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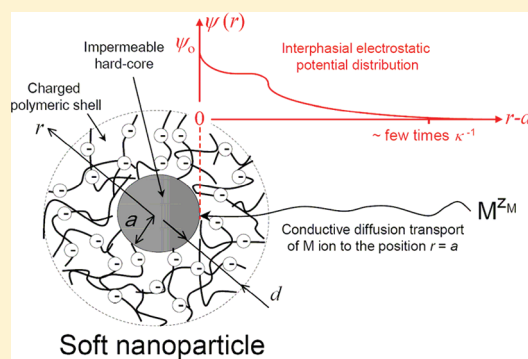
# Rates of Ionic Reactions With Charged Nanoparticles In Aqueous Media

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**ABSTRACT:** A theory is developed to evaluate the electrostatic correction for the rate of reaction between a small ion and a charged ligand nanoparticle. The particle is assumed to generally consist of an impermeable core and a shell permeable to water and ions. A derivation is proposed for the ion diffusion flux that includes the impact of the equilibrium electrostatic field distribution within and around the shell of the particle. The contribution of the extra- and intraparticle field is rationalized in terms of a conductive diffusion factor,  $f_{el}$ , that includes the details of the particle geometry (core size and shell thickness), the volume charge density in the shell, and the parameters defining the electrostatic state of the particle core surface. The numerical evaluation of  $f_{el}$ , based on the nonlinear Poisson–Boltzmann equation, is successfully complemented with semianalytical expressions valid under the Debye–Hückel condition in the limits of strong and weak electrostatic screening. The latter limit correctly includes the original result obtained by Debye in his 1942 seminal paper about the effect of electrostatics on the rate of collision between two ions. The significant acceleration and/or retardation possibly experienced by a metal ion diffusing across a soft reactive particle/solution interphase is highlighted by exploring the dependence of  $f_{el}$  on electrolyte concentration, particle size, particle charge, and particle type (i.e., hard, core/shell, and entirely porous particles).



## 1. INTRODUCTION

Almost a century ago, von Smoluchowski<sup>1,2</sup> calculated the purely diffusion-controlled frequency of collisions,  $\nu$ , between spherical particles dispersed in a liquid medium. It resulted in the well-known expression  $\nu = 16\pi Dr_p c$ , where  $D$  is the diffusion coefficient,  $r_p$  is the particle radius and  $c$  is the volume concentration of the dispersed particles (see, e.g., ref 3 for background and details). The frequency of collisions between identical particles, as derived by von Smoluchowski, is strongly related to the steady state diffusive flux,  $J$ , of small molecular/ionic species to dispersed particles. Thus it provides us with a useful starting point in analyzing the rates of reactions between small ions or molecules and reactive nanoparticles.

A few decades after the appearance of von Smoluchowski's collision theory, Debye<sup>4</sup> extended the mere diffusion approach to charged particles by invoking the impact of electrostatic interactions on the collision frequency  $\nu$ . This was realized by incorporating the electric term for the Coulombic forces between the dispersed particles and the diffusing ionic species into the basic transport equation. The solution is found after the integration of the electric interaction potential,  $U$ , over the separation between the particles in a collision event. The result was represented by a correction factor,  $f_{el}$ , in the von Smoluchowski equation. For particles with the same charge sign,  $f_{el}$  is  $<1$  (retardation), whereas for opposite charge signs  $f_{el}$  is  $>1$  (acceleration). The effect of screening by the background electrolyte leads to a

modification of  $f_{el}$  by additional terms in  $\kappa l_B$ , where  $\kappa^{-1}$  is the Debye length and  $l_B$  is the Bjerrum length defined by  $z_1 z_2 e^2 / (4\pi\epsilon k_B T)$  with  $z_1$  and  $z_2$  representing the charge numbers of the colliding particles,  $k_B T$  the thermal energy and  $\epsilon$  the dielectric permittivity of the medium.

The von Smoluchowski–Debye theory has been applied as a basic framework for the reaction kinetics in various fields of chemistry, e.g., enzyme kinetics<sup>5,6</sup> and chemodynamics of metal ion complexation.<sup>7–10</sup> For charged reactant particles in the size range of nanometers and higher (nanoparticles and colloids), however, the Coulombic formulation of the electrostatic impact on their reaction rates seems a priori inadequate. The charge of such particles is smeared-out, either over the surface or over some part of the particle volume, and an interfacial electric double layer hosts the generally asymmetric potential profile from the medium phase to the particle phase. Reactive sites at the particle surface or inside the particle body can be reached by reactants in the medium only after passage through the relevant part of the potential profile. For colloidal particles with radii much larger than the Debye length  $\kappa^{-1}$  of the medium, it may be anticipated

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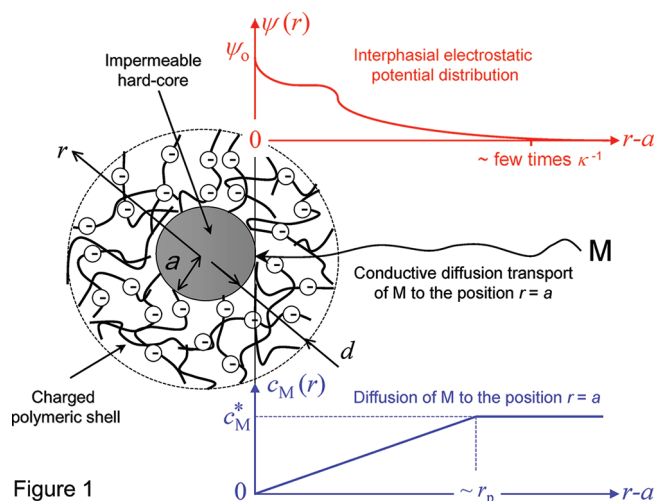


