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Electrostatic interaction between ion-penetrable multi-layered membranes

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A theory of the double layer interaction regulated by the Donnan potential between two ion-penetrable membranes in an electrolyte solution developed previously by Ohshima and Kondo is extended to the case in which the membranes consist of many layers having different thicknesses and densities of membrane-fixed charges. The interaction force is found to be determined mainly by the contributions from layers located within the depth of $1/\kappa$ (κ, Debye-Hückel parameter) from the membrane surface. It is also predicted that the interaction force may alter its sign with changing electrolyte concentration.

1. Introduction

As a model for the electrostatic interaction between biological cells, we have developed a theory of the double layer interaction between ion-penetrable charged membranes [1–8]. This theory, unlike the conventional models for interactions of colloidal particles at constant surface potential or constant surface charge density [9–12], assumes that the potential far inside the membranes remains constant at the Donnan potential during interaction. We thus term this type of interaction the Donnan-potential regulated interaction. In previous papers [2,4,6–8], we confined ourselves mainly to uniformly charged membranes. Since, however, in the membranes of real cells the distribution of membrane-fixed charges may actually be non-uniform rather than uniform, it is necessary to extend our theory to cover the case of arbitrary distributions of membrane-fixed charges. In the present paper we shall consider the electrostatic interaction of ion-penetrable multilayered membranes as a model for real cell membranes.

2. Basic equations

Consider two parallel planar ion-penetrable membranes 1 and 2, which may not be identical, at separation h in a symmetrical electrolyte solution of valency v and bulk concentration n (fig. 1). We take an x-axis perpendicular to the membranes with its origin at the surface of membrane 1. The electric potential $\psi(x)$ at position x between the membranes (relative to the bulk solution phase, where $\psi(x)$ is set equal to zero) is assumed to be small so that the linearized Pois-

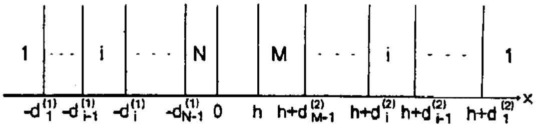

Fig. 1. Interaction of two ion-penetrable membranes 1 and 2 consisting of N and M layers, respectively.

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son-Boltzmann equation can be employed. Membranes 1 and 2, respectively, consist of N and M layers. All the layers are perpendicular to the x-axis. Let the thickness and the density of membrane-fixed charges of the i-th layer of membrane j ($j = 1, 2$) be $d_i^{(j)}$ and $\rho_i^{(j)}$. The linearized Poisson-Boltzmann equation for the i-th layer of membrane j is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi - \frac{\rho_i^{(1)}}{\epsilon_r\epsilon_0}, \quad -d_{i-1}^{(1)} < x < -d_i^{(1)} \quad (1 \leqq i \leqq N), \tag{1}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi - \frac{\rho_i^{(2)}}{\epsilon_r\epsilon_0}, \quad h + d_i^{(2)} < x < h + d_{i-1}^{(2)} \quad (1 \leqq i \leqq M), \tag{2}$$

and

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi, \quad 0 < x < h, \tag{3}$$

with

$$\kappa = \left(2n\nu^2e^2/\epsilon_r\epsilon_0 kT\right)^{1/2}, \tag{4}$$

where ϵ_r and κ are, respectively, the relative permittivity and the Debye-Hückel parameter of the electrolyte solution; ϵ_0 is the permittivity of a vacuum; e denotes the elementary electric charge; k is Boltzmann's constant; T is the absolute temperature; and we have defined $d_N^{(1)} = d_M^{(2)} = 0$ and $d_0^{(1)} = d_0^{(2)} = \infty$. The second term of the right-hand side of both eqs 1 and 2 arises from the contribution of membrane-fixed charges. Eq. 3 is the usual linearized Poisson-Boltzmann quation. It is convenient to introduce the Donnan potential $\psi_{\mathrm{DON},i}^{(j)}$ of the respective layers. Since the Donnan potential satisfies $\mathrm{d}^2\psi/\mathrm{d}x^2 = 0$, we have from eqs 1 and 2

$$\psi_{\mathrm{DON},i}^{(j)} = \frac{\rho_i^{(j)}}{\epsilon_r\epsilon_0\kappa^2}. \tag{5}$$

Now we assume that the distribution of mobile electrolyte ions is always at thermodynamic equilibrium within the membranes as well as in the surrounding solution, then the potential far inside the membranes remains constant during interaction. In the present system the potentials far inside membranes 1 and 2, respectively, remain constant at $\psi_{\mathrm{DON},1}^{(1)}$ and at $\psi_{\mathrm{DON},2}^{(2)}$.

