = 1.68$ ($r_g = 1.19$). The broken line shows the theoretical curve calculated by means of Eq. 18 on the assumption of $r_g = 1$ (symmetric membrane) with $\theta_s g = -2.8 \times 10^{-3}$, $\tau_0 = 0.14$ and $\rho' = 2$ ($r_g = 1$).

(b) Two Components of the Membrane Potential Shown in Fig. 5a

Solid lines and broken lines have the same meaning as in Fig. 5a.

lines, separately. In Figs. 5a and 5b, the broken lines show the result of analysis treating the cellulose membrane as a symmetric membrane. From Figs. 5a and 5b, it can be seen that our treatment explains the experimental results well.

The treatment as a symmetric membrane disagrees with the experimental results in the low concentration region. This is because only the counter ion is partitioned at the membrane surface at the lower concentration limit, and the total amount is determined by the surface charge density. The membrane potential, therefore, becomes determined mainly by ΔE_D as shown in Fig. 5b. As ΔE_D is determined by the bulk concentration ratio at the lower concentration limit, a relatively small difference in the bulk concentration ratio could result in a large potential change. In a membrane system asymmetric due to the standard chemical potential, the bulk concentration ratio, r , is modified to ρ' ($=r/r_g$). This phenomenon gives the membrane potential the same effect as a change of the bulk concentration ratio, as discussed in section 1-1. A relatively small change of r_g , therefore, greatly changes the membrane potential.

5 Confirmation of Membrane Asymmetry

Next, experimental methods to confirm the asymmetry of membranes are discussed. Here, we consider a membrane in which one sublayer is different from the other sublayer with respect to the standard chemical potential.

If the membrane is asymmetric, the following phenomena will be observed. First, the membrane potential at the lower concentration limit is different from that expected from the symmetric membrane theory, as discussed above. Secondly, if we turn the membrane inside-out, a potential change will be observed, since ρ' is changed from $\rho' = r/r_g$ to rr_g by this operation. Thirdly, the membrane potential at the bulk concentration ratio $r=1$ will not be

zero, because $\rho' (=r/r_g)$ is not unity but $1/r_g$.

The considerations discussed here are applicable to a membrane in which one surface is different from the other surface with respect to the surface charge density, if the diffusion potential within the membrane is negligible.

Conclusion

In order to develop experimental methods to obtain information on the asymmetry of membrane structure from potential measurements, the asymmetric membrane potential was theoretically investigated.

It was concluded that the effect of asymmetry of the surface charge density on the membrane potential is not measurable experimentally except in a membrane system in which the diffusion potential within the membrane is negligible, because the changes of ΔE_D and ΔE_M due to the asymmetry of surface charge density compensate for each other.

When the diffusion potential within the membrane is not negligible, the effect of the asymmetry with respect to the standard chemical potential can be measured experimentally. The asymmetry with respect to the standard chemical potential modifies the bulk concentration ratio, and affects the partition of ions between the bulk solution and the membrane surface. Therefore, both the surface potential and the diffusion potential within the membrane are affected by the asymmetry of the standard chemical potential, and the membrane potential is greatly affected.

Experimental methods to determine the values of parameters were also investigated and applied to find the membrane potential of cellulose membrane. It was shown that our theory could explain the experimental results well. On the basis of our theory, it is possible to test experimentally whether a membrane is asymmetric or symmetric.

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