Figure 1

**Figure 1.** Schematic representation of a soft (core-shell) reactant nanoparticle/solution interphase. The conductive diffusion of a metal ion  $M$  from/to the particle core surface is illustrated. For nanoparticles, the characteristic length scale  $\kappa^{-1}$  for the interphasial potential distribution  $\psi(r)$  (top) is typically of the same order of magnitude than the thickness of the diffusion layer (bottom) that is comparable to the particle size  $r_p = a + d$ .

that the accelerating effect on the diffusion rate of an oppositely charged reactant from the medium will be modest because the diffusion scale is a much larger one than the electric field scale. However, in the nanoparticulate regime these two scales typically are of the same order of magnitude. For the sake of illustration, we recall that in an aqueous medium containing  $10^{-3}$  M 1:1 electrolyte, the Debye screening length is the same as the radius of a 10 nm nanoparticle. Therefore, to understand the conductive diffusion of charged reactants in the nanoparticulate domain, it will be necessary to expand the Debye approach with non Coulombic extraparticulate and intraparticulate electric fields. The aim of the present study is to explore this expansion and to generate basic physicochemical understanding on the rates of reactions of simple ions with larger charged reactant(s), from the molecular to the nanoparticulate and colloidal size ranges.

## 2. FORMULATION OF THE PROBLEM

Let us consider a spherical reactant nanoparticle composed of an impermeable core and a soft outer shell, which is permeable to water and ions (Figure 1). The spherical core has a radius  $a$  and the shell has a thickness  $d$ . The overall particle radius, frequently denoted as  $r_p$ , equals  $a + d$ . Below we shall use this core/shell model as a general case, which encompasses the limits of “hard” particles and “porous” particles corresponding to  $d \rightarrow 0$  and  $a \rightarrow 0$ , respectively. Unless indicated otherwise, the permittivity and viscosity of the shell liquid will be assumed to be equal to those of the bulk aqueous medium, implying that, e.g., differences in ionic diffusion coefficients between the shell and the surrounding medium will be disregarded. By way of example and for the sake of clarity, we shall continue for the case of a small cationic reactant  $M_{aq}^{z_M}$  (with  $z_M$  usually 2+) and a particle with arbitrary core and shell charges. Evidently, a negative charge will accelerate the transport of an incoming cation whereas a positive charge will give rise to retardation. For a core/shell particle with core and shell charges of opposite sign the net effect on the transport rate will be more differentiated.

The target ion  $M_{aq}^{z_M}$  (or  $M$  in short) is assumed to be a minor ion in the presence of a large excess of background electrolyte. Under such conditions, the setting/adjusting of electric potential in the double layer at the particle/medium interphase is governed by the background electrolyte, which will allow us to analyze the transport of the reactive ion  $M$  toward the particle under conditions of the equilibrium electric potential profile in the interphasial double layer. In many cases it will also be acceptable to ignore the initial transient stage in the diffusive transport of  $M$  toward the particles. For a particle radius of 10 nm and a diffusion coefficient  $D_M = 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, this transient occurs at time scales on the order of  $10^{-7}$  s. For times beyond this transient stage, and using  $r_p \gg r_M$  (and  $D_p \ll D_M$ ) the limiting value of the stationary diffusive flux of  $M$  is given by

$$J_M^* = -4\pi r_p D_M c_M^* N_{AV} \quad (1)$$

with  $J_M^*$  expressed as the number of metal ions per particle per second,  $c_M^*$  the bulk concentration of  $M$ , and  $N_{AV}$  the Avogadro number. Debye<sup>4</sup> incorporated the electric force term  $dU(r)/dr$  in the flux equation for  $J_M^*$ , with  $U(r)$  being the electrostatic energy between the charged particle and the ion  $M$  at distance  $r$ . He found the general solution for any type of potential profile and represented it by an additional coefficient  $f_{el}$  in the pure diffusion eq 1. This general solution incorporates an integral term involving  $U$  according to

$$f_{el} = \left\{ r_p \int_{r_p}^{\infty} r^{-2} \exp(U(r)/k_B T) dr \right\}^{-1} \quad (2)$$

Assuming the electric force to be of a purely Coulombic nature with a  $1/r^2$  dependence on the charge separation  $r$ , Debye easily found the straightforward solution

$$f_{el} = \tilde{U} / [\exp(\tilde{U}) - 1] \quad (3)$$

where  $\tilde{U} = z_M z_p e^2 / (4\pi\epsilon k_B T r_p)$ .

Obviously, the Coulombic point charge approach is not really appropriate for colloidal and nanoparticulate systems where the charges are spatially distributed over the surface (hard core-only particles) or over the volume (entirely porous permeable particles), or both (core/shell type particles). The energy term  $U$  involved in the integral of eq 2 then has to be defined in terms of the actual potential field in and/or outside the particle body, i.e., the potential profile in the interphasial double layer. In its most basic form a double layer profile is defined by an exponential function with the Debye length  $\kappa^{-1}$  as the argument.<sup>11</sup> For the sake of completeness, we recall this crucial parameter

$$\kappa = [2F^2 z^2 c^* / (\epsilon R T)]^{1/2} \quad (4)$$

where  $F$  is the Faraday,  $T$  is the temperature,  $R$  is the gas constant.  $z$  denotes the charge number of the symmetrical  $z_+/z_-$  electrolyte considered here, and  $c^*$  its bulk concentration.

