EXACT SOLUTION OF THE UNIDIMENSIONAL POISSON-BOLTZMANN EQUATION FOR A 1:2 (2:1) ELECTROLYTE

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ABSTRACT The unidimensional Poisson-Boltzmann equation for a 1:2 (2:1) electrolyte has been solved analytically. The results have been compared with those obtained from the linearized equation. It is shown that in physiological conditions the difference may be greater than 10%. The value of the derivative of the potential in $x = 0$, $(d\psi/dx)_{x=0}$, has been used by many authors in the evaluation of the superficial charges of biological membranes. The value of $(d\psi/dx)_{x=0}$ have also been compared with the ones derived from the linearized equation. The difference may be greater than 25%. Our results suggest that the linearization of the Poisson-Boltzmann equation for a 1:2 (2:1) electrolyte may be greatly misleading.

INTRODUCTION

In recent years many investigators studying ionic currents across cell membranes, in order to explain a number of experimental results, postulated the existence of superficial potentials at the membrane-solution interface (see, for example, Chandler et al. [1], Adrian [2], Horowicz et al. [3], and Gilbert and Ehrenstein [4]). These superficial potentials arise from the interaction of the ionic charges in the solution with membrane charges. Moreover models have been developed describing the potential profile inside (Mauro [5]) and outside (1, 5) the membrane. These authors assume that the potential varies only in the direction perpendicular to the membrane surface, reducing the problem to the unidimensional case. Mauro considered a uniform charge density in the whole membrane volume, while Chandler et al. derived their model assuming a uniform superficial distribution of charges at the membrane-solution interface. In both cases the potential profile in the external solution, as it may be predicted from the nonlinear unidimensional Poisson-Boltzmann equation, is determined by the value of the superficial potential.

The Poisson-Boltzmann equation has been widely used, in physiological and biophysical investigations, mostly in its linearized form (taking the name of Debye-Hückel theory). This procedure introduces two kind of errors, one related to the fact that the theory is valid only for dilute solutions, the other due to the linearization itself. No general solution of the three-dimensional nonlinear Poisson-Boltzmann equation has been found (Olivares and McQuarrie [6]). Instead in the unidimensional case and for a 1:1 electrolyte the analytical solution has been found (1). One of the purposes of the present communication is to extend the analytical solution to the 1:2 (2:1) electrolyte case. This in fact may be of some relevance because in many cases electrolytes as K_2SO_4 or $CaCl_2$ are used in physiological solutions.

ANALYTICAL SOLUTION

According to the unidimensional Poisson-Boltzmann equation, we have

$$d^2\psi/dx^2 = -4\pi\rho/\epsilon_w, \tag{1}$$

where ψ is the electrical potential, ρ is the volume charge density, and ϵ_w is the dielectric constant of water. With a 1:2 electrolyte ρ will be expressed by (Glasstone [7], p. 82)

$$\rho = qn_+(e^{-q\psi/kT} - e^{2q\psi/kT}), \tag{2}$$

where n_+ is the number of positive ions per unit volume of solution, q is the magnitude of the electronic charge, k is the Boltzmann constant, and T is the absolute temperature.

From Eqs. 1 and 2 we get

$$d^2\psi/dx^2 = -(4\pi qn_+/\epsilon_w)(e^{-q\psi/kT} - e^{2q\psi/kT}). \tag{3}$$

Making the substitution $d\psi/dx = \tau(x)$, so that $d^2\psi/dx^2 = \tau d\tau/d\psi$, and integrating once, we obtain

$$\tau = \pm[(\alpha/\beta)(2e^{-\beta\psi} + e^{2\beta\psi}) + C_1]^{1/2} \tag{4}$$

where $\alpha = 4\pi qn_+/\epsilon_w$, $\beta = q/kT$, and C_1 is an integration constant, which may be determined remembering that $\psi \rightarrow 0$ and $(d\psi/dx) \rightarrow 0$ when $x \rightarrow \infty$. In this way we find $C_1 = -3\alpha/\beta$. The sign of the square root in Eq. 4 will depend on the initial condition $\psi(0) = \psi_0$. For physical reasons it will be positive for $\psi_0 < 0$, negative for $\psi_0 > 0$.

Making the substitution $e^{-\beta\psi} = t$ we obtain after some rearrangements

$$dx = \mp dt/[(2\alpha\beta)(t - 1)^2(t + 1/2)]^{1/2}. \tag{5}$$

Taking into account the sign of $(t - 1)$, Eq. 5 may be rewritten, for positive and negative values of ψ_0, as

$$dx = -2ds/[(s - \sqrt{3\phi})(s + \sqrt{3\phi})], \tag{6}$$

where $s = (2\phi t + \phi)^{1/2}$ and $\phi = \alpha\beta$. Eq. 6 is a rational integral and may be easily integrated. Finally we find

$$x = -(1/\sqrt{3\phi})\ln(|s - \sqrt{3\phi}|/|s + \sqrt{3\phi}|) + C_2, \tag{7}$$

where C_2 is the second integration constant.

