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Experimental Verification of the Theory of Membrane Potential for Collodion Membranes with Asymmetric Charge Distribution

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The theory of asymmetric membrane potential is developed for a membrane system having a large asymmetric membrane charge distribution. The theory suggests that there are two kinds of typical asymmetric membrane potential profiles: 1) the membrane potential shows both a minimum and a maximum depending upon the bulk concentration, and 2) it shows either a minimum or a maximum. A parameter which represents the asymmetry of the distribution of the membrane charge density was introduced into the theory. A collodion membrane asymmetric with respect to the membrane charge density was prepared to experimentally check the validity of the theory. The experimental results were in agreement with the theory.

Keywords——membrane potential; asymmetric membrane; asymmetric membrane potential; membrane charge density; asymmetric collodion membrane

Introduction

Asymmetry of membrane structure is closely related to membrane function.[1,2] The asymmetry of membrane structure results from differences in the porosity or the components of the membrane between the internal and external surfaces. This induces a difference in the surface properties and affects the membrane potential through the partition of ions between the bulk solution and the membrane surface.

Information on the asymmetry of membrane structure could be obtained from analysis of the asymmetric membrane potential. On an asymmetric membrane, it has been reported that facilitated or reverse transport can take place in addition to passive transport.[3] Further studies on asymmetric membrane should improve our understanding of drug transport across biomembranes, and of molecular separation using artificial membrane.

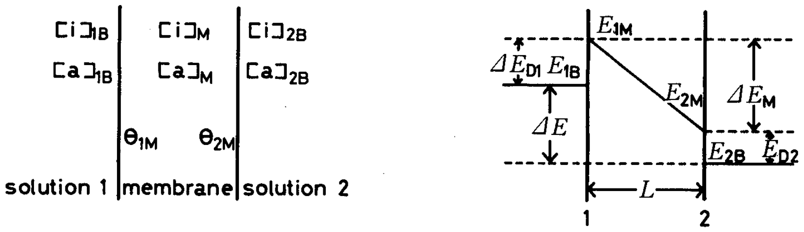
In our previous paper,[4] equations were derived for the standard chemical potential and the surface charge density of a membrane having different surfaces. In that paper, a membrane system having a relatively small asymmetric charge distribution was discussed. It was pointed out that the effect of the asymmetry of surface charge density on the membrane potential could not be analyzed experimentally except in a membrane system in which the diffusion potential within the membrane is negligible.

In this paper, a membrane system having a large asymmetric charge density is theoretically studied. The theory developed is applied to the experimental results obtained with an asymmetric collodion membrane.

Theory

General Equation

Figure 1a shows a diagram of the membrane system. One surface is different from the other surface with respect to the fixed charge density. Ions partitioned on the membrane



(a) (b)

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

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

b) Schematic Diagram of Asymmetric Membrane Potential

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; $\Delta E_D = \Delta E_{D2} - \Delta E_{D1}$, $\Delta E = \Delta E_D + \Delta E_M$.

surface permeate through the membrane. The volume flow across the membrane is neglected.

The membrane potential, ΔE, can be represented as a sum of two surface potentials and the diffusion potential within the membrane[5,6] and is given by Eq. 1, as shown in Fig. 1b.

$$\Delta E = \Delta E_{D2} - \Delta E_{D1} + \Delta E_M = \Delta E_D + \Delta E_M \tag{1}$$

where ΔE_M is the diffusion potential within the membrane and is given by Henderson's equation.[7] ΔE_{D1} and ΔE_{D2} are the surface potentials at interfaces 1 and 2, respectively, and are obtained from the Donnan equilibrium condition derived from the continuity of the electrochemical potential at the bulk solution–membrane interface.[8]

The membrane potential is obtained as follows[9]:

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

where k represents all the 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. Suffixes 1 and 2 denote interfaces 1 and 2, respectively. M and B denote the membrane and the bulk solution, respectively. g_{k1} and g_{k2} are the g_k values at interfaces 1 and 2, respectively, and are given by Eq. 3.

$$g_k = \gamma_{kM}/b_k\gamma_{kB} \tag{3}$$

γ_k is the activity coefficient of the k-th ion, and

$$b_k = \exp(-\Delta\mu_k^\circ/\boldsymbol{R}T) \tag{4}$$

where $\Delta\mu_k^\circ = \mu_{kM}^\circ - \mu_{kB}^\circ$ and μ_k° is the standard chemical potential of the k-th ion. $\boldsymbol{R}$ is the gas constant, T the absolute temperature and $\boldsymbol{F}$ the Faraday constant. B_k is the mobility of the k-th ion within the membrane.

