Charging mechanism in colloidal particles leading to a linear relation between charge and size

Filip Strubbe,* Filip Beunis, Matthias Marescaux, and Kristiaan Neyts

Ghent University, Electronics and Information Systems, Sint-Pietersnieuwstraat 41, Ghent B-9000, Belgium
(Received 14 August 2006; revised manuscript received 9 November 2006; published 30 March 2007)

Colloidal particles that are dissolved in a liquid can become charged by preferential adsorption or dissociation of surface molecules. The assumption of a constant surface charge density leads to a particle charge that is proportional to the square of the radius. Recent experiments however have shown that in a number of cases the charge is linearly proportional to its size. We present a simple model for the charging of colloidal particles leading to a linear relation between charge and size in the framework of the mean-field Poisson-Boltzmann theory. The model is based on preferential adsorption or dissociation of surface molecules, in combination with a large concentration of chargeable surface sites. The model also predicts a surface potential that is independent of the particle size. Numerical simulations show that this model is in good agreement with analytical approximations.

　　　　PACS number(s): 82.70.Dd, 82.65.+r, 82.70.Uv, 82.30.Fi

I. INTRODUCTION

Charged colloidal particles are used in different applications, such as pharmaceuticals, soil mechanics, engine oils, and paints. In recent years, fundamental research has been carried out on the nucleation and growth of electrostatically stabilized colloidal crystals used as a model system for atomic systems [1], as well as on the interaction potential between charged colloidal particles [2,3]. A practical application is found in electrophoretic displays [4,5]. It is clear that the properties of colloidal dispersions depend strongly on the electrical charge of the particles. Since it is difficult to measure the charge of a particle directly, it is usual to determine the particle mobility in an electrical field and to use a model to relate the mobility to the charge. Several methods have been developed to determine the mobility of colloidal suspensions (electroacoustics [6], electrophoretic light scattering [7], video microscopy electrophoresis [8], optical tweezing electrophoresis [9]). In order to model the movement of a single colloidal particle in an electrical field, three problems have to be addressed: The chemical equilibrium for charging the surface of the particle, the electrostatic distribution around the particle related to ions in the liquid, and finally the hydrodynamic motion of the particle in the liquid. These problems influence each other and have to be solved simultaneously. The simplest model uses a perfectly spherical particle with a uniform surface potential surrounded by a double layer of ions and counter ions. The ions have a Boltzmann distribution around the charged particle, and the interaction with the electric field is taken into account by the Poisson equation. The combined mean-field Poisson-Boltzmann equation yields a relation between the surface potential of the particle and its charge. The Stokes law for the friction on a spherical particle in a liquid can be used to link the surface potential to the particle mobility [10].

A colloidal particle can obtain a charge by preferential adsorption of charges or by dissociation of ions from the surface. Sometimes the chemical composition of the surface gives an indication for the charging mechanism. It is known for example that the principal mechanism by which silica particles acquire a charge in contact with water at high pH, is the dissociation of sylanol groups: $SiOH \rightleftharpoons SiO^- + H^+$. In many other cases it is not obvious to predict how the charging occurs. One way to determine the charging mechanism is to measure the particle charge for a variety of parameters: Different solvents, different electrolyte concentrations, and different particle sizes [11,12]. The observation of the isoelectric point where the charge shifts from positive to negative or vice versa for increasing pH, is one example of this.

Recent experiments on charged pigment particles in non-aqueous media and on particles with different surface chemistry in aqueous media suggest that the charging mechanism often leads to a surface potential that is more or less independent of the particle size [12,13]. A good way to test the hypothesis of a constant surface potential in the framework of the Poisson-Boltzmann model is to check if there is a linear relation between the particle charge and the size for small particles. Garbow *et al.* have indeed demonstrated such a linear relation in low-salt aqueous media [12]. This result does not correspond to a particle charge that is proportional to the surface area, because this leads to a quadratic relation between charge and size. The explanation for the linear charge-size relation has to originate from a specific charging model. In the next section two basic charging mechanisms are discussed, namely preferential adsorption and dissociation of surface ions, providing a simple model for the linear charge-size dependency.

II. THEORY

Consider a single spherical colloidal particle with radius R and surface area $4\pi R^2$ suspended in a liquid with dielectric constant ϵ_r. The liquid contains potential-determining ions that are responsible for the development of a surface charge, and indifferent ions that are not chemically interacting with the particle surface. The potential-determining ions are modeled as an electrolyte containing positive and negative charges in the form of ions in aqueous media or inverse

*Corresponding author. Electronic address:
filip.strubbe@elis.ugent.be

micelles in nonaqueous media. In the following we will use the term ions to refer to both types of charged particles. In a continuous mean-field model, the concentrations of positive and negative potential-determining ions at infinity are denoted as $\bar{p}(m^{-3})$ and $\bar{n}(m^{-3})$. When a particle that is initially neutral is placed in this medium, it can obtain a charge through mechanisms like preferential adsorption or dissociation of surface molecules.

