Surface Science 607 (2013) 197–202

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Analytical solutions of the nonlinear Poisson–Boltzmann equation in mixture of electrolytes

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ARTICLE INFO

Keywords:
Potential distribution
Concentration distribution
Surface charge
Poisson–Boltzmann equation

ABSTRACT

The Poisson–Boltzmann theory is still considered as an exact theory under low or even moderate electrolyte concentrations. As of today, however, just the analytical solutions in a single electrolyte were obtained, while people often meet mixed electrolytes in practical applications. Thus the analytical solutions of Poisson–Boltzmann equation (PBE) in different mixed electrolytes are still an important issue. The analytical solutions of PBE in mixed electrolytes with monovalent and bivalent counterions were firstly derived in the present study. The potential distribution and concentration profile curves in EDL were obtained with one dimensional space by the analytical solutions of PBE. The potential distribution curves of different mixtures showed that the power of the screen surface charge for bivalent counterion was stronger than that for monovalent counterion, thus the concentration of bivalent counterion in EDL was larger than that of monovalent counterion.

1. Introduction

The electric double layer (EDL) adjacent to a charged surface is very vital to many interfacial phenomena [1,2]. The importance of EDL has led to numerous studies and a great many models proposed in the past, of which the best-known is the Gouy–Chapman model [3]. The Gouy–Chapman theory describes the EDL structure through the solution of the Poisson–Boltzmann equation (PBE). The PBE has a wide range of applications in potential and ion distributions around a charged planer, cylinder or sphere [4–10] and adsorption of ions to charged particle surfaces [11,12]. The potential distribution affects the electric repulsive force between charged particles [13,14], the electrostatic adsorption energy of counterion-surface in EDL and the stability of colloid suspensions. The concentration profiles of ions in EDL can be calculated once the potential distributions are derived from PBE. Thus the question turns into obtaining the analytical solution of PBE.

The approximate analytical solutions of PBE were firstly obtained by Debye–Hückel under a low potential condition [15], while the exact analytical solutions were derived for a single symmetrical electrolyte by Gouy–Chapman [12,16] and for a single asymmetrical electrolyte of the 1:2 and 2:1 types respectively by Grahame and Andrietti [12,17,18]. The above analytical solutions of PBE were derived only for single electrolyte (there are only counterions from a charged particle and no other ions); however, the exact analytical solution could not be derived from mixed electrolytes up to now. Although Eriksson has solved the charge density distribution in binary symmetric electrolytes (1:1 + 2:2 electrolytes) [19], the potential distribution was not derived. Grahame holds that, for a mixed salt with a different type of valence, there is no analytical solution but only a numerical solution for PBE [17].

Under high electrolyte concentrations, the ionic volume effects and the dispersion forces become important [20,21]. Nevertheless, under low or even moderate electrolyte concentrations of bulk solution with ionic strength lower than 0.5 mol/l, the Poisson–Boltzmann equation will still be exact [11]. On the other hand, either in scientific research or chemical engineering, people often meet mixed electrolyte solutions rather than a single electrolyte solution, therefore the solution of the Poisson–Boltzmann equation in mixed electrolyte solutions will still be an important issue.

In the present paper, the analytical solutions (potential distribution functions) of PBE for mixed electrolytes (i.e. 1:1 + 2:1, 1:1 + 1:2, 1:1 + 2:2, 2:1 + 1:2 and 2:1 + 2:2 electrolytes) will be discussed, and then the potential and ion distribution curves in EDL can be obtained.

