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Evaluation of the Donnan model for polyelectrolytes using the composite Poisson–Boltzmann equations

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Abstract: The validity of the macroscopic Donnan model for polyelectrolytes in an electrolyte solution is examined by taking into account the effects of the varying potential distribution across the boundary between a polyelectrolyte and the surrounding solution, using the composite Poisson–Boltzmann equations for the polyelectrolyte interior and the surrounding solution. Calculations are made for a planar polyelectrolyte of thickness $2d$ and a planar polyelectrolyte layer of thickness d covering a rigid surface, both showing the identical potential distribution. A simple expression for a correction factor for these effects is derived which enables to evaluate various corrected quantities in the polyelectrolyte interior such as the average potential, the average ionic concentration, the average degree of dissociation and the apparent dissociation constant of ionizable groups in the polyelectrolyte. It is found that when $\kappa d \gg 1$ (where κ indicates the Debye-Hückel parameter) the macroscopic Donnan model can safely be applied, while as κd decreases the effects of the varying potential distribution become appreciable.

Key words: Donnan model – Donnan potential – polyelectrolyte – counterion binding – potential distribution

1. Introduction

When charged polyelectrolytes are immersed in an electrolyte solution, the macroscopic potential difference is established between the polyelectrolyte interior and the external electrolyte solution. The distribution of electrolyte ions between these two regions has often been treated by a two-phase model, or the macroscopic Donnan model [1–10], where the potential of the polyelectrolyte interior phase, measured relative to the external solution phase is called the Donnan potential. The thermodynamic expression for the Donnan potential is derived from the equilibrium condition for the distribution of small mobile ions, which can exist in both phases, that is, by equating the electrochemical potentials of these ions in the two phases. Marinsky and coworkers, in particular, have recently proposed computational procedures to estimate the volume of the internal region of a polyelectrolyte by use of the polyelectrolyte-counterion binding equilibria as a probe [3–10].

Even though it has been shown that the macroscopic Donnan model can be used for the analysis of complexation equilibria in systems of not only cross-linked polyelectrolytes but also linear polyelectrolytes [9, 10], the definition of the phase boundary still remains arbitrary. Owing to the thermal motion of the electrolyte ions, the potential actually varies continuously (or essentially exponentially) across the polyelectrolyte/solution boundary (see Fig. 1). In a model taking into account the effects of this potential distribution, that is, the microscopic Donnan model, the potential distribution is given by solving the composite Poisson-Boltzmann equations for the polyelectrolyte phase and the external solution phase [11–12]. The microscopic Donnan model has been developed also in the problems of the potential

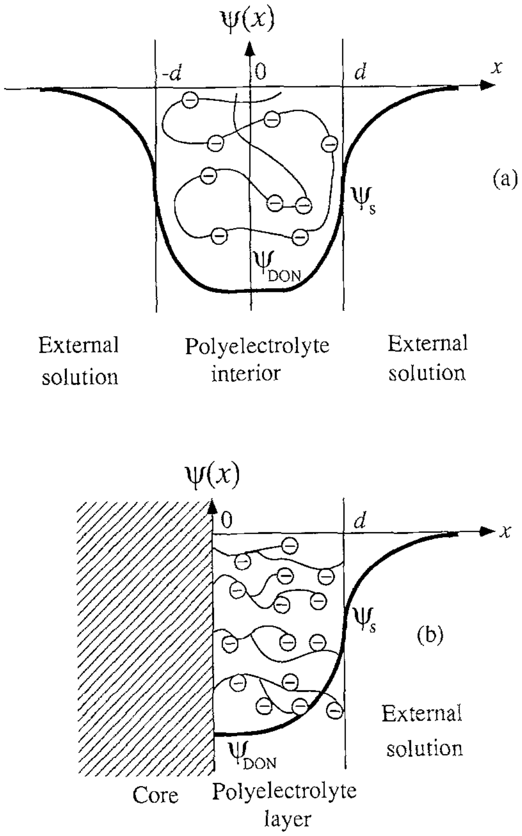

Fig. 1. A planar polyelectrolyte of thickness $2d$ (a) and a planar polyelectrolyte layer of thickness d adsorbed on a rigid surface. (b). ψ_{DON} = Donnan potential and ψ_s = surface potential

distribution across ion-penetrable membranes [13–15] and the electrophoresis of biological cells [16].