For simplicity, we treat, hereafter, the system which contains one kind of uni-univalent electrolyte (i^+, a^-). The molar concentration of each ion is C_{1B} in bulk solution 1 and C_{2B} in bulk solution 2. The ion concentration at the membrane surface is obtained from the Donnan equilibrium condition with electroneutrality in each phase as follows[4,9]:

$$[\mathrm{i}]_{1\mathrm{M}}g_1/C_{1\mathrm{B}}=\sqrt{\vartheta_{1\mathrm{M}}^2+1}-\vartheta_{1\mathrm{M}}, \quad [\mathrm{i}]_{2\mathrm{M}}g_2/C_{2\mathrm{B}}=\sqrt{\vartheta_{2\mathrm{M}}^2+1}-\vartheta_{2\mathrm{M}} \tag{5}$$

$$[\mathrm{a}]_{1\mathrm{M}}g_1/C_{1\mathrm{B}}=\sqrt{\vartheta_{1\mathrm{M}}^2+1}+\vartheta_{1\mathrm{M}}, \quad [\mathrm{a}]_{2\mathrm{M}}g_2/C_{2\mathrm{B}}=\sqrt{\vartheta_{2\mathrm{M}}^2+1}+\vartheta_{2\mathrm{M}} \tag{6}$$

where $\vartheta_{1\mathrm{M}}=\theta_{1\mathrm{M}}g_1/2C_{1\mathrm{B}}$, $\vartheta_{2\mathrm{M}}=\theta_{2\mathrm{M}}g_2/2C_{2\mathrm{B}}$, $g_1^2=g_{\mathrm{i}1}\cdot g_{\mathrm{a}1}$ and $g_2^2=g_{\mathrm{i}2}\cdot g_{\mathrm{a}2}\cdot\theta_{\mathrm{M}}$ is the fixed charge density within the membrane. $g_{\mathrm{i}1}$, $g_{\mathrm{a}1}$, $g_{\mathrm{i}2}$ and $g_{\mathrm{a}2}$ are defined by Eq. 3.

Membrane System Having Asymmetric Membrane Charge Density

Here, we assume that $\theta_{1\mathrm{M}}\neq\theta_{2\mathrm{M}}$ but $g_{k1}=g_{k2}=g_k$, and put the relation between $\theta_{1\mathrm{M}}$ and $\theta_{2\mathrm{M}}$ as follows:

$$\theta_{1\mathrm{M}}=r_\theta\theta_{2\mathrm{M}} \tag{7}$$

This membrane system can be realized by chemically modifying one surface of a membrane with a charged substance, or by oxidizing the surface.

Substituting Eqs. 5, 6 and 7 into Eq. 2, we have

$$\Delta E=\Delta E_{\mathrm{D}}+\Delta E_{\mathrm{M}}$$

$$=\pm\frac{RT}{F}\left\{\ln\left(\rho''\frac{\sqrt{\vartheta''^2+1}+|\vartheta''|}{\sqrt{\vartheta''^2+\rho''^2}+|\vartheta''|}\right)+K''\ln\left(\frac{1}{r_\theta}\frac{\sqrt{\vartheta''^2+1}-\tau_0|\vartheta''|}{\sqrt{\vartheta''^2+\rho''^2}-\tau_0|\vartheta''|}\right)\right\} \tag{8}$$

where

$$K''=\frac{\tau_0(r_\theta\sqrt{\vartheta''^2+\rho''^2}-\sqrt{\vartheta''^2+1})-(r_\theta-1)|\vartheta''|}{r_\theta\sqrt{\vartheta''^2+\rho''^2}-\sqrt{\vartheta''^2+1}-\tau_0(r_\theta-1)|\vartheta''|} \tag{9}$$

$$C_{1\mathrm{B}}=rC_{2\mathrm{B}}, \quad \vartheta''=\vartheta_{2\mathrm{M}}''=\rho''\vartheta_{1\mathrm{M}}''=\theta_{2\mathrm{M}}g/2C_{2\mathrm{B}}, \quad g^2=g_1^2=g_2^2=g_k^2 \quad \text{and}$$

$$\rho''=r/r_\theta \tag{10}$$

$\tau_0=(B_{\mathrm{c}}-B_{\mathrm{g}})/(B_{\mathrm{c}}+B_{\mathrm{g}})$ where suffix c denotes a co-ion and g denotes a counter-ion for the membrane charge. The double sign for the potential takes the same sign as that of the membrane charge. For $r_\theta=1$, Eq. 8 reduces to the equation for a symmetric membrane.[8)]

