Colloid Polym Sci 273:881–885 (1995)
© Steinkopff Verlag 1995

ORIGINAL CONTRIBUTION

J.-P. Hsu
Y.-C. Kuo

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

Received: 25 October 1994
Accepted: 8 March 1995

Prof. J.P. Hsu (✉) · Y.-K. Kuo
Department of Chemical Engineering
National Taiwan University
Taipei, Taiwan 10617, R.O.C.

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]:

$$\frac{d^2 Y}{dX^2} = \frac{\exp(bY) - \exp(-aY)}{a+b} \tag{1}$$

In this expression, $Y = e\phi/k_B T$, $X = \kappa r$, $\kappa^2 = 4\pi e^2(a^2 n_a^0 + b^2 n_b^0)/\varepsilon T_B T$, ϕ is the electrostatic potential, r represents the distance measured from one of the two surfaces, ε and T are, respectively, the dielectric constant and absolute temperature, n_a^0 and n_b^0 denote the number concentration of cation and that of anion in the bulk liquid phase, respectively, and k_B and κ are, respectively, the Boltzmann constant and the reciprocal Debye length. One of the boundary conditions associated with Eq. (1) is

$$Y \to Y_m \quad \text{and} \quad dY/dX \to 0 \quad \text{as} \quad X \to L/2\,, \tag{1a}$$

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

$$\begin{aligned} dY/dX = {} & -\operatorname{Sgn}(Y_m)[2/(a+b)]^{1/2}\{(1/b)[\exp(bY) \\ & - \exp(bY_m)] + (1/a)[\exp(-aY) \\ & - \exp(-aY_m)]\}^{1/2} \end{aligned} \tag{2}$$

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

$$dY/dX = -\operatorname{Sgn}(Y_m)(a/k)^{1/2}[\xi_2 y^k - (\xi_1 + \xi_2)y^2 + \xi_1]^{1/2}, \tag{3}$$

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 Göuy and Chapman [1]. In general, solving Eq. (3) analytically is nontrival. 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

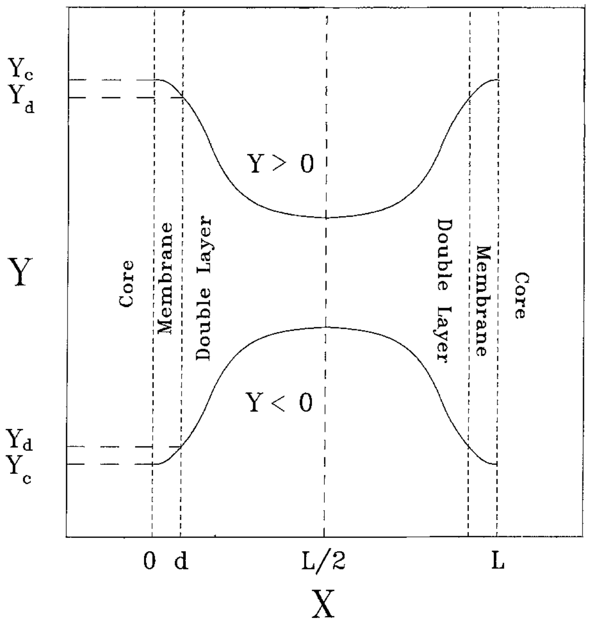

Fig. 1 Schematic representation of the system under consideration

$$AH \rightarrow A^- + H^+ , \tag{4}$$

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

$$K_a = (n_{A^-})(n_{H^+})/n , \tag{5}$$

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,

$$N_A N_0 = n_{AH} + n_{A^-} , \tag{6}$$

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

$$n_{H^+} = n^0_{H^+} \exp(-Y) , \tag{7}$$

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

$$d^2Y/dX^2 = g_i/U, \quad i = 0, 1 , \tag{8}$$

where

$$g_i = n^0_{\mathrm{OH}^-}\exp(Y) - n^0_{\mathrm{H}^+}\exp(-Y) + bn^0_{\mathrm{b}}\exp(bY) - an^0_{\mathrm{a}}\exp(-aY) + iN_{\mathrm{m}1}, \quad i = 0, 1 \tag{8a}$$

