

Study on the Radius of an Electrical Spherical Micelle: Functional Theoretical Approach

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For the purpose of eliminating restriction, the Poisson-Boltzmann (PB) equation, which represents the potential of the electrical double layer of spherical micelles, can be solved analytically only under the lower potential condition, a kind of iterative method in functional analysis theory has been used. The radius of the spherical particle can be obtained from the diagram of the second iterative solution of the potential versus the distance from the center of the particle. The influences of the concentration of the ions, the charge number of ions, the aggregation number of the particle, the dielectric constant of solvent and the temperature of system on the radius also have been studied.

Keywords radius of spherical micelle, electrical double layer, functional analysis theory

Introduction

It is well known, according to the diffuse double layer model of Gouy and Chapman (GC model), that the electric potential in the electrolyte solution surrounding a colloid particle is governed by the so-called PB equation. The equation, which is used in a plane interface between a particle and its solution, can be solved analytically.^{1,2} But with a spherical micelle, its PB equation is a second order nonlinear differential one, which can not be solved analytically by traditional methods; only the numerical solution has been given so far.³ However, in most of surfactant solutions, the particles are spherical and the distribution of charges in their electrical diffuse layer plays a significant role in calculating or studying the many properties of these systems, such as the adsorption of interface, the state and structures of interfacial films between phases, as well as the diffusion, effusion, stability and rheology.⁴ The distribution also forms the basis of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.⁴⁻⁷ Therefore, to get the analytical solution of the PB equation accurately for a spherical particle is very important. The conventional method uses the low potential approximation, which is also called Debye and Hückel (DH) approximation, to change the equation into a second order linear differential equation and solve it.⁸ But at a higher potential, this approximate method becomes invalid. To get over the difficulty brought about by a high potential, many revising methods have been presented.⁹⁻¹⁴ Unfortunately, the shortage has not been gotten rid of up to now.

In the authors' previous work, the PB equation under general potential condition has been worked out by using the iterative method in functional analysis theory. The first and the second order analytical expressions have been obtained on the basis of GC model.¹⁵ The results tested from the points of mathematics and physical chemistry show that this iterative method is superior to the conventional ones because it has thoroughly gotten rid of the restriction of the low potential.¹⁶ The present work is, based on the results of the second order iterative solution of the potential, to work out the radius of the spherical micelle and find out the relations of the radius with each of the parameters which have the main influence on the radius, such as the concentration of the ions, the charge of the particle and so on.

Results and discussion

Iterative method in functional theory

For a set C composed of functions (ψ, ϕ, \dots) which are continuous and exist at least second-order derivative in an open interval (a, b) , where a and b are two different real numbers, define a norm^{17,18}

$$\|\psi\| = \max |\psi(r)| \quad (1)$$

$$a < r < b$$

Then it is easy to prove that any functions in this set can satisfy the following axioms of norm. That is, if

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$\psi, \phi \in C$, one will have^{17,18}

$$\|\psi\| \geq 0;$$

$$\|\psi + \phi\| \leq \|\psi\| + \|\phi\|;$$

$$\|\lambda\psi\| = |\lambda| \|\psi\| \quad (\lambda \text{ is a real}).$$

According to the functional analysis theory, the set C forms a Banach space B . Considering an operator \hat{P} acting on the space B , the result of the operator \hat{P} operating on the function ψ in the space B gives an identical ψ . That is¹⁸

$$\psi = \hat{P}\psi \quad (2)$$

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

$$\|\hat{P}\psi - \hat{P}\phi\| \leq \alpha \|\psi - \phi\| \quad (\psi, \phi \in B) \quad (3)$$

where α is called Lipschitz constant, then beginning with any function ψ_0 (where $\psi_0 \in B$), one can get

$$\psi_{n+1}(r) = \hat{P}\psi_n(r) \quad (n=0, 1, 2, \dots) \quad (4)$$

and as $n \rightarrow \infty$,

$$\psi_n(r) \rightarrow \psi(r) \quad (5)$$

Here $\psi(r)$ is the only solution of equation¹⁸

$$\psi(r) = \hat{P}\psi(r) \quad (6)$$

And $\psi_n(r)$ is generally called the approximate solution of n th-order iteration of Eq. (4).

Solution of the PB equation under general conditions by using the iterative method

According to the GC model, the PB equation describing the relation between the electrical potential ψ and the distance from the center of the spherical particle r is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \psi = -\frac{en_0z}{\epsilon} \left[\exp\left(-\frac{ze}{kT}\right) - \exp\left(\frac{ze}{kT}\right) \right] \quad (7)$$

(in the electrical double layer)

$$\text{and } \nabla_r^2 \psi = 0 \quad (\text{inside the particle}) \quad (7')$$

with the boundary conditions: $\psi \rightarrow 0$ (in the bulk) and $\psi = \psi_R$ (at the particle surface).

