

Letter to the Editor

Comment on “The surface potential of a spherical colloid particle:
Functional theoretical approach”

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Received 15 March 2006; accepted 22 April 2006

Available online 13 June 2006

Abstract

In a work published in this journal by Z.W. Wang, G.Z. Li, D.R. Guan, X.Z. Yi, and A.J. Lou [J. Colloid Interface Sci. 246 (2002) 302], an iterative method for the determination of the potential around a colloidal particle is presented. It is claimed that successive terms of the iteration series converge to the exact solution of the Poisson–Boltzmann equation. This claim seems to be unfounded when the analytical expressions of the iteration terms are compared with well established numerical data.

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Keywords: Poisson–Boltzmann equation; Spherical colloid particle

In Ref. [1], and in a series of previous works [2–5], the authors use an iterative method based on functional analysis in order to find an approximate analytical expression for the equilibrium electric potential ψ of a colloidal particle. They consider that the particle is spherical and is suspended in a binary symmetrical electrolyte solution, so that the Poisson–Boltzmann equation to be solved is

$$\nabla_r^2 \psi(r) = \frac{2 \times 10^3 z e N_A c}{\varepsilon} \sinh \left[\frac{z e}{k T} \psi(r) \right]. \quad (1)$$

In this expression r is the distance to the center of the particle,

$$\nabla_r^2 = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \quad (2)$$

is the radial part of the Laplacian operator in spherical coordinates, z the valence of the ions, e the elementary charge, N_A the Avogadro constant, c the electrolyte concentration far from the particle (mol/L), ε the absolute permittivity of the electrolyte solution, k the Boltzmann constant, and T the absolute temperature.

The proposed procedure consists in iteratively calculating successive approximations to the potential,

$$\psi_{n+1}(r) = \frac{k T}{z e} \sinh^{-1} \left[\frac{z e}{k T} \psi_n(r) \right], \quad (3)$$

and it is claimed that $\psi_n(r)$ converges to the real solution of Eq. (1) for $n \rightarrow \infty$. The initial term in the iterative series is chosen as the well-known Debye–Hückel approximation,

$$\psi_0(r) = \frac{A}{r} e^{-\kappa r}, \quad (4)$$

where A is an integration constant and

$$\kappa = \sqrt{\frac{2 \times 10^3 e^2 N_A c z^2}{\varepsilon k T}} \quad (5)$$

is the reciprocal Debye length. They so obtain

$$\psi_1(r) = \frac{k T}{z e} \sinh^{-1}(F), \quad (6)$$

$$\psi_2(r) = \frac{k T}{z e} \sinh^{-1} \left\{ \frac{F}{\sqrt{1 + F^2}} \left[1 - \frac{F^2}{1 + F^2} \left(1 + \frac{1}{\kappa r} \right)^2 \right] \right\}, \quad (7)$$

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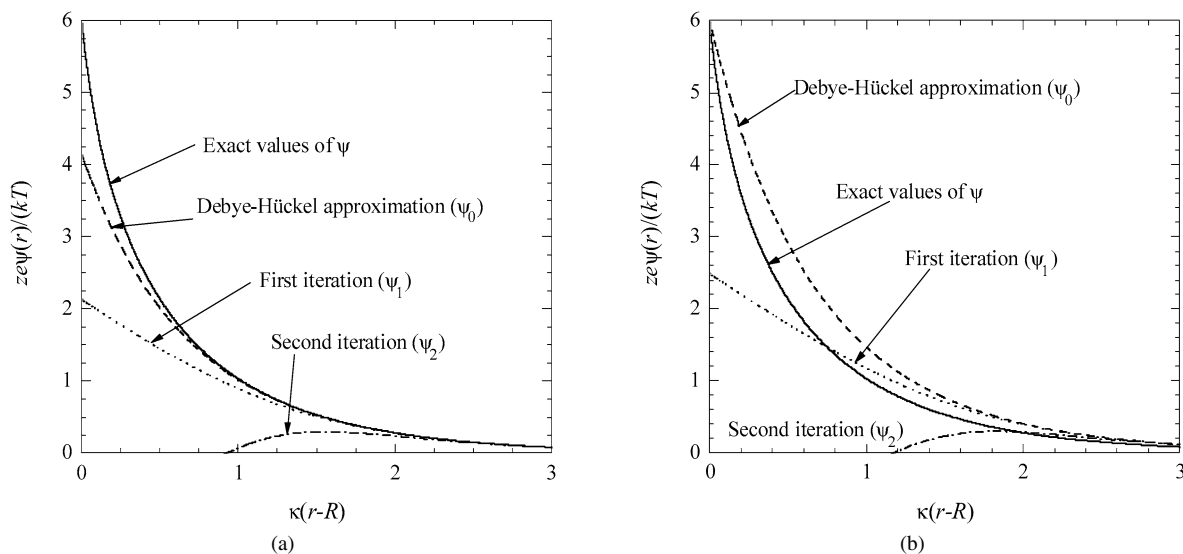


Fig. 1. Reduced electric potential in the electrolyte solution surrounding a charged spherical particle of radius R . Comparison of the “exact” numerical solution [6] with the Debye–Hückel approximation, Eq. (4), and the results of the first and second iterations, Eqs. (6) and (7). Calculations performed for $z = 1$, $\kappa R = 2$, and $ze\psi(R)/(kT) = 6$, considering for the determination of the coefficient A in Eq. (4) that $\psi_0(r)$ and the exact solution of Eq. (1) have the same limiting behavior far from the particle (a), or reduce to the same value on the surface of the particle (b).

where

$$F = \frac{ze}{kT} \psi_0(r), \quad (8)$$

and claim that “the first- or the second-order iterative solution is accurate enough for most chemical problems.”

We tried to verify the validity of this method by comparing its results to a well-established numerical solution of the Poisson–Boltzmann equation. In order to do this, the value of the integration constant A in Eq. (4) must be determined. We tried two possibilities:

- Impose that $\psi_0(r)$ and the exact solution of Eq. (1) have the same limiting behavior far from the particle.
- Impose that $\psi_0(r)$ and the exact solution of Eq. (1) reduce to the same value on the surface of the particle.

Our results appear in Figs. 1a and 1b, which reproduce Fig. 2 in the classical work of Loeb et al. [6], together with the potential profiles corresponding to the first and second iterations, Eqs. (6) and (7). According to Fig. 1a, successive iterations diverge from the numerical solution instead of converging to it, so that $\psi_2(r)$ appears to be a poorer approximation to the exact solution than the Debye–Hückel expression $\psi_0(r)$ in the whole range $r \geq R$.

As for Fig. 1b, successive iterations diverge from the numerical solution in a region close to the particle and, furthermore, they do not converge to the numerical solution far from the particle. These conclusions do not seem to be a result of a particular choice of the parameter values, since the ψ_0 , ψ_1 , and ψ_2 curves in Figs. 1a and 1b have precisely the same shapes and the same relative positions as the three curves in Fig. 1 of Ref. [1].

We hope that the authors will clarify this situation by either pointing at our mistake in the interpretation of their work or by correcting their results.

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