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帶電個體在電解質溶液中的表面電位

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一、中文摘要

　　求解一帶電個體在一電解質溶液中之電位分佈在基礎與應用方面皆扮演重要角色的現象；它在膠體與界、表面科技領域中是主要研究課題之一。在過去近一個世紀的研究中，唯一可解出正解(解析解)的問題為一個無限平板處於一對稱電解質溶液中。由於實際應用上的需求，求解其他更廣義的問題，如球、圓柱或橢球形的情況是相關領域研究者相當有興趣的問題。不過，目前所求得的仍以近似解或半解析解為主。本研究中，吾人探討這方面的問題，以圓柱粒子為目標，採用 Wang 等人求解球形粒子的方法(Z.W. Wang, G.Z. Li, D.R. Guan, X.Z Yi, A.J. Lou, J. Colloid Interface Sci., 246, 302, 2002)，並以數值法求解描述電位分佈之波松-波茲曼方程式的方式探討所得結果之適用性。經由這一系列的分析後，吾人將可以系統化的方式描述簡單幾何形狀的帶電個體在一電解質溶液中之電位分佈問題。所得結果將可提供下一階段計算帶電個體間之靜電作用力之基礎。

關鍵詞: 電解質溶液, 電位分佈, 波松-波茲曼方程式, 圓柱形粒子

Abstract

Determining the electrical potential distribution for the case a charged entity is placed in an electrolyte solution is of fundamental and practical significance; it is one of the basic problems in colloid and interface science. Up to now, the only exactly solvable problem is an infinite plate in a symmetric electrolyte solution. Apparently, deriving results for a more general case is highly desirable from practical point of view. In the present study attempt is made to derive approximate analytical result based on the method proposed recently by Wang et al. (Z.W. Wang, G.Z. Li, D.R. Guan, X.Z Yi, A.J. Lou, J. Colloid Interface Sci., 246, 302, 2002). We focus on the case of a cylindrical surface. The performance of the approximate results are examined by comparing with the results obtained by solving numerically the

corresponding Poisson-Boltzmann equation. The results obtained provide necessary information for the calculation of the electrical interaction force between two charged entities.

Keywords: electrolyte solution, electrical potential, Poisson-Boltzmann equation, cylindrical surface

二、緣由與目的

In the DLVO theory, the electrical double layer interaction can be evaluated on the basis of the nonlinear Poisson-Boltzmann equation [1,2]. Even though there are disputes over the validity of the Poisson-Boltzmann theory, corrections are generally negligible for symmetric univalent electrolytes at the concentrations of interest to colloid scientists [3]. In spite of the relative simplicity of the Poisson-Boltzmann theory for the electrical potential, the equation can be solved in closed form only in a planar geometry or under simplified conditions. For curved surfaces, one often resort to the approximation under extreme conditions and/or use the numerical methods. For instances, the Debye-Huckel approach is based on the assumption that the magnitude of the ionic potential energy is far smaller than the thermal energy everywhere so that the nonlinear Poisson-Boltzmann equation can be linearized [1,2]. Under some circumstances, the analytical results can be found under the Debye-Huckel condition. So far only the numerical analyses can provide an overall insight into the properties of the electrical double layer without restriction against the electrical potential. Due to the significance of the electrical double layer in colloid and interface science, however, a solution to the Poisson-Boltzmann equation that fits all potential is desirable for the practical utility.

From the perspective on the functional theory, the Poisson-Boltzmann equation for a symmetric electrolyte can be solved iteratively without any restriction of potential [4-6]. For example, Wang et al. [7] solved the Poisson-Boltzmann equation for an arbitrary potential with an iterative method in the functional theory. They pointed out that this method is superior to the conventional ways since it has entirely eliminated the limit of low potential. In addition, this method can readily provide the information about the radius and the surface potential of a spherical colloidal particle [8,9]. In the extended studies, Wang et al. [8,9] investigated the surface potential of a spherical particle, and the effects of system parameters on the surface potential have been examined. They concluded that the surface potential of a spherical colloidal particle is a function of the temperature, the micellar aggregation number, the concentration of bulk ions, the dielectric constant of the medium, and the ionic

valence.

In this study, the radius and the surface potential of a cylindrical colloidal particle have been estimated. For simplicity, the second-order solution is adopted as the exact solution to the Poisson-Boltzmann equation. The radius and the surface potential of the particle is determined by finding the maximum of the electrical potential. Also, the applicability of the iterative method to a cylindrical geometry is verified and the effect of the choice of the zero-th order solution is also discussed.