In Eq. (7), e, n_0, z, ϵ, k and T represent the elementary charge, the concentrations of the ions far from the particle (number/m³), the valance of the ions, the

the dielectric constant of the surrounding solution, the Boltzmann's constant and the absolute temperature of the system, respectively. For the sake of convenience, the two points that ϵ is not changing with r and that the ion pair is a symmetric z - z type are considered in this paper.

Eq. (7) is a second-order nonlinear differential equation of ψ and cannot be solved by a usual method. But if DH approximation $ze\psi \ll kT$ is introduced, the analytical solution of the equation can be reached as

$$\psi(r) = \frac{A}{r} \exp(-\kappa r) \quad (8)$$

where A is the integral constant and $\kappa^2 = 2e^2 n_0 z^2 / \epsilon kT = 2 \times 10^3 e^2 N_0 c z^2 / \epsilon kT$ is called Debye reciprocal length in which N_0 represents the Avogadro's number and c , the molar concentration of ion (mol·L⁻¹).

Using Eq. (8) as the zero order approximate solution $\psi_0(r)$ of the potential, and setting the operator \hat{P} from the general BP equation [Eq. (7)] as

$$\hat{P} = \frac{kT}{ze} \sin h^{-1} \left[\frac{\epsilon}{2en_0z} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] \quad (9)$$

where $\sin h^{-1}$ is the anti-operator of the hyperbolic sine operator $\sin h$, then from Eqs. (8), (9) and (4) one can get the first order iterative approximate solution of Eq. (7)

$$\begin{aligned} \psi_1(r) &= \hat{P}\psi_0(r) \\ &= \frac{kT}{ze} \sin h^{-1} \left[\frac{ze}{kT} \frac{A}{r} \exp(-\kappa r) \right] \\ &= \frac{kT}{ze} \sin h^{-1} F \end{aligned} \quad (10)$$

and the second-order iterative approximate solution:

$$\begin{aligned} \psi_2(r) &= \hat{P}\psi_1(r) \\ &= \frac{kT}{ze} \sin h^{-1} \left\{ \frac{F}{\sqrt{1+F^2}} \left[1 - \frac{F^2}{1+F^2} \left(1 + \frac{1}{\kappa r} \right)^2 \right] \right\} \end{aligned} \quad (11)$$

Here $F = ze\psi_0/kT$ is a dimensionless function of r . As $\psi_0(r)$ is one of the solutions of $\psi(r)$, so are $\psi_1(r)$ and $\psi_2(r)$. But since the operator \hat{P} is set up strictly based on PB equation, both $\psi_1(r)$ and $\psi_2(r)$ are also different from $\psi_0(r)$ in that they have eliminated the restriction of the condition $ze\psi \ll kT$.

Generally speaking, though it is true in principle that the choice of a $\psi_0(r) \in B$ is arbitrary according to the functional analysis theory, the convergence velocity of functions $\psi_n(r)$ ($n=0, 1, 2, \dots$) to the precise solution $\psi(r)$ varies with different $\psi_0(r)$ and \hat{P} . The experience of practical calculation shows that if they are selected correctly, only the first or the second order it-

erative solution is accurate enough for most chemical problems. Any over elaborate work is not needed.¹⁷

The examination of the validity of this iterative method is done mathematically by substituting the low potential condition $ze\psi \ll kT$ into $\psi_1(r)$ and $\psi_2(r)$, and both can reduce to $\psi_0(r)$ in the limit of low potential.¹⁵ It is also done with the use of the flat plate model, which has both DH approximate solution and precise one.⁴ And the results show that the data from this iterative method are much closer than those from the DH approximation to the precise solution.¹⁶

Solutions and the radius of the sphere micelle

In the above equations the integral constant is determined as $A=R\psi_R \exp(\kappa R)$ for DH approximation by using the boundary condition at $r=R$ in Eq. (7). Here R is the radius and ψ_R is the surface potential of particle. Though each of them R and ψ_R has its clear physical meaning, there is not any method to determine them so far. Therefore, A remains an undetermined constant.

However, if the infinite dilution of the particle condition is used, it can be determined by means of elementary physics anyway.⁴

$$A=Q/\varepsilon=mze/\varepsilon \quad (12)$$

where Q and m represent the total charge and the aggregation number of the micelle, respectively. As a result, by using condition Eq. (12) one can get such a diagram of the curves of $\psi_0(r)$, $\psi_1(r)$ and $\psi_2(r)$ as Figure 1 (A) for any fixed case of z , m , c , T and ε .