A. Preferential adsorption

1. Model

The reaction for preferential adsorption at the surface can be expressed by the following formulas:

$$S + P \rightleftarrows SP, \tag{1}$$

$$T + N \rightleftarrows TN, \tag{2}$$

with S an unoccupied adsorption site for positive ions, P a free positive ion with charge z_P, and SP a positively charged surface site, with corresponding concentrations $\nu_S(m^{-2})$, $p(m^{-3})$, and $\nu_{SP}(m^{-2})$. Similarly, T is an adsorption site for negative ions, N a free negative ion with charge $-z_N$, and TN a negatively charged site, with corresponding concentrations $\nu_T(m^{-2})$, $n(m^{-3})$, and $\nu_{SN}(m^{-2})$. When the adsorption of one type of ion is preferred, the particle obtains a charge Z in units of the elementary charge e. For example, in an electrolyte with $R'NH_3^+$ and Cl^- ions with R' being a hydrocarbon chain, preferential adsorption of $R'NH_3^+$ leads to a positively charged particle. The equations describing the equilibrium at the particle surface are

$$\frac{\nu_{SP}}{\nu_S p} = K_P, \tag{3}$$

$$\frac{\nu_{TN}}{\nu_T n} = K_N, \tag{4}$$

where K_P and K_N represent the equilibrium constants of Eqs. (1) and (2). The total concentrations of adsorption sites that can be positively or negatively charged are respectively given by $\nu_S^{\max}$ and $\nu_T^{\max}$ and therefore

$$\nu_S^{\max} = \nu_S + \nu_{SP}, \tag{5}$$

$$\nu_T^{\max} = \nu_T + \nu_{TN}, \tag{6}$$

The equilibrium particle charge Z is determined by the number of positive and negative charges on the surface:

$$Z = (\nu_{SP} z_P - \nu_{TN} z_N) 4\pi R^2. \tag{7}$$

When the particle charge is high, ions in the liquid with the same sign are repulsed, while ions with the opposite sign are attracted. The electrical potential in equilibrium at distance r from the particle center is $\Phi(r)$, with dimensionless value $\Psi(r) = e\Phi(r)/k_B T$, with k_B the Boltzmann constant and T the temperature. The equilibrium between electrostatic forces and thermal diffusion leads to a Boltzmann distribution of the ions, in which the surface concentrations p and n

are determined by the surface potential $\Psi_0 = \Psi(R)$:

$$p = \bar{p} \exp(-z_P \Psi_0), \tag{8}$$

$$n = \bar{n} \exp(z_N \Psi_0). \tag{9}$$

The relation between Ψ_0 and Z is found by solving the Poisson-Boltzmann equation (PBE) for a spherical particle [Eq. (10)] in combination with Gauss' law [Eq. (11)] and $\Psi(\infty) = 0$. The summation goes over all ionic species including indifferent ions with bulk concentration n_{i0} and valency z_i:

$$\nabla^2 \Psi = -\frac{e}{\varepsilon_0 \varepsilon_r k_B T} \sum_i z_i e n_{i0} \exp(-z_i \Psi), \tag{10}$$

$$\left.\frac{d\Psi}{dr}\right|_R = -\frac{Z\lambda_B}{R^2}, \tag{11}$$

with Bjerrum length $\lambda_B = e^2/4\pi\varepsilon_0\varepsilon_r k_B T$. For sufficiently low potentials ($\Psi_0 \ll 1$) the PBE can be linearized:

$$\nabla^2 \Psi = \frac{e^2}{\varepsilon_0 \varepsilon_r k_B T} \sum_i z_i^2 n_{i0} \Psi = \kappa^2 \Psi, \tag{12}$$

with $\kappa^{-1} = \sqrt{\varepsilon_0 \varepsilon_r k_B T / e^2 \Sigma_i n_{i0} z_{i0}^2}$ the Debye length. The solution of Eq. (12) is the well known screened Coulomb potential $\Psi(r) = \Psi_0(R/r)e^{-\kappa(r-R)}$ [14], and together with Eq. (11) the surface potential can be related to the particle charge:

$$\Psi_0 = \frac{Z\lambda_B}{R(1 + \kappa R)} = \frac{Z}{Z_A}, \tag{13}$$

with the definition $Z_A = R(1 + \kappa R)/\lambda_B$.

2. Equilibrium charge

The equilibrium charge is found by eliminating $\nu_S, \nu_{SP}, p, \nu_T, \nu_{TN}, n$ in Eqs. (3)–(9):

$$Z = \frac{K_P \bar{p} z_P \nu_S^{\max} 4\pi R^2}{e^{z_P \Psi_0} + K_P \bar{p}} - \frac{K_N \bar{n} z_N \nu_T^{\max} 4\pi R^2}{e^{-z_N \Psi_0} + K_N \bar{n}}, \tag{14}$$

and by stating that the equilibrium surface potential Ψ_0 is related to the charge Z through equations (10) and (11). Equation (14) reflects an electrostatic feedback mechanism in which the particle charge Z is determined by the ion concentrations p and n at the particle surface. The concentrations close to the surface depend on the surface potential Ψ_0, and Ψ_0 is determined by the particle charge Z.