2. The analytical solutions in mixed electrolytes with monovalent and bivalent charge

The nonlinear PBE: the basic equation for electrolyte of any valence types was given from PBE [12,19]:

$$\frac{dy}{dx} = -\operatorname{sgn}(y)\sqrt{\frac{8\pi F^2}{\varepsilon RT}\sum_i \left(f_i \ \exp^{-Z_i y} - 1\right)} \qquad (1)$$

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http://dx.doi.org/10.1016/j.susc.2012.09.008

where $y = F\varphi/RT$, R (J K^{-1} mol^{-1}) is the universal gas constant; T (K) is the absolute temperature; F (C mol^{-1}) is the Faraday constant, ε is the dielectric constant (8.9×10^{-10} C^2 J^{-1} dm^{-1} for water), and f_i and Z_i are the concentration and valence, respectively, of the ith ion species. Eq. (1) denotes the analytical solution for charge density distribution near the surface from PBE. The following solutions for Eq. (1) in binary mixture of electrolytes are the analytical solutions for potential distributions of a negative charged particle surface.

2.1. The analytical solutions for potential distributions of PBE in 1:1 +2:1 electrolytes

1:1 + 2:1 (i.e. $AB + CD_2$, e.g. NaCl + Ca(NO$_3$)$_2$) electrolytes: here f_A, f_B, f_C and f_D are denoted as the concentration of ions for electrolytes respectively. In this mixture, $Z_A = 1$, $Z_C = 2$ and $Z_B = Z_D = -1$; $f_A = f_B$ and $f_D = 2f_C$. Therefore, Eq. (1) is changed as:

$$\frac{dy}{dx} = -\operatorname{sgn}(y)\sqrt{\frac{8\pi F^2}{\varepsilon RT}\begin{bmatrix} f_A\left(e^{-Z_A y}-1\right)+f_B\left(e^{-Z_B y}-1\right) \\ +f_c\left(e^{-Z_c y}-1\right)+f_D\left(e^{-Z_D y}-1\right)\end{bmatrix}}. \tag{2}$$

For a negative charged particle surface ($y<0$, so $\operatorname{sgn}(y) = -1$), Eq. (2) can be also expressed as:

$$\frac{dy}{dx} = \sqrt{\frac{8\pi F^2}{\varepsilon RT}\left[f_A(e^{-y}-1)+f_A(e^{y}-1)+f_C(e^{-2y}-1)+2f_C(e^{y}-1)\right]}. \tag{3}$$

Solving the differential Eq. (3), we have (see Appendix A):

$$\varphi(x) = \frac{RT}{F}\ln\left[\left(\frac{f_A+3f_C}{f_A+2f_C}\right)\left(\frac{1-\lambda_1 e^{-\kappa x}}{1+\lambda_1 e^{-\kappa x}}\right)^2 - \frac{f_C}{f_A+2f_C}\right] \tag{4}$$

where

$$\lambda_1 = \frac{\sqrt{f_A+3f_C}-\sqrt{(f_A+2f_C)e^{y_0}+f_C}}{\sqrt{f_A+3f_C}+\sqrt{(f_A+2f_C)e^{y_0}+f_C}}$$

$$\kappa = \sqrt{\frac{8\pi F^2(f_A+3f_C)}{\varepsilon RT}} = \sqrt{\frac{8\pi F^2\left(0.5\sum f_i Z_i^2\right)}{\varepsilon RT}}. \tag{5}$$

If there is only a single electrolyte in bulk solution, i.e. $f_A = 0$ or $f_C = 0$. Therefore, Eq. (3) educes the solution of a single 1:1 or 2:1 electrolyte respectively [12]:

$$\varphi(x) = \frac{2RT}{F}\ln\left(\frac{1-\lambda_{1:1}e^{\kappa x}}{1+\lambda_{1:1}e^{\kappa x}}\right) \tag{6}$$

$$\varphi(x) = \frac{RT}{F}\ln\left[\frac{3}{2}\left(\frac{1-\lambda_{2:1}e^{-\kappa x}}{1+\lambda_{2:1}e^{-\kappa x}}\right)^2 - \frac{1}{2}\right] \tag{7}$$

$$\lambda_{1:1} = \frac{1-\sqrt{e^{y_0}}}{1+\sqrt{e^{y_0}}} \quad \text{and} \quad \lambda_{2:1} = \frac{\sqrt{3}-\sqrt{2e^{y_0}+1}}{\sqrt{3}+\sqrt{2e^{y_0}+1}}. \tag{8}$$