From the initial condition $\psi(0) = \psi_0$ we find

$$C_2 = -(1/\sqrt{3\phi})\ln(|\sqrt{2\phi e^{-\beta\psi_0} + \phi} + \sqrt{3\phi}|/|\sqrt{2\phi e^{-\beta\psi_0} + \phi} - \sqrt{3\phi}|). \tag{8}$$

Inverting Eq. 7 we get for $\psi_0 < 0$

$$\psi = -\frac{1}{\beta}\ln\left[\frac{3}{2}\left(\frac{1 + e^{\sqrt{3\phi}(x - C_2)}}{e^{\sqrt{3\phi}(x - C_2)} - 1}\right)^2 - \frac{1}{2}\right], \tag{9}$$

and for $\psi_0 > 0$

$$\psi = -\frac{1}{\beta}\ln\left[\frac{3}{2}\left(\frac{1 - e^{\sqrt{3\phi}(x - C_2)}}{1 + e^{\sqrt{3\phi}(x - C_2)}}\right)^2 - \frac{1}{2}\right], \tag{9A}$$

where C_2 is given by Eq. 8.

DISCUSSION

If we linearize the second term of Eq. 3 and we use the appropriate boundary conditions [$\psi(x) \rightarrow 0$ for $x \rightarrow \infty$ and $\psi(0) = \psi_0$] we find

$$\psi_{\text{lin}} = \psi_0 e^{-\sqrt{3\phi}x} \tag{10}$$

From Eq. 10, at $T = 300°\text{K}$, we may compute a space constant $x = 1/\sqrt{3\phi}$ of 22.46 Å (solute concentration 1 mM), 7.10 Å (10 mM), and 2.24 Å (100 mM), about twice less than the thickness of the ionic atmosphere in water for 1:2 and 2:1 electrolytes (ref. 7, p. 85).

We have plotted Eqs. 9, 9 A, and 10 in Fig. 1 for $\psi_0 = \pm 25$ mV and two values of solute concentration (10 mM and 100 mM). We may see that the linearized equations are symmetrical with respect to the x axis while the nonlinear are not. Moreover the difference between the two solutions is greater when $\psi_0 > 0$. It may be of interest to compare our results with those of Chandler et al. (1). They found that the values of the

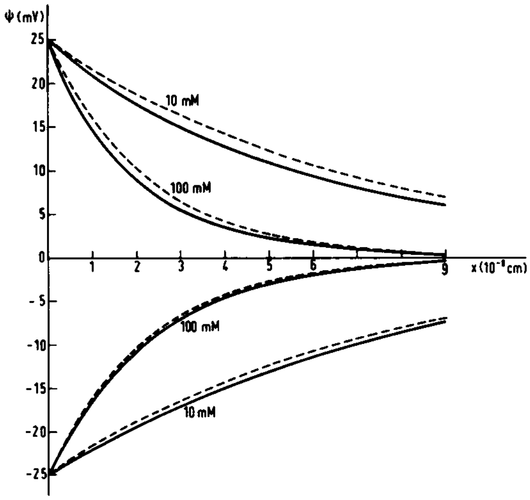

FIGURE 1 Exact and linearized solutions of the Poisson-Boltzmann equation. Solid curves are computed according to Eqs. 9 and 9 A; dashed curves according to Eq. 10, for $\psi_0 = \pm 25$ mV and two values of solute concentration (10 mM and 100 mM).

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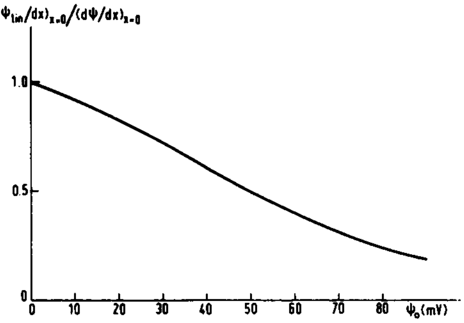

FIGURE 2 Comparison of the derivatives in $x = 0$ of the exact and linearized solutions of the Poisson-Boltzmann equation for different values of ψ_0.

linearized equation are accurate to within about 5% up to $|\psi| = 25$ mV. From Fig. 1 we may see that the error in our case may be greater than 10%.

In order to estimate the density of superficial charge, Chandler et al. (1) used the value of $(d\psi/dx)_{x=0}$. The derivative of ψ with respect to x computed in $x = 0$ is given by

$$(d\psi/dx)_{x=0} = (1 - e^{\beta\psi_0})(2\phi e^{-\beta\psi_0} + \phi)^{1/2}/\beta. \tag{11}$$

This equation holds for both positive and negative values of ψ_0.

We obtain instead from the linearized Eq. 10

$$(d\psi_{\text{lin}}/dx)_{x=0} = -\psi_0\sqrt{3\phi}. \tag{12}$$

The ratio of Eq. 12 to Eq. 11 is independent from the concentration. In Fig. 2 this ratio is plotted as a function of ψ_0. At $\psi_0 = 25$ mV $(d\psi_{\text{lin}}/dx)_{x=0}$ is about 25% less than $(d\psi/dx)_{x=0}$ and the error increases rapidly with the potential. In the case of 2:1 electrolyte we may obtain the same results simply interchanging ψ with $-\psi$.

Received for publication 19 April 1976.

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