## 3. CONDUCTIVE DIFFUSION OF AN ION TO A CHARGED CORE/SHELL PARTICLE

**3.1. Equilibrium Potential Profile Across the Soft Particle/Solution Interphase.** The equilibrium electrostatic potential distribution,  $\psi(r)$ , around and within the soft surface layer of a core/shell particle is governed by the Poisson equation

$$\nabla^2 \psi(r) = -[\rho_{ion}(r) + \rho_{fix}(r)] / \epsilon_0 \epsilon_r \quad (5)$$

where  $\nabla^2 = r^{-2} d(r^2 d/dr) / dr$  is the radial component of the Laplacian operator in spherical geometry. For the sake of

simplicity, the dielectric permittivity of the electrolyte solution,  $\varepsilon = \varepsilon_o \varepsilon_r$ , is taken to be identical to that of the particle core and shell components. The term  $\rho_{\text{ion}}(r)$  in eq 5 denotes the local space charge density stemming from the mobile ions that are distributed within and outside the ion-permeable shell. At equilibrium, ion concentration profiles follow Boltzmann statistics so that, in the case of a  $z:z$  background electrolyte of bulk concentration  $c^*$ ,  $\rho_{\text{ion}}(r)$  reads as

$$\rho_{\text{ion}}(r) = -2zFc^* \sinh(zF\psi(r)/RT) \quad (6)$$

This formulation implies that in case of a reaction with a specific minor ion, the potential profile is established/adjusted by the background electrolyte. The quantity  $\rho_{\text{fix}}(r)$  in eq 5 corresponds to the local volume charge density that originates from the immobile charged sites in the soft material composing the particle shell. To further define  $\rho_{\text{fix}}(r)$ , we adopt the formulation of soft diffuse interphases introduced by Duval et al. in electrokinetic theories for soft particles<sup>12</sup> and soft planar surfaces,<sup>13</sup> and in the modeling of electrostatic interaction between soft multilayered (bio)particles.<sup>14</sup> In that representation, the density of structural charges in the shell depends on the radial position  $r$  according to

$$\begin{aligned} \rho_{\text{fix}}(r)/\rho_o &= g_\alpha(r) \\ &= \chi(1 - \tanh\{[r - (a + d)]/\alpha\})/2 \end{aligned} \quad (7)$$

where  $g_\alpha(r)$  is a continuous tanh-like function expressing the gradual distribution of structural charges from the core/shell interface ( $r = a$ ) to the bulk electrolyte solution ( $r \rightarrow \infty$ ). The function  $g_\alpha(r)$  satisfies the condition  $g_\alpha(r \rightarrow \infty) \rightarrow 0$ , which expresses the required vanishing of the polymeric shell and its structural charges for  $r \rightarrow \infty$ . The length  $\alpha$  characterizes the extent of diffuseness of the interphase, i.e., the degree of inhomogeneity of the radial soft material distribution across the shell/solution interphase. In the limit  $\alpha \rightarrow 0$ ,  $g_{\alpha \rightarrow 0}(a \leq r < a+d) = 1$  and  $g_{\alpha \rightarrow 0}(r \geq a+d) = 0$  so that the density of charges  $\rho_{\text{fix}}(r)$  becomes independent of  $r$  within the shell ( $\rho_{\text{fix}}(a \leq r < a+d) = \rho_o$ ) and is zero outside the shell. This situation is that of a step function-like soft interphase. The dimensionless parameter  $\chi$  involved in eq 7 ensures the required conservation of charges amount upon modification of the soft material density distribution, i.e., when the diffuseness degree  $\alpha/d$  of the interphase is varied (see details in ref 12). In the limit  $\alpha \rightarrow 0$  that we shall consider in section 4 below, we have  $\chi \rightarrow 1$ . After eqs 5–7 are combined, the distribution of the dimensionless potential  $y = zF\psi/RT$  at the diffuse soft particle/solution interphase is given by the Poisson–Boltzmann type of equation

$$\begin{aligned} d^2y(X)/dX^2 + 2(X + \kappa a)^{-1} dy(X)/dX \\ - \sinh(y(X)) = \bar{\rho}_o g_\alpha(r) \end{aligned} \quad (8)$$

with  $X = \kappa(r - a)$  is the dimensionless space variable,  $\kappa$  is the reciprocal Debye length defined by eq 4, and  $\bar{\rho}_o = -\rho_o/(2zFc^*)$ . Modifications of eq 8 to include the pH and ionic-strength dependence of the density of charges carried by the particle as well as the impact of free protons and hydroxyl ions in solution (when present in amounts comparable to that of ions from background electrolyte) may be straightforwardly incorporated along the lines detailed elsewhere.<sup>14,15</sup> One of the two required boundaries associated with the above nonlinear differential equation of the second-order expresses bulk electroneutrality condition at large distances from the particle, i.e.

$$y(X \rightarrow \infty) \rightarrow 0 \quad (9)$$

The second boundary condition reflects the electrostatic state of the particle core surface. Depending on the nature of the system investigated, the latter may be written in terms of a surface potential,  $\psi_o$ , or a surface charge density,  $\sigma_o$ , i.e.

$$\begin{aligned} y(X=0) &= y_o \quad \text{or} \\ dy(X)/dX|_{X=0} &= -\bar{\sigma}_o \end{aligned} \quad (10a, b)$$

where  $y_o$  and  $\bar{\sigma}_o$  are the dimensionless surface potential and surface charge density defined by  $y_o = zF\psi_o/RT$  and  $\bar{\sigma}_o = zF\sigma_o/(RT\varepsilon_o\varepsilon_r\kappa)$ , respectively. For the practical case of a porous particle devoid of a core, the boundary defined in eq 10 is replaced by

$$dy(X)/dX|_{X=0} = 0 \quad (11)$$

which expresses the symmetry of the potential distribution around the center of the particle.