In the present paper we treat planar isolated polyelectrolytes or polyelectrolytes adsorbed on the surface of a rigid particle in an aqueous solution containing electrolytes. In the polyelectrolyte interior, ionizable groups are assumed to be uniformly distributed. The composite Poisson–Boltzmann equations are applied to inside and outside the polyelectrolyte. We derive simple analytic expressions for average quantities within a polyelectrolyte and evaluate the validity of the macroscopic Donnan model.

2. Basic equations

Imagine isolated polyelectrolytes or polyelectrolytes adsorbed on the surface of a rigid particle in an aqueous solution containing 1:1 symmetrical univalent electrolytes. Let n (in units of m^{-3}) be the total bulk number density of salt cations plus H^+ ions and that of salt anions plus OH^- ions. As a model for polyelectrolytes, it may be most appropriate to consider cylindrical or spherical geometry. In the following, however, we consider for simplicity a planar model. That is, we deal with a planar polyelectrolyte of thickness $2d$ (see Fig. 1(a)) and a planar polyelectrolyte layer of thickness d covering the rigid particle core (see Fig. 1(b)). We assume that univalent acidic dissociable groups of intrinsic dissociation constant K are distributed at a uniform density N within the polyelectrolyte. We take an x-axis in the direction of the polyelectrolyte thickness with its origin at the mid-plane in the polyelectrolyte (Fig. 1(a)) or at the surface of the particle core (Fig. 1(b)). For the system shown in Fig. 1(b), by symmetry we need to consider only the region $0 \leq x \leq d$. Note that the potential distribution in the region $0 \leq x \leq d$ in Fig. 1(a) is identical to that in the region $0 \leq x \leq d$ in Fig. 1(b) so that the following formulation is applicable to both systems in Figs. 1(a) and 1(b). In Fig. 1(b) the effects of the internal field within the particle core (in the region $x < 0$) are assumed negligible. We assume that the polyelectrolyte is permeable to small mobile ions (electrolyte ions, H^+ and OH^-). Also, we assume that these small mobile ions obey a Boltzmann distribution and the electric potential $\psi(x)$ (relative to the bulk solution phase, where $\psi(x)$ is set equal to zero) for the regions $x > d$ and $0 < x < d$ satisfies the following composite Poisson–Boltzmann equations:

$$\frac{d^2\psi}{dx^2} = \frac{2en}{\varepsilon_r\varepsilon_0}\sinh\frac{e\psi(x)}{kT}, \quad x > d, \tag{1}$$

$$\frac{d^2\psi}{dx^2} = \frac{2en}{\varepsilon_r\varepsilon_0}\sinh\frac{e\psi(x)}{kT} - \frac{\rho_{\mathrm{fix}}(x)}{\varepsilon_r\varepsilon_0}, \quad 0 < x < d. \tag{2}$$

In Eqs. (1) and (2) e is the elementary electric charge, ε_r is the relative permittivity, ε_0 is the permittivity of a vacuum, k is the Boltzmann constant, T is the absolute temperature and $\rho_{\mathrm{fix}}(x)$ is the fixed-charge density resulting from the dissociation of acidic groups distributed in the polyelectrolyte. Here, we have assumed that the relative permittivity ε_r is the same for both the surrounding solution phase and the polyelectrolyte interior. From the mass action law for the dissociation reaction of acidic groups AH, viz., $AH = A^- + H^+$, it follows that the number density $N^-(x)$ of dissociated acidic groups A^- is expressed as

$$N^-(x) = \alpha(x)N = \frac{N}{1 + \dfrac{n_H(x)}{K}}, \quad 0 < x < d , \quad (3)$$

where $\alpha(x)$ is the degree of dissociation of the acidic groups at position x and $n_H(x)$ is the number density of H^+ ions at position x. Since we assume a Boltzmann distribution for H^+ ions, viz.,

$$n_H(x) = n_H^0 \exp\left[-\frac{e\psi(x)}{kT}\right], \quad (4)$$

where n_H^0 is the bulk number density of H^+ ions, then Eq. (3) becomes

$$N^-(x) = \frac{N}{1 + \dfrac{n_H^0}{K}\exp\left[-\dfrac{e\psi(x)}{kT}\right]}, \quad 0 < x < d , \quad (5)$$

and $\alpha(x)$ is expressed as

$$\alpha(x) = \frac{1}{1 + \dfrac{n_H^0}{K}\exp\left[-\dfrac{e\psi(x)}{kT}\right]}, \quad 0 < x < d . \quad (6)$$

