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Short communicaion

Analytical model for surface charge property of pH-regulated nanorods

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ABSTRACT

An analytical model for the zeta potential and the surface charge density of pH-regulated nanorod particles is derived for the first time. This extends existing models by taking account of the effects of multiple ionic species, surface chemistry reactions, Stern layer, and surface curvature, all of practical significance. Our model predicts excellently the experimental data in the literature for the zeta potential of 11-mercaptoundecanoic acid functionalized gold nanorod. The validated analytical multi-ion model provides valuable information for applications involving pH-tunable nanorods.

1. Introduction

Metallic nanorod particles, such as gold nanorods [1–4], silver [5–7] and ZnO [8–10] nanowires, have received significant attention for their diverse applications in many fields. Metallic nanorods functionalized with biocompatible surface coatings also provide a board new materials in biological applications such as biosensors [11–13] and drug delivery [14,15]. Developing relevant applications of nanorod particles requires a fundamental understanding of the electrostatic interaction between two particles, which strongly depend upon the charged properties of their surface such as zeta potential and charge density. Many experimental results [16–18] revealed that these properties, which stem from surface deprotonation/protonation reactions of functional groups, are influenced by the background solution properties like pH and salt concentration.

In an attempt to better understand the aforementioned influences on the surface charge properties of nanorod particles, we develop for the first time an analytical multi-ion model (MIM) for the zeta potential and surface charge density of pH-regulated nanorods. Our model extends that of Dougherty et al. [17], in which the curvature of the nanorod surface and the presence of H^+ and OH^- are neglected, to a more general case by taking account of multiple ionic species, surface chemistry reactions, Stern layer, and the curvature of nanorod surface. The MIM developed is capable of predicting the variations of the zeta potential and the surface charge density of pH-regulated nanorods with nanorod radius, background salt concentration, and pH for the case where the double layer is sufficiently thin, and the nanorod is sufficiently long.

2. Mathematical model

We consider a long nanorod of radius a_R and length L suspended in an infinite aqueous electrolyte solution containing N types of ionic species. Suppose that the background salt is NaCl (or KCl), and the solution pH is adjusted by HCl and NaOH (or KOH). Therefore, four kinds of ionic species (i.e., $N = 4$) need be considered: Na^+ (or K^+), Cl^-, H^+, and OH^-. Let C_{i0} (in the unit of mM), $i = 1, 2, 3$, and 4, be the bulk concentrations of these ions, respectively. Then $C_{10} = C_{NaCl}$, $C_{20} = C_{NaCl} + 10^{(-pH+3)} - 10^{-(14-pH)+3}$, $C_{30} = 10^{(-pH+3)}$, and $C_{40} = 10^{-(14-pH)+3}$ for pH ≤ 7; $C_{10} = C_{NaCl} - 10^{(-pH+3)} + 10^{-(14-pH)+3}$, $C_{20} = C_{NaCl}$, $C_{30} = 10^{(-pH+3)}$, and $C_{40} = 10^{-(14-pH)+3}$ for pH > 7 [19,20]. Here, C_{NaCl} (C_{KCl}) is the background salt concentration when NaCl (KCl) is used.

Suppose that the nanorod surface carries dissociable functional groups ~AH (e.g., ~COOH) capable of undergoing the following dissociation/association reactions [16,21]: $\sim AH \leftrightarrow \sim A^- + H^+$ and $\sim A^- + M^+ \leftrightarrow \sim AM$, where M^+ is metal cations (Na^+ or K^+). Let $K_A = (N_{A^-}[H^+]_s)/N_{AH}$ and $K_B = N_{AM}/(N_{A^-}[M^+]_s)$ be the equilibrium constants of these surface reactions, where N_{AH}, N_{A^-}, and N_{AM} denote the surface site densities of ~AH, $\sim A^-$, and ~AM, respectively, and $[H^+]_s$ and $[M^+]_s$ be the molar concentrations of H^+ and M^+ at the nanorod/liquid interface, respectively. If the total number site density of AH on the nanorod

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surface is N_t $(= N_{AH} + N_{A^-} + N_{AM})$ and the spatial distributions of H^+ and M^+ follow the Boltzmann distribution, the surface charge density of the nanorod, σ_s, can be expressed as

$$\sigma_s = -FN_{A^-} = -FN_t\left\{\frac{K_A}{K_A + 10^{-\mathrm{pH}}\exp\left(-\frac{F\psi_s}{RT}\right) + K_AK_BC_{10}\exp\left(-\frac{F\psi_s}{RT}\right)}\right\}. \tag{1}$$

Here ψ_s is the surface potential of the nanorod; F, R, and T are the Faraday constant, universal gas constant, and the absolute temperature, respectively.

