

An application of functional analysis method to the potential of electrical double layer for spherical micelles

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With the help of the iterative method in functional analysis theory based on the Gouy–Chapman model in the colloid and interface chemistry an analytic solution of the potential of electrical double layer of spherical micelles has been obtained. This method has eliminated the restriction that the Poisson–Boltzmann equation, which represents the distribution of the potential in the double layer, can be solved only under the condition of $ze\psi \ll kT$ so far. The connections between the present results and those from Verwey and Overbeek's previous work have also been discussed. Our approach provides a simple but effective method for the calculation of the potential of electrical double layer under general potential condition.

KEY WORDS: spherical micelle, potential of electrical double layer, functional analysis theory

1. Introduction

There exists an electrical double layer (EDL) between the surface of a micelle and the bulk solution. The distribution of the charge of ions in the layer plays a significant role to many properties of a colloid solution, such as the adsorption of interface, the state of interfacial film between phases, the diffusion, effusion and rheology of micelles [1–3], and the interaction among the micelles in solution [4–6]. The properties of the EDL are characterized by the so-called Poisson–Boltzmann (PB) equation of potential. For that reason, a solution of the equation has been sought in colloid and interface science field for a long time. To our knowledge only the PB equation of the Gouy–Chapman's (GC) flat-plate model has been solved [2–4]. For a spherical particle, its structure of PB equation is different from that of the flat-plate EDL. Therefore, except the commonly used Debye–Hückel (DH) approximation [2,4], though some other approximate methods have been introduced for dealing with the equation [2,4–6], there is still not enough progress made so far.

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The solution given by the DH approach is restricted by the condition $ze\psi \ll kT$, which means that the potential must be very low for a spherical particle at usual temperature. But in most cases this condition cannot be satisfied for an actual colloid solution. Therefore, a much more accurate solution of the equation is still in urgent need.

The aim of the present work is, with the help of functional analysis theory and on the basis of the GC model, to give an analytic solution of the potential ψ for the EDL of a spherical particle under general potential condition.

2. The model of EDL [2–4]

According to the colloids and interface scientific theory, EDLs exist between different phases (such as gas/liquid, solid/liquid and liquid/liquid phases) and a few of theoretical models have been presented to explain the potential of the layer thus far. All the aims of those models can be summarized to solve the potential represented by the following PB equation [1–5]:

$$\nabla^2\psi = -\frac{4\pi e}{\varepsilon} \sum_i z_i n_{i0} \exp\left(-\frac{z_i e\psi}{kT}\right). \quad (1)$$

Here ψ , e , ε , k and T are the potential of the EDL, the elementary charge, the dielectric constant, the Boltzmann constant and the temperature of the studied system, respectively. z_i and n_{i0} are the valence numbers of ions and their concentration in the bulk phase far away from the interface of phases, respectively, and ∇^2 is the Laplace operator. In the spherical coordinates, the Laplace operator takes the following form:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2}. \quad (2)$$

For the symmetry $z-z$ type ion pair, the concentrations of cations and anions n_0^+ and n_0^- as well as their valence numbers z^+ and z^- are related as follows: $n_0^+ = n_0^- = n_0$ and $z^+ = z^- = z$. So, equation (1) can be rewritten as

$$\nabla^2\psi = -\frac{4\pi z e n_0}{\varepsilon} \left[\exp\left(-\frac{ze}{kT}\psi\right) - \exp\left(\frac{ze}{kT}\psi\right) \right]. \quad (3)$$

Supposing a flat-plate carrying a positive charge, when we consider its potential distribution, we define the plate being infinite in both the positive and negative directions of y and z . In this case, equation (1) becomes

$$\frac{d^2}{dx^2}\psi = -\frac{4\pi z e n_0}{\varepsilon} \left[\exp\left(-\frac{ze}{kT}\psi\right) - \exp\left(\frac{ze}{kT}\psi\right) \right]. \quad (4)$$

Equation (4) is a second-order nonlinear differential equation in ψ . It is difficult to solve with conventional methods.