The charge density $\rho_{fix}(x) = -eN^-(x)$ is then given by

$$\rho_{fix}(x) = -\frac{eN}{1 + \dfrac{n_H^0}{K}\exp\left[-\dfrac{e\psi(x)}{kT}\right]}, \quad 0 < x < d , \quad (7)$$

Note that the degree of dissociation $\alpha(x)$, the number density $N^-(x)$ of dissociated acidic groups A^-, and the charge density $\rho_{fix}(x)$ are all functions of position x. By substituting Eq. (7) into Eq. (2), the Poisson–Boltzmann equation for the polyelectrolyte interior is rewritten as

$$\frac{d^2\psi}{dx^2} = \frac{2en}{\varepsilon_r\varepsilon_0}\sinh\frac{e\psi(x)}{kT} + \frac{1}{\varepsilon_r\varepsilon_0}\frac{eN}{1 + \dfrac{n_H^0}{K}\exp\left[-\dfrac{e\psi(x)}{kT}\right]}, \quad 0 < x < d . \quad (8)$$

The Donnan potential of the polyelectrolyte interior is defined as the potential value that makes the right-hand side of Eq. (8) zero, viz.,

$$\sinh\frac{e\psi_{DON}}{kT} + \frac{N}{2n}\frac{1}{1 + \dfrac{n_H^0}{K}\exp\left[-\dfrac{e\psi_{DON}}{kT}\right]} = 0 , \quad (9)$$

which can also be derived by equating the electrochemical potential of mobile ions in the region where the potential equals the Donnan potential with that in the external bulk solution phase.

The boundary conditions for $\psi(x)$ are

$$\psi(d-0) = \psi(d+0) , \quad (10)$$

$$\left.\frac{d\psi}{dx}\right|_{x=d-0} = \left.\frac{d\psi}{dx}\right|_{x=d+0} , \quad (11)$$

$$\psi(x) \to 0 \text{ and } \frac{d\psi}{dx} \to 0 \text{ as } x \to \infty , \quad (12)$$

and

$$\left.\frac{d\psi}{dx}\right|_{x=+0} = 0 . \quad (13)$$

Equation (13) is a result of symmetry of the system shown in Fig. 1(a), while in the system in Fig. 1(b) it corresponds to the assumption that the fields inside the particle core are negligible.

The coupled equations (1) and (8) subject to the boundary conditions (10)–(13) completely determine the potential distribution $\psi(x)$ in the whole region for both systems shown in Figs. 1(a) and 1(b).

3. Numerical calculation and approximate expression for potential distribution

We introduce the dimensionless potential

$$y = \frac{e\psi}{kT}, \quad (14)$$

then the Poisson–Boltzmann equations (1) and (8) become

$$\frac{d^2y}{dx^2} = \kappa^2 \sinh y, \quad x > d , \quad (15)$$

$$\frac{d^2y}{dx^2} = \kappa^2\left[\sinh y + \frac{N}{2n}\,\frac{1}{1+\frac{n_{\mathrm{H}}^0}{K}\exp(-y)}\right], \qquad 0 < x < d\,, \tag{16}$$

where

$$\kappa = \left(\frac{2ne^2}{\varepsilon_{\mathrm{r}}\varepsilon_0 kT}\right)^{1/2} \tag{17}$$

is the Debye-Hückel parameter. The Poisson–Boltzmann equation (15) for the external solution phase ($x > d$) subject to the boundary condition (12) is readily integrated to yield [17]

$$\frac{dy}{dx} = -2\kappa\sinh\left(\frac{y}{2}\right), \quad x > d\,. \tag{18}$$