In Sec. III Eq. (14) is solved numerically to find the equilibrium charge Z. Some cases result in a particle charge Z that is proportional to the surface area $4\pi R^2$ or in other words in a surface charge density that is independent of the size. On the other hand, the parameters are often well described by a constant surface potential, for instance when the concentrations of surface sites $\nu_S^{\max}$ and $\nu_T^{\max}$ are sufficiently large. We will discuss this case in more detail in the next sections. In this regime it is found that the charge of small particles ($\kappa R \ll 1$) is proportional to their radius.

3. Large concentrations of surface sites

In a number of cases, the system of equations (10), (11), and (14) determining the surface potential Ψ_0 can be simplified considerably. Let us assume for example that the surface site concentrations $\nu_S^{\max}$ and $\nu_T^{\max}$ are sufficiently large in order to have

$$\frac{K_P \bar{p} \cdot z_P \cdot \nu_S^{\max} 4\pi R^2}{e^{z_P \Psi_0} + K_P \bar{p}} \gg |Z|, \quad \frac{K_N \bar{n} \cdot z_N \cdot \nu_T^{\max} 4\pi R^2}{e^{-z_N \Psi_0} + K_N \bar{n}} \gg |Z|. \tag{15}$$

In this case, the two terms on the right-hand side in Eq. (14) will be approximately equal. Setting both terms equal yields an equation for the surface potential in which the particle size does not appear:

$$\frac{K_P \bar{p} \cdot z_P \cdot \nu_S^{\max}}{e^{z_P \Psi_0^A} + K_P \bar{p}} = \frac{K_N \bar{n} \cdot z_N \cdot \nu_T^{\max}}{e^{-z_N \Psi_0^A} + K_N \bar{n}}. \tag{16}$$

The solution of this equation Ψ_0^A is often a good approximation for the surface potential Ψ_0. The fact that Ψ_0^A is independent of the particle size may seem surprising. It can be understood by the important role of the particle charge in the charging mechanism: the particle repels ions with a charge of the same sign and attracts ions of the opposite sign.

Equation (16) can only be solved analytically when some additional assumptions are made. In the next sections we will discuss the value of Ψ_0^A as well as the size and concentration dependency for some special cases.

(i) *Most surface sites not occupied.* When most surface sites are not occupied we have $\nu_{SP} \ll \nu_S$ and $\nu_{TN} \ll \nu_T$. In this case the chemical balance of reactions (1) and (2) is largely shifted to the left and we have [Eqs. (3) and (4)] $K_P \bar{p} \ll 1$ and $K_N \bar{n} \ll 1$. Equation (16) then reduces to

$$\frac{K_P \bar{p} \cdot z_P \cdot \nu_S^{\max}}{e^{z_P \Psi_0^A}} = \frac{K_N \bar{n} \cdot z_N \cdot \nu_T^{\max}}{e^{-z_N \Psi_0^A}}, \tag{17}$$

which can be solved analytically to give an approximate expression for the potential Ψ_0^A:

$$\Psi_0^A = \frac{1}{(z_P + z_N)} \ln\left(\frac{K_P \bar{p} \cdot z_P \cdot \nu_S^{\max}}{K_N \bar{n} \cdot z_N \cdot \nu_T^{\max}} \right) \equiv A, \tag{18}$$

where the latter equation defines the quantity A. We find a surface potential that is independent of the particle size and independent of the electrolyte concentration in the case of charge neutrality $\bar{p} z_P = \bar{n} z_N$ for the potential-determining ions. There is a small dependency on the electrolyte concentration when $\bar{p} z_P \neq \bar{n} z_N$.

(ii) *Generalization of formula (18).* The result in Eq. (18) has a limited validity. In the case that $z_P = z_N = z$, Eq. (16) reduces to a quadratic equation in $e^{z\Psi_0}$ and the following solution is valid for arbitrary values of $K_P \bar{p}$ and $K_N \bar{n}$:

$$\Psi_0^A = \frac{1}{z} \ln\left(\frac{K_P \bar{p} K_N \bar{n}(\nu_S^{\max} - \nu_T^{\max}) + \sqrt{[K_P \bar{p} K_N \bar{n}(\nu_S^{\max} - \nu_T^{\max})]^2 + 4 K_P \bar{p} K_N \bar{n} \nu_S^{\max} \nu_T^{\max}}}{2 K_N \bar{n} \nu_T^{\max}} \right). \tag{19}$$

Obviously, Eq. (19) reduces to Eq. (18) for $K_P \bar{p} \ll 1$ and $K_N \bar{n} \ll 1$.