A charged surface immersed in an electrolyte solution is associated with an electric double layer (EDL), including a Stern layer and a diffusive layer. The counterions in the former are immobile, reducing the surface potential to a lower value, known as the zeta potential ψ_d, an experimentally measurable quantity. Assuming a Stern layer thickness of ca. 1–3 times of ion size [22], which is much smaller than the nanorod radius, Behrens and Grier [23] and Xue et al. [24] used a basic Stern layer model to elucidate the effect of that layer. If we let C_s and σ_d be the surface capacitance of the Stern layer and the charge density of the diffusive layer, respectively, then

$$\psi_s - \psi_d = \frac{\sigma_d}{C_s}, \tag{2}$$

Suppose that the nanorod is long compared with its radius (i.e., $L \gg a_R$). Then for the considered electrolytes, the electric potential ψ in cylindrical coordinates with the origin on the nanorod's axis can be described by the Poisson-Boltzmann equation [25],

$$\frac{d^2\psi}{dr^2} + \frac{1}{r}\frac{d\psi}{dr} = -\frac{1}{\varepsilon_f}\sum_{i=1}^{4} Fz_iC_{i0}\exp\left(-\frac{z_iF\psi}{RT}\right) = \frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\psi}{RT}\right), \tag{3}$$

where ε_f is the permittivity of the liquid phase, z_i the valence of the ith ionic species with $z = |z_i|$, and $\kappa = \sqrt{2z^2F^2C_0/\varepsilon_f RT}$ the reciprocal Debye length. $C_0 = C_{10} + C_{30} = C_{20} + C_{40} = C_{NaCl} + 10^{(-\mathrm{pH}\ +\ 3)}$ for pH ≤ 7 and $C_{NaCl} + 10^{-\ (14\ -\ \mathrm{pH})\ +\ 3}$ for pH > 7 [25]. Note that if the effect of multiple ionic species is not considered, that is, the presence of H^+ and OH^- is neglected, then $C_0 = C_{NaCl}$, regardless of the level of pH. The boundary equations for Eq. (3) are: (i) $\psi = \psi_d$ as $r \to a_R$, and (ii) $\psi = d\psi/dr = 0$ as $r \to \infty$. If $\kappa a_R \ge 1$, solving Eq. (3) subject to these boundary conditions yields the charge density of the diffusive layer [26],

$$\sigma_d = -\varepsilon_f\left.\frac{d\psi}{dr}\right|_{r\to a_R} = \beta_1\sinh\left(\frac{\bar{\psi}_d}{2}\right)\left\{1+\frac{(\beta_2-1)}{\cosh^2\left(\frac{\bar{\psi}_d}{4}\right)}\right\}^{\frac{1}{2}}, \tag{4}$$

where $\beta_1 = 4zFC_0/\kappa$, $\beta_2 = [K_1(\kappa a_R)/K_0(\kappa a_R)]^2$, $\bar{\psi}_d = \psi_d/(zF/RT)$, and K_n is the nth-order modified Bessel function of the second kind.

The electroneutrality implies that $\sigma_s - \sigma_d = 0$, and substituting Eqs. (1), (2), and (4) into this expression yields

$$\frac{FN_tK_A}{K_A + 10^{-\mathrm{pH}}\exp\left[-\frac{F}{RT}\left(\psi_d+\frac{\sigma_d}{C_s}\right)\right] + K_AK_BC_{10}\exp\left[-\frac{F}{RT}\left(\psi_d+\frac{\sigma_d}{C_s}\right)\right]} + \sigma_d = 0, \tag{5}$$

where σ_d is defined in Eq. (4). Once ψ_d is determined by solving this equation with, for example, Matlab function *fzero*, σ_d, ψ_s, and σ_s can be calculated by Eqs. (4), (2), and (1), respectively.

