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Journal of Colloid and Interface Science 297 (2006) 644–653
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

A rapidly convergent series for calculation of the interaction between two similar plane double-layers for $z_+/z_- = -2$ asymmetric electrolytes at positive surface potential

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Received 8 September 2005; accepted 29 October 2005

Available online 28 November 2005

Abstract

A rapidly convergent series for calculation of the interaction energies between two similar plane double-layers for $z_+/z_- = -2$ asymmetric electrolytes at positive surface potential are obtained by introducing a parameter λ in elliptical integral. When dimensionless surface potential is less or equal to 20, the number of the series terms required to obtain the interaction energies with six significant digits are not more than 4. The accurate numeral results are given and they can be used to check up the validity of approximate expressions people obtain. The present results are also fit for $z_+/z_- = -1/2$ asymmetric electrolytes at negative surface potential.

Keywords: Rapidly convergent series; Double layers; Interaction energies; Asymmetric electrolytes; Elliptical integral

1. Introduction

Interactions of symmetric electrolytes have been studied extensively [1–16]. But for interactions of asymmetric electrolytes, only a few of investigations are reported [17–19], and the accurate numeral results have never been seen. In this paper, a rapidly convergent series for calculation of the interaction energies between two similar plane double-layers for $z_+/z_- = -2$ asymmetric electrolytes at positive surface potential is obtained by introducing a parameter λ in elliptical integral. When dimensionless surface potential $y_0 \leqslant 20$, the number of the series terms required to obtain the interaction energies with six significant digits are not more than 4. The accurate numeral results are given and they can be used to check up the validity of approximate expressions people obtain. The present results are also fit for $z_+/z_- = -1/2$ asymmetric electrolytes at negative surface potential.

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doi:10.1016/j.jcis.2005.10.065

2. Interaction between two plates

For convenience we define following dimensionless quantity:

$$\kappa = \sqrt{8\pi n_0 z^2 e^2/(\varepsilon kT)}, \tag{1}$$

$$\xi = \kappa x, \qquad \xi_d = \kappa d, \tag{2}$$

$$y = ze\varphi/(kT), \qquad y_0 = ze\varphi_0/(kT), \tag{3}$$

$$V' = \kappa V/(2n_0 kT), \qquad p' = p/(2n_0 kT), \tag{4}$$

where κ is Debye parameter, n_0 is the electrolyte concentration of the bulk solution, $z = \min(z_+, |z_-|)$, e is the proton charge, ε is the dielectric constant of the solution, k is Boltzmann constant, and T is the absolute temperature; ξ is the dimensionless distance and x is the distance from left plate; ξ_d is the dimensionless distance and d is the distance between two plates; y is the dimensionless potential and φ is the potential between two plates; y_0 is the dimensionless surface potential and φ_0 is the surface potential on two plates; V' is the dimensionless interaction energies and V is the interaction energies between two plates; p' is the dimensionless repulsive force and p is the repulsive force between two plates.

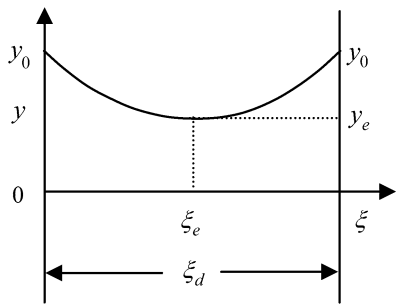

Fig. 1. The y–ξ curve of asymmetric electrolytes for $z_+/z_- = -2$ at $y > 0$.

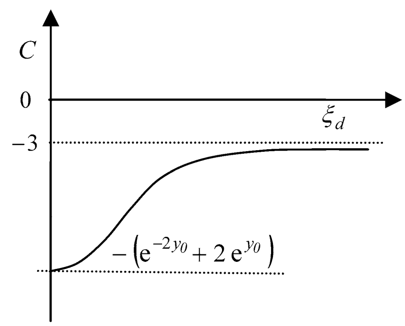

Fig. 2. The C–ξ_d curve of asymmetric electrolytes for $z_+/z_- = -2$ at $y > 0$.

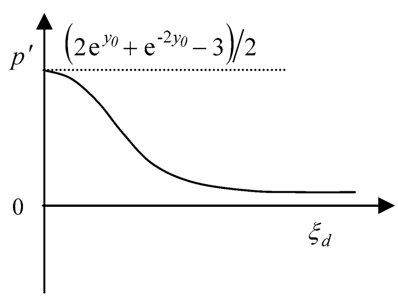

Fig. 3. The p'–ξ_d curve of asymmetric electrolytes for $z_+/z_- = -2$ at $y > 0$.