(iii) *Particle charge and mobility.* The approximated value Ψ_0^A of the surface potential can now be related to the particle charge Z. Combination of Eq. (18) and the linearized solution of the PBE [Eq. (13)] which is valid for $\Psi_0 \ll 1$ as well as for $\kappa R \ll 1$, leads to the following value for the particle charge:

$$Z = \frac{R(1 + \kappa R)}{\lambda_B} \Psi_0^A. \tag{20}$$

For small particles ($\kappa R \ll 1$), the equilibrium charge becomes

$$Z = \frac{\Psi_0^A R}{\lambda_B}, \tag{21}$$

representing the remarkable linear charge-size relation. Larger particles ($\kappa R \gg 1$) show a quadratic proportionality according to Eq. (20).

The surface potential Ψ_0^A can also be used to find the corresponding electrophoretic mobility. For low ion concentrations the Debye length is large and the electrical potential decays slowly. In that case we can assume that the surface potential $\Phi(R)$ is equal to the zeta potential ς, and we can obtain an approximation for the mobility. For small values of the surface potential (let us say $\Psi_0 < 3$) Henry's equation $\mu = f(\kappa R)[2\varepsilon_0 \varepsilon_r \Phi(R)/3\eta] = f(\kappa R)(\Psi_0 z e/6\pi\eta\lambda_B)$ can be used, with $f(\kappa R)$ varying monotonically between 1 for $\kappa R \ll 1$ and 1.5 for $\kappa R \gg 1$ [10]. The reduced mobility $\mu_{\text{red}} = (2/3) z e \eta \mu / \varepsilon_0 \varepsilon_r k_B T$ corresponding to a particle with the surface potential Ψ_0^A becomes

$$\mu_{\text{red}} = \frac{4\Psi_0^A}{9} f(\kappa R). \tag{22}$$

This reduced mobility is only slightly dependent on the particle size through the function f. In the regions $\kappa R \ll 1$ and $\kappa R \gg 1$ the mobility is independent of the size.

B. Dissociation of surface molecules

1. Model

We again consider a particle with radius R suspended in a liquid containing potential-determining and indifferent ions.

Instead of the previously described preferential adsorption, the particle can now obtain a charge through dissociation of specific molecules at the surface. In such a dissociation process, a neutral surface molecule splits into a charged part that remains attached to the surface, and an oppositely charged part that becomes a free ion. We consider two types of specific molecules on the particle surface, and we will reuse some notations from the preferential adsorption model. The chemical reactions at the particle surface are described by the following formulas:

$$S \rightleftarrows SP + N, \tag{23}$$

$$T \rightleftarrows TN + P. \tag{24}$$
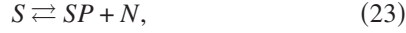
S represents a molecule with surface concentration $\nu_S(m^{-2})$ for which the positive part remains attached to the particle, while T with concentration $\nu_T(m^{-2})$ represents a molecule for which the negative part remains attached. The charged molecules on the surface, SP and TN have concentrations $\nu_{SP}(m^{-2})$ and $\nu_{TN}(m^{-2})$ and valencies respectively z_P and $-z_N$. The dissociated free ions N and P have valencies $-z_P$ and z_N and concentrations $n(m^{-3})$ and $p(m^{-3})$ close to the surface. We assume that the bulk concentrations $\bar{p}$ and $\bar{n}$ of positive and negative ions and indifferent ions are unchanged by the additional release of dissociated ions. An example of this mechanism is the dissociation of hydrogen from acidic surface groups $R'COOH \rightleftarrows R'COO^- + H^+$ leading to a negatively charged particle. For basic surface groups $R'OH \rightleftarrows R'^+ + OH^-$ the dissociation leads to a positively charged particle. The equations describing chemical equilibrium at the particle surface are

$$\frac{\nu_{SP} \cdot n}{\nu_S} = K_P, \tag{25}$$

$$\frac{\nu_{TN} \cdot p}{\nu_T} = K_N, \tag{26}$$

where K_P and K_N are the equilibrium constants of Eqs. (25) and (26). The total concentrations of surface sites that can be positively or negatively charged are respectively given by $\nu_S^{\max}$ and $\nu_T^{\max}$ and therefore

$$\nu_S^{\max} = \nu_S + \nu_{SP}, \tag{27}$$

$$\nu_T^{\max} = \nu_T + \nu_{TN}. \tag{28}$$

The equilibrium charge is

$$Z = (\nu_{SP} z_P - \nu_{TN} z_N) S. \tag{29}$$

The surface concentrations p and n are related to the bulk concentrations $\bar{p}$ and $\bar{n}$ by

$$p = \bar{p} \exp(- z_N \Psi_0), \tag{30}$$

$$n = \bar{n} \exp(z_P \Psi_0). \tag{31}$$

The relation between the charge and the surface potential is again found by solving Eqs. (10) and (11).