### 3.2. Numerical Evaluation of the Potential Distribution and Its Impact on Ion Diffusion to a Charged Soft Particle.

The complexity of eqs 8–11 requires numerical procedures for deriving the electrostatic potential distribution  $y(X)$ . For that purpose, we developed a Fortran 77 program and used the subroutine COLSYS that approximates the solution through spline collocation at Gaussian nodes and selects the mesh subdivision following an autoadaptive strategy.<sup>16</sup> The prescribed accuracy for the searched potential  $y(X)$  and electric field  $dy(X)/dX$  was set to  $10^{-5}$ , a value that ensures fast convergence. Using the dimensionless space and potential variables introduced above,  $X$  and  $y(X)$ , respectively, the expression for the local electrostatic correction factor  $f_{\text{el}}$  (eq 2) for the conductive diffusion of a cation  $M$  with charge  $z_M$  from the bulk solution to a position  $r$  within the particle shell becomes a function of  $r$  (or  $X$ ) according to

$$\begin{aligned} f_{\text{el}}(X) &= [(\kappa a + X) \int_X^\infty (\kappa a + u)^{-2} \\ &\times \exp(z_M y(u)/z) du]^{-1} \end{aligned} \quad (12)$$

where  $u$  is a dimensionless dummy integration variable. Once the potential distribution  $y(X)$  had been determined according to the aforementioned numerical strategy, the integral involved in eq 12 was evaluated using the Simpson rule.<sup>17</sup> The function  $f_{\text{el}}(X)$  could then be estimated for an arbitrary set of discrete positions  $X_{j=1,\dots,N}$  within the shell volume, where  $N$  is an integer satisfying  $N \gg 1$ . The overall effective  $\bar{f}_{\text{el}}$  that pertains to the conductive diffusion of the ion  $M$  toward the entire shell volume of a soft particle, may then be written in the form

$$\bar{f}_{\text{el}} = 3\kappa^{-3} \int_0^{\kappa d} (X + \kappa a)^2 f_{\text{el}}(X) dX / [(a + d)^3 - a^3] \quad (13)$$

which holds for  $\alpha \rightarrow 0$ . For cases where  $\alpha > 0$ , the spatial boundary between the diffuse shell particle and the medium cannot be defined unambiguously so that  $d$  loses the physical meaning it has for uniform soft surface layers. In such situations, the upper boundary  $\kappa d$  in the integral of eq 13 may be replaced by  $\kappa d(1 + 2.3\alpha/d)$ , which corresponds to the position where the density of charges  $\rho_{\text{fix}}$  (eq 7) is only  $\sim 1$ –2% of the value  $\rho_o$  in the bulk shell volume.<sup>12</sup> Estimation of  $\bar{f}_{\text{el}}$  on the basis of eq 13 was performed after integrating the spline-interpolated form of  $f_{\text{el}}(X_{j=1,\dots,N})$  according to the trapeze method.<sup>17</sup> For cases where the metal ion  $M$  is able to reach only a defined fraction of the shell volume, eq 13 can be easily extended by appropriate change of the boundaries in the involved integral and modification of the volume normalization term appearing in the denominator.



**3.3. Limiting Situations for Low Potential and Extreme Values of  $\kappa r_p$ .** It will be useful to compare the rigorous result computed on the basis of the numerical algorithm described in the previous section with semianalytical expressions of  $f_{el}(X)$  that we derive below for a number of limiting situations. These include the low potential regime  $y(X) \ll 1$  and limiting situations of electric double layers that are infinitely thin or thick as compared to the soft particle radius, i.e.,  $\kappa r_p \gg 1$  (strong screening) and  $\kappa r_p \ll 1$  (weak screening) respectively.

**3.3.1. Low Potential Debye–Hückel Regime.** For cases where the local electrostatic potential  $y(X)$  satisfies the inequality  $y(X) \ll 1$  at any position  $X \geq 0$ , the  $\sinh(y(X))$  term in eq 8 may be linearized according to  $\sinh(y(X)) \sim y(X)$ . Then the resulting Debye–Hückel formulation of the Poisson–Boltzmann equation for a homogeneous shell ( $\alpha \rightarrow 0$ ) has the general solution

$$y(X) = \frac{A}{X + \kappa a} \exp(X) + \frac{B}{X + \kappa a} \exp(-X) + \frac{\bar{\rho}_o \exp(X)}{2(X + \kappa a)} \int_0^X (u + \kappa a) \exp(-u) g_\alpha(u) du - \frac{\bar{\rho}_o \exp(-X)}{2(X + \kappa a)} \int_0^X (u + \kappa a) \exp(u) g_\alpha(u) du \quad (14)$$

$$y(X) = \begin{cases} \frac{\bar{\rho}_o(1 + \kappa r_p)}{2} \frac{\exp(X - \kappa d)}{(X + \kappa a)} + \left( B + \frac{\bar{\rho}_o(\kappa a - 1)}{2} \right) \frac{\exp(-X)}{(X + \kappa a)} - \bar{\rho}_o & \text{for } X \leq \kappa d \\ \left\{ B - \frac{\bar{\rho}_o(\kappa a - 1)}{2} \left[ \frac{(\kappa r_p - 1)\exp(\kappa d)}{\kappa a - 1} - 1 \right] \right\} \frac{\exp(-X)}{(X + \kappa a)} & \text{for } X \geq \kappa d \end{cases} \quad (17a, b)$$