Figure 1 (A) shows that for a fixed case of z , m , c , T and ε , at lower potentials the three curves are coincident. It further confirms that the DH approximation is reasonable at low potentials. On the other hand, the use of the iterative method in the functional theory to solve the potential of a spherical micelle is also favorable.

At the higher potentials, $\psi_2(r) < \psi_1(r) < \psi_0(r)$. This phenomenon is rational since $\psi_0(r)$ is the roughest approximate function and the others are more accu-

rate than it to the precise potential $\psi(r)$ in the set composed of all the solutions $\psi_n(r)$. Under the low potential, the distance from the center of the particle r is long; the radius of the particle R is so small in comparison with the distance that it can be neglected and the particle can be treated as a point charge. So all iterative solutions can get together under the low potential. But at a higher potential (or shorter distance), the real situation of the particle is far away from the point charge model of the DH approximation [Eq. (8) with Eq. (12) as the integral constant] and the radius cannot be neglected. For that reason, they get apart from each other. Furthermore, since all three are the approximate solutions of the potential $\psi(r)$, the operator \hat{P} is set up strictly based on PB equation, and the DH approximation $\psi_0(r)$ is the basic iterative function, the other two solutions $\psi_1(r)$ and $\psi_2(r)$ must be more accurate than $\psi_0(r)$, and $\psi_2(r)$ more accurate than $\psi_1(r)$ according to the functional theory.¹⁷

The phenomenon is also interesting in which this method can give us the information of the radius of the particle. In Figure 1 (A), $\psi_1(r)$ is almost similar to $\psi_0(r)$ in shape except that the former is lower than the latter at a shorter distance. For $\psi_2(r)$, as the r gets shorter from a long distance, it grows up as $\psi_0(r)$ and $\psi_1(r)$ do, then becomes slower than both of them up to the distance R , where it reaches its maximum ψ_R . So we can define R as the radius and ψ_R , the surface potential of the particle.

The validity of this definition can be proved from the following considerations:

Firstly, the PB equation of the spherical particle for the GC model is a universal one and it must include the information of the radius of the particle. Therefore, according to the functional analysis theory, despite that we begin with the point model, the radius should appear when the number of iterative order goes to a specific level.

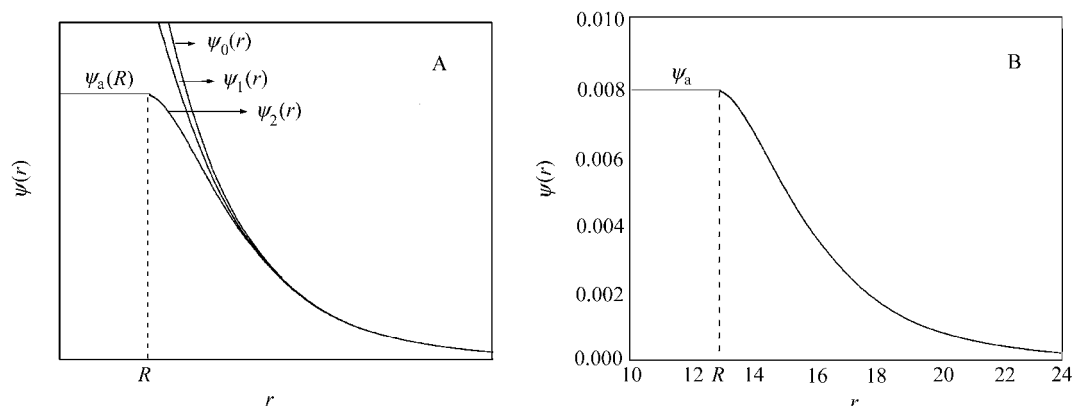


Figure 1 (A) The diagram of the potential of a double layer of a spherical micelle ψ vs. the distance from the center of the particle r for any fixed case of z , m , c , T , and ε : ψ_0 (the right), ψ_1 (the middle) and ψ_2 (the left); (B) The radius of a spherical micelle R determined from the potential ψ_2 vs. the distance r for a special case $z=1$, $m=50$, $c=0.01 \text{ mol} \cdot \text{L}^{-1}$, $T=298.6 \text{ K}$ and $\varepsilon=6.954 \times 10^{-10} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^{-1}$.