2.2. The analytical solutions for potential distributions of PBE in 1:1 + 1:2 electrolytes

1:1 + 1:2 (i.e. $AB + E_2F$) electrolytes: similarly, in these electrolytes, $Z_E = 1$, $Z_F = -2$ and $f_F = 0.5f_E$. Therefore, we have:

$$\frac{dy}{dx} = \sqrt{\frac{8\pi F^2}{\varepsilon RT}\left[f_A(e^{-y}-1)+f_A(e^{y}-1)+f_E(e^{-y}-1)+0.5f_E(e^{2y}-1)\right]}. \tag{9}$$

Solving the differential Eq. (9), we have (see Appendix B):

$$\varphi(x) = \frac{RT}{F}\ln\left[1-\frac{(4f_A+6f_E)\lambda_2 e^{\kappa x}}{(\lambda_2 e^{\kappa x}+f_A+2f_E)^2-f_E(2f_A+3f_E)}\right] \tag{10}$$

with

$$\lambda_2 = \frac{2f_A+3f_E}{1-e^{y_0}}-f_A-2f_E+\sqrt{2f_A+2f_E}\sqrt{\frac{2f_A+3f_E}{(1-e^{y_0})^2}-\frac{2f_A+4f_E}{1-e^{y_0}}+f_E}$$

$$\kappa = \sqrt{\frac{8\pi F^2(f_A+1.5f_E)}{\varepsilon RT}} = \sqrt{\frac{8\pi F^2\left(0.5\sum f_i Z_i^2\right)}{\varepsilon RT}}. \tag{11}$$

If $f_E = 0$, Eq. (10) reduces to Eq. (6) with a single 1:1 electrolyte; on the other hand, if $f_A = 0$, Eq. (10) reduces to the solution of single 1:2 electrolyte [12]:

$$\varphi(x) = \frac{RT}{F}\ln\left[1-\frac{6\lambda_{1:2}e^{\kappa x}}{(\lambda_{1:2}e^{\kappa x}+2)^2-3}\right] \tag{12}$$

$$\lambda_{1:2} = \frac{\lambda_2}{f_E} = \frac{3}{1-e^{y_0}}-2+\sqrt{6}\sqrt{\frac{1.5}{(1-e^{y_0})^2}-\frac{2}{1-e^{y_0}}+\frac{1}{2}}. \tag{13}$$

2.3. The analytical solutions for potential distributions of PBE in 1:1 +2:2 electrolytes

1:1 + 2:2 (i.e. $AB + GH$) electrolytes: in these electrolytes, $Z_G = 2$, $Z_H = -2$ and $f_H = f_G$. Therefore, we have:

$$\frac{dy}{dx} = \sqrt{\frac{8\pi F^2}{\varepsilon RT}\left[f_A(e^{-y}-1)+f_A(e^{y}-1)+f_G(e^{-2y}-1)+f_H(e^{2y}-1)\right]}. \tag{14}$$

Solving the differential Eq. (14), we have (see Appendix C):

$$\varphi(x) = \frac{RT}{F}\ln\left[1-\frac{4(f_A+4f_G)\lambda_3 e^{\kappa x}}{(\lambda_3 e^{\kappa x}+f_A+4f_G)^2-4f_G(f_A+4f_G)}\right]. \tag{15}$$

with

$$\lambda_3 = \left[\frac{2(f_A+4f_G)}{1-e^{y_0}}-f_A-4f_G+2\sqrt{f_A+4f_G}\sqrt{\frac{f_A+4f_G}{(1-e^{y_0})^2}-\frac{f_A+4f_G}{1-e^{y_0}}+f_G}\right]$$

$$\kappa = \sqrt{\frac{8\pi F^2(f_A+4f_G)}{\varepsilon RT}} = \sqrt{\frac{8\pi F^2\left(0.5\sum f_i Z_i^2\right)}{\varepsilon RT}}. \tag{16}$$