$$U = a^2 n^0_{\mathrm{a}} + b^2 n^0_{\mathrm{b}} + n^0_{\mathrm{H}^+} + n^0_{\mathrm{OH}^-} \tag{8b}$$

$$\kappa^2 = 4\pi e^2 U/\varepsilon k_{\mathrm{B}} T\,. \tag{8c}$$

In these expressions, $n^0_{\mathrm{OH}^-}$ is the number concentration of OH^- in the bulk liquid phase and i denotes a region index: $i = 0$ for double-layer region, and $i = 1$ for membrane phase. The definitions of the rest symbols are the same as those in Eq. (1). The distribution of fixed charges $N_{\mathrm{m}1}$ can be determined by Eqs. (5) through (7) as

$$N_{\mathrm{m}1} = N_{\mathrm{A}} N_0 / [1 + (n^0_{\mathrm{H}^+}/K_{\mathrm{a}})\exp(-Y)]\,. \tag{9}$$

Single surface

For an easier illustration, we consider first a single surface. In this case, the boundary conditions associated with Eq. (8) are

$$Y \to 0 \quad \text{and} \quad (dY/dX) \to 0 \quad \text{as} \quad X \to \infty \tag{10a}$$

$$Y(X \to d^-) = Y(X \to d^+) = Y_{\mathrm{d}} \quad \text{and}$$

$$(dY/dX)_{\mathrm{d}^-} = (dY/dX)_{\mathrm{d}^+} \tag{10b}$$

$$Y \to Y_{\mathrm{c}} \quad \text{and} \quad (dY/dX) \to 0 \quad \text{as} \quad X \to 0\,, \tag{10c}$$

where Y_{c} and Y_{d} are, respectively, the value of Y at the outer boundary of the uncharged core and that at the membrane-liquid interface.

For the membrane phase, integrating Eq. (8) with $i = 1$ subject to Eq. (10c) yields

$$dY/dX = Q_{\mathrm{m}}\,, \tag{11}$$

where

$$Q_{\mathrm{m}} = (2/U)^{1/2}\{n^0_{\mathrm{OH}^-}[\exp(Y) - \exp(Y_{\mathrm{c}})] + n^0_{\mathrm{H}^+}[\exp(-Y) - \exp(-Y_{\mathrm{c}})] + n^0_{\mathrm{b}}[\exp(bY) - \exp(bY_{\mathrm{c}})] + n^0_{\mathrm{a}}[\exp(-aY) - \exp(-aY_{\mathrm{c}})] + N_{\mathrm{m}2} - N_{\mathrm{m}2}(Y_{\mathrm{c}})\}^{1/2} \tag{11a}$$

$$N_{\mathrm{m}2} = N_{\mathrm{A}} N_0 \ln[\exp(Y) + (n^0_{\mathrm{H}^+}/K_{\mathrm{a}})]\,. \tag{11b}$$

We define

$$f_i = n^0_{\mathrm{OH}^-}\exp(Y) + n^0_{\mathrm{H}^+}\exp(-Y) + n^0_{\mathrm{b}}\exp(bY) + n^0_{\mathrm{a}}\exp(-aY) + iN_{\mathrm{m}2}, \quad i = 0, 1\,. \tag{12a}$$

It can be shown that

$$f_i = (U/2)Q^2_{\mathrm{m}} + n^0_{\mathrm{OH}^-}\exp(Y_{\mathrm{c}}) + n^0_{\mathrm{H}^+}\exp(-Y_{\mathrm{c}}) + n^0_{\mathrm{b}}\exp(bY_{\mathrm{c}}) + n^0_{\mathrm{a}}\exp(-aY_{\mathrm{c}}) + iN_{\mathrm{m}2}(Y_{\mathrm{c}}), \quad i = 0, 1\,. \tag{12b}$$

Differentiating Eq. (11a) with respect to Y gives

$$dQ_{\mathrm{m}}/dY = g_1/UQ_{\mathrm{m}}\,. \tag{13}$$

Equations (11) and (13) lead to

$$dX/dQ_{\mathrm{m}} = U/g_1\,. \tag{14}$$

For a given Q_{m}, f_1 is evaluated by Eq. (12b), $\exp(Y)$ and g_1 are then determined by Eqs. (12a) and (8a), respectively, and Eq. (14) can be integrated numerically.

