Study of the Electrical Double Layer of a Spherical Micelle: Functional Theoretical Approach

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Abstract: By using the iterative method in functional theory, an analytic expression of the Poisson-Boltzmann equation (PB eq.), which describes the distribution of the potential of electrical double layer of a spherical micelle, has been carried out under the general potential condition for the first time. The method also can give the radius, the surface potential, and the thickness of the layer.

Keywords: Functional analytic theory, spherical micelle, electrical double layer.

The electrical double layer theory is the base of the colloid stability theory (DLVO theory), and the PB eq. is a key to the study of the layer[1,2]. For a spherical particle, the PB eq. is

$$r^{-2}\frac{d}{dr}(r^2\frac{d}{dr}\psi) = -\frac{1}{\varepsilon}\sum_i z_i e n_{i0}\exp(\frac{-z_i e}{kT}\psi) \tag{1}$$

where ε, z, e, n, k and T are the dielectric constant of the medium, the valence of ions, the elementary charge, the concentration of ions far away from the particle, the Boltzmann's constant and the temperature of the system, respectively. Since this eq. is a second order nonlinear differential one, only the analytical solution for the z-z type ion-pair and for the low potential (Debye and Hückel(DH) appr.) has been worked out so far. This appr. gives

$$\psi(r) = A\exp(-\kappa r)/r \tag{2}$$

where κ is the Debye reciprocal length and A is the integral constant, which can be determined by further using the infinitive dilution condition of the ions in elementary physics.

In the present work, we have proved that for any two solutions of the PB eq. ψ and ϕ, they can satisfy the axioms of norm[3]: (a) $\|\psi\| \geq 0$, (b) $\|\psi+\phi\| \leq \|\psi\|+\|\phi\|$, (c) $\|\lambda\psi\| = |\lambda|\|\psi\|$ and the Lipschitz condition[4]: $\|\hat{p}\psi - \hat{p}\phi\| \leq \alpha\|\psi-\phi\|$ (where ψ and ϕ are functions in the Banach Space, $\hat{p}$ is an operator, λ is a real number and α is the Lipschitz constant). So according to the functional theory, the PB eq. can be solved iteratively by appointing eq. (2) as the zero order appr. solution ψ_0 and setting the corresponding operator from *eq.*(1):

$$\psi(r)_{n+1} = \hat{p}\,\psi(r)_n \quad (\text{where } \hat{p} = \frac{kT}{ze} sh^{-1}[\frac{ze}{kT\kappa^2}\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr})] \text{ and } n = 0,1,2,\cdots) \quad (3)$$

The examination of the validity of this iterative method has been done mathematically by substituting the low potential condition into any order solution ψ_n to see if it can reduce to ψ_0 in the limit of low potential. It also has been done with the use of the flat plat model, which has both DH appr. solution and precise one and the results show that the data from this method are much closer than those from the DH appr. to the precise solution, *e.g.*, in an aqueous solution with T=298K, z=1, c=0.01mol·L^{-1} and ψ_d (the surface potential) =77.1mV, for those distances away from the surface x=3, 4 and 5nm, the DH appr. solution ψ_0 =28.7, 20.7, 14.9mV; the 1st iterative solution ψ_1 =24.7, 18.9, 14.1mV; and the precise one ψ_r =24.8, 17.7, 12.7 mV.

Though eq. (3) is also an appr. solution, it has got rid of the restriction of low potential. Furthermore, from the second order solution

$$\psi_2(r) = \frac{kT}{ze} sh^{-1}\{\frac{\frac{ze}{kT}A\frac{\exp(-\kappa r)}{r}}{[1+\frac{ze}{kT}A\frac{\exp(-\kappa r)}{r}]^{\frac{1}{2}}} - \frac{(\frac{1}{\kappa r}+1)^2[\frac{ze}{kT}A\frac{\exp(-\kappa r)}{r}]^3}{[1+\frac{ze}{kT}A\frac{\exp(-\kappa r)}{r}]^{\frac{3}{2}}}\} \quad (4)$$

and the corresponding diagram of this eq., the radius R and the surface potential $\psi(R)$ of the particle can be defined and figured out by using the diagram method or solved with the Newton iterative method.

The thickness of the double layer of a spherical particle also can be inferred by further using the capacitor model of the electrical double layer with a same center. For example, in the extreme cases the expressions of the thickness are

$$\delta = [\psi(R)\frac{3Rze}{2\pi kT\kappa^2}]^{1/3} \exp[\frac{ze}{3kT}\psi(R)] \qquad (R \ll \delta) \quad (5)$$

$$\delta = [\psi(R)\frac{ze}{2\pi kT\kappa^2}]^{1/2} \exp[\frac{ze}{2kT}\psi(R)] \qquad (R \gg \delta) \quad (6)$$

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