Secondly, according to the GC model, the charges of particle are concentrated on the surface and as a result, Eq. (7) should have a sole maximum value at the particle surface. From the viewpoint of physical chemistry, for a spherical micelle, the polarization vector $\mathbf{P} = \epsilon \mathbf{E}$ (where \mathbf{E} is the electric field density vector) should also be the maximum when $r=R$ which can be further confirmed by the following example. For a spherical particle composed of cationic surfactants $C_{12}H_{25}N^+(CH_3)_3$ each carrying a positive charge, the net charge distribution on this surfactant ion calculated with the quantum chemistry theory¹⁹ shows that most of the charge (+0.91354e) is concentrated on the head of the molecule. This molecule charge distribution means that most of the particle charges are on its surface and almost no polarization takes place in the particle (in Figure 2). The curve expressed by $\psi_2(r)$ having a sole maximum value just coincides with above phenomena.

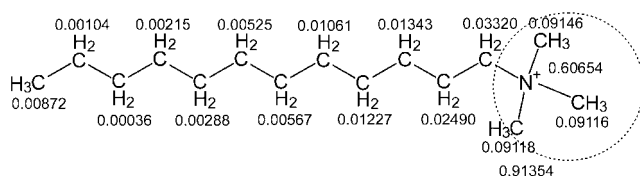


Figure 2 Distribution of charge on the cationic surfactant $C_{12}H_{25}N^+(CH_3)_3$.

Thirdly, the range of R is fit for the micelle radius. For example, for a particle composed by 50 ions each carrying a basic positive charge in the $T=298.16$ K, $c=0.01 \text{ mol}\cdot\text{L}^{-1}$ aqueous solution, R is about 13 nm [Figure 1 (B)]. This length is reasonable for the micelle radius.

Factors influencing the radius

Besides the distance from the center of the particle, the expression of $\psi_2(r)$ also includes the parameters c , z , m , T and ϵ , so it can be predicted that the radius R must be influenced at some level by these parameters. Figures 3—7 illustrate all the influences and the corresponding expressions of the fitting curve for each parameter are listed in Table 1. In most cases, the system under study is at room temperature; the concentration, in the range 10^{-5} — $10^{-1} \text{ mol}\cdot\text{L}^{-1}$; the aggregation number, in the range 20—200; the charge number of ion, between 1 and 3 and the solvent, water. Therefore, except for the spatial study, for all Figures, the following numerical values have been used: $z=1$, $m=50$, $c=0.01 \text{ mol}\cdot\text{L}^{-1}$, $T=298.16$ K, $\epsilon = \epsilon_{H_2O}\epsilon_0 = 78.54 \times 8.854 \times 10^{-12} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1} = 6.954 \times 10^{-12} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$. In Figure 4, for the convenience of making the curve, the non-integral charge numbers have been used. And in Figure 7, besides that of water, the other relative dielectric constants ϵ (293.16 K): glycerin (56.2), methanol (31.2), alcohol (27.8), ethyl ether (4.30), carbon tetrahalide (2.24), and hexane (1.80) have been used.

The results in Figures 3—7 and Table 1 show that, in

the studying range of the parameters, the radius reduces as the ion concentration and the ion valance in the solution grow up. The probable reason is that the exclusive force between ions and particle will grow up with the increase of the two parameters, and as a result of the exclusion, the volume of the particle will be reduced. And with the same reason, the increases of the aggregative number of particle, the dielectric constants

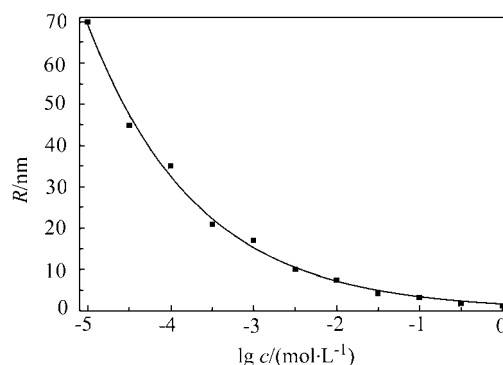


Figure 3 Influence of the concentration of ions on the radius of the particle R in the case $z=1$, $m=50$, $T=298.16$ K and $\epsilon = 6.954 \times 10^{-10} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$.

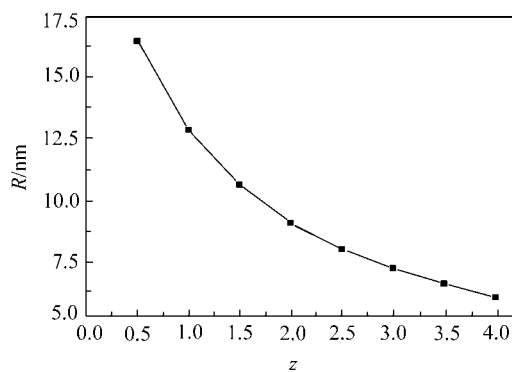


Figure 4 Influence of charge number of ion z on the radius of the particle R in the case $m=50$, $c=0.01 \text{ mol}\cdot\text{L}^{-1}$, $T=298.16$ K and $\epsilon = 6.954 \times 10^{-10} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$.