The limiting values of Eq. 8 are

$$C_{2\mathrm{B}}\to\infty \quad (\text{or } |\vartheta''|\to 0) \qquad \Delta E=\pm\frac{RT}{F}\tau_0\ln\frac{1}{r} \tag{11}$$

and

$$C_{2\mathrm{B}}\to 0 \quad (\text{or } |\vartheta''|\to\infty) \qquad \Delta E=\pm\frac{RT}{F}\ln r \tag{12}$$

Equations 11 and 12 are the same as the limiting equations of the symmetric membrane potential.[9)]

Bulk Concentration Dependency

Next, we consider the bulk concentration dependence of Eq. 8. Hereafter, we treat a membrane system in which the bulk concentration ratio, r, is larger than unity and is constant. The considerations discussed here are easily applicable to a membrane system of $r<1$.

In a membrane system in which $r_\theta\gg r>1$, ρ'' $(=r/r_\theta)$ is much smaller than unity. Therefore, Eq. 8 can be rewritten as follows except in the limiting bulk concentration region where $\vartheta''\gg 1$ or $\vartheta''\ll\rho''$.

In the region where $\vartheta''\gg\rho''$ but ϑ'' is not much larger than unity (lower bulk concentration),

$$\Delta E = \pm\frac{RT}{F}\left\{\ln\left(\rho''\frac{\sqrt{\vartheta''^2+1}+|\vartheta''|}{2|\vartheta''|}\right)+K''\ln\left(\frac{1}{r_\theta}\frac{\sqrt{\vartheta''^2+1}-\tau_0|\vartheta''|}{(1-\tau_0)|\vartheta''|}\right)\right\} \tag{13}$$

where

$$K''=\frac{\tau_0(r_\theta|\vartheta''|-\sqrt{\vartheta''^2+1})-(r_\theta-1)|\vartheta''|}{r_\theta|\vartheta''|-\sqrt{\vartheta''^2+1}-\tau_0(r_\theta-1)|\vartheta''|} \tag{14}$$

In the region where $\vartheta''\ll 1$ but ϑ'' is not negligibly small compared with ρ'' (higher bulk concentration),

$$\Delta E = \pm\frac{RT}{F}\left\{\ln\left(\rho''\frac{1}{\sqrt{\vartheta''^2+\rho''^2}+|\vartheta''|}\right)+K''\ln\left(\frac{1}{r_\theta}\frac{1}{\sqrt{\vartheta''^2+\rho''^2}-\tau_0|\vartheta''|}\right)\right\} \tag{15}$$

where

$$K''=\frac{\tau_0(r_\theta\sqrt{\vartheta''^2+\rho''^2}-1)-(r_\theta-1)|\vartheta''|}{r_\theta\sqrt{\vartheta''^2+\rho''^2}-1-\tau_0(r_\theta-1)|\vartheta''|} \tag{16}$$

For $r_\theta=1$, Eqs. 13 and 15 correspond to the symmetric membrane system in which $r\ll 1$. In addition, as is shown in Eqs. 11 and 12, the limiting value of Eq. 8 is independent of the asymmetry of membrane structure. This indicates that the membrane potential has both a minimum and a maximum depending upon the bulk concentration.

In a membrane system in which $r_\theta\ll 1<r$, ρ'' is much larger than unity. Therefore, there is a bulk concentration region where $\vartheta''\gg 1$ but ϑ'' is not much larger than ρ''. The corresponding conditions in a symmetric membrane system arise only for the membrane system in which $r\gg 1$. In this region, the absolute magnitude of the asymmetric membrane potential will be larger than that expected for the symmetric membrane of bulk concentration ratio, r. As mentioned above, the limiting magnitudes of the asymmetric membrane are the same as for the symmetric membrane. Therefore, in the case where $r_\theta\ll 1$, the asymmetric membrane potential will show either a minimum or a maximum, depending upon the bulk concentration.