Further integration of Eq. (18) gives [17]

$$y(x) = 2\ln\left(\frac{1+\tanh(y_{\mathrm{s}}/4)\cdot\exp[-\kappa(x-d)]}{1-\tanh(y_{\mathrm{s}}/4)\cdot\exp[-\kappa(x-d)]}\right), \qquad x \geq d\,, \tag{19}$$

with

$$y_{\mathrm{s}} = \frac{e\psi_{\mathrm{s}}}{kT} = \frac{e\psi(d)}{kT}\,, \tag{20}$$

where $\psi_{\mathrm{s}} \equiv \psi(d)$ is the surface potential of the polyelectrolyte, i.e., the potential at the boundary $x = d$ between the polyelectrolyte and the surrounding solution and $y_{\mathrm{s}} \equiv y(d)$ is the dimensionless surface potential. On the other hand, solving the Poisson–Boltzmann equation (16) for the polyelectrolyte interior requires numerical calculation. It is most convenient to use the Taylor expansion series of $y(x)$ around $x = +0$

$$y(x) = y(0) + \sum_{n=1}^{\infty} A_n(\kappa x)^{2n}, \quad 0 < x < d\,, \tag{21}$$

with

$$A_n = \frac{1}{(2n)!\,\kappa^{2n}}\left.\frac{d^{2n}y}{dx^{2n}}\right|_{x=+0}, \tag{22}$$

where we have used the fact that all terms with the odd power of κx vanish, which can be proven using Eq. (13). The coefficients A_n can be obtained from Eq. (16) (for $n = 1$) and by successive differentiation of Eq. (16) (for $n \geq 2$). The explicit expressions for A_n ($n = 1$–4) are listed below:

$$A_1 = B_1/2 \tag{23}$$

$$A_2 = B_1B_2/24 \tag{24}$$

$$A_3 = B_1(3B_1B_3 + B_2^2)/720 \tag{25}$$

$$A_4 = B_1(15B_1^2B_4 + 18B_1B_2B_3 + B_2^3)/40320\,, \tag{26}$$

where

$$B_1 = \sinh y(0) + \frac{N}{2n}\,\frac{1}{1+\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))} \tag{27}$$

$$B_2 = \cosh y(0) + \frac{N}{2n}\,\frac{\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))}{\left[1+\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\right]^2} \tag{28}$$

$$B_3 = \sinh y(0) - \frac{N}{2n}\,\frac{\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\left[1-\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\right]}{\left[1+\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\right]^3} \tag{29}$$

$$B_4 = \cosh y(0) + \frac{N}{2n}\,\frac{\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\left[1-\frac{4n_{\mathrm{H}}^0}{K}\exp(-y(0)) + \left\{\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\right\}^2\right]}{\left[1+\frac{n_{\mathrm{H}}^0}{K}\exp(-y(0))\right]^4} \tag{30}$$

By evaluating the values of y and dy/dx at $x = d$ from Eqs. (19) and (21) and matching them via the boundary conditions (10) and (11), we can obtain simultaneous equations for $y(0)$ and $y(d)$. Using the obtained values of $y(0)$ and $y(d)$, we can calculate $y(x)$ by again using Eqs. (19) and (21).

Although this numerical procedure is not difficult, it is inconvenient to calculate various quantities relating to the potential distribution $y(x)$ in the polyelectrolyte. We thus here employ a method of "quasi-linearization" in order to find an approximate solution for the polyelectrolyte interior ($0 < x < d$), as will be shown below. By putting $y(x) = y_{\mathrm{DON}} + \Delta y(x)$, $y_{\mathrm{DON}} \equiv e\psi_{\mathrm{DON}}/kT$ being the dimensionless Donnan potential, and linearizing Eq. (16) with respect to $\Delta y(x)$, we obtain

$$\frac{d^2 \Delta y}{dx^2} = \kappa_{\mathrm{m}}^2 \Delta y, \quad 0 < x < d\,, \tag{31}$$

where

$$\kappa_{\mathrm{m}} = \kappa[\cosh y_{\mathrm{DON}} - (1 - \alpha_{\mathrm{DON}})\sinh y_{\mathrm{DON}}]^{1/2}\,, \tag{32}$$

and

$$\alpha_{\mathrm{DON}} = \frac{1}{1 + \dfrac{n_{\mathrm{H}}^0}{K}\exp(-y_{\mathrm{DON}})}\,. \tag{33}$$

