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Relationship among the surface potential, Donnan potential and charge density of ion-penetrable membranes

Hiroyuki Ohshima and Tamotsu Kondo

Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162, Japan

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Calculation of the potential distribution across a uniformly charged ion-penetrable membrane that we developed previously is extended to derive a relationship among the surface potential, Donnan potential and charge density of an ion-penetrable membrane in a mixed solution of 2-1 and 1-1 electrolytes. We also present an approximate method for calculating the surface potential/Donnan potential/charge density relationship for membranes with an arbitrary distribution of membrane-fixed charges.

1. Introduction

The surface potential and surface charge density of a colloidal particle are important parameters characterizing the particle surface. When a plate-like particle is immersed in a symmetrical electrolyte solution of valency v and bulk concentration n, its surface potential ψ_0 and surface charge density σ are often related to each other via the following familiar formula [1–3]:

$$\psi_0 = \frac{2kT}{ve}\text{arcsinh}\left[\frac{\sigma}{(8n\epsilon_r\epsilon_0 kT)^{1/2}}\right], \tag{1}$$

where k is Boltzmann's constant, T the absolute temperature, e the elementary electric charge, ϵ_r the relative permittivity of the solution and ϵ_0 the permittivity of a vacuum.

However, it should be borne in mind that eq. 1 is only applicable to particles with ion-impenetrable surfaces and thus cannot be employed in the case of biocolloids such as cells, which have ion-penetrable surfaces. Recently, we proposed a novel membrane model [4–7] applicable to biocolloids and calculated the potential profile across an ion-penetrable membrane immersed in an electrolyte solution. We have shown that the potential deep within the membrane is in practice equal to the Donnan potential, which we denote ψ_{DON}, and that the potential in the membrane interior varies nearly exponentially from the surface potential ψ_0 to ψ_{DON}, as depicted schematically in fig. 1. On the basis of this membrane model, we have derived expressions for ψ_{DON} and ψ_0 of an ion-penetrable membrane in which charged groups of valency z are distributed at a uniform density N, and immersed in a symmetrical electrolyte, viz.,

$$\psi_{DON} = \frac{kT}{ve}\text{arcsinh}\left(\frac{zN}{2vn}\right) = \frac{kT}{ve}\ln\left[\frac{zN}{2vn} + \left\{\left(\frac{zN}{2vn}\right)^2 + 1\right\}^{1/2}\right], \tag{2}$$

Correspondence address: T. Kondo, Faculty of Pharmaceutical Sciences, Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.

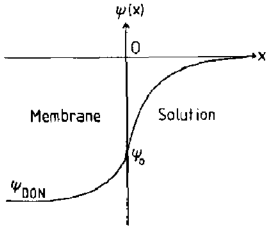

Fig. 1. Schematic representation of the potential profile across an ion-penetrable membrane with the surface potential ψ_0 and Donnan potential ψ_{DON}.

and

$$\psi_0 = \psi_{DON} - \frac{kT}{\nu e}\tanh\left(\frac{\nu e \psi_{DON}}{2kT}\right), \tag{3}$$

which, on being combined, yield

$$\psi_0 = \frac{kT}{\nu e}\left(\ln\left[\frac{zN}{2\nu n} + \left\{\left(\frac{zN}{2\nu n}\right)^2 + 1\right\}^{1/2}\right] + \frac{2\nu n}{zN}\left[1 - \left\{\left(\frac{zN}{2\nu n}\right)^2 + 1\right\}^{1/2}\right]\right), \tag{4}$$

Eq. 4 is quite different from eq. 1 in that the latter involves a surface charge density σ whereas N appearing in eq. 4 represents a volume charge density. It has been found [8] that the dependence of the surface potential of microcapsules upon electrolyte concentration can be explained very well by eq. 4 rather than by eq. 1. A number of other studies have also reported analyses of the charge distribution on the surfaces of microcapsules [9] and biological cells [10].

In the present paper, we generalize eq. 4 to cover the case in which an ion-penetrable membrane is immersed in a mixture of 2-1 and 1-1 electrolytes (e.g., $CaCl_2 + NaCl$). In addition, a transcendental equation is presented whose root provides an approximate value of the surface potential for a membrane having a non-uniform distribution of fixed charges.

2. Basic equations

Consider an ion-penetrable planar membrane immersed in a mixed solution of 1-1 electrolyte of bulk concentration n_1 and 2-1 electrolyte of bulk concentration n_2. Let ϵ_r and ϵ_r', respectively, denote the relative permittivity of the solution phase and that of the membrane phase. We take the x-axis as perpendicular to the membrane with its origin at the membrane surface, such that the region $x > 0$ corresponds to the solution phase and $x < 0$ to the membrane phase (fig. 1). We assume that membrane-fixed charges are distributed at a uniform density ρ within the membrane. Below, we first derive the relation between the Donnan potential ψ_{DON} and charge density ρ. We then obtain the relation between ψ_{DON} and the surface potential ψ_0 $(= \psi(0))$.