In our previous paper,[4] it was reported that the effect of asymmetric distribution of membrane charge density on the membrane potential is hardly detectable experimentally in the case where $0.5\leqq r_\theta\leqq 5$. However, in the case where $r_\theta\ll 1$ or $r_\theta\gg 1$, the effect of the asymmetric membrane charge density should be detectable experimentally.

The bulk concentration dependence of Eq. 8 is shown in Figs. 2—4 for constant r. 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 $(\theta_{1M}+\theta_{2M})/2$. θ_{1M} and θ_{2M} satisfy the following relations:

$$\theta_{1M}=r_\theta\theta_{2M}, \qquad \theta_{1M}+\theta_{2M}=2\theta_{av} \tag{17}$$

ϑ'' in Eq. 8 is related with θ_{av} by Eq. 18.

$$\vartheta''=\frac{2}{1+r_\theta}\frac{\theta_{av}g}{2C_{2B}}=\frac{2}{1+r_\theta}\vartheta_{av} \tag{18}$$

Figure 2 shows the bulk concentration dependence of Eq. 8 as a function of $\log|1/\vartheta_{av}|$ for various values of r_θ. Line f in Fig. 2 is for the symmetric membrane, since $r_\theta=1$. From Fig. 2, it is clear that the potential shows both a minimum and a maximum in the case where $r_\theta\gg 1$ and that shows a maximum (a minimum in the case where θ_M is negative) in the case where $r_\theta\ll 1$.

Figures 3 and 4 show the bulk concentration dependence of Eq. 8 as a function of $\log|1/\vartheta_{av}|$ for various values of τ_0, Fig. 3 for $r_\theta\gg 1$ and Fig. 4 for $r_\theta\ll 1$.

In the case where $r_\theta\gg 1$, from Figs. 2 and 3, it is found that the magnitude of the

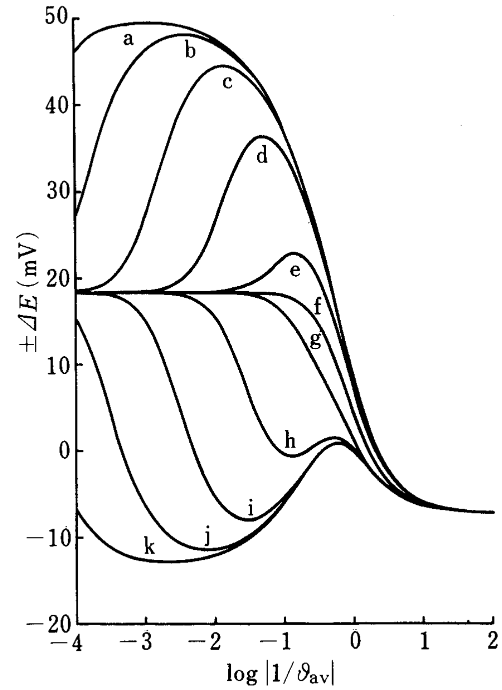


Fig. 2. Membrane Potential of an Asymmetric Membrane with Respect to the Membrane Charge Density at $r=2$, $\tau_0=0.4$ and 34 °C

$\vartheta_{av}=\theta_{av}g/2C_{2B}$ and $\theta_{av}=(\theta_{1M}+\theta_{2M})/2$. The double sign for the potential takes the same sign as that of the membrane charge. $r_\theta=0.00001$ (a), 0.0001 (b), 0.001 (c), 0.01 (d), 0.1 (e), 1 (f), 10 (g), 100 (h), 1000 (i), 10000 (j), 100000 (k).

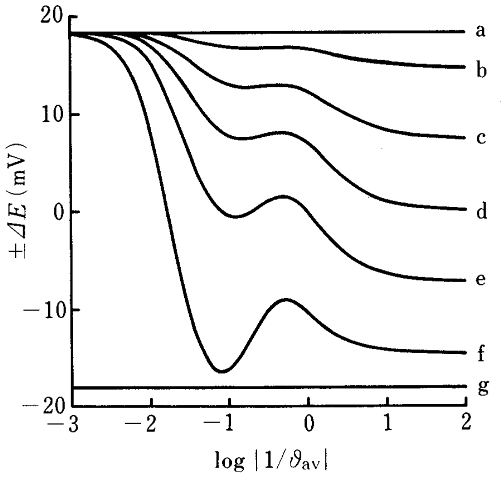


Fig. 3. Membrane Potential of an Asymmetric Membrane with Respect to the Membrane Charge Density at $r=2$, $r_\theta=100$ and 34 °C

$\tau_0=-1$ (a), −0.8 (b), −0.4 (c), 0 (d), 0.4 (e), 0.8 (f), 1 (g).