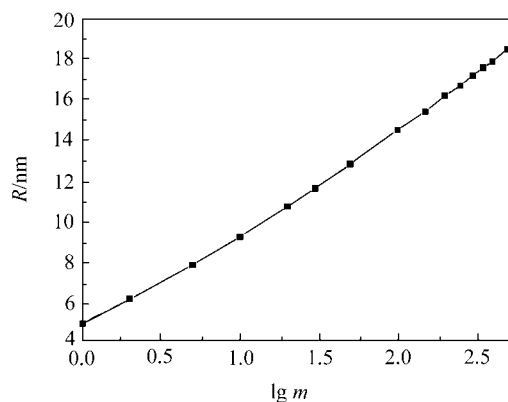


Figure 5 Influence of the aggregation number of particle m on the radius of the particle R in the case $z=1$, $c=0.01 \text{ mol}\cdot\text{L}^{-1}$, $T=298.16$ K and $\epsilon = 6.954 \times 10^{-10} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$.

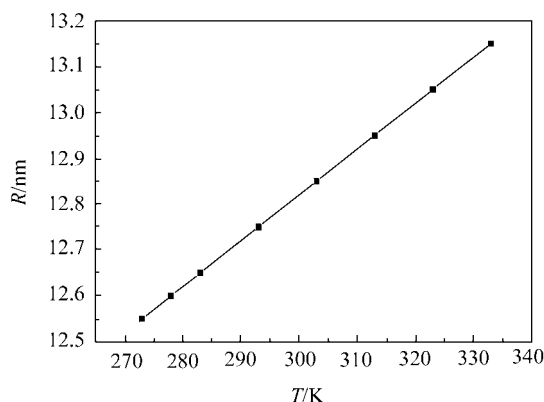


Figure 6 Influence of the temperature of system T on the radius of the particle R in the case $z=1$, $m=50$, $c=0.001 \text{ mol}\cdot\text{L}^{-1}$, $T=298.16 \text{ K}$ and $\varepsilon=6.954\times 10^{-10} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$.

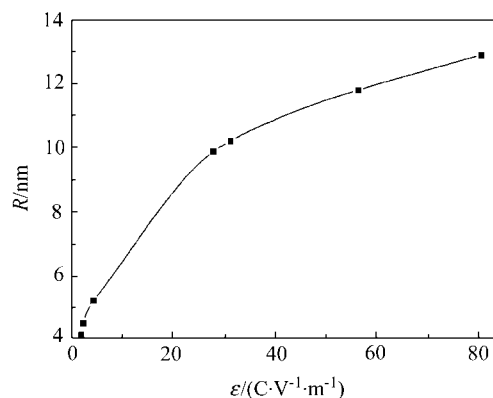


Figure 7 Influence of the different dielectric constant ε on the radius of the particle R in the case: $z=1$, $m=50$, $c=0.001 \text{ mol}\cdot\text{L}^{-1}$ and $T=298.16 \text{ K}$.

Table 1 Relations of the radius of a spherical micelle (R) with some parameters

Parameters	Relation of R (m) with each factor	Correlation coefficient (r^2)
c	$R=2.817\exp(-\lg c/1.241)$	0.9991
z	$R=5.059+16.36\exp(-z/1.372)$	0.9992
m	$R=4.352+5.135\lg m$	0.9984
T	$R=9.82+0.01000T$	1.0000
ε	$R=3.788+0.3433\varepsilon-5.291\times 10^{-3}\varepsilon^2+3.021\times 10^{-5}\varepsilon^3$	0.9970

of the solvent and the system temperature will reduce the exclusive force and make the change of radius contrary. All absolute value of the correlation coefficients in Table 1 being over 0.99 illustrates that the fitting expressions for the parameters are dependable.

Conclusions

(1) To solve the potential PB equation of electric diffuse double layer of a spherical micelle, an iterative method in functional analysis theory has been used. With the help of the method the general analytical solution for the potential under general potential condition has been obtained.

(2) From the diagram of $\psi_2(r)$, the radius of the micelle can be defined and the factors influencing the scale of the radius have been studied.

(3) This method can be not only used successfully for resolving the PB equation of the diffuse double electric layer of the spherical micelle analytically, which has been puzzling people so far, and presenting a method of obtaining the radius of the particle, but also used as a useful and simple means in further studying of the DLVO theory^{7,20} and in dealing with many other physical chemistry problems.

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