**3.3.2. Infinitely Thin Double Layer Regime ( $\kappa r_p \gg 1$ ).** Under the condition ( $y(X) \ll 1$ ), the expression 12 for the electrostatic correction to the rate of diffusion of an ion M from bulk solution ( $X \rightarrow \infty$ ) to a position  $X$  within the particle shell ( $0 \leq X \leq \kappa d$ ),  $f_{el}(X)$ , may be linearized and rewritten according to

$$f_{el}(X) = [1 + (z_M/z)(\kappa a + X) \times (\Omega_{out}^H + \Omega_{in}^H(X))]^{-1} \quad (18)$$

with

$$\Omega_{out}^H = \int_{\kappa d}^{\infty} (\kappa a + u)^{-2} y(u) du \quad (19)$$

and

$$\Omega_{in}^H(X) = \int_X^{\kappa d} (\kappa a + u)^{-2} y(u) du \quad (20)$$

The superscript H in  $\Omega_{out}^H$  and  $\Omega_{in}^H(X)$  denotes “high  $\kappa r_p$  regime”. The scalar  $\Omega_{out}^H$  represents the contribution of the electric double layer field located outside the soft particle ( $X \geq \kappa d$ ) whereas the function  $\Omega_{in}^H(X)$  corresponds to the conductive-diffusion of metal ions across the intraparticle electric double layer field, i.e., from the position  $X = \kappa d$  to the position  $X$ . After substitution of eq 17b into eq 19 and evaluation of the resulting integral, we obtain for  $\Omega_{out}^H$

where  $u$  is a dummy integration variable.  $A$  and  $B$  are constants that follow from the boundary conditions defined in eqs 9 and 10. The use of eqs 9 and 14 in the limit  $\alpha \rightarrow 0$  leads to

$$A = -(\bar{\rho}_o/2)(1 + \kappa a) \times [1 - (1 + \kappa r_p)(1 + \kappa a)^{-1} \exp(-\kappa d)] \quad (15)$$

The expression for the constant  $B$  depends on the core/shell interface conditions, i.e., whether a constant surface potential or a constant surface charge applies at the particle core surface. After straightforward algebraic manipulations, the combination of eqs 10 and 14 provides

$$B = \begin{cases} (\kappa a)y_o - A & \text{for } y(X=0) = y_o \\ (1 + \kappa a)^{-1}[(\kappa a)^2 \bar{\sigma}_o + (\kappa a - 1)A] & \text{for } dy(X)/dX|_{X=0} = -\bar{\sigma}_o \end{cases} \quad (16)$$

where  $A$  is given by eq 15. By combining eqs 10, 14, and 15, we may write the expressions for the electrostatic potential distribution inside and outside the shell, within the framework of the Debye–Hückel approximation ( $y(X) \ll 1$ ), in the form

$$\Omega_{out}^H = (\omega_o/2) \exp(\kappa a) \{E_-(\kappa r_p) - (\kappa r_p)^{-1} \times [1 - (\kappa r_p)^{-1}] \exp(-\kappa r_p)\} \quad (21)$$

where  $\omega_o$  is given by  $\omega_o = B - [\bar{\rho}_o(\kappa a - 1)/2][1 - (\kappa r_p - 1)\exp(\kappa d)/(\kappa a - 1)]$  and  $E_-(x) = \int_x^\infty u^{-1} \exp(-u) du$  is a tabulated exponential integral function. Following a similar procedure, the combination of eqs 17a and 20 leads to

$$\Omega_{in}^H(X) = \bar{\rho}_o[(\kappa r_p)^{-1} - (X + \kappa a)^{-1}] + \frac{\omega_+}{2} \left\{ [E_+(X + \kappa a) - E_+(\kappa r_p)] \exp(-\kappa r_p) + \left[ \frac{1 + (X + \kappa a)^{-1}}{X + \kappa a} \right] \exp(X - \kappa d) - \left[ \frac{1 + (\kappa r_p)^{-1}}{\kappa r_p} \right] \right\} + \frac{\omega_-}{2} \left\{ [E_-(X + \kappa a) - E_-(\kappa r_p)] \exp(\kappa a) + \left[ \frac{1 - (\kappa r_p)^{-1}}{\kappa r_p} \right] \exp(-\kappa d) - \left[ \frac{1 - (X + \kappa a)^{-1}}{X + \kappa a} \right] \exp(-X) \right\} \quad (22)$$

where the constants  $\omega_+$  and  $\omega_-$  are defined by  $\omega_+ = \bar{\rho}_o(1 + \kappa r_p)/2$  and  $\omega_- = (B + \bar{\rho}_o(\kappa a - 1)/2)$ , respectively, and the exponential integral function  $E_+(x)$  is given by  $E_+(x) = \int_x^\infty u^{-1} \exp(u) du$ . The set of eqs 18, 21, and 22