Here, κ_{m} can be interpreted to be the Debye–Hückel parameter of the polyelectrolyte interior and α_{DON} is the degree of dissociation in the region where the potential $\psi(x)$ (or $y(x)$) equals the Donnan potential ψ_{DON} (or y_{DON}). Equation (32) shows that κ_{m} is always greater than κ. In terms of y_{DON} and α_{DON}, Eq. (9) is rewritten as

$$\sinh y_{\mathrm{DON}} + \frac{N}{2n}\alpha_{\mathrm{DON}} = 0\,, \tag{34}$$

which is a transcendental equation for y_{DON}. In the present case, where the polyelectrolyte-fixed charges arise from dissociation of acidic groups, y_{DON} is negative. In the special case of $\alpha_{\mathrm{DON}} = 1$, Eq. (34) reduces to

$$\begin{aligned} y_{\mathrm{DON}} &= -\operatorname{arcsinh}\left(\frac{N}{2n}\right) \\ &= -\ln\left[\frac{N}{2n} + \left\{\left(\frac{N}{2n}\right)^2 + 1\right\}^{1/2}\right]. \end{aligned} \tag{35}$$

The solution to Eq. (31) subject to the boundary conditions (10) and (13) is given by

$$\Delta y(x) = (y_{\mathrm{s}} - y_{\mathrm{DON}})\frac{\cosh(\kappa_{\mathrm{m}}x)}{\cosh(\kappa_{\mathrm{m}}d)}, \quad 0 \le x \le d\,, \tag{36}$$

or

$$y(x) = y_{\mathrm{DON}} + (y_{\mathrm{s}} - y_{\mathrm{DON}})\frac{\cosh(\kappa_{\mathrm{m}}x)}{\cosh(\kappa_{\mathrm{m}}d)}, \quad 0 \le x \le d\,. \tag{37}$$

The value of ψ_{s} (or y_{s}) can be determined as follows. Evaluating Eq. (18) at $x = d$ and equating the result with the derivative of Eq. (37) at $x = d$ (Eq. (11)) yields the following transcendental equation for y_{s}:

$$(y_{\mathrm{s}} - y_{\mathrm{DON}})\kappa_{\mathrm{m}}\tanh(\kappa_{\mathrm{m}}d) = -2\kappa\sinh(y_{\mathrm{s}}/2)\,. \tag{38}$$

If $|y_{\mathrm{s}}|/2$ is small, then Eq. (38) can be further simplified by approximating $\sinh(y_{\mathrm{s}}/2)$ by $y_{\mathrm{s}}/2$. This approximation does not lead to serious errors, because it is not required that $|y_{\mathrm{DON}}|$ is also small. Equation (38) is then approximated by

$$y_{\mathrm{s}} = \frac{(\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}}d)}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}}d)}\,y_{\mathrm{DON}}\,. \tag{39}$$

Substituting Eq. (39) into Eqs. (36) and (37) yields

$$\Delta y(x) = -\frac{y_{\mathrm{DON}}}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}}d)}\,\frac{\cosh(\kappa_{\mathrm{m}}x)}{\cosh(\kappa_{\mathrm{m}}d)}, \quad 0 \le x \le d\,, \tag{40}$$

and

$$y(x) = y_{\mathrm{DON}}\left[1 - \frac{1}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}}d)}\,\frac{\cosh(\kappa_{\mathrm{m}}x)}{\cosh(\kappa_{\mathrm{m}}d)}\right], \quad 0 \le x \le d\,. \tag{41}$$

Equation (41) is the required approximate expression for the potential distribution within the polyelectrolyte. The accuracy of Eq. (41) is quite good, as will be described later. The following analyses will be based on Eq. (41).

