

Analysis of Ionic Transport through NPN Type Bipolar Membranes

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A NPN type bipolar membrane has a sandwich-like structure with negatively charged layers (layer N) and positively charged layer (layer P). We calculated the ionic transport in a model system consisting of the membrane and mixed salt solutions by computer simulations to analyze the relationship between the ionic transport and the charged layer structure of the membrane. The simulations show that the charge density of each charged layer in the NPN type bipolar membrane can be estimated by fitting the data of membrane potential-concentration curve into the simulation. In a dialysis system where the concentration gradient of CaCl_2 between the two chambers is in opposite direction of that of KCl , the facilitate transport of both the cations occurs. In a dialysis system where the concentration gradient of CaCl_2 is in the same direction of that of KCl , the *uphill* transport of the bivalent ions occurs.

Key words: Ionic transport, charged membrane, facilitate transport, membrane potential, bipolar

1. INTRODUCTION

A bipolar membrane has a sandwich-like structure of a positively charged layer, P, and a negatively charged layer, N, joined together in series. This membrane has many interesting transport phenomena such as rectification properties [1-3], permselectivity for univalent ion [4-6] and water splitting [7-18] and electrical oscillations [19,20]. Theoretical treatment of ionic transport across the membrane was pioneered by Mauro [1] and Coster [2]. These authors considered the ionic PN-junction as a simple model of biological membranes and derived its electrical characteristics in close analogy to those of the electronic PN-junction of semiconductor physics.

A NPN type bipolar membrane has a sandwich-like structure with a negatively-charged layer and two positively-charged ones. The characteristics of the membrane in ionic transport will be also considered in close analogy to those of the electronic NPN-junction of transistors. Ionic transport across the membrane are very important clues for developing highly selective membranes as well as for making clear the mechanism of ionic transport in biological systems. However, there have been no studies reported on the ionic transport through a NPN type bipolar membrane because of the complexity of its charge structure.

This study aims to analyze the relationship between

the ionic transport and the charged layer structure of the membrane. Hence, we calculated the ionic transport in a model system consisting of the membrane and mixed electrolyte solutions by computer simulations based on the Donnan equilibrium and the Nernst-Planck equation.

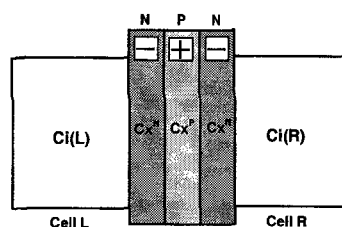


Fig. 1 A system consisting of a NPN bipolar membrane and electrolyte solutions.

2. SIMULATION METHOD

Fig. 1 shows a system on which calculations were made. A NPN type bipolar membrane separates the two electrolyte solutions. Initially, the solution in cell L and cell R contain a single or mixed salt solution at the concentration of $C_i(L)$ and $C_i(R)$, respectively. Ionic transport in the system is simulated using the same calculation method as in ref. 21 under the following assumptions: (a) the surfaces of both of the charged

layers are always in a state of the Donnan equilibrium; (b) the boundary effects on the surfaces are negligible; (c) all the electrolytes dissolve perfectly, and ionic activity coefficients are unity both in the aqueous solutions and in the two charged layers; (d) the standard chemical potentials of ions in the two layers are equal to those in the solutions, respectively. The Donnan equilibrium and the electroneutrality condition give the following equation [21, 22]:

$$\sum z_i (K_{(j,k)})^{z_i} C_i^R(j) + z_x(k) C_x(k) = 0 \quad (1)$$

where z_i is the valence of the i th ion and $K_{(j,k)}$ is the Donnan equilibrium constant at the interface between layers j and k :

$$(K_{(j,k)})^{z_i} = \frac{C_i^L(k)}{C_i^R(j)} = \exp(-z_i F \Delta \phi_{don(j,k)} / RT) \quad (2)$$

where F , R and T are the Faraday constant, the gas constant and the absolute temperature, respectively; $C_i^L(k)$ and $C_i^R(j)$ are the ionic concentration at the left-hand side in layer k and the right-hand side in layer j , respectively. $\Delta \phi_{don(j,k)}$ is the Donnan potential at the interface between layers j and k . The flux of the i th ion in layer k , $J_i(k)$, is given as [23]

$$J_i(k) = -\frac{RTz_i\omega_i}{d_k} \ln \beta \frac{C_i^R(k) - C_i^L(k)\beta^{z_i}}{\beta^{z_i} - 1} \quad (3)$$

where d_k is the thickness of layer k ; ω_i is the mobility of the i th ion, respectively; β is defined as

$$\beta = \exp(-F \Delta \phi_{diff}(k) / RT) \quad (4)$$

where $\Delta \phi_{diff}(k)$ is the diffusion potential in layer k . β is the solution of the following equation:

$$(B_1 + 4B_2)\beta^2 + (B_1 - A_1)\beta - (A_1 + 4A_2) = 0 \quad (5)$$

where

$$\begin{aligned} A_z &= \sum \omega_{i,z+} C_{i,z+}^R(k) + \sum \omega_{i,z-} C_{i,z-}^L(k), \\ B_z &= \sum \omega_{i,z+} C_{i,z+}^L(k) + \sum \omega_{i,z-} C_{i,z-}^R(k). \end{aligned} \quad (6)$$