Debye and Hückel [3] used an approximate method to solve the equation. They supposed $ze\psi \ll kT$ (it is true in some special situations), then the right side of equa-

tion (4) can be expanded as a Taylor series. And if the terms of ψ in the series are only retained to the first order, equation (4) can be transformed into

$$\frac{d^2}{dx^2} \psi = \frac{8\pi e^2 n_0 z^2}{\varepsilon k T} \psi. \tag{5}$$

Equation (5) is a second-order linear differential equation in ψ and can be solved easily by using the conventional method.

In order to eliminate the restriction of the condition $ze\psi \ll kT$, Gouy and Chapman [3] made an appropriate treatment of equation (4). Multiplication of both sides of equation (4) by $2 d\psi/dx$ gives [2,3]

$$2 \frac{d\psi}{dx} \frac{d^2}{dx^2} \psi = -\frac{8\pi en_0 z}{\varepsilon} \left[\exp\left(-\frac{ze}{kT} \psi\right) - \exp\left(\frac{ze}{kT} \psi\right) \right] \frac{d\psi}{dx}. \tag{6}$$

Equation (6) is just the derivation of equation

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi n_0 k T}{\varepsilon} \left[\exp\left(-\frac{ze}{kT} \psi\right) - \exp\left(\frac{ze}{kT} \psi\right) \right]^2. \tag{7}$$

Then, equation (7) can be simplified as

$$\frac{d\psi}{dx} = \left(\frac{8\pi n_0 k T}{\varepsilon}\right)^{1/2} \left[\exp\left(-\frac{ze}{kT} \psi\right) - \exp\left(\frac{ze}{kT} \psi\right) \right]. \tag{8}$$

Equation (8) is a first-order differential equation, and also can be solved easily in terms of the conventional method.

For the EDL of a spherical shape, its symmetry properties transform equation (1) as [3]

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \psi = -\frac{4\pi en_0 z}{\varepsilon} \left[\exp\left(-\frac{ze}{kT} \psi\right) - \exp\left(\frac{ze}{kT} \psi\right) \right]. \tag{9}$$

It is also a second-order nonlinear differential equation in ψ with constant coefficients, but different from equation (6) in shape. Therefore, it cannot be solved by the similar Gouy–Chapman method as above. However, if the iterative method in functional analysis theory is used, this work can be done. In the next sections we will illustrate validity of this method.

3. The iteration method in Banach space [7–10]

For a set C composed of functions (ψ, ϕ, \dots) that are continuous and have at least second-order derivative in the open interval (a, b) , where a and b are two different real numbers, we can define a norm [7,8]

$$\|\psi\| = \max_{a < r < b} |\psi(r)|. \tag{10}$$

It is easy to prove that any functions in the set can satisfy the following axioms of norm. That is, if $\psi, \phi \in C$, then [7,8] we have

- (i) $\|\psi\| \geq 0$;
- (ii) $\|\psi + \phi\| \leq \|\psi\| + \|\phi\|$;
- (iii) $\|\lambda\psi\| = |\lambda| \|\psi\|$ (λ is a real).

For example, we may take $a = 0, b \rightarrow \infty$. According to the functional analysis theory, the set C forms a Banach space B . Considering an operator \widehat{P} acting on the space B , then the operator \widehat{P} operates on the function ψ in this space to give an identical ψ , i.e.,

$$\psi = \widehat{P}\psi. \quad (11)$$

And if the operator \widehat{P} also satisfies the Lipschitz condition

$$\|\widehat{P}\psi - \widehat{P}\phi\| \leq \alpha\|\psi - \phi\|, \quad \psi, \phi \in B, \quad (12)$$

where α is called the Lipschitz constant, in that case beginning with any function ψ_0 (where $\psi_0 \in B$), we can get

$$\psi_{n+1}(r) = \widehat{P}\psi_n(r), \quad n = 0, 1, 2, \dots, \quad (13)$$

and

$$\lim_{n \rightarrow \infty} \psi_n(r) = \psi(r). \quad (14)$$

Here $\psi(r)$ is the only solution of equation [7,8]

$$\psi(r) = \widehat{P}\psi(r), \quad (15)$$

and $\psi_n(r)$ is called the approximate solution of n th-order iteration of equation (15).