4. Results and discussion

According to the macroscopic Donnan model, the internal region of polyelectrolytes is regarded as a uniform "polyion domain" or "Donnan phase" so that the potential everywhere in this region equals the Donnan potential. Actually, however, the potential in the polyelectrolyte interior is not uniform but varies near the polyelectrolyte/solution boundary, as schematically shown in Fig. 1. We have derived a simple approximate expression for the potential distribution in the polyelectrolyte interior ($0 \le x \le d$) (Eq. (41)). Figure 2 shows an example of the potential distribution $y(x)$ as a function of κx for $\kappa d = 5$ and $y_{\mathrm{DON}} = -0.5$, -1 and -2 calculated from Eq. (41) for the polyelectrolyte interior and from Eq. (19) for the external solution. It is seen that the potential $y(x)$ tends to the Donnan potential y_{DON} for the respective cases in the deep interior of the polyelectrolyte, but varies over some distance of order $\kappa (x \ge d)$ or order $\kappa_{\mathrm{m}} (0 \le x \le d)$ on both sides of the boundary between the polyelectrolyte and the surrounding solution. One must take into account this potential distribution $y(x)$ unless $\kappa d \gg 1$, as shown below.

The average value over the polyelectrolyte interior, i.e., the region $0 \le x \le d$ for an arbitrary function $f(x)$ is calculated via

$$\langle f(x) \rangle = \frac{1}{d} \int_0^d f(x) dx \, . \tag{42}$$

We give below the average values of several functions of x:

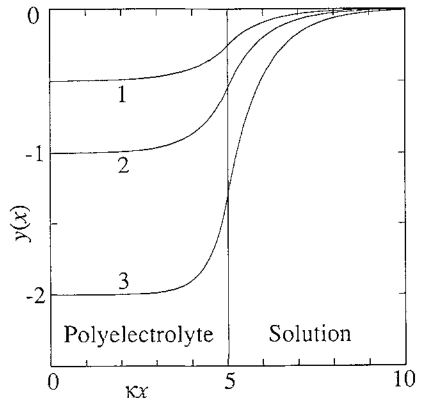

Fig. 2. Potential distribution $\psi(x)$ inside and outside a planar polyelectrolyte of scaled thickness $\kappa d = 10$ or an adsorbed polyelectrolyte layer of scaled thickness $\kappa d = 5$ for several values of y_{DON} at $\alpha_{\mathrm{DON}} = 1$. Curves: 1, $y_{\mathrm{DON}} = -0.5$ ($N/n = 1.04$); 2, $y_{\mathrm{DON}} = -1$ ($N/n = 2.35$); 3, $y_{\mathrm{DON}} = -2$ ($N/n = 7.25$)

a) Average potential

Substituting Eqs. (40) and (41) into Eq. (42), we have

$$\langle \Delta y(x) \rangle = -\frac{y_{\mathrm{DON}}}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}} d)} \frac{\tanh(\kappa_{\mathrm{m}} d)}{\kappa_{\mathrm{m}} d} \tag{43}$$

and

$$\langle y(x) \rangle = y_{\mathrm{DON}} \left[1 - \frac{1}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}} d)} \frac{\tanh(\kappa_{\mathrm{m}} d)}{\kappa_{\mathrm{m}} d} \right], \tag{44}$$

or

$$\langle \psi(x) \rangle = \psi_{\mathrm{DON}} \left[1 - \frac{1}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}} d)} \frac{\tanh(\kappa_{\mathrm{m}} d)}{\kappa_{\mathrm{m}} d} \right]. \tag{45}$$

The effects of the potential distribution within the polyelectrolyte are characterized by the ratio of the average potential to the Donnan potential, viz.,

$$f(y_{\mathrm{DON}}, d) = \frac{\langle y(x) \rangle}{y_{\mathrm{DON}}} = \frac{y_{\mathrm{DON}} + \langle \Delta y(x) \rangle}{y_{\mathrm{DON}}} = 1 - \frac{1}{1 + (\kappa_{\mathrm{m}}/\kappa)\tanh(\kappa_{\mathrm{m}} d)} \frac{\tanh(\kappa_{\mathrm{m}} d)}{\kappa_{\mathrm{m}} d}, \tag{46}$$

which is a function of y_{DON} and d.