define the local electrostatic correction  $f_{\text{el}}(X)$  for the diffusion of the ion  $M$  from the bulk solution toward a position  $X$  within the charged particle shell. These semianalytical equations are valid for sufficiently low local potentials at any position from the particle core surface to the electrolyte bulk solution ( $y(X) \ll 1$ ). In particular, this condition is met for an efficient screening of the particle charge by ions present in the electrolyte medium (providing  $y_0 \ll 1$ ). It is therefore achieved for sufficiently large electrolyte concentrations or, for that matter, sufficiently compressed electric double layers ( $\kappa r_p \gg 1$ ). For the practical case of conductive diffusion of an ion  $M$  from bulk solution to the outer periphery of a charged core/shell particle ( $X = \kappa d$ ), we have  $\Omega_{\text{in}}^{\text{H}}(X) = 0$  and eq 18 then reduces to

$$f_{\text{el}}(X = \kappa d) = \{1 + [z_M \omega_0 / (2z)] \exp(\kappa a) \times \{(\kappa r_p) E_-(\kappa r_p) - [1 - (\kappa r_p)^{-1}] \times \exp(-\kappa r_p)\}\}^{-1} \quad (23)$$

The limit of a hard particle is retrieved upon replacing  $\kappa d$  and  $\kappa r_p$  in eq 23 by 0 and  $\kappa a$ , respectively. It is useful to note that in this limit we further have  $\omega_0 = B$  and  $A = 0$ .

**3.3.3. Infinitely Thick Electric Double Layer Regime ( $\kappa r_p \ll 1$ ).** For sufficiently low bulk electrolyte concentration  $c^*$  the thickness of the electric double layer may well exceed the size of the soft particle, i.e.,  $\kappa r_p \ll 1$ . To account for the impact of the electric double layer field on the diffusion of a metal toward a position  $X$  within the shell for such a situation, we now write  $f_{\text{el}}(X)$  in the form

$$f_{\text{el}}(X) = \{(\kappa a + X)(\Omega_{\text{out}}^{\text{L}} + \Omega_{\text{in}}^{\text{L}}(X))\}^{-1} \quad (24)$$

with

$$\Omega_{\text{out}}^{\text{L}} = \int_{\kappa d}^{\infty} (\kappa a + u)^{-2} \exp(z_M y(u)/z) du \quad (25)$$

and

$$\Omega_{\text{in}}^{\text{L}}(X) = \int_X^{\kappa d} (\kappa a + u)^{-2} \exp(z_M y(u)/z) du \quad (26)$$

The superscript L in  $\Omega_{\text{out}}^{\text{L}}$  and  $\Omega_{\text{in}}^{\text{L}}(X)$  denotes “low  $\kappa r_p$  regime”. In the regime  $\kappa r_p \ll 1$ , it is sufficient to conserve the first-order term in the Taylor expansion of the electric double layer field in terms of the power law for  $\kappa r$  or for that matter  $X$  so that the potential distribution (eqs 17a,b) derived from the linearized Poisson–Boltzmann equation simplifies to

$$y(X) \approx \begin{cases} (X + \kappa a)^{-1} \{\omega_+ \exp(-\kappa d)(1 + X) + \omega_-(1 - X)\} - \bar{\rho}_0 & \text{for } X \leq \kappa d \\ \omega_0(X + \kappa a)^{-1}(1 - X) & \text{for } X \geq \kappa d \end{cases} \quad (27a, b)$$

where  $\omega_0$ ,  $\omega_+$ ,  $\omega_-$ , and  $\bar{\rho}_0$  are the constants introduced before. By substituting eq 27b into eq 25, we obtain the following expression for  $\Omega_{\text{out}}^{\text{L}}$

$$\Omega_{\text{out}}^{\text{L}} = [z_M \omega_0 (1 + \kappa a) / z]^{-1} \exp(-z_M \omega_0 / z) \times \{\exp[z_M \omega_0 (1 + \kappa a) (\kappa r_p)^{-1} / z] - 1\} \quad (28)$$

Combining eq 27a and eq 26 and performing the integration further yields

$$\begin{aligned} \Omega_{\text{in}}^{\text{L}}(X) = & (z/z_M) [\omega_+ (1 - \kappa a) \exp(-\kappa d) \\ & + \omega_- (1 + \kappa a)]^{-1} \exp(-z_M \bar{\rho}_0 / z) \\ & \times [\exp\{(z_M/z)(X + \kappa a)^{-1} [\omega_+ (1 + X) \\ & \times \exp(-\kappa d) + \omega_- (1 - X)]\} \\ & - \exp\{(z_M/z)(\kappa r_p)^{-1} [\omega_+ (1 + \kappa d) \\ & \times \exp(-\kappa d) + \omega_- (1 - \kappa d)]\}] \quad (29) \end{aligned}$$

The set of eqs 24, 28, and 29 define the function  $f_{\text{el}}(X)$  in the regime  $\kappa r_p \ll 1$  provided that the condition  $y(X) \ll 1$  is satisfied, recalling that the linearized form of the Poisson–Boltzmann equation (eq 17) serves as a basis for the mathematical developments. Starting from eqs 28 and 29, we show that in the limit  $\kappa r_p \ll 1$  the conductive diffusion of an ion  $M$  from bulk solution to the outer periphery of a core/shell particle ( $X = \kappa d$ ) is given by

$$f_{\text{el}}(X = \kappa d) = [z_M \omega_0 (1 + \kappa a) (\kappa r_p)^{-1} / z] \exp(z_M \omega_0 / z) \times \{\exp[z_M \omega_0 (1 + \kappa a) (\kappa r_p)^{-1} / z] - 1\}^{-1} \quad (30)$$