In the above theoretical method, there are two aspects that should be paid attention to:

- (1) Most of the differential (or integral) equations and their corresponding operator \widehat{P} in physical chemistry problems can satisfy the above condition, so the solutions in any order iteration can be obtained. Therefore, this iterative method appears to have wide range of validity if the problems can satisfy the above conditions.
- (2) Though it is true in principle that the choice of a $\psi_0(r)$ ($\psi_0(r) \in B$) is arbitrary, where $\psi_0(r)$ is called the zero-order iterative approximate solution, the convergence velocity of functions $\psi_n(r)$ ($n = 0, 1, 2, \dots$) to the precise solution $\psi(r)$ is rather different for different $\psi_0(r)$. The experience of practical calculation shows that if $\psi_0(r)$ is selected correctly, only the solution in the first (or the second) order iteration is accurate enough for most chemical problems. To the potential of the EDL, it is not difficult to understand that $\psi(r)$ is a continuous function and has the first and the second order derivatives that are continuous in the open interval (a, b) in the views of both physical chemistry

and mathematics, where a and b are the two boundary sides of the EDL. Since the maximum of the continuous function $\psi(r)$ must exist in the open interval $(0, \infty)$, so the norm expressed by equation (10) can be defined. And it can be easily proved that $\|\psi\|$ satisfies the axioms of norm (i), (ii) and (iii), therefore, we have $\psi(r) \in B$. The operator \widehat{P} corresponding to equation (9) is defined as

$$\widehat{P} = \frac{kT}{ze} \sinh^{-1} \left[\frac{\varepsilon}{8\pi en_0 z} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right], \quad (16)$$

where \sinh^{-1} is the anti-operator of the hyperbolic sine operator \sinh . So, equation (9) can be rewritten as

$$\psi(r) = \widehat{P}\psi(r). \quad (17)$$

In the next section, we will solve this equation (or equation (9)) by means of the iteration method.

4. A solution to the PB equation of the EDL of a spherical particle with the iterative method

If the condition $ze\psi \ll kT$ is used, which means that the potential $\psi(r)$ is very low at a usual temperature, we can expand the functions $\exp(ze\psi/(kT))$ and $\exp(-ze\psi/(kT))$ to the first order in the Taylor series. From equation (9), we can obtain

$$\frac{1}{r^2} \frac{d}{dr^2} \left(r^2 \frac{d}{dr} \psi \right) = \kappa^2 \psi, \quad (18)$$

where $\kappa^2 = 8\pi e^2 n_0 z^2 / (\varepsilon kT)$. Equation (18) is a second-order linear differential equation with the consistent coefficients, and, as mentioned above, it can be solved easily in terms of conventional methods. Its general solution is [3]

$$\psi(r) = \frac{A}{r} \exp(-\kappa r) + \frac{B}{r} \exp(\kappa r), \quad (19)$$

where A and B are two arbitrary constants and only can be determined separately by choosing two different conditions. The first one (boundary condition) is [3]

$$\lim_{r \rightarrow \infty} \psi(r) = 0. \quad (20)$$

Under this condition, B becomes zero, and equation (19) changes to [3]

$$\psi(r) = \frac{A}{r} \exp(-\kappa r). \quad (21)$$

And the second one (infinite dilution condition) is

$$\lim_{\kappa \rightarrow 0} \psi(r) = \frac{q}{\varepsilon r} = \frac{ze}{\varepsilon r}. \quad (22)$$

So, we have $A = q/\varepsilon$ (where $q = ze$) and $\psi(r) = q \exp(-\kappa r)/(\varepsilon r)$. This is the work done by Verwey and Overbeek [2,3] for the potential of a spherical particle under the condition $ze\psi \ll kT$. But for the convenience of discussion with iterative method in the following steps, we do not use this condition $A = q/\varepsilon$ temporarily. This means that A remains an arbitrary constant, which needs to be determined.