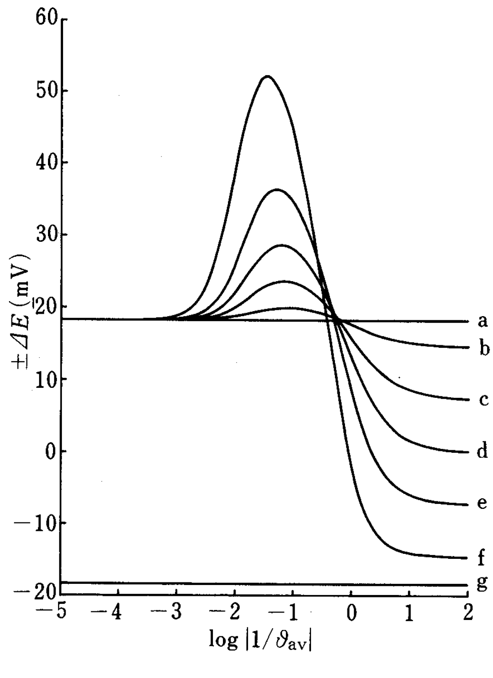


Fig. 4. Membrane Potential of an Asymmetric Membrane with Respect to the Membrane Charge Density at $r=2$, $r_\theta=0.01$ and 34 °C

$\tau_0=-1$ (a), −0.8 (b), −0.4 (c), 0 (d), 0.4 (e), 0.8 (f), 1 (g).

minimum potential and the value of ϑ_{av} at the minimum point vary systematically with the value of τ_0 and r_θ. From Fig. 2, in the case where $r_\theta \gg 1$, it is also found that the maximum potential and the value of ϑ_{av} at the maximum point scarcely depend on the value of r_θ.

Equations 15 and 16 can be rewritten as follows using ϑ_{av}:

$$\Delta E = \pm\frac{RT}{F}\ln\frac{r}{\sqrt{(2\vartheta_{av})^2+r^2}+2|\vartheta_{av}|}+K''\ln\frac{1}{\sqrt{(2\vartheta_{av})^2+r^2}-2\tau_0|\vartheta_{av}|} \tag{19}$$

where

$$K''=\frac{\tau_0(\sqrt{(2\vartheta_{av})^2+r^2}-1)-2|\vartheta_{av}|}{\sqrt{(2\vartheta_{av})^2+r^2}-1-2\tau_0|\vartheta_{av}|} \quad (20)$$

Equation 19 shows the potential for $r_\theta \gg 1$ in the region where $\vartheta'' \ll 1$ but ϑ'' is not negligibly small compared with ρ''. It does not include r_θ. For $\vartheta'' \ll \rho''$, the potential is given by Eq. 11 and does not depend on r_θ. Consequently, the membrane potential for $\vartheta'' \ll 1$ ($\vartheta_{av} \ll (1+r_\theta)/2$) does not depend on r_θ, but depends on r, τ_0 and ϑ_{av}. From Figs. 2 and 3, in the case where $r_\theta \gg 1$, it is clear that the maximum potential appears in the region where $\vartheta'' \ll 1$ ($\vartheta_{av} \ll (1+r_\theta)/2$).

In the case where $r_\theta \ll 1$, from Figs. 2 and 4, it is found that the magnitude of the maximum potential and the value of ϑ_{av} at the maximum point vary systematically with the values of r_θ and τ_0.

In the case where only the counter-ion for the membrane charge permeates through the membrane ($\tau_0=-1$) and the case where only the co-ion permeates through the membrane ($\tau_0=1$), the potential is determined by only the bulk concentration ratio,[4] as is shown in Figs. 3 and 4 (lines a and g).