2. Equilibrium charge

The equilibrium charge is the solution of Eqs. (25)–(31):

$$Z = \frac{K_P \cdot z_P \cdot \nu_S^{\max} 4\pi R^2}{K_P + \bar{n} e^{z_P \Psi_0}} - \frac{K_N \cdot z_N \cdot \nu_T^{\max} 4\pi R^2}{K_N + \bar{p} e^{-z_N \Psi_0}}, \tag{32}$$

where Ψ_0 is a function of Z through Eqs. (10) and (11). In Sec. III B the equilibrium charge Z is calculated numerically. We find again that in some cases the particle charge is proportional to the surface area $4\pi R^2$. When the concentrations of surface sites are sufficiently large there is again a regime where the surface potential is independent of the size, and where the particle charge is proportional to the particle size. Since many conclusions are similar to those of the preferential adsorption model (Sec. II A), the discussion is shortened considerably.

3. Large concentrations of surface sites

As in Sec. II A 3 we make the assumption that the surface site concentrations $\nu_S^{\max}$ and $\nu_T^{\max}$ are sufficiently large so that both terms at the right-hand side of Eq. (32) are—in absolute value—much larger than $|Z|$:

$$\frac{K_P \cdot z_P \cdot \nu_S^{\max} 4\pi R^2}{K_P + \bar{n} e^{z_P \Psi_0}} \gg |Z|, \quad \frac{K_N \cdot z_N \cdot \nu_T^{\max} 4\pi R^2}{K_N + \bar{p} e^{-z_N \Psi_0}} \gg |Z|. \tag{33}$$

In many cases a good approximation for the potential Ψ_0^A can be obtained by setting the two terms on the right-hand side in Eq. (32) equal to each other:

$$\frac{K_P \cdot z_P \cdot \nu_S^{\max}}{K_P + \bar{n} e^{z_P \Psi_0^A}} = \frac{K_N \cdot z_N \cdot \nu_T^{\max}}{K_N + \bar{p} e^{-z_N \Psi_0^A}}. \tag{34}$$

The surface potential Ψ_0^A is again independent of the particle size.

In the following sections we will derive analytical equations for Ψ_0^A in some special cases and discuss the size and concentration dependency.

(i) Most surface sites not dissociated. When most surface sites are not dissociated we have $\nu_{SP} \ll \nu_S$ and $\nu_{TN} \ll \nu_T$. In this case the chemical balance of reactions (23) and (24) is largely shifted to the left and we have [Eqs. (25) and (26)] $K_P \ll \bar{n}$ and $K_N \ll \bar{p}$. Equation (34) then reduces to

$$\frac{K_P \cdot z_P \cdot \nu_S^{\max}}{\bar{n} e^{z_P \Psi_0^A}} = \frac{K_N \cdot z_N \cdot \nu_T^{\max}}{\bar{p} e^{-z_N \Psi_0^A}}. \tag{35}$$

Equation (35) can be solved analytically to give an approximate value for the surface potential Ψ_0^A:

$$\Psi_0^A = \frac{1}{(z_P + z_N)} \ln\left(\frac{K_P \bar{p} z_P \nu_S^{\max}}{K_N \bar{n} z_N \nu_T^{\max}}\right) \equiv A, \tag{36}$$

which is similar to Eq. (18).

(ii) Generalization of formula (36). For larger values of $K_P/\bar{p}$ and $K_N/\bar{n}$ an analytical solution Ψ_0^A of formula (34) can be found in the case that $z_P = z_N = z$:

$$\Psi_0^A = \frac{1}{z} \ln\left(\frac{K_P K_N (\nu_S^{\max} - \nu_T^{\max}) + \sqrt{[K_P K_N (\nu_S^{\max} - \nu_T^{\max})]^2 + 4 K_P \bar{p} K_N \bar{n} \nu_S^{\max} \nu_T^{\max}}}{2 K_N \bar{n} \nu_T^{\max}} \right). \tag{37}$$

It can be verified that Eq. (37) reduces to Eq. (36) for $K_P \ll \bar{n}$ and $K_N \ll \bar{p}$.

(iii) Particle charge and mobility. The surface potential Ψ_0^A can be related to the particle charge and mobility as explained in Sec. II A 3. As a result, small particles ($\kappa R \ll 1$) will again show a linear charge-size relation.

III. SIMULATIONS

The main goal of the simulations is to verify the validity of the derived analytical solutions, and to find the size and concentration dependency of the equilibrium charge, since this can be compared to experimental data. The input parameters are κ, R, K_P, K_N, $\bar{p}$, $\bar{n}$, z_P, z_N, λ_B, $\nu_S^{\max}$, $\nu_T^{\max}$ and the output parameters are Z and Ψ_0. Simulation results are shown for the case of a symmetrical electrolyte without indifferent ions: $z_P = z_N = 1$ and $\bar{p} = \bar{n}$.