In order to solve equation (9) with iterative method, we choose equation (21) as the zero-order approximate solution $\psi_0(r)$. From equations (13) and (16), we get the first-order approximate solution of equation (9),

$$\begin{aligned}\psi_1 &= \frac{kT}{ze} \sinh^{-1} \left[\frac{\varepsilon}{8\pi en_0 z} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] \frac{A}{r} \exp(-\kappa r) \\ &= \frac{kT}{ze} \sinh^{-1} \left[\frac{ze}{kT} \frac{A}{r} \exp(-\kappa r) \right].\end{aligned}\quad (23)$$

Equation (23) also can be rewritten as

$$\sinh \left[\frac{ze}{kT} \psi_1(r) \right] = \frac{ze}{kT} \frac{A}{r} \exp(-\kappa r). \quad (24)$$

Both equations (24) and (23) are different from equation (21) because they have got rid of the restriction of the very low potential condition $ze\psi \ll kT$.

If the condition $ze\psi \ll kT$ is used in equation (24), and also if we expand the function $\sinh[(ze/(kT))\psi_1(r)]$ only to the first order in Taylor series, we can get

$$\psi_1(r) = \frac{A}{r} \exp(-\kappa r), \quad (25)$$

which is identical with equation (21) under the very low potential condition. It, thus, confirms that the iterative method used for solving equation (9) is reasonable and the choice of the zero-order approximate solution $\psi_0(r)$ is appropriate.

Further using equations (13), (16) and (9), we can get the solution in the second-order iteration $\psi_2(r)$ from $\psi_1(r)$ as

$$\psi_2(r) = \hat{P}\psi_1(r) = \frac{kT}{ze} \sinh^{-1} f(r), \quad (26)$$

where

$$\begin{aligned}f(r) &= \frac{(ze/(kT))(A/r) \exp(-\kappa r)}{\sqrt{1 + [(ze/(kT))(A/r) \exp(-\kappa r)]^2}} \\ &\times \left\{ 1 - \frac{[(ze/(kT))(A/r) \exp(-\kappa r)]^2}{\sqrt{1 + [(ze/(kT))(A/r) \exp(-\kappa r)]^2}} \left(1 + \frac{1}{\kappa r} \right)^2 \right\}.\end{aligned}\quad (27)$$

If the condition $ze\psi \ll kT$ is used also in equation (27), we have

$$f(r) = \frac{ze}{kT} \frac{A}{r} \exp(-\kappa r). \quad (28)$$

And substituting equation (28) into equation (26), we will get the result which is the same as equation (25) again. Comparing equation (26) with equation (25), we can find that $\psi_2(r)$ in equation (26) is further approaching the real potential $\psi(r)$. With the above processes, we can obtain the potential $\psi_n(r)$ up to any accuracy of $\psi(r)$.

5. Conclusions

We have described an iterative method in functional analysis theory for solving the PB equation of the EDL for a spherical particle, and obtained a general analytical solution for the potential under general potential condition. We have also deduced the solutions in the first and the second order iteration for potential: $\psi_1(r)$ and ψ_2 . Following the similar procedure, we can obtain the solutions of the potential to any accuracy $\psi_n(r)$. The method is superior to the conventional ones in that it has thoroughly got rid of the difficulty, which was puzzling people for a long time, that the PB equation can be solved only under the very low potential condition $ze\psi \ll kT$. And this iterative method is very valuable for the practical calculation of the potential of EDL with spherical structure particles in colloid and interface science field since it can be used not only for any cases of potential but also for any values of the charge number and of the temperature of the system. With the much more accurate results of potential, we can further precisely illustrate many other properties of micelles as we have mentioned in the introduction. And we expect the functional analysis method also to be a very useful tool to solve many other similar problems in chemistry.

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