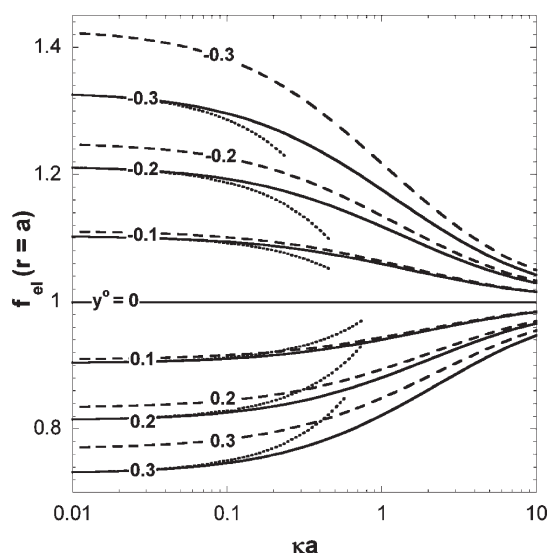
which is the counterpart of eq 23 previously derived for  $\kappa r_p \gg 1$ . For the hard particle case ( $\kappa d = 0$ ), eq 30 further simplifies to

$$f_{\text{el}}(X = 0) = [z_M B (1 + \kappa a) (\kappa a)^{-1} / z] \exp(z_M B / z) \times \{\exp[z_M B (1 + \kappa a) (\kappa a)^{-1} / z] - 1\}^{-1} \quad (31)$$

with  $B = (\kappa a) y_0$  or  $B = (\kappa a)^2 \bar{\sigma}_0 / (1 + \kappa a)$  depending on the surface state of the particle considered. In the case of a hard particle (eq 31), it is possible to relate surface potential and surface charge realizing that the particle surface charge must be counterbalanced by the diffuse ionic charge distributed across the surrounding electric double layer, which in turn leads to  $y_0 = (\kappa a) \bar{\sigma}_0 / (1 + \kappa a)$ .<sup>11</sup> By substituting the definition of  $\bar{\sigma}_0 = z F \sigma_0 / (R T \epsilon_0 \epsilon_r \kappa)$  in the above relationship that connects  $y_0$  and  $\bar{\sigma}_0$ , we obtain  $y_0 = z_p z e^2 / [4 \pi a (1 + \kappa a) \epsilon_0 \epsilon_r k_B T]$  with  $k_B$  the Boltzmann constant and  $z_p e \equiv 4 \pi a^2 \sigma_0$  the total surface charge of the hard particle. In turn, for  $\kappa a \ll 1$ , eq 31 simplifies to

$$f_{\text{el}}(X = 0) = (l_B/a) \exp[(1 + \kappa a)^{-1} \kappa l_B] \times \{\exp(l_B/a) - 1\}^{-1} \quad (32)$$

where  $l_B = z_p z M e^2 / (4 \pi \epsilon_0 \epsilon_r k_B T)$  is the Bjerrum length. This equation is similar to the classical Coulombic Debye equation;<sup>4</sup> see section 2. The equivalence between eq 32 and the equation derived by Debye is clear after setting  $R_1 = R_2 = 2a$  ( $R_1$  and  $R_2$  are radii of colliding particles in Debye's notations), and realizing that the quantities  $\gamma = (1 + \kappa a)^{-1} \exp(\kappa a)$  introduced by Debye and  $(1 + \kappa a)$  involved in eq 32 are approximately unity in the regime  $\kappa a \ll 1$ , where linearization of the electrostatic potential distribution with respect to position (eq 27) is physically justified. The slight difference between eq 32 and Debye's expression is explained by his linearization of the potential distribution with respect to the position  $\kappa r$  and not to  $X = \kappa(r - a)$ . The latter, however, is the physically relevant space variable that encompasses all positions accessible by ions, recalling that the core is not permeable to ions.



**Figure 2.** Electrostatic correction factor  $f_{el}$  at the position  $r = a$  for a hard particle of radius  $a = 40$  nm and surface potential  $y_0$  ( $|y_0| \leq 0.3$ , indicated). Numerical results (solid lines) are reported as a function of dimensionless  $\kappa a$ . Dashed lines: evaluation from eqs 18, 21, and 22 valid under Debye–Hückel condition ( $|y(r)| \ll 1$ ) (section 3.3.2). Short dotted lines: evaluation from eqs 24, 28, and 29 valid under Debye–Hückel condition in the thick double layer limit ( $\kappa a \ll 1$ ) (section 3.3.3).

#### 4. COMPUTATIONAL RESULTS FOR SOME EXAMPLE CASES

Using the numerical procedure outlined in section 3, we now proceed to computing the properties of the conductive transport coefficient  $f_{el}$  for a number of basic types of particles. The results will be given as a function of  $\kappa a$  for core-only and core/shell particles, or  $\kappa d$  for entirely porous particles. As much as possible, comparison will be made between the rigorous numerical result and the outcome for the analytical expressions in the linearized low-potential regime and the thick or thin double layer regimes ( $\kappa r_p \ll 1$  and  $\kappa r_p \gg 1$ , respectively).