The Poisson-Boltzmann equation for the electric potential $\psi(x)$ at position x in the membrane phase reads

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\epsilon_r'\epsilon_0}\left[n_1 \exp(-e\psi/kT) + 2n_2 \exp(-2e\psi/kT) - (n_1 + 2n_2)\exp(e\psi/kT)\right] - \frac{\rho}{\epsilon_r'\epsilon_0}, \quad x < 0. \tag{5}$$

The right-hand side of eq. 5 arises from the contribution of mobile electrolyte ions and from that of the membrane fixed charges. We introduce the reduced potential

$$y = e\psi/kT \tag{6}$$

and a function of y

$$F(y) = -\frac{1-\eta}{2}e^{-y} - \frac{\eta}{3}e^{-2y} + \frac{3-\eta}{6}e^{y}, \tag{7}$$

where

$$\eta = \frac{3n_2}{n_1 + 3n_2} \tag{8}$$

is a dimensionless parameter $(0 \leqq \eta \leqq 1)$. Eq. 5 then becomes

$$\frac{d^2y}{dx^2} = \kappa'^2 F(y) - \frac{\rho}{\epsilon_r'\epsilon_0}\frac{e}{kT}, \quad x < 0. \tag{9}$$

In the bulk membrane phase, i.e., far inside the membrane, $d^2y/dx^2 \to 0$ and y becomes the reduced Donnan potential y_{DON}, defined by

$$y_{DON} = e\psi_{DON}/kT, \tag{10}$$

which is the solution to

$$F(y_{DON}) - \frac{e\rho}{\epsilon_r'\epsilon_0\kappa'^2 kT} = 0, \tag{11}$$

or

$$F(y_{DON}) - \frac{\rho}{2eI} = 0, \tag{12}$$

where

$$I = n_1 + 3n_2 \tag{13}$$

corresponds to the ionic strength and

$$\kappa' = \left[\frac{2Ie^2}{\epsilon_r'\epsilon_0 kT}\right]^{1/2} \tag{14}$$

represents the Debye-Hückel parameter of the membrane phase. Eq. 12 expresses the relation between y_{DON} (or ψ_{DON}) and ρ.

Now, we rewrite eq. 9, by using eq. 11, as

$$\frac{d^2y}{dx^2} = \kappa'^2[F(y) - F(y_{DON})], \quad x < 0, \tag{15}$$

which is integrated to yield

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa'^2[G(y) - G(y_{DON}) - (y - y_{DON})F(y_{DON})], \quad x < 0, \tag{16}$$

where $G(y)$ is defined as

$$G(y) = \frac{1-\eta}{2}e^{-y} + \frac{\eta}{6}e^{-2y} + \frac{3-\eta}{6}e^{y}. \tag{17}$$

The Poisson-Boltzmann equation for the solution phase is obtained by replacing ϵ_r' by ϵ_r and putting $\rho = 0$ in eq. 5, viz.,

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\epsilon_r\epsilon_0}[n_1 \exp(-e\psi/kT) + 2n_2 \exp(-2e\psi/kT) - (n_1 + 2n_2)\exp(e\psi/kT)], \quad x > 0, \tag{18}$$

which can be integrated to give

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa^2[G(y) - (1 - \eta/2)], \quad x > 0, \tag{19}$$

where

$$\kappa = \left[\frac{2Ie^2}{\epsilon_r\epsilon_0 kT}\right]^{1/2} \tag{20}$$

is the Debye-Hückel parameter of the solution phase. As a result of the continuity of the electric displacement, y must satisfy the following boundary condition at $x = 0$:

$$\epsilon_r'\frac{dy}{dx}\bigg|_{x=-0} = \epsilon_r\frac{dy}{dx}\bigg|_{x=+0}. \tag{21}$$

We evaluate eq. 16 at $x = -0$ and eq. 19 at $x = +0$, substituting the results into eq. 21. Then, by noting that y is continuous at $x = 0$, we obtain

$$G(y_0) - \left(1 - \frac{\eta}{2}\right) - \left(\frac{\epsilon_r'}{\epsilon_r}\right)[G(y_0) - G(y_{DON}) - (y_0 - y_{DON})F(y_{DON})] = 0, \tag{22}$$

which expresses the required relation between y_0 and y_{DON}.

3. Results and discussion

The principal results of the present paper are eqs 12 and 22, which determine the relationship among the reduced surface potential y_0 ($= e\psi_0/kT$), reduced Donnan potential y_{DON} ($= e\psi/kT$) and charge density ρ of an ion-penetrable membrane immersed in a mixed solution of 1-1 and 2-1 electrolytes. A number of examples illustrating the results of calculation via eqs 12 and 22 are given in figs 2–4, where the sign of ρ is chosen to be negative so that y_0 and y_{DON} are also negative, since biocolloids are usually negatively charged.