A. Preferential adsorption

1. Size dependency

Simulations have been carried out using the model of preferential adsorption as described in Sec. II A. Equation (14) is solved numerically with parameters $\kappa^{-1} = 750$ nm, $\lambda_B = 7.03 \times 10^{-10}$ m, $\bar{p} = \bar{n} = 10^{20}$ m^{-3}, and $z_P = z_N = 1$. The equilibrium constants $K_P = 10^{-19}$ m^3 and $K_N = 10^{-21}$ m^3 result in a value for $A = 3.45$ [Eq. (18)]. Simulations are shown in Fig. 1 for particles with radius between 1 nm and 10 μm. Each line corresponds to one value of $\nu_S^{\max}$ going from 10^{10} m^{-2} up to 10^{20} m^{-2} in steps of a factor 10. $\nu_T^{\max}$ is always chosen 10 times smaller than $\nu_S^{\max}$; thus $\nu_T^{\max} = 0.1 \cdot \nu_S^{\max}$. Since the solution Ψ_0^A of Eq. (16) depends only on the ratio of $\nu_S^{\max}$ and $\nu_T^{\max}$, the corresponding value of Ψ_0^A is the same for all lines.

In Fig. 1(a) we find that for low values of $\nu_S^{\max}$, the charge can be approximated by a simplified version of Eq. (14) in which the charge is proportional with R^2:

$$Z = \left(\frac{K_P \bar{p} \cdot z_P \cdot \nu_S^{\max}}{1 + K_P \bar{p}} - \frac{K_N \bar{n} \cdot z_N \cdot \nu_T^{\max}}{1 + K_N \bar{n}} \right) 4\pi R^2. \tag{38}$$

For increasing values of $\nu_S^{\max}$, the charge approaches the analytical solution $Z_A \Psi_0^A$ [Eq. (20)] for all radii. Notice the linear charge-size relation for sizes between 1 nm and 0.1 μm (corresponding to $\kappa R \ll 1$) changing to a quadratic relation for sizes above 0.5 μm ($\kappa R \gg 1$).

Figure 1(b) shows the results for the surface potential Ψ_0. As expected the potential becomes $\Psi_0^A = 3.45$ if the concentration $\nu_S^{\max}$ is sufficiently high.

2. Concentration dependency

The dependency of the equilibrium charge on the electrolyte concentration is simulated in Fig. 2, using the same pa-

rameters as in Fig. 1. A fixed value $R = 400$ nm was chosen for the particle radius. The equilibrium charge was calculated for electrolyte concentrations $\bar{p} = \bar{n}$ varying from 10^{18} m^{-3} to 10^{23} m^{-3}. The lower charges in Fig. 2(a) can again be described by Eq. (38). This means that the charge Z is proportional with the electrolyte concentration for $K_P \bar{p} \ll 1$ and saturates for large electrolyte concentrations ($K_P \bar{p} \gg 1$) when all adsorption sites are charged.

For high values of $\nu_S^{\max}$ the charge saturates at a value $Z_A \Psi_0^A$ according to Eq. (20). The saturation value is constant for small electrolyte concentrations [Eq. (18)], and increases for high concentrations $\bar{p}$, because the Debye length κ^{-1} decreases and because the potential increases as described by Eq. (37). Figure 2(b) shows that the saturated value of the equilibrium surface potential Ψ_0^A is constant for low concentrations $\bar{p}$, and increases according to Eq. (37) for high concentrations when most of the sites are charged.
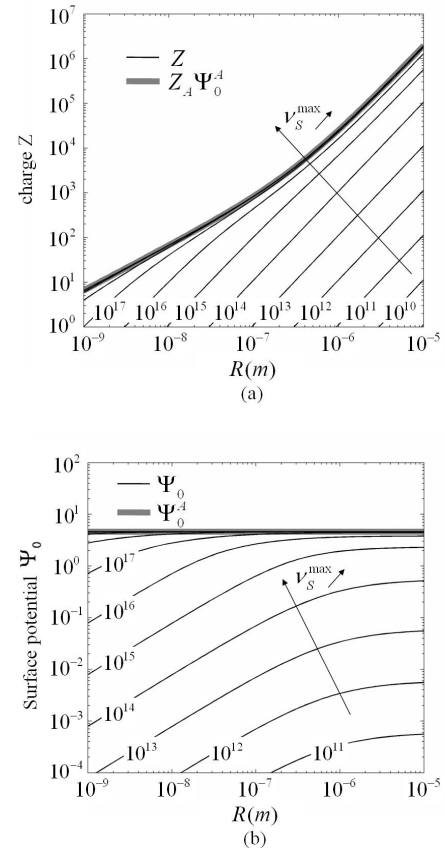