From Figs. 2, 3 and 4, it is also clear that a very wide range of the bulk concentration is required to obtain the full potential curve, compared with a symmetric membrane system. This is because, in a symmetric membrane system, the required range of the bulk concentration is from $\vartheta'' \ll 1$ to $\vartheta'' \gg r$. On the other hand, the required concentration range in the asymmetric membrane system is from $\vartheta'' \ll \rho''$ ($\vartheta_{av} \ll r/2$) to $\vartheta'' \gg 1$ ($\vartheta_{av} \gg r_\theta/2$) for $r_\theta \gg 1$, and from $\vartheta'' \ll 1$ ($\vartheta_{av} \ll 1/2$) to $\vartheta'' \gg \rho''$ ($\vartheta_{av} \gg r/2r_\theta$) for $r_\theta \ll 1$.

Determination of Parameters

The value of τ_0 can be determined from Eq. 11, since r is known from the experimental conditions.

The value of r_θ can be determined by utilizing the systematic change of the minimum and the maximum. In the case where $r_\theta \gg 1$, Fig. 5 shows $\vartheta_{av}(\text{min})/\vartheta_{av}(\text{max})$ as a function of $\log r_\theta$ for various values of τ_0, where $\vartheta_{av}(\text{min})$ and $\vartheta_{av}(\text{max})$ indicate the value of ϑ_{av} at the minimum point and the maximum point, respectively. Figure 6 shows plots of ΔE_{min} *versus* ΔE_{max} for various values of τ_0 and r_θ, where ΔE_{min} indicates the magnitude of the minimum potential and ΔE_{max} the magnitude of the maximum potential.

From Fig. 6, it is apparent that values of τ_0 and r_θ can be determined by the data on ΔE_{min} and ΔE_{max} without data on the limiting potential at $C_{2B} \to \infty$. In Fig. 6, it may be difficult to determine a value of r_θ more than 10000. In that case, the value of r_θ can be determined by using Fig. 5.

In the case where $r_\theta \ll 1$, Fig. 7 shows ΔE_{max} as a function of τ_0 for various values of r_θ. If the value of τ_0 is determined by Eq. 11, the value of r_θ can be determined by using Fig. 7. After

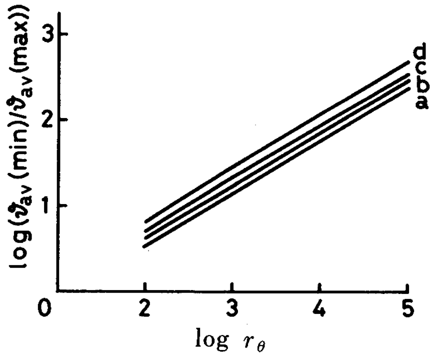


Fig. 5. r_θ Dependency of $\vartheta_{av}(\text{min})/\vartheta_{av}(\text{max})$ at $r=2$

$\vartheta_{av}(\text{min})$ and $\vartheta_{av}(\text{max})$ indicate the value of ϑ_{av} at the minimum point and the maximum point, respectively. For the calculation, the membrane charge was assumed to be positive. $\tau_0=-0.8$ (a), -0.6 (a), -0.4 (a), -0.2 (a), 0 (a), 0.2 (a), 0.4 (b), 0.6 (c), 0.8 (d).

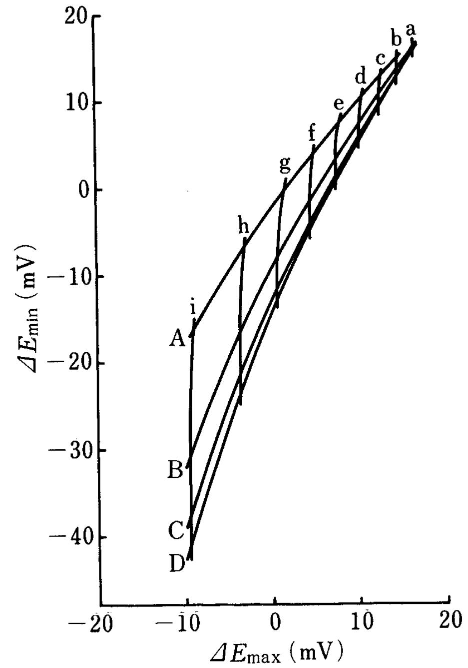


Fig. 6. τ_0 and r_θ Dependency of $\Delta E_{\min}$ and $\Delta E_{\max}$ in the Case where $r_\theta \gg 1$ at $r=2$ and 34 °C

$\Delta E_{\min}$ and $\Delta E_{\max}$ indicate the magnitude of the minimum potential and the maximum potential, respectively. For the calculation, the membrane charge was assumed to be positive. $\tau_0 = -0.8$ (a), -0.6 (b), -0.4 (c), -0.2 (d), 0 (e), 0.2 (f), 0.4 (g), 0.6 (h), 0.8 (i); $r_\theta = 100$ (A), 1000 (B), 10000 (C), 100000 (D).