三、理論

Let us consider a set C, which comprises the functions $(Æ, w, \dots)$. These functions are continuous, and have at least second-order derivatives in an open interval (a,b), where a and b are two different real numbers. The maximum norm of $Æ$ is defined as [5,6]

$$\|Æ\| = \underset{a<r<b}{Max}|Æ(r)| \tag{1}$$

It can be shown that, for any two functions $Æ$ and w in C and $\}$ a real number,

$$\|Æ\| \geq 0 \tag{2a}$$
$$\|Æ\| + \|w\| \geq \|Æ + w\| \tag{2b}$$
$$\|\}Æ\| = |\}|\|Æ\| \tag{2c}$$

According to the functional theory, the set C forms a Banach space B. We consider the operator $\hat{P}$, which has the property

$$Æ = \hat{P}Æ, \quad Æ \in B \tag{3}$$

Also, if $\hat{P}$ satisfies the Lipschitz condition, then

$$\left\|\hat{P}Æ - \hat{P}w\right\| \leq r\|Æ - w\|, \quad Æ, w \in B \tag{4}$$

where r is the Lipschitz constant ($0 \leq r < 1$). Then, beginning with an arbitrary function $Æ_0 \in B$, we have [5]

$$Æ_{n+1} = \hat{P}Æ_n, \quad n=0,1,2,\dots \tag{5}$$

and

$$\lim_{n\to\infty} Æ_n(r) = Æ(r) \tag{6}$$

Here, $Æ_n(r)$ is the nth-order iterative approximate solution of Eq. (5), and $Æ(r)$ is the exact solution of the equation

$$\mathcal{E}(r) = \hat{P}\mathcal{E}(r) \tag{7}$$

As will be illustrated latter, this approach is applicable to the case of cylindrical coordinates. In this case, $\hat{P}$ can be constructed as

$$\hat{P} = \frac{k_B T}{ze}\sinh^{-1}\left[\frac{v}{2n_0 ze}\nabla_r^2\right] = \frac{k_B T}{ze}\sinh^{-1}\left[\frac{ze}{k_B T/^2}\nabla_r^2\right] \tag{8}$$

It can be also shown that [8]

$$\hat{P}\mathcal{E} = \frac{k_B T}{ze}\sinh^{-1}\left[\frac{ze}{k_B T/^2}\nabla_r^2\right]\mathcal{E} = \frac{k_B T}{ze}\sinh^{-1}\left[\frac{ze}{k_B T/^2}\nabla_r^2\mathcal{E}\right] \tag{9}$$

Here, $\mathcal{E}(r) = \frac{2t}{v}K_0(/r)$ is adopted as the initial or zeroth-order iterative solution $\mathcal{E}_0(r)$, where t is the linear charge density (C/m) of the particle and K_ϵ is the v-th order Bessel function of the second kind and the higher-order iterative solutions, $\mathcal{E}_n(r)$, $n=1,2,\ldots$, are generated by Eqs. (5) and (9). Among these, the first and the second iterative solutions are

$$\mathcal{E}_1(r) = \hat{P}\mathcal{E}_0(r) = \frac{k_B T}{ze}\sinh^{-1}\left[\frac{ze}{k_B T}\mathcal{E}_0(r)\right] = \frac{k_B T}{ze}\sinh^{-1}f \tag{10}$$

$$\mathcal{E}_2(r) = \hat{P}\mathcal{E}_1(r) = \frac{k_B T}{ze}\sinh^{-1}\left\{\frac{f}{\sqrt{1+f^2}}\left[1 - \frac{1}{1+f^2}\left(\frac{1}{/}\frac{df}{dr}\right)^2\right]\right\} \tag{11}$$

where $f = ze\mathcal{E}_0/k_B T$ is a dimensionless function of r.

For the present case, $\mathcal{E}_2(r)$ is satisfactory to stand for the exact solution in comparison with $\mathcal{E}_0(r)$ and $\mathcal{E}_1(r)$. Note that Eq. (10) can be rewritten as

$$\sinh[\frac{ze}{k_B T}\mathcal{E}_1(r)] = \frac{ze}{k_B T}\mathcal{E}_0(r) \tag{12}$$

Under Debye-Huckel condition, expanding the left-hand side of this expression in Taylor series in terms of $\mathcal{E}_1(r)$ and retaining the linear term, we obtain

$$\mathcal{E}_1(r) \cong \mathcal{E}_0(r) \tag{13}$$

Similarly, it can be shown under Debye-Huckel condition, $\mathcal{E}_n(r) \cong \mathcal{E}_{n-1}(r)$, which implies that $\mathcal{E}_n(r) \cong \mathcal{E}_0(r)$. With the use of the functional theory in the solution of the Poisson-Boltzmann equation, however, the particle radius can be theoretically estimated [8,9].