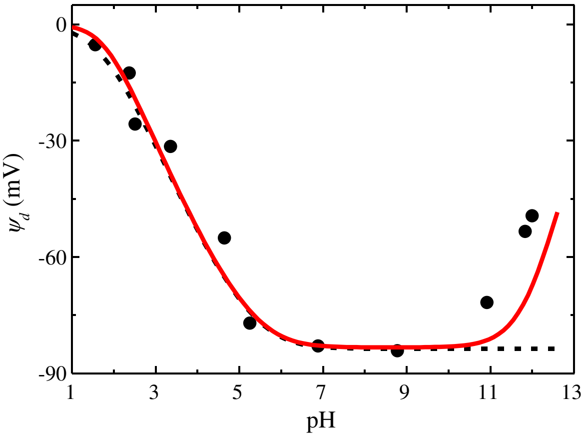

Fig. 1. Dependence of the zeta potential ψ_d on pH for 11-mercaptoundecanoic acid functionalized gold nanorods of radius $a_R = 125$ nm in a 10 mM NaCl solution. Symbols: experimental data of Dougherty et al. [17]; solid curve: results based on the present analytical MIM, Eq. (5) at $C_s = 0.6$ F/m^2, pK_A = 2.7, pK_B = 3, and $N_t = 2.99 \times 10^{-7}$ mol/m^2; dashed curve: results based on the analytical model, Eq. (6).

3. Results and discussion

To verify the applicability of the present analytical MIM, it is used to predict the experimental data of the zeta potential of 11-mercaptoundecanoic acid functionalized gold nanorods of radius $a_R = 125$ nm and length $L = 6$ μm [17]. Since $L \gg a_R$, the problem under consideration is one-dimensional. Because the nanorod surface bears carboxylic acid-terminated functional groups, ~COOH, its charged properties depend highly upon the solution properties like pH and salt concentration [16,21]. Fig. 1 shows the dependence of the zeta potential ψ_d on pH for a 10 mM NaCl solution. Both the experimental data (symbols) and the results based on our analytical MIM, Eq. (5) (solid curve), are presented. For comparison, the corresponding results based on the analytical model of Dougherty et al. [17] (dashed curve) below are also shown,

$$\frac{FN_tK_A}{K_A + 10^{-\mathrm{pH}}\exp\left\{-\frac{F}{RT}\left[\psi_d+\frac{4zFC_{NaCl}}{\kappa C_s}\sinh\left(\frac{\bar{\psi}_d}{2}\right)\right]\right\}} + \frac{4zFC_{NaCl}}{\kappa}\sinh\left(\frac{\bar{\psi}_d}{2}\right) = 0. \tag{6}$$

This model neglects the curvature effect, that is, the nanorod surface is assumed to be planar. In addition, only the one-site dissociation model

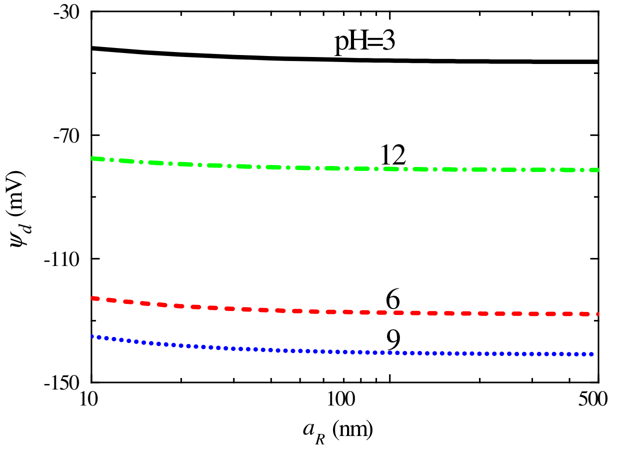

Fig. 2. Variation of the zeta potential ψ_d of a nanorod with its radius a_R for various values of pH at the background salt concentration C_{NaCl} = 1 mM.