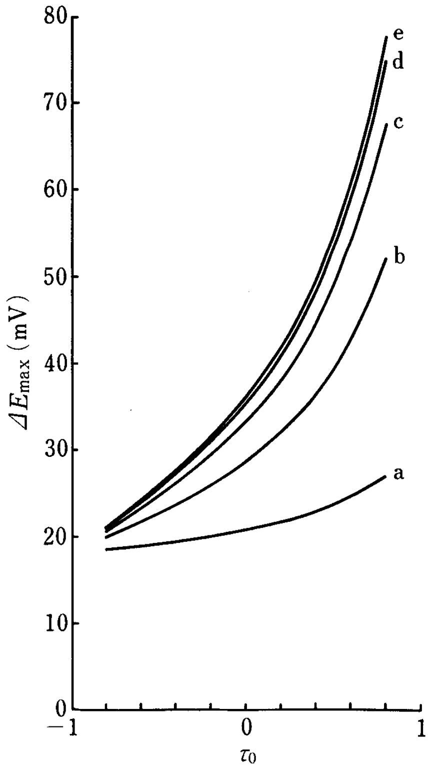


Fig. 7. τ_0 Dependency of $\Delta E_{\max}$ in the case where $r_\theta \ll 1$ at $r=2$ and 34 °C

$\Delta E_{\max}$ indicates the magnitude of the maximum potential. For the calculation, the membrane charge was assumed to be positive. $r_\theta = 0.1$ (a), 0.01 (b), 0.001 (c), 0.0001 (d), 0.00001 (e).

the determination of the values of τ_0 and r_θ, ϑ'' is determined by Eq. 8 and $\theta_{2M}g$ $(=2\vartheta'' C_{2B})$ is also determined.

In the case where $r_\theta \ll 1$, it is clear from Figs. 2 and 4 that nearly the full potential curve, including the limiting magnitude of the membrane potential at $C_{2B} \rightarrow \infty$, is required to obtain the values of parameters. Sometimes, it may be impossible to investigate a sufficiently wide bulk concentration range. This is because it is usually difficult to measure a membrane potential in the low bulk concentration range. In the case where $r_\theta \gg 1$, the values of parameters can be determined only from the magnitudes of the minimum and the maximum potentials. The appropriate bulk concentration range is narrow compared with that in the case of $r_\theta \ll 1$. It is, therefore, desirable to use conditions where $r_\theta \gg 1$. The condition $(r_\theta \gg 1)$ is established by turning the membrane inside-out.

Experimental

To check the validity of the theory, the membrane potential of a collodion membrane with asymmetric membrane charge density was investigated.

The membrane was prepared as follows.[10] A solution of collodion in ether-alcohol (Kishida Chem. Co., Ltd.) was poured into test-tubes which were rotated slowly in a horizontal position. After drying and soaking the film formed, 1 M sodium hydroxide solution was poured into the tubular collodion membrane (still held within the test-tube), and left to stand for 10 min. After several hours of soaking, the collodion membrane was dried at 43% relative humidity.

The measurement of the membrane potential was attempted using NaCl (guaranteed reagent grade) under the condition of $r=2$ at 34 °C. The potential difference, ΔE_{ob}, was measured by inserting Ag-AgCl electrodes directly into the bulk solutions. The membrane potential, ΔE, is given as follows[11]:

$$\Delta E = \Delta E_{ob} - \frac{RT}{F} \ln \frac{a^{I}}{a^{II}} \tag{21}$$

where a^{I} and a^{II} are the activities of chloride ion[12] in the bulk solutions 1 and 2, respectively. The experimental equipment and procedures were the same as those of Nakagaki and Miyata.[11]

Results

The experimental results are shown in Fig. 8 by open circles. The potential shows both a minimum and a maximum, as expected from the theory.