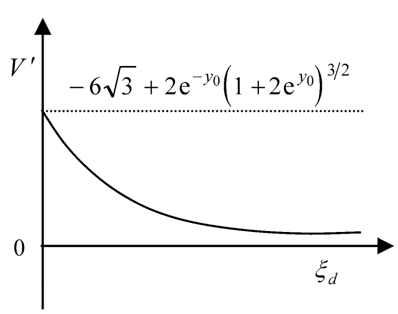

Fig. 4. The V'–ξ_d curve of asymmetric electrolytes for $z_+/z_- = -2$ at $y > 0$.

With the aid of analytic method, the $y - \xi$, C–ξ_d, p'–ξ_d, and V'–ξ_d curves are shown in Figs. 1–4 (see Appendices A, D, E, and F). C in Fig. 2 is integral constant.

The $z_+/z_- = -2$ electrolytes belong to $CaCl_2$ type. If we change the symbol of the charge number of ions in $CaCl_2$, we obtain the $z_+/z_- = -1/2$ electrolytes at once which belong to Na_2SO_4 type. The change of the symbol of potential between two plates is equivalent to the change of the symbol of the charge number of ions. Thus the $|y|$–ξ, C–ξ_d, p'–ξ_d, and V'–ξ_d curves for $z_+/z_- = -1/2$ asymmetric electrolytes at $y < 0$ are similar to those in Figs. 1–4, respectively, and all results for $z_+/z_- = -2$ asymmetric electrolytes at $y > 0$ can be applied to $z_+/z_- = -1/2$ asymmetric electrolytes at $y < 0$ as long as we replace y in the results with $|y|$.

ξ_d for $z_+/z_- = -2$ can be expressed as (see Appendix B)

$$\xi_d = 2\int_{y_e}^{y_0} \frac{dy}{\sqrt{e^{-2y} + 2e^{y} + C}}. \tag{5}$$

V' for $z_+/z_- = -2$ have the form (see Appendix C)

$$\begin{aligned} V' &= -6\sqrt{3} + 2e^{-y_0}(1 + 2e^{y_0})^{3/2} \\ &\quad + \int_{y_e}^{y_0} \frac{(C+3)\,dy}{\sqrt{e^{-2y} + 2e^{y} + C}} \\ &\quad - 2\int_{y_e}^{y_0} \sqrt{e^{-2y} + 2e^{y} + C}\,dy. \end{aligned} \tag{6}$$

For integral constant C we have the following relation (see Appendix B):

$$C = -\left(e^{-2y_e} + 2e^{y_e}\right) \tag{7}$$

and $-(e^{-2y_0} + 2e^{y_0}) < C < -3$. Substituting Eq. (7) into Eq. (5), we obtain

$$\xi_d = \int_{y_e}^{y_0} \frac{-2\,de^{-y}}{e^{-y}\sqrt{e^{-2y} + 2e^{y} - e^{-2y_e} - 2e^{y_e}}}. \tag{8}$$

Let $e^{-y} = w^2$, thus

$$\begin{aligned} \xi_d &= \int_{w_e}^{w_0} \frac{-4\,dw}{w\sqrt{w^4 + 2/w^2 - w_e^4 - 2/w_e^2}} \\ &= \int_{w_e}^{w_0} \frac{-4w_e\,dw}{\sqrt{w_e^2 - w^2}\sqrt{2 - w_e^4 w^2 - w^4 w_e^2}} \\ &= \int_{w_e}^{w_0} \frac{-2\sqrt{2}w_e\,dw}{\sqrt{w_e^2 - w^2}\sqrt{1 + \beta^2 w^2}\sqrt{1 - \alpha^2 w^2}}, \end{aligned} \tag{9}$$

where

$$\alpha^2 = \frac{w_e}{4}\left(w_e^3 + \sqrt{w_e^6 + 8}\right), \tag{10}$$

$$\beta^2 = 2w_e \Big/ \left(w_e^3 + \sqrt{w_e^6 + 8}\right). \tag{11}$$

When w_e increases from 0 to 1, α and β monotonously increase from 0 to 1 and from 0 to 1/2, respectively. Let

$$w^2 = \frac{u^2}{1 + \beta^2(1 - u^2)} \tag{12}$$

or

$$u = \frac{w\sqrt{1 + \beta^2}}{\sqrt{1 + \beta^2 w^2}}. \tag{13}$$