For the double layer region, integrating Eq. (8) with $i = 0$ subject to Eq. (10a) yields

$$dY/dX = Q_{\mathrm{d}}\,, \tag{15}$$

where

$$Q_{\mathrm{d}} = (2/U)^{1/2}\{n^0_{\mathrm{OH}^-}[\exp(Y) - 1] + n^0_{\mathrm{H}^+}[\exp(-Y) - 1] + n^0_{\mathrm{b}}[\exp(bY) - 1] + n^0_{\mathrm{a}}[\exp(-aY) - 1]\}^{1/2}\,, \tag{15a}$$

where f_0 is defined in Eq. (12a), which can be recast as

$$f_0 = (U/2)Q^2_{\mathrm{d}} + 2n_0 \tag{15b}$$

$$n_0 = n^0_{\mathrm{OH}^-} + n^0_{\mathrm{b}} = n^0_{\mathrm{H}^+} + n^0_{\mathrm{a}} \tag{15c}$$

Following the same procedure as that employed in the derivation of Eq. (14), we obtain

$$dX/dQ_{\mathrm{d}} = U/g_0 \tag{16}$$

For a given Q_{d}, f_0 is evaluated by Eq. (15b), $\exp(Y)$ and g_0 are then determined by Eqs. (12a) and (8a), respectively. Equation (16) can be integrated numerically.

The numerical procedure is similar to that presented in [6].

Two parallel surfaces

In this case the boundary conditions associated with Eq. (8) are Eqs. (1a), (10b), and (10c). It can be shown that the potential distribution in the membrane phase is governed by Eq. (14), and that in the double-layer region is the same as that derived by Kuo and Hsu [6] for two rigid surfaces. The numerical procedure is similar to that presented in [6]. The electrostatic pressure at each dimensionless separation distance L, $P(L)$, can be calculated by

$$P(L) = k_{\mathrm{B}}T[n^0_{\mathrm{H}^+}\exp(-Y_{\mathrm{m}}) + n^0_{\mathrm{OH}^-}\exp(Y_{\mathrm{m}}) + n^0_{\mathrm{a}}\exp(-aY_{\mathrm{m}}) + n^0_{\mathrm{b}}\exp(bY_{\mathrm{m}}) - n_0]\,. \tag{17}$$

The interaction free energy per unit surface area, $E(L)$, is evaluated by

$$E(L) = \int_L^\infty P(L')\,dL'\,. \tag{18}$$

Donnon Potential.

If a membrane is thick enough, $Y \to Y_{\mathrm{Don}}$ as $X \to 0$, Y_{Don} being the dimensionless Donnan potential, and the right-hand side of Eq. (8) vanishes. We have

$$\begin{aligned} & n^0_{\mathrm{OH^-}} \exp(Y_{\mathrm{Don}}) - n^0_{\mathrm{H^+}} \exp(-Y_{\mathrm{Don}}) + bn^0_{\mathrm{b}} \exp(bY_{\mathrm{Don}}) \\ & \quad - an^0_{\mathrm{a}} \exp(-aY_{\mathrm{Don}}) + N_{\mathrm{m1}}(Y_{\mathrm{Don}}) = 0 \,. \end{aligned} \tag{19}$$

Rearranging this expression and applying Eq. (9), we obtain

$$\begin{aligned} \exp(Y_{\mathrm{Don}}) = {} & \{[an^0_{\mathrm{a}} \exp(-aY_{\mathrm{Don}}) - bn^0_{\mathrm{b}} \exp(bY_{\mathrm{Don}})] \\ & \times [\exp(Y_{\mathrm{Don}}) + (n^0_{\mathrm{H^+}}/K_{\mathrm{a}}) \\ & + (n^0_{\mathrm{H^+}})^2/[K_{\mathrm{a}} \exp(Y_{\mathrm{Don}})] - n^0_{\mathrm{OH^-}} \exp(2Y_{\mathrm{Don}}) \\ & + n^0_{\mathrm{H^+}}\}/[N_{\mathrm{A}} N_0 + n^0_{\mathrm{H^+}} n^0_{\mathrm{OH^-}}/K_{\mathrm{a}}] \,. \end{aligned} \tag{20}$$