From Fig. 8, the magnitudes of the minimum and the maximum potential are obtained as -12.5 ± 0.5 mV for ΔE_{min} and as 1.5 ± 0.5 mV for ΔE_{max}. The positions of the minimum and the maximum are also obtained from Fig. 8 as $\log C_{2B}(\text{min}) = -2.65 \pm 0.1$ for the minimum and as $\log C_{2B}(\text{max}) = -0.75 \pm 0.1$ for the maximum, where $C_{2B}(\text{min})$ and $C_{2B}(\text{max})$ indicate the values of C_{2B} at the minimum point and the maximum point, respectively. From Fig. 6, the values of parameters are determined to be $\tau_0 = 0.4$ and $r_\theta \doteqdot 10000$ using the magnitudes of ΔE_{min} and ΔE_{max}. As the value of r_θ is nearly 10000, it is difficult to determine the value of r_θ exactly from Fig. 6. From Eq. 18, the value of $\log \vartheta_{av}(\text{min})/\vartheta_{av}(\text{max})$ is equal to the value of $\log C_{2B}(\text{max})/C_{2B}(\text{min})$. Thus, from Fig. 5, the value of r_θ is determined to be 10000 using the line for $\tau_0 = 0.4$ with the values of $\log C_{2B}(\text{min})$ and $\log C_{2B}(\text{max})$.

The value of $\theta_{av} g$ is determined from the best fit of the theoretical curve to the experimental data. The theoretical curve is calculated as a function of $\log 1/\vartheta_{av}$ with $\tau_0 = 0.4$ and $r_\theta = 10000$. The value of $\theta_{av} g$ is determined to be 0.56 mol/l. From Eq. 17, $\theta_{1M} g$ and $\theta_{2M} g$ are determined to be 1.12 and 1.12×10^{-4} mol/l, respectively. θ_{1M} is the charge density at the surface treated with NaOH.

The solid line in Fig. 8 shows the theoretical curve calculated from Eq. 8 by using these values as parameters. From Fig. 8, it can be seen that the theory is in agreement with the experimental results. This supports the validity of the present theory.

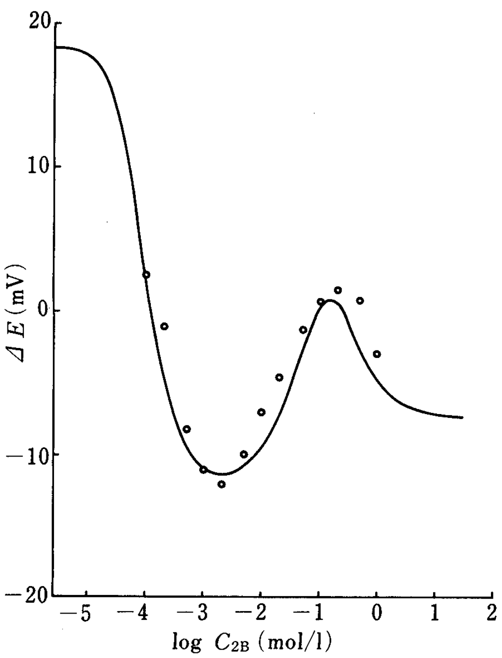


Fig. 8. Membrane Potential of the Asymmetric Collodion Membrane with Respect to the Membrane Charge Density at $r=2$ and 34 °C

Open circles show the experimental results. The solid line shows the theoretical curve calculated from Eq. 8 using the values of $\tau_0 = 0.4$, $r_\theta = 10000$ and $\theta_{av} g = 0.56$.

Conclusion

The theory of an asymmetric membrane potential was developed. It is theoretically pointed out that, in the case where $r_\theta \gg 1$, asymmetric membrane potential has both a minimum and a maximum, depending upon the bulk concentration. In the case where $r_\theta \ll 1$, the asymmetric membrane potential has either a minimum or a maximum. The value of r_θ, which represents the asymmetry of the membrane charge density, could be determined from the magnitudes of the minimum and the maximum potentials and the relative positions of the minimum and the maximum points.

In order to check the validity of the theory, an asymmetric collodion membrane with respect to the membrane charge density was prepared. The membrane potential of this collodion membrane showed both a minimum and a maximum depending upon the bulk concentration, as expected from our theory. The collodion membrane was asymmetric with respect to the membrane charge density, the value of r_θ being 10000.

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