The interaction force $P(h)$ driving the two membranes apart per unit area is generally expressed as [9,10,12]

$$P(h) = 2nkT\left[\cosh\left(\frac{\nu e\psi(0)}{kT}\right) - 1\right] - \tfrac{1}{2}\epsilon_r\epsilon_0\left(\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=0}\right)^2, \tag{6}$$

where the first and second terms are, respectively the difference in osmotic pressure and that in Maxwell's stress between $x = 0$ and the bulk solution phase. When the potentials are small, eq. 6 can be approximated by

$$P(h) = \tfrac{1}{2}\epsilon_r\epsilon_0\kappa^2\left[\psi^2(0) - \left(\frac{1}{\kappa}\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=0}\right)^2\right]. \tag{7}$$

The solution to eqs 1–3 subject to the boundary conditions that ψ and its derivative are, respectively, continuous at the boundaries $x = -d_i^{(1)}$ and $x = h + d_i^{(2)}$ can easily be obtained. Since only the values of ψ and its derivative at $x = 0$ are required to calculate $P(h)$ via eq. 7, we give explicitly the solution to eq. 3 below.

$$\psi(x) = \psi_{1\infty}e^{-\kappa x} + \psi_{2\infty}e^{-\kappa(h-x)}, \tag{8}$$

where $\psi_{1\infty}$ and $\psi_{2\infty}$ are, respectively, given by

$$\begin{aligned}\psi_{1\infty} = {} & \tfrac{1}{2}\psi_{\mathrm{DON},1}^{(1)}\exp\left(-\kappa d_1^{(1)}\right) \\ & + \tfrac{1}{2}\sum_{i=2}^{N-1}\psi_{\mathrm{DON},i}^{(1)}\left[\exp\left(-\kappa d_i^{(1)}\right) - \exp\left(-\kappa d_{i-1}^{(1)}\right)\right] \\ & + \tfrac{1}{2}\psi_{\mathrm{DON},N}^{(1)}\left[1 - \exp\left(-\kappa d_{N-1}^{(1)}\right)\right],\end{aligned} \tag{9}$$

and

$$\begin{aligned}\psi_{2\infty} = {} & \tfrac{1}{2}\psi_{\mathrm{DON},1}^{(2)}\exp\left(-\kappa d_1^{(2)}\right) \\ & + \tfrac{1}{2}\sum_{i=2}^{M-1}\psi_{\mathrm{DON},i}^{(2)}\left[\exp\left(-\kappa d_i^{(2)}\right) - \exp\left(-\kappa d_{i-1}^{(2)}\right)\right] \\ & + \tfrac{1}{2}\psi_{\mathrm{DON},M}^{(2)}\left[1 - \exp\left(-\kappa d_{M-1}^{(2)}\right)\right].\end{aligned} \tag{10}$$

Evaluating ψ and its derivative at $x = 0$ via eq. 8 and substituting the result into eq. 7, we obtain

$$P(h) = 2\epsilon_r\epsilon_0\kappa^2\psi_{1\infty}\psi_{2\infty}e^{-\kappa h}. \tag{11}$$

It is interesting to note that $\psi_{1\infty}$ and $\psi_{2\infty}$ are, respectively, the unperturbed surface potentials of membranes 1 and 2 (i.e., the surface potentials at $h = \infty$), as can be seen from eq. 8 and that eq. 11 states that the interaction force is proportional to the product of the unperturbed surface potentials of the interacting membranes. This is generally true for the Donnan-potential regulated interaction between two ion-penetrable membranes in which the distribution of the membrane-fixed charges far inside the membranes is uniform but may be arbitrary in the region near the membrane surfaces [13].

3. Results and discussion

We have derived expressions for the unperturbed surface potentials (eqs 9 and 10) of ion-penetrable multilayered membranes, from which the interaction force between them can be calculated with the help of eq. 11. Each layer in the membranes is characterized by its thickness and density of membrane-fixed charges. We have introduced the Donnan potential in place of the charge density. Our treatment is based upon the assumption that the Donnan potential of the innermost layer of each membrane ($\psi_{\mathrm{DON},1}^{(1)}$ and $\psi_{\mathrm{DON},1}^{(2)}$) remains constant during interaction.