FIG. 1. Simulation results and analytical equations (a) of the equilibrium particle charge Z and (b) of the surface potential Ψ_0 as a function of the particle radius R and the concentration of adsorption sites $\nu_S^{\max}$. Each line corresponds to a value of $\nu_S^{\max}$ (the value of $\nu_S^{\max}$ in m^2 is written for some lines).
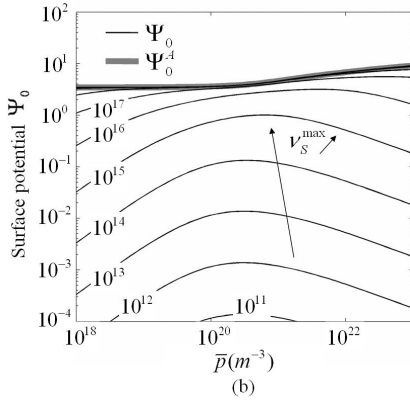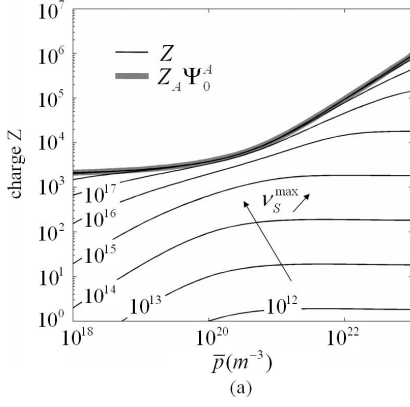
FIG. 2. Simulation results and analytical equations (a) of the equilibrium charge Z and (b) of the surface potential Ψ_0 as a function of the electrolyte concentration $\bar{p}$ and the concentration of adsorption sites $\nu_S^{\max}$. Each line corresponds to a value of $\nu_S^{\max}$ (the value of $\nu_S^{\max}$ in m^2 is written for some lines).

B. Dissociation of surface molecules

1. Size dependency

The size dependency of charge and potential in the case of dissociation of surface molecules is very similar to preferential adsorption and will not be discussed in detail. Small charges ($\Psi_0 \ll 1$) are described by the reduced form of Eq. (32):

$$Z = \left(\frac{K_P \cdot z_P \cdot \nu_S^{\max}}{K_P + \bar{n}} - \frac{K_N \cdot z_N \cdot \nu_T^{\max}}{K_N + \bar{p}} \right) 4\pi R^2, \qquad (39)$$

which has a similar relation between the charge and the size as Eq. (38). For high values of $\nu_S^{\max}$ the potential will saturate at the value Ψ_0^A [Eq. (34)], while the charge approaches the value $Z_A \Psi_0^A$ [Eq. (20)], quite similar to what can be seen in Fig. 1.

2. Concentration dependency

The concentration dependency in the case of dissociation is different from the case of preferential adsorption. In Fig. 3 the particle charge and surface potential are simulated. Simulation parameters are $\kappa^{-1} = 750$ nm, $\lambda_B = 7.03 \times 10^{-10}$ m, and $z_P = z_N = 1$. The equilibrium constants are $K_P = 10^{20}$ m^{-3} and
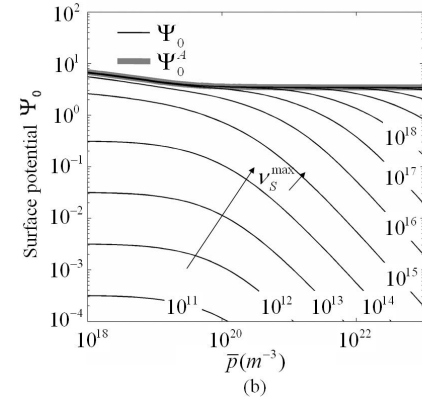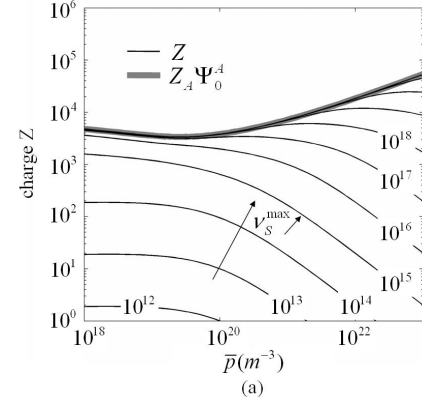
FIG. 3. Simulation results and analytical equations (a) of the equilibrium charge Z and (b) of the surface potential Ψ_0 as a function of the electrolyte concentration $\bar{p}$ and the concentration of adsorption sites $\nu_S^{\max}$. Each line corresponds to a value of $\nu_S^{\max}$ (the value of $\nu_S^{\max}$ in m^2 is written for some lines).

$K_N = 10^{18}$ m^{-3}, resulting in a value $A = 3.45$, and the particle radius was chosen to be $R = 400$ nm. The equilibrium charge was calculated for electrolyte concentrations $\bar{p} = \bar{n}$ varying between 10^{18} m^{-3} and 10^{23} m^{-3}, and for values of $\nu_S^{\max}$ ranging from 10^{11} m^{-2} to 10^{22} m^{-2}. Each line corresponds to one value of $\nu_S^{\max}$ and $\nu_T^{\max}$ is always chosen 10 times smaller than $\nu_S^{\max}$; thus $\nu_T^{\max} = 0.1 \cdot \nu_S^{\max}$. Since the ratio of $\nu_S^{\max}$ and $\nu_T^{\max}$ is fixed, the corresponding values of Ψ_0^A are the same for all the lines [Eq. (34)].

Low charges in Fig. 3(a) are described by Eq. (39), this means a constant charge for small concentrations $\bar{p}$ and an inverse relationship ($\sim 1/\bar{p}$) for higher concentrations. For increasing $\nu_S^{\max}$ the charge Z saturates towards the value given by Eq. (20). Notice that the resulting charge Z may be many thousand times smaller than in the case without electrostatic feedback.