The permeability coefficient in layer k , $P_i(k)$, is given as

$$P_i(k) = \frac{J_i(k)d_k}{(C_i^L(k) - C_i^R(k))} \quad (7)$$

The total membrane potential, $\Delta \phi$, are also simulated. These potentials are defined as

$$\begin{aligned} \Delta \phi_{don} &= \Delta \phi_{don(L,N1)} + \Delta \phi_{don(N1,P)} \\ &\quad + \Delta \phi_{don(P,N2)} + \Delta \phi_{don(N2,R)} \end{aligned} \quad (9)$$

$$\Delta \phi_{diff} = \Delta \phi_{diff(N1)} + \Delta \phi_{diff(P)} + \Delta \phi_{diff(N2)} \quad (10)$$

$$\Delta \phi = \Delta \phi_{don} + \Delta \phi_{diff} \quad (11)$$

We simulated ionic transport of the two ions, varying the charge density ratio, r_x , of the two charged layers. The ratio of the charge densities is defined as:

$$r_x = C_x^P / C_x^N \quad (12)$$

where C_x^P and C_x^N are the charge density of layers P and N, respectively. We assume that for all the ions, the mobility at the two charged layers has the same values as that in an aqueous solution, respectively. The value of the mobility of K^+ , Ca^{2+} and Cl^- ion are $7.9 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, $3.0 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$ and $8.2 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, respectively. In all the simulations, the thickness of the two layers $d = 30 \text{ } \mu\text{m}$; $C_x^N = 5.0 \times 10^{-1} \text{ mol/dm}^3$.

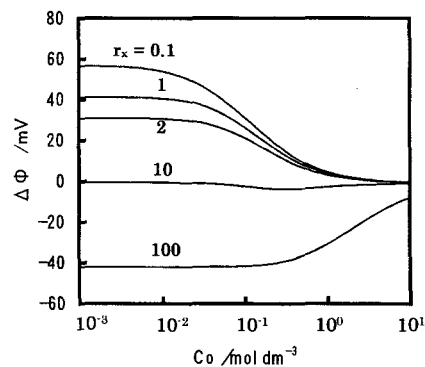


Fig. 2 The simulations of the total membrane potential in a single KCl system as a function of the ionic concentration at cell L, C_o . r_x is the charge density ratio of the two charged layers. $r_m = \omega_{Ca} / \omega_K = 1$.

3. RESULTS AND DISCUSSION

3.1 Membrane potential in a single KCl system.

In order to estimate the charged structure of the NPN type bipolar membrane, the membrane potential-ionic concentration curve in a single KCl system is calculated. In the system, cell L and cell R in Fig. 1 contain KCl solutions at different concentrations. The concentration ratio, $r = C_i(R)/C_i(L)$ is 10. Figure 2 shows the simulations of the total membrane potential as a function of the ionic concentration at cell L, C_o for a few values of r_x . Where both $C_x^P \ll C_o$ and $C_x^N \ll C_o$, the potentials are almost equal to zero for all the values of r_x because the Donnan potentials are zero and the diffusion potential in the three charged layers hardly appear in KCl solutions. The absolute value of the potentials increases with decreasing C_o and reaches a constant values when $C_x^P \gg C_o$ and $C_x^N \gg C_o$. The simulations where $r_x = 0.1$ show almost the same profile as that in the systems with negatively-charged membranes calculated from the Teorell-Meyer-Sievers (TMS) theory [21]. This fact supports the adequacy of our calculations because the NPN bipolar membrane of $r_x = 0.1$ has almost same charged structure as a homogeneous negatively-charged membrane. The potential in the plateau region at low C_o

decreases with increasing r_x . This means that the charge density of each charged layer in the NPN type bipolar membrane can be estimated by fitting the data of the membrane potential-concentration curve into the simulation.

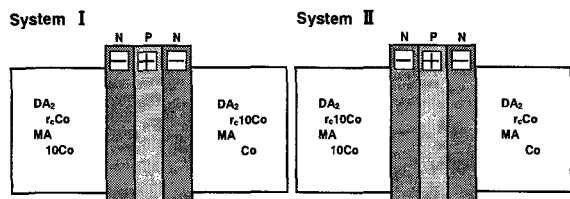


Fig. 3 A system consisting of NPN bipolar membrane and mixed KCl and CaCl₂ solutions. In system I, the concentration gradient of CaCl₂ between the two chambers is in opposite direction of that of KCl. In system II, the concentration gradient of CaCl₂ is in the same direction of that of KCl. Where $r_c = [\text{CaCl}_2]/[\text{KCl}]$.

