An algorithm for the calculation of the electrostatic repulsion between surface coated with a charge membrane

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Abstract We propose a numerical procedure for the calculation of the electrostatic repulsion force between two identical, parallel surfaces immersed in an a:b electrolyte solution. These surfaces are coated with an ion-penetrable membrane carrying fixed charges. The amount of fixed charges is governed by the dissociation of the functional groups in the membrane phase. The effect of pH on the degree of dissociation of these functional groups is taken into account. The difficulty of extensive use of Jacobi elliptic function in the numerical treatment of Poisson-Boltzmann equation can be circumvented by resorting to the present algorithm.

Key words Electrostatic repulsion - ion-penetrable charged membrane - electrostatic potential distribution - Poisson-Boltzmann equation - arbitrary electrolytes

Introduction

The electrostatic potential distribution between two identical, charged, rigid, parallel planar surfaces immersed in an a:b electrolyte solution is described by the following Poisson-Boltzmann equation [1]:

\[
\frac{d^2 Y}{dX^2} = \frac{\exp(bY) - \exp(-aY)}{a + b}
\]

(1)

In this expression, \( Y = e\phi/k_B T \), \( X = kr \), \( \kappa^2 = 4\pi\varepsilon^2 (a^2 n_0^+ + b^2 n_0^-)/e^2 T_k \), \( \phi \) is the electrostatic potential, \( r \) represents the distance measured from one of the two surfaces, \( \varepsilon \) and \( T \) are, respectively, the dielectric constant and absolute temperature, \( n_0^+ \) and \( n_0^- \) denote the number concentration of cation and that of anion in the bulk liquid phase, respectively, and \( k_B \) and \( \kappa \) are, respectively, the Boltzmann constant and the reciprocal Debye length. One of the boundary conditions associated with Eq. (1) is

\[
Y \rightarrow Y_m \quad \text{and} \quad dY/dX \rightarrow 0 \quad \text{as} \quad X \rightarrow L/2, \quad (1a)
\]

where \( Y_m \) is the value of \( Y \) at the midpoint between two interacting surfaces, \( X = L/2, L \) being the dimensionless separation distance. Integrating Eq. (1) once subject to Eq. (1a) yields

\[
dY/dX = -\text{Sgn}(Y_m) \left[ \frac{2}{a + b} \right]^{1/2} \left\{ \frac{1}{b} \left[ \exp(bY) - \exp(bY_m) \right] + \frac{1}{a} \left[ \exp(-aY) - \exp(-aY_m) \right] \right\}^{1/2}
\]

(2)

If we define \( y = \exp[a(Y - Y_m)/2] \), \( \xi_1 = \exp(-aY_m)/a \), and \( \xi_2 = \exp(bY_m)/b \), then Eq. (2) becomes

\[
dY/dX = -\text{Sgn}(Y_m) \left( \frac{a/k}{4 + 2(b/a)} \right)^{1/2} \left\{ \xi_2 y^2 - (\xi_1 + \xi_2) y^2 + \xi_1 \right\}^{1/2},
\]

(3)

where \( k = 2 + 2(b/a) \). If the electrolyte is symmetric (\( k = 4 \)), and two surfaces are infinitely apart, Eq. (3) can be integrated to yield the classic result of Gouy and Chapman [1]. In general, solving Eq. (3) analytically is nontrivial. The solutions which involve Jacobi elliptic functions were derived for some special cases [2-4]. Apparently, extensive use of elliptic functions is necessary if these solutions are
used to investigate the electrostatic behaviour of the system under consideration. Since tabulated values for elliptic functions are based on specific values of relevant parameters, e.g., surface charge density, surface potential, and type of electrolytes, a more efficient numerical scheme is highly desirable. Chan et al. [5] proposed an algorithm for the resolution of Eq. (2) which does not utilize the Jacobi elliptic function. The discussion, however, was mainly focused on 1:1 electrolytes. The analysis was extended by Kuo and Hsu [6] to arbitrary a:b electrolytes and to a mixed solution of a:b and c:d electrolytes.

Among various types of colloidal particles, biocolloids play a significant role in numerous areas. Typical examples include blood cells and protein aggregates. These particles are characterized by having an ion-penetrable surface, which carries fixed charges due to the dissociation of functional groups. More often than not, a biocolloid is simulated by a particle having an inner uncharged core and an outer ion-penetrable membrane. Clearly, the property of the membrane has a significant effect on the behaviour of a particle. In contrast to the available results for a rigid surface, the analyses for a non-rigid or ion-penetrable surface are limited. The mathematical treatment of the Poisson–Boltzmann equation governing the potential distribution of the latter is more complicated than that of the former, as expected. In practice, either a numerical solution is presented [7], or approximate results are derived under drastic assumptions [8–12]. Ninham and Parsegian [2] derived the electrostatic potential distribution between surfaces bearing ionizable groups. The analysis was extended to an amphoteric surface by Chan and coworkers [3, 4]. The surface equilibrium was assumed to be governed by the chemical potential of potential determining ions in bulk solution. In these cases, the fixed charges are distributed over a rigid surface, rather than in a finite volume in space. The potential distribution obtained involves elliptic integral.

The purpose of this study is to extend the algorithm for the resolution of Poisson–Boltzmann equation for rigid surfaces [6] to the case of a rigid surface coated with an ion-penetrable membrane immersed in an arbitrary electrolyte solution. In particular, the effect of pH on the dissociation of the functional groups in membrane is discussed. The system under consideration was examined by Ohshima and Kondo (13) for the case of 1:1 electrolytes.

**Analysis**

By referring to Fig. 1, we consider two identical, parallel planar surfaces immersed in an a:b electrolyte solution separated by a dimensionless distance \( L \). Note that if \( L \) approaches to infinity, the problem under consideration reduces to an isolated surface. The surfaces comprise an uncharged, rigid core and a charged, ion-penetrable membrane with a dimensionless thickness \( d \). The fixed charges in membrane arise from the dissociation of the functional groups it bears according to the reaction

\[
AH \rightarrow A^- + H^+, \quad (4)
\]

where \( AH \) and \( A^- \) denote the acidic functional groups and its conjugated basic groups, respectively. At equilibrium,

\[
K_a = \frac{(n_{A^-})(n_{H^+})}{n_{AH}}, \quad (5)
\]

where \( K_a \) is the equilibrium constant, \( n_{A^-} \), \( n_{AH} \), and \( n_{H^+} \), represent, respectively, the number concentrations of \( A^- \), \( AH \), and \( H^+ \). Suppose that the functional groups in membrane are uniformly distributed with density \( N_0 \). Apparently,

\[
N_0 N_A = n_{AH} + n_{A^-}, \quad (6)
\]

where \( N_A \) is the Avogadro number. The distribution of \( H^+ \) follows the Boltzmann distribution

\[
n_{H^+} = n_{H^+}^0 \exp(-Y), \quad (7)
\]

where \( n_{H^+}^0 \) is the number concentration of \( H^+ \) in the bulk liquid phase. In this case, the Poisson–Boltzmann equation can be written as

\[
d^2Y/dX^2 = g_i/U, \quad i = 0, 1, \quad (8)
\]