This expression needs to be solved for $\exp(Y_{\mathrm{Don}})$, which can be used to calculate Y_{Don}. Apparently, a numerical scheme is required. We suggest using the initial guess for $\exp(Y_{\mathrm{Don}})$, $\exp(Y^i_{\mathrm{Don}})$, defined by

$$\begin{aligned} \exp(Y^i_{\mathrm{Don}}) = {} & \left[\frac{-\delta_5}{2} + \left(\frac{\delta_5^2}{4} + \frac{\delta_4^3}{27}\right)^{1/2}\right]^{1/3} \\ & - \left[\frac{\delta_5}{2} + \left(\frac{\delta_5^2}{4} + \frac{\delta_4^3}{27}\right)^{1/2}\right]^{1/3} - \frac{\delta_1}{3} \,, \end{aligned} \tag{21}$$

where

$$\delta_5 = (2\delta_1^3 - 9\delta_1\delta_2 + 27\delta_3)/27 \tag{21a}$$

$$\delta_4 = (3\delta_2 - \delta_1^2)/3 \tag{21b}$$

$$\delta_3 = -n^0_{\mathrm{H^+}}/K_{\mathrm{a}} \tag{21c}$$

$$\delta_2 = -1 \tag{21d}$$

$$\delta_1 = (n^0_{\mathrm{H^+}}/K_{\mathrm{a}}) + (N_{\mathrm{A}} N_0/n_0) \,. \tag{21e}$$

Substituting Eq. (21) into the right-hand side of Eq. (20) yields a new value of $\exp(Y_{\mathrm{Don}})$. This procedure is continued until two successive values of $\exp(Y_{\mathrm{Don}})$ are close enough. It can be shown that Eq. (21) is the exact result for 1:1 electrolytes.

Discussion

The amount of fixed charges in the membrane phase is determined by the degree of dissociation of AH, which is closely related to pH. If pH is high, Eq. (5) yields

$$n_{\mathrm{A^-}}/n_{\mathrm{AH}} = K_{\mathrm{a}} \exp(Y)/n^0_{\mathrm{H^+}} \to \infty \,. \tag{22}$$

This implies that the dissociation of the functional groups in the membrane phase is complete. According to Eq. (9), $N_{\mathrm{m1}} \to N_{\mathrm{A}} N_0$. In other words, the fixed charges distribute uniformly in the membrane phase. In this case, Eqs. (8a), (12a), and (12b) reduce to, respectively,

$$\begin{aligned} g_{\mathrm{i,h}} = {} & n^0_{\mathrm{OH^-}} \exp(Y) + bn^0_{\mathrm{b}} \exp(bY) \\ & - an^0_{\mathrm{a}} \exp(-aY) + iN_{\mathrm{A}} N_0, \quad i = 0, 1 \end{aligned} \tag{23a}$$

$$\begin{aligned} f_{\mathrm{i,h}} = {} & n^0_{\mathrm{OH^-}} \exp(Y) + n^0_{\mathrm{b}} \exp(bY) + n^0_{\mathrm{a}} \exp(-aY) \\ & + iN_{\mathrm{A}} N_0 Y, \quad i = 0, 1 \end{aligned} \tag{23b}$$

$$\begin{aligned} f_{\mathrm{i,h}} = {} & (U/2) Q^2_{\mathrm{m,h}} + n^0_{\mathrm{OH^-}} \exp(Y_{\mathrm{c}}) + n^0_{\mathrm{b}} \exp(bY_{\mathrm{c}}) \\ & + n^0_{\mathrm{a}} \exp(-aY_{\mathrm{c}}) + iN_{\mathrm{A}} N_0 Y_{\mathrm{c}}, i = 0, 1 \,, \end{aligned} \tag{23c}$$

where

$$\begin{aligned} Q_{\mathrm{m,h}} = {} & (2/U)^{1/2} [n^0_{\mathrm{OH^-}} [\exp(Y) - \exp(Y_{\mathrm{c}})] + n^0_{\mathrm{b}} [\exp(bY) \\ & - \exp(bY_{\mathrm{c}})] + n^0_{\mathrm{a}} [\exp(-aY) - \exp(-aY_{\mathrm{c}})] \\ & + N_{\mathrm{A}} N_0 (Y - Y_{\mathrm{c}})\}^{1/2} \end{aligned} \tag{23d}$$