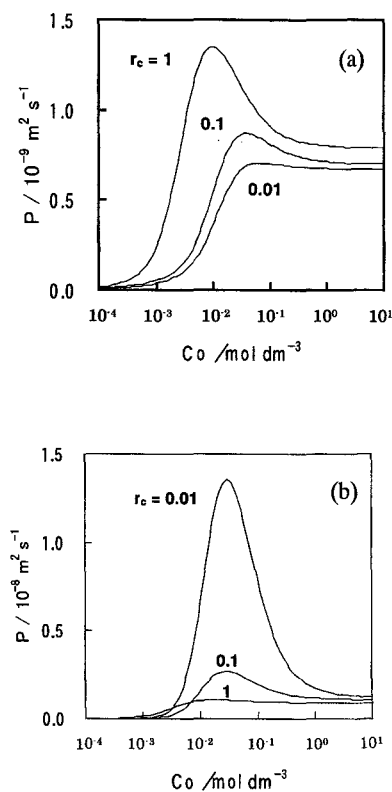


Fig. 4 The simulations of the permeation coefficient of ions in system I as a function of the ionic concentration, Co. (a) the data for K⁺ ions; (b) for Ca²⁺ ions. Where $r_m = 2$; $r_x = 5$.

3.2 Permeability coefficient of ions in system I

Fig. 4 shows the simulations of the permeation

coefficient of K⁺ ions and Ca²⁺ ions, P_K and P_{Ca} , respectively, as a function of the ionic concentration, Co in system I. As shown in Fig. 3, the chamber of cell L in the system contains r_c Co mol dm⁻³ of CaCl₂ and 10 Co mol dm⁻³ of KCl; that of cell R contains 10 r_c Co mol dm⁻³ of CaCl₂ and Co mol dm⁻³ of KCl. Hence, in the system, the concentration gradient of CaCl₂ between the two chambers is in opposite direction of that of KCl. When $C_x^P \ll Co$ and $C_x^N \ll Co$, P_K and P_{Ca} are almost equal to the permeability coefficient of these ions, respectively, through a neutral membrane for all the values of r_x because the charges of the three layers do not affect on the permeability of ions under these conditions. When $C_x^P \gg Co$ and $C_x^N \gg Co$, both P_K and P_{Ca} become to zero because the cations can not permeate through the positively-charged layer under these conditions. When the charge density of the two charged layers is almost equal to the ionic concentration, both P_K and P_{Ca} has a maximum value. This means that facilitate transport of both the cations occurs. The maximum value of P_K increases with increasing r_c while that of P_{Ca} decreases with increasing r_c . The reason why the facilitate transport occurs is that under the conditions, the concentration of the cations in layer N is much larger than that of the external solutions and the facilitate transport of the cations is driven by the diffusion of the other cations.

3.3 Permeability coefficient of ions in system II

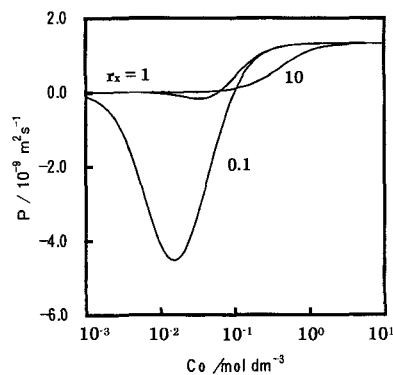


Fig. 5 The simulations of the permeation coefficient of Ca²⁺ ions in system II as a function of the ionic concentration, Co. Where $r_m = 2$; $r_c = 0.01$.

Fig. 5 shows the simulations of the permeation coefficient of the divalent ions as a function of the ionic concentration Co in system II. As well as the permeability coefficient in system I, P_{Ca} in system II is

almost equal to that through a neutral membrane for all the values of r_x when $C_x^P \ll C_o$ and $C_x^N \ll C_o$, and becomes to zero when $C_x^P \gg C_o$ and $C_x^N \gg C_o$. In the case of $r_x = 0.1$, when $C_o < 0.1 \text{ mol dm}^{-3}$, P_{Ca} has negative values. This means that the ions are transported against their concentration gradient from the low-concentration side to the high-concentration side. The diffusion of the univalent ions becomes the driving force of this *uphill* transport of the bivalent ions [24]. P_{Ca} has a minimum value when the charge density of the two charged layers is almost equal to the ionic concentration because the bivalent ions can not permeate when $C_x^P \gg C_o$ and $C_x^N \gg C_o$.

4. CONCLUSION

In this study, we calculated the ionic transport in a model system consisting of a NPN type bipolar membrane and mixed salt solutions by computer simulations. The simulations show that the membrane potential in the plateau region at low electrolyte concentration decreases with increasing the charge density ratio between the two charged layers. This means that the charge density of each charged layer in the NPN type bipolar membrane can be estimated by fitting the data of membrane potential-concentration curve into the simulations. In the system where the concentration gradient of CaCl_2 between the two chambers is in opposite direction of that of KCl , facilitate transport of both the cations occurs when the charge density of the two charged layers is almost equal to the ionic concentration. In a dialysis system where the concentration gradient of CaCl_2 is in the same direction of that of KCl , the *uphill* transport of the bivalent ions occurs under appropriate conditions.

5. ACKNOWLEDGMENT

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