Let us examine the relative contributions from each layer of membrane 1 to the surface potential $\psi_{1\infty}$. From eq. 10 it follows that the contribution from the innermost layer, i.e., a semi-infinite layer having the Donnan potential $\psi_{\mathrm{DON},1}^{(1)}$ occupying the region $-\infty < x < -d_1$, is seen to be

$$\tfrac{1}{2}\psi_{\mathrm{DON},1}^{(1)} \exp\left(-\kappa d_1^{(1)}\right). \tag{12}$$

The contribution of the i-th layer, having a finite thickness $d_i^{(1)} - d_{i-1}^{(1)}$ $(2 \leqq i \leqq N-1)$ and the Donnan potential $\psi_{\mathrm{DON},i}^{(1)}$, can thus be expressed as the difference in contribution between two semi-infinite layers, both having the same Donnan potential $\psi_{\mathrm{DON},i}^{(1)}$ occupying the regions $-\infty < x < -d_i^{(1)}$ and $-\infty < x < -d_{i-1}^{(1)}$, i.e.,

$$\tfrac{1}{2}\psi_{\mathrm{DON},i}^{(1)}\left[\exp\left(-\kappa d_i^{(1)}\right) - \exp\left(-\kappa d_{i-1}^{(1)}\right)\right]. \tag{13}$$

For the outermost layer (the N-th layer), we have

$$\tfrac{1}{2}\psi_{\mathrm{DON},N}^{(1)}\left[1 - \exp\left(-\kappa d_{N-1}^{(1)}\right)\right]. \tag{14}$$

Eqs 12–14 show that owing to the factor $\exp(-\kappa d_i^{(1)})$ the contribution of the i-th layer $(1 \leqq i \leqq N-1)$ becomes negligible if $\kappa d_i^{(1)} \gg 1$. In other words, the unperturbed surface potential $\psi_{1\infty}$ is determined mainly by the contribution from layers located within the depth of $1/\kappa$ from the membrane surface. This implies that variation of the electrolyte concentration (and thus of $1/\kappa$) changes the relative contributions to the unperturbed surface potentials from the respective layers of the interacting membranes so that the interaction force may also alter with electrolyte concentration. It is of particular interest to note that if layers forming the region within the depth of $1/\kappa$ are not of the same sign, the surface potential may alter even its sign with changing electrolyte concentration. This implies the existence of isoelectric points with respect to variation of the electrolyte concentration. Note, however, that the isoelectric point introduced here is the value of the electrolyte concentration at which the unperturbed surface potential becomes zero and does not have the usual meaning that the total (net) amount of membrane-fixed charges is zero. It immediately follows from the existence of isoelectric points that if the two interacting membranes have different isoelectric points, then the interaction force alters its sign at these isoelectric points (note that the interaction force between membranes with the same isoelectric point does not change its sign). An examples is given in fig. 2, which shows the interaction force between two membranes with different isoelectric points in a monovalent symmetrical electrolyte solution as a function of the electrolyte concentration. It is seen that the interaction force is positive (i.e., repulsive) at concentrations less than 0.07 M and higher than 0.18 M and negative (i.e., attractive) between 0.07 and 0.18 M, corresponding to the isoelectric points at 0.07 M for membrane 1 and 0.18 M for membrane

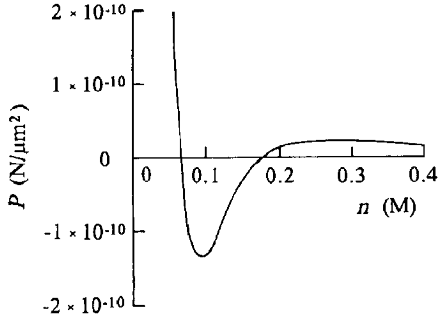

Fig. 2. Electrostatic force P between two ion-penetrable membranes, each consisting of two layers, immersed in a monovalent symmetrical electrolyte solution as a function of the electrolyte concentration n (M). The Donnan potentials at $n = 0.1$ M in the respective layers are as follows. $\psi_{\mathrm{DON},1}^{(1)} = -20$ mV, $\psi_{\mathrm{DON},2}^{(1)} = +15$ mV, $\psi_{\mathrm{DON},1}^{(2)} = -10$ mV, $\psi_{\mathrm{DON},2}^{(2)} = +10$ mV. $d_1^{(1)} = 10$ Å, $d_1^{(2)} = 5$ Å, $h = 25$ Å, $\epsilon_r = 78.5$, $T = 298$ K. $P > 0$ corresponds to repulsion and $P < 0$ to attraction.

2. Membranes consisting of more than two layers may exhibit more than one isoelectric point. The interaction force between such membranes will show complicated behavior on variation of the electrolyte concentration.

The present study has revealed that the sign of the interaction force $P(h)$ is determined not by the net or total amount of membrane-fixed charges but, rather, depends strongly on the isoelectric points of the interacting membranes. This behavior is not predicted by the conventinal interaction models assuming constant surface potential or constant surface charge density. We would therefore suggest a possibility of selective aggregation in the system of ion-penetrable membranes with different isoelectric points by using the difference between their isoelectric points.

In the present paper we have discussed the behavior of two interacting ion-penetrable multilayered membranes. A similar behavior may be expected in a system of an ion-penetrable membrane and a solid particle. The interaction force in the system is, to a first approximation, proportional to the product of their unperturbed surface potentials [14]. The interaction force may thus change its sign at the isoelectric point of the ion-penetrable membrane.

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