The case of $f(y_{\mathrm{DON}}, d) = 1$ corresponds to the simple Donnan model, which ignores the potential distribution across the polyelectrolyte/solution boundary. Figure 3 shows the dependence of $f(y_{\text{DON}}, d)$ upon κd for various values of y_{DON} for the simple case where $\alpha_{\text{DON}} = 1$. We see that in the limit $\kappa d \to \infty$, the simple Donnan model (i.e., $f(y_{\text{DON}}, d) \to 1$) exactly results and for $\kappa d \gg 1$ the macroscopic Donnan model is a good approximation. With decreasing κd, however, the value of $f(y_{\text{DON}}, d)$ decreases, tending to zero, so that the deviation from the macroscopic Donnan model becomes appreciable. That is, for small κd one should take into account the potential distribution inside the polyelectrolyte. When $d = 10$ nm and $n = 0.1$ M, for instance, in which case $1/\kappa = 1$ nm (i.e., $\kappa d = 10$), we obtain $f(y_{\text{DON}}, d) = 0.95$. If, however, the electrolyte concentration is decreased to $n = 0.001$ M, then κd becomes 1 so that $f(y_{\text{DON}}, d)$ is decreased down to 0.5, implying the considerable effects of the potential distribution inside the polyelectrolyte. Note that for $\kappa d \to 0$, the Donnan model becomes inappropriate because the potential inside the polyelectrolyte never takes the value of the Donnan potential even approximately.

Figure 3 also shows the corresponding exact numerical results. The accuracy of Eq. (46), which is based on Eq. (41), is good. The error of Eq. (46) relative to the exact numerical solution is less than 5% for $\kappa d \geq 1$. Even at $\kappa d = 0.5$, the error is about 15%.

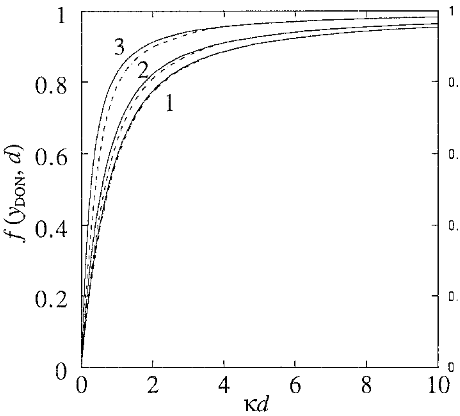

Fig. 3. Correction factor $f(y_{\text{DON}}, d)$ defined by Eq. (46) as a function of κd for several values of the dimensionless Donnan potential y_{DON} at $\alpha_{\text{DON}} = 1$. Curves: 1, $y_{\text{DON}} = -0.5$ ($N/n = 1.04$); 2, $y_{\text{DON}} = -1$ ($N/n = 2.35$); 3, $y_{\text{DON}} = -2$ ($N/n = 7.25$). The corresponding exact numerical results are also shown as dashed lines

b) Average concentrations of univalent cations and anions

We calculate the average concentrations of cations and of anions as

$$\begin{aligned}\langle n^{\pm}(x)\rangle &= n\langle \exp(\mp\, y(x))\rangle \\ &= n\langle \exp(\mp\, (y_{\text{DON}} + \Delta y(x))\rangle \\ &\approx n\exp(\mp\, y_{\text{DON}})(1 \mp \langle \Delta y(x)\rangle) \\ &= n\exp(\mp\, y_{\text{DON}})[1 \pm y_{\text{DON}} \\ &\quad \times (1 - f(y_{\text{DON}}, d))]\ . \qquad (47\text{a}) \\ &\approx n\exp[\mp\, y_{\text{DON}} f(y_{\text{DON}}, d)]\ . \qquad (47\text{b})\end{aligned}$$

Note that Eq. (47b) equals $\exp(\mp\,\langle y(x)\rangle)$, that is, in the present approximation (based on the linearization with respect to $\Delta y(x) = y(x) - y_{\text{DON}}$), $\langle\exp(\mp\, y(x))\rangle$ coincides with $\exp(\mp\,\langle y(x)\rangle)$. The product $\langle n^{\pm}(x)\rangle d$ represents the total amount of mobile cations or anions trapped (or purely electrostatically bound) in the polyelectrolyte interior ($0 \leq x \leq d$).