As can be observed in Fig. 3(b), the saturated value of the surface potential is $A = 3.45$ for high concentrations and increases as described by Eq. (37) for low concentrations.

IV. DISCUSSION

There are a lot of analogies between the models of preferential adsorption and dissociation of surface molecules. In

both models there is a range in the parameter space for which the surface potential does not depend on the radius of the particle. Therefore, both models are able to explain a linear relation between particle charge and size for sufficiently small particles. The similarity between both models implies that it is not easy to distinguish which mechanism is responsible for the behavior. Only a detailed study of the concentration dependency of the charging behavior or direct evidence about the chemical reactions makes it possible to determine the appropriate model.

At this point it is interesting to compare experimental data available from the literature with the analytical expressions we have obtained in Sec. II. The experimental results of Garbow *et al.* [12] on isolated particles in low-salt aqueous media with a radius between 50 nm and 1.5 μm show a linear relation between charge and size that can be fitted well with Eq. (21) with the value $\Psi_0^A \cong 2$. The linear relation between charge and size is visible over more than a decade and is observed in water as well as in mixed water/glycerol solutions, for particles of different surface chemistry and titrated charge numbers. The interpretation of the fitted value $\Psi_0^A \cong 2$ can be illustrated by using Eq. (18). From Eq. (18) we find that for the case of a symmetrical 1:1 electrolyte with charge neutrality $z_P \bar{p} = z_N \bar{n}$ and equal concentrations of surface sites $\nu_S^{\max} = \nu_T^{\max}$, the value $\Psi_0^A \cong 2$ corresponds to a ratio $K_P/K_N \cong 55$, which is a reasonable result. In addition Garbow *et al.* found that the particles of very different sizes and surface chemistries show the same reduced mobilities [12]. With Eq. (22) this is identical with saying that the particles have the same surface potential, and it is an indication that the proportion of the equilibrium constants K_P/K_N is more or less the same for different surface chemistries.

The models described in this paper are only valid for systems with a simple double layer, in which the discrete ions can be described by a continuum charge density. In practice this is fine if the particle charge Z and number of ions in the double layer are sufficiently large.

In the presented models a necessary condition to achieve a linear charge-size relation is a large number of chargeable surface sites [Eq. (15) and Eq. (33)]. We will now verify if the surface density $\nu_S^{\max} = \nu_T^{\max} = 1$ nm^{-2} (which is much less than the atomic surface density) is sufficiently high to reach the condition expressed in Eq. (15). Using the parameters $R = 100$ nm, $\kappa^{-1} = 750$ nm, $\lambda_B = 0.7$ nm, $K_P \bar{p} = 1$, and $K_N \bar{n} = 0.1$, we find that the surface potential $\Psi_0 = 1.147$ is almost equal to $\Psi_0^A = 1.151$ and that the two terms on the right-hand side of Eq. (14) are both much larger than Z [Eq. (14) becomes $Z = 186 = 30284 - 30098$]. A similar result is found for Eq. (33).

Combining the Poisson-Boltzmann equation for isolated colloidal particles [Eq. (10)] and Gauss' law [Eq. (11)] leads to a relation between the particle charge Z and the particle surface potential Ψ_0. The charging mechanisms described in Sec. II provide a third equation that is needed to determine the values of Z and Ψ_0. Usually this third equation is not included and either a fixed particle charge or a fixed surface potential is assumed. The results of Sec. II can be a basis for selecting the most appropriate parameter value for the particle. The surface potential is found to be more or less constant over a large range of particle sizes and electrolyte concentrations. For particles with a high number of chargeable sites [according to the necessary conditions (15) and (33)] that can be modeled in first approximation with a simple double layer it is better justified to use a constant surface potential. However, when the concentration of surface sites is low or in the case of complete dissociation or complete occupation of chargeable sites, the constant surface charge density is a better approximation.

V. CONCLUSION

Two basic charging mechanisms for a particle dispersed in an electrolyte have been studied in the framework of the mean-field Poisson-Boltzmann theory: Preferential adsorption of ions and dissociation of surface ions. Analytical expressions are derived for the concentration and size dependency of the equilibrium charge, surface potential, and particle mobility. As long as the surface potential is sufficiently low, the equilibrium particle charge is proportional to the surface area of the particle, as expected. However, if the number of chargeable sites is sufficiently large, the potential increases and an electrostatic feedback mechanism sets in, leading to a linear charge-size relation for both mechanisms. Experimental data suggesting a linear charge-size relation, as for instance found by Garbow *et al.* [12], can be fitted to the analytical equation $Z = \Psi_0^A R / \lambda_B$ [Eq. (21)]. In this work, it is explained how the fitting parameter Ψ_0^A can be related to the properties of the electrolyte and the equilibrium constants of the charge determining reactions at the particle surface.

ACKNOWLEDGMENTS

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