Eq. 12 expresses the relation between y_{DON} and ρ. It should be noted that this relation does not involve the relative permittivities ϵ_r or ϵ_r'. Fig.

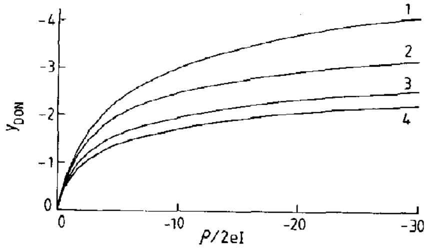

Fig. 2. Reduced Donnan potential y_{DON} ($= e\psi_{DON}/kT$) as a function of the charge density ρ for several values of η. Curves: 1, $\eta = 0$; 2, $\eta = 0.1$; 3, $\eta = 0.5$; 4, $\eta = 1$.

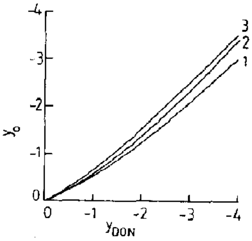

Fig. 3. Reduced surface potential y_0 ($= e\psi_0/kT$) as a function of the reduced Donnan potential y_{DON} ($= e\psi_{DON}/kT$) for several values of η. $\epsilon_r'/\epsilon_r = 1$. Curves: 1, $\eta = 0$; 2, $\eta = 0.1$; 3, $\eta = 1$.

2 shows y_{DON} plotted as a function of $\rho/2eI$ for several values of η, where $\eta = 0$ corresponds to a simple 1-1 electrolyte and $\eta = 1$ to a simple 2-1 electrolyte. When $\eta = 0$, in which case $F(y) = \sinh y$, we have the following familiar formula:

$$\sinh y_{DON} = \rho/2eI, \tag{23}$$

or

$$y_{DON} = \text{arcsinh}(\rho/2eI) = \ln\left[\frac{\rho}{2eI} + \left\{\left(\frac{\rho}{2eI}\right)^2 + 1\right\}^{1/2}\right]. \tag{24}$$

In the limit of small $|y_{DON}|$, eq. 24 reduces to

$$y_{DON} = \rho/2eI, \tag{25}$$

which is independent of η.

The relation between y_{DON} and y_0 is given by eq. 22. For the special case of $\epsilon_r'/\epsilon_r = 1$, eq. 22 becomes

$$y_0 = y_{DON} - \frac{[\exp(y_{DON}) - 1][(3-\eta)\exp(y_{DON}) + \eta]}{(3-\eta)\exp(y_{DON})[\exp(y_{DON}) + 1] + 2\eta}. \tag{26}$$

When $\eta = 0$, in particular, eq. 26 reduces to

$$y_0 = y_{DON} - \tanh(y_{DON}/2). \tag{27}$$

By combining eqs 24 and 27, we obtain y_0 as a function of ρ, i.e.,

$$y_0 = \ln\left[\frac{\rho}{2eI} + \left\{\left(\frac{\rho}{2eI}\right)^2 + 1\right\}^{1/2}\right] + \frac{2eI}{\rho}\left[1 - \left\{\left(\frac{\rho}{2eI}\right)^2 + 1\right\}^{1/2}\right]. \tag{28}$$

Eqs 24, 27 and 28 are, respectively, equivalent to eqs 2, 3 and 6, if ρ is set equal to zeN. In the limit of large $|y_{DON}|$, we have

$$|y_0| = |y_{DON}| - 1, \quad \eta = 0, \tag{29}$$

$$|y_0| = |y_{DON}| - 1/2, \quad \eta \neq 0. \tag{30}$$

Indeed, as demonstrated in fig. 3, which depicts y_0 as a function of y_{DON} at $\epsilon_r'/\epsilon_r = 1$ for several values of η, the curves with $\eta \neq 0$ have asymptotes to $|y_0| = |y_{DON}| - 1/2$. In the opposite limit of small $|y_{DON}|$, we have

$$y_0 = y_{DON}/2, \tag{31}$$

irrespective of the value of η. It follows from eqs 29–31, that

$$|y_{DON}|/2 < |y_0| < |y_{DON}|. \tag{32}$$

Consider next the effects of ϵ_r' on y_0. Fig. 4 shows plots of y_0 as a function of y_{DON} at $\eta = 0$ for several values of ϵ_r'/ϵ_r. One observes that y_0 becomes smaller in magnitude with decreasing ϵ_r'.