If pH is low, Eq. (5) suggests that

$$n_{\mathrm{A^-}}/n_{\mathrm{AH}} = K_{\mathrm{a}} \exp(Y)/n^0_{\mathrm{H^+}} \to 0 \,. \tag{24}$$

This means that the dissociation of the functional groups in the membrane phase is negligible. In this case Eq. (9) yields $N_{\mathrm{m1}} \to 0$, and the membrane contains no fixed charges.

For intermediate pH values the concentrations of H^+ and OH^- are relatively smaller than those of electrolytes, Eqs. (8a), (12a), and (12b) become, respectively,

$$g_{\mathrm{i,int}} = bn^0_{\mathrm{b}} \exp(bY) - an^0_{\mathrm{a}} \exp(-aY) + iN_{\mathrm{m1}}, \quad i = 0, 1 \tag{25a}$$

$$f_{\mathrm{i,int}} = n^0_{\mathrm{b}} \exp(bY) + n^0_{\mathrm{a}} \exp(-aY) + iN_{\mathrm{m2}}, \quad i = 0, 1 \tag{25b}$$

$$\begin{aligned} f_{\mathrm{i,int}} = {} & (U/2) Q^2_{\mathrm{m,int}} + n^0_{\mathrm{b}} \exp(bY_{\mathrm{c}}) + n^0_{\mathrm{a}} \exp(-aY_{\mathrm{c}}) \\ & + iN_{\mathrm{m2}}(Y_{\mathrm{c}}), \quad i = 0, 1 \,, \end{aligned} \tag{25c}$$

where

$$\begin{aligned} Q_{\mathrm{m,int}} = {} & (2/U)^{1/2} \{n^0_{\mathrm{b}} [\exp(bY) - \exp(bY_{\mathrm{c}})] + n^0_{\mathrm{a}} [\exp(-aY) \\ & - \exp(-aY_{\mathrm{c}})] + N_{\mathrm{A}} N_0 (Y - Y_{\mathrm{c}})\}^{1/2} \,. \end{aligned} \tag{25d}$$

The numerical procedure is similar to that presented in [6].

Note that, regardless of the value of pH, if $K_{\mathrm{a}} \to 0$, the membrane is free of fixed charges, and if $K_{\mathrm{a}} \to \infty$, the fixed charges are uniformly distributed in membrane. If the distance between two surfaces approaches to infinity, $Y_{\mathrm{m}} \to 0$, and the system can be treated as two isolated surfaces.

Acknowledgement This work is supported by the National Science Council of the Republic of China.

References

1. Hunter RJ (1989) In: Foundations of colloid science, Vol 1, Oxford University Press, Oxford
2. Nimhan BW, Parsegian VA (1971) J Theor Biol 31:405
3. Chan DYC, Perram JW, White LR, Healy TW (1975) J Chem Soc Faraday Trans I 71:1046
4. Chan DYC, Healy TW, White LR (1976) J Chem Soc Faraday Trans I 72:2844
5. Chan DYC, Pashley RM, White LR (1980) J Colloid Interface Sci 77:283
6. Kuo YC, Hsu JP (1993) J Colloid Inter Sci 156:250
7. Hsu WC, Hsu JP, Chang YI (1993) J Colloid Inter Sci 155:1
8. Ohshima H, Ohki S (1985) Biophys J 47:673
9. Ohshima H, Makino K, Kondo T (1986) J Colloid Inter Sci 113:369
10. Ohshima H (1994) J Colloid Inter Sci 163:474
11. Hsu JP, Hsu WC, Chang YI (1994) J Colloid Inter Sci 165:1
12. Ohshima H, Kondo T (1993) J Colloid Inter Sci 155:499
13. Ohshima H, Kondo T (1988) Biophys Chem 32:161