**4.1. Hard Particle Limit.** We consider the diffusion of a cation  $M$  with  $z_M = 2+$  to a core-only particle with a fixed surface potential  $y_0$ . In Figure 2, the dependence of  $f_{el}(X=0)$  (or  $f_{el}(r=a)$ ) on  $\kappa a$  is presented for a broad range of values of  $y_0$ , covering both negatively and positively charged surfaces. As a consequence,  $f_{el}(r=a)$  covers both the acceleration regime ( $f_{el}(r=a) > 1$ ) and the retardation regime ( $f_{el}(r=a) < 1$ ). The computational range covers a wide range of  $\kappa a$  values from well below to well above unity. Evidently, all curves tend to unity for  $\kappa a$  approaching infinity, i.e., for a complete compression of the particle double layer by ions in the medium. This corresponds to the situation where the effective gradient in electric potential at the particle/solution interface is much steeper than the gradient in the reactant concentration  $c_M$ . Hence, the conductive acceleration/retardation is of a very local nature, covering only a small fraction of the diffusive gradient of  $M$ . In other words, for large  $\kappa a$  the coefficient  $f_{el}(r=a)$  incorporates no more than a brief enhancement/reduction (scale of  $1/\kappa$ ) of the transport rate over the relatively long distance (scale of  $a$ ) to the particle surface. Note that the acceleration and retardation regimes of  $f_{el}(r=a)$  are not symmetrical with respect to each other: a very strong local potential jump may significantly slow down diffusion whereas acceleration

remains limited. The figure also compares the numerical solution with the small particle/thick double layer limit where  $\kappa a$  is much less than unity. As demonstrated in section 3.3.3, this limit leads us to the situation of essentially Coulombic interaction and applicability of the corresponding Debye type relationship between  $f_{el}(r=a)$  and particle charge. Indeed, our results illustrate that eq 32 holds very well in the regime of  $\kappa a$  below 0.1. The low-potential Debye–Hückel regime (section 3.3.2) applies over the whole range of  $\kappa a$  but loses accuracy for normalized surface potentials beyond few tens of millivolts. The discrepancy between numerical and analytical results then becomes significant with decreasing  $\kappa a$ , i.e., with increasing the magnitude of the local potentials across the electric double layer. In turn, the use of the linearized Poisson–Boltzmann equation for evaluating  $f_{el}(r=a)$  (section 3.3.1) at low  $\kappa a$ , is rendered approximate.

It appears that for particles with a modest charge, the impact of conductive effects on the diffusive transport of ions toward the surface is fairly modest with  $f_{el}(r=a)$  ranging between 0.7 and 1.3 in the most sensitive low  $\kappa a$  domain under the conditions of particle surface potential and particle size of Figure 2. For highly charged particles, however, the picture is changing drastically, as illustrated by Figure 3. For very small  $\kappa a$  and  $a = 40$  nm, the Coulombic thick double layer limit still works well, *albeit* that with increasing charge one has to go to smaller and smaller  $\kappa a$  to reach agreement with the rigorous solution. Obviously, with  $M^{2+}$  ions the low potential Debye–Hückel limit at large  $\kappa a$  is utterly useless in the potential regime beyond some 10 mV.

**4.2. Core/Shell Particle.** Here we consider an example core/shell particle with a core radius,  $a$ , of 40 nm and a shell thickness,  $d$ , of 20 nm. The conductive coefficient was calculated for  $r = a$ , implying that we count the transport of an  $M^{2+}$  ion all the way through the shell layer to the supposedly reactive core surface. In the case where reactive sites are also contained in the shell, an average  $\bar{f}_{el}$  should be invoked for the reaction of  $M^{2+}$  with the shell sites (see section 3.2, eq 13, and section 4.3 below on the completely porous particle case). The present example case (Figure 4A) holds for a core with a fixed negative surface potential ( $y_0 = -1$ ) and a range of space charge densities in the shell, covering both positive and negative charge densities  $\rho_0$ . Note that for  $\rho_0 = 0$  we retrieve the hard particle limit as discussed in section 4.1 above. As expected, a negative shell charge compounds the acceleration of  $M^{2+}$  on its way to the particle. However, for positively charged shells, “anomalous” dependencies of  $f_{el}(r=a)$  on  $\kappa a$  may result. For  $\rho_0/F$  on the order of  $1 \text{ mol m}^{-3}$  (1 mM),  $f_{el}(r=a)$  increases from less than unity for very low ionic strength ( $\kappa a < 1$ ) to a maximum well above unity in the millimolar ionic strength regime. With the shell charge increasing to more and more positive charges,  $f_{el}(r=a)$  is strongly reduced over a broad range of  $\kappa a$  values. Here the repelling effect of the shell on the incoming  $M^{2+}$  is dominant over the eventual attraction by the negative core surface. By combining different core potentials and shell charges, we may envisage many variations of this theme. These variations are connected to the diverse ways in which the interphasial double layer field distribution is affected by the electrolyte concentration in case of particles characterized by shell charge and core potential/charge of different signs. For further details, the reader is referred to the work by Duval et al. on electrostatics of multilayered soft interphases.<sup>18</sup> Parts B and C of Figure 4 illustrate the accuracy of the semianalytical expressions derived for  $f_{el}$  in the high and low  $\kappa a$  regimes (eqs 18, 21, 22 and eqs 24, 28, 29, respectively). Although the expressions for  $\kappa a \gg 1$