We regard $\mathcal{E}_2(r)$ as the exact electrical potential profile. In this consideration,

the phenomenon: $\Phi_2(r) < \Phi_1(r) < \Phi_0(r)$ in the vicinity of surface is reasonable since $\Phi_0(r)$ is the roughest approximate solution and the others are more accurate than it to the exact potential $\Phi(r)$ in the set comprised by the solutions $\Phi_n(r)$. When the distance from the center of the particle, r, is much larger than the particle radius R, the Debye-Huckel condition is satisfied and the particle can be viewed as a charged line segment. It accounts for that all the iterative solutions coincide if r is large enough. But at a higher potential or shorter distance, the particle is far from the charged segment model under the Debye-Huckel condition and its radius has to be taken into consideration. The curves are apart from each other as a result.

As have been mentioned above, the iterative method can induce us to define the maximum of $\Phi_2(r)$ as the surface potential $\Phi(R)$ and R as the radius of the particle. This method of estimation can be realized from the following considerations: First, the solution of the Poisson-Boltzmann equation based on Gouy-Chapman model describes the electrical potential in the electrical double layer and it must include the information of the radius and the surface potential of the particle. Therefore, starting the iterative process with $\Phi(r) = \dfrac{2t}{v}K_0(\kappa r)$, the radius and the surface potential of particle appear while the number of iterative order is enough. Second, according to Poisson-Boltzmann equation, the space charge density inside the particle is assumed zero. The governing Laplace equation inside and the fixed surface potential suggests that the electrical potential should be uniform over the whole particle and a maximum exists on the surface even though the constructed operator is no longer valid inside the particle surface.

As a consequence, the radius R and the surface potential $\Phi(R)$ of a cylindrical particle can be estimated by applying the condition

$$\frac{d\Phi_2(r)}{dr} = 0 \tag{14}$$

Incorporating Eqs. (11) into (14) yields

$$F(r) = \frac{d\Phi_2(r)}{dr} = \kappa^2 K_1^2(\kappa r) + \kappa^4 K_0^2(\kappa r)\cdot(K_0^2(\kappa r) - 2K_1^2(\kappa r))$$
$$+ \kappa^2 K_0(\kappa r)K_2(\kappa r)\cdot(1 + \kappa^2 K_0^2(\kappa r)) - 1 = 0$$

$$\tag{15}$$

where $\kappa = zeA/k_B T$. In the following analysis, we assume a 1:1 bulk electrolyte, namely, $z=1$ for simplicity. This nonlinear algebraic equation can be solved by Newton-Raphson method. We suggest using the initial estimate of $R=5/\kappa$. Usually, a convergent root can be obtained after several iterations.

四、結果與討論

The results show that the surface potential of the cylindrical particle increases as the aggregation number and the temperature of the system increase, but decreases with increasing in the dielectric constant, the valence of the carried ions, and the length of the cylindrical particle while the other factors are fixed. The surface potential of the cylindrical particle increases with increasing of the linear charge density. However, the surface potential is independent of the concentration of the electrolyte, which differs from that obtained by Wang et al. [9]. This can be comprehended from that, with the increase in the concentration of electrolyte, the interaction between the particle and the bulk ions also increases. This interaction compresses the electrical double layer, and the estimated radius of the particle should be smaller if the surface potential remains constant. The radius of the cylindrical particle increases with increasing in the dielectric constant, the temperature of the system and the length of the particle. On the other hand, the estimated particle radius may decrease with the increases in the aggregation number, the concentration of the electrolyte and the valence of the carried ions.

The required number of iterations for an accurate result is closely related to the choice of the zero-th iterative solution, $Æ_0$. In summary, with the use of the iterative method in the functional theory, the nonlinear Poisson-Boltzmann equation for a symmetric electrolyte can be solved under the general potential conditions. The surface potential and the radius of a cylindrical particle can be estimated from the second iterative solution of potential. The surface potential has been found to increase with increasing in both the temperature of the system and the linear charge density, decrease with increasing in the dielectric constant of medium and the valence of carried ions. However, while the electrolyte concentration increases the particle radius under estimation reduces and the surface potential remains fixed, which differs from that of a spherical particle.

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