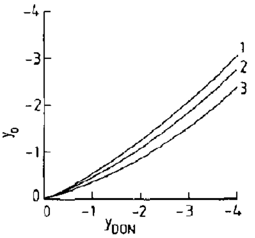

Fig. 4. Reduced surface potential y_0 ($= e\psi_0/kT$) as a function of the reduced Donnan potential y_{DON} for several values of ϵ_r'/ϵ_r. $\eta = 0$. Curves: 1, $\epsilon_r'/\epsilon_r = 1$; 2, $\epsilon_r'/\epsilon_r = 0.5$; 3, $\epsilon_r'/\epsilon_r = 0.2$.

The reason for this is that $y(x)$ in the membrane interior changes more sharply for smaller ϵ_r', as is also evident from eq. 21. In the limit of small y_0, we obtain

$$y_0 = \frac{1}{1+(\epsilon_r/\epsilon_r')^{1/2}} y_{DON}, \tag{33}$$

which does not depend on η.

Finally, we describe an approximate method for calculating y_0. We expand $F(y)$ around $y = y_{DON}$ as

$$F(y) = F(y_{DON}) + \left.\frac{dF(y)}{dy}\right|_{y=y_{DON}} \cdot (y - y_{DON})$$
$$= F(y_{DON}) + H(y_{DON})(y - y_{DON}), \tag{34}$$

where $H(y)$ is defined as

$$H(y) = \frac{1-\eta}{\eta} e^{-y} + \frac{2\eta}{3} e^{-2y} + \frac{3-\eta}{6} e^{y}. \tag{35}$$

The Poisson-Boltzmann equation (eq. 15) is then approximated by

$$\frac{d^2y}{dx^2} = \kappa_m^2 (y - y_{DON}), \tag{36}$$

where

$$\kappa_m = \kappa' [H(y_{DON})]^{1/2}. \tag{37}$$

Eq. 36 can easily be integrated to give

$$y(x) = y_{DON} + (y_0 - y_{DON}) \exp(\kappa_m x), \qquad x < 0, \tag{38}$$

From the condition of continuity of the electric displacement and of the potential at $x = 0$, we obtain from eqs 19, 21 and 38

$$G(y_0) - \left(1 - \frac{\eta}{2}\right) - \frac{\epsilon_r'}{2\epsilon_r} H(y_{DON})(y_0 - y_{DON})^2 = 0. \tag{39}$$

This is a transcendental equation for y_0 for a given value of y_{DON}. When $\epsilon'/\epsilon = 1$ and $\eta = 0$, in particular, eq. 43 becomes

$$(y_0 - y_{DON})^2 \cosh y_{DON} - 2(\cosh y_0 - 1) = 0. \tag{40}$$

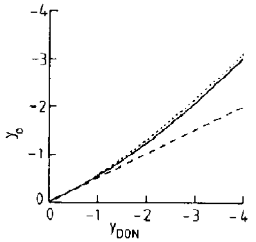

Fig. 5. Comparison of approximate results with the exact data. (———) Exact (eq. 27); (······) approximation (eq. 40); (- - - - -) approximation (eq. 31).

Fig. 5 shows the approximate results (eq. 40) in comparison with the exact data (eq. 27). It is seen that the approximation is excellent with the maximum error of about 4% and much better than the linear approximation: $y_0 = y_{DON}/2$ (eq. 31). Eqs 39 and 40 can provide a useful method when exact analytical solutions are not available. As an important example, we consider the case in which the membrane fixed charge distribution is homogeneous only deep within the membrane but is inhomogeneous near the membrane surface. This may be the case for real biological membranes. We assume that ρ is given by

$$\rho(x) = \rho_0 + \Delta\rho(x), \qquad x < 0, \tag{41}$$

with

$$\Delta\rho(x) \xrightarrow[x \to -\infty]{} 0, \tag{42}$$

where ρ_0 corresponds to a uniform bulk charge distribution and $\Delta\rho$ to a non-uniform distribution near the membrane surface. It can be shown that

$$\left.\frac{dy}{dx}\right|_{x=-0} = \kappa_m(y_0 - y_{DON}) - \frac{e}{\epsilon_r'\epsilon_0 kT} \int_{-\infty}^{0} \Delta\rho(x) \times \exp(\kappa_m x)\, dx. \tag{43}$$

Combining eqs 19, 21 and 43, we obtain a transcendental equation for y_0, viz.,

$$G(y_0) - \left(1 - \frac{\eta}{2}\right) - \frac{\epsilon_r'}{2\epsilon_r} H(y_{DON}) \times \left[y_0 - y_{DON} - \frac{\overline{\Delta\rho}}{2eIH(y_{DON})} \right]^2 = 0, \tag{44}$$

with

$$\overline{\Delta\rho} = \kappa_m \int_{-\infty}^{0} \Delta\rho(x) \exp(\kappa_m x) \, dx, \tag{45}$$

which can readily be solved numerically.

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