c) Average degree of dissociation

The degree of dissociation α is a function of position x so that its average is calculated as

$$\begin{aligned}\langle\alpha(x)\rangle &= \left\langle \frac{1}{1 + \dfrac{n_{\text{H}}^{0}}{K}\exp(-y(x))} \right\rangle \\ &\approx \left\langle \frac{1}{1 + \dfrac{n_{\text{H}}^{0}}{K}\exp(-y_{\text{DON}})[1 - \Delta y(x)]} \right\rangle \\ &\approx \frac{1}{1 + \dfrac{n_{\text{H}}^{0}}{K}\exp(-y_{\text{DON}})} \\ &\quad \times \left[1 + \frac{\dfrac{n_{\text{H}}^{0}}{K}\exp(-y_{\text{DON}})}{1 + \dfrac{n_{\text{H}}^{0}}{K}\exp(-y_{\text{DON}})} \langle \Delta y(x)\rangle\right] \\ &= \alpha_{\text{DON}}[1 - (1 - \alpha_{\text{DON}}) y_{\text{DON}} \\ &\quad \times \{1 - f(y_{\text{DON}}, d)\}]\ . \qquad (48)\end{aligned}$$

Note that in the present approximation we have

$$\langle \alpha(x) \rangle = \frac{1}{1 + \frac{n_H^0}{K} \exp(-\langle y(x) \rangle)} \,. \tag{49}$$

d) Apparent dissociation constant

The apparent dissociation constant K_{app} is related to the average degree of dissociation $\langle \alpha(x) \rangle$ and the intrinsic dissociation constant K as

$$\langle \alpha(x) \rangle = \frac{1}{1 + \frac{n_H^0}{K} \exp(-\langle y(x) \rangle)} = \frac{1}{1 + \frac{n_H^0}{K_{app}}} \,, \tag{50}$$

which gives

$$K_{app} = K \exp(\langle y(x) \rangle) = K \exp[y_{DON} f(y_{DON}, d)] \,. \tag{51}$$

We thus have

$$\Delta pK = pK_{app} - pK = -\frac{1}{2.303} \langle y(x) \rangle = -\frac{1}{2.303} y_{DON} f(y_{DON}, d) \,, \tag{52}$$

or, equivalently,

$$10^{\Delta pK} = \exp[-y_{DON} f(y_{DON}, d)] \,. \tag{53}$$

In this way the average value of an arbitrary quantity over the polyelectrolyte interior can be expressed in terms of the correction factor $f(y_{DON}, d)$ (Eq. 46)).

Finally, we derive a relationship between the polyelectrolyte thickness d, the above corrected quantities and the total amount of the fixed-charges in the polyelectrolyte layer, $M \equiv Nd$. The value of d corresponds to the volume of a planar polyelectrolyte, and equals the amount of solvent uptake by the polyelectrolyte. Marinsky, Miyajima, and coworkers have derived an expression for the volume of a polyelectrolyte on the basis of a macroscopic Donnan model modified with introduction of the practical osmotic coefficient of the polyelectrolyte [4, 5, 8–10]. We now derive an equation for d, expressed in terms of $f(y_{DON}, d)$.

By integrating both sides of the Poisson–Boltzmann Eq. (2) for the polyelectrolyte interior from 0 to d, and noting that

$$\left.\frac{dy}{dx}\right|_{x=d} = -y_{DON} \kappa_m^2 d \{1 - f(y_{DON}, d)\} \,, \tag{54}$$

which follows from Eq. (41), we obtain

$$d = \frac{\frac{\langle \alpha(x) \rangle M}{2n}}{\sinh[-y_{DON} \cdot f(y_{DON}, d)] - y_{DON} \frac{\kappa_m^2}{\kappa^2} \{1 - f(y_{DON}, d)\}} \,, \tag{55}$$

or, by using Eq. (53)

$$d = \frac{\frac{\langle \alpha(x) \rangle M}{n}}{10^{\Delta pK} - 10^{-\Delta pK} - 2y_{DON} \frac{\kappa_m^2}{\kappa^2} \{1 - f(y_{DON}, d)\}} \,. \tag{56}$$

This expression may facilitate a better analysis of the solvent uptake by the polyelectrolyte.

In this paper we have considered a planar model for polyelectrolytes. If the length *d* can be considered to be a characteristic length of polyelectrolytes of arbitrary geometry, then the present treatment can be applied to other geometries. For example, for spherical polyelectrolytes and cylindrical polyelectrolytes, *d* corresponds to their radii.

The surfaces of biological cells are usually covered by a layer of polyelectrolytes. The thickness of this layer (corresponding to *d*) is typically of the order of 10 nm. The theory presented in this paper would also be useful to study the electric properties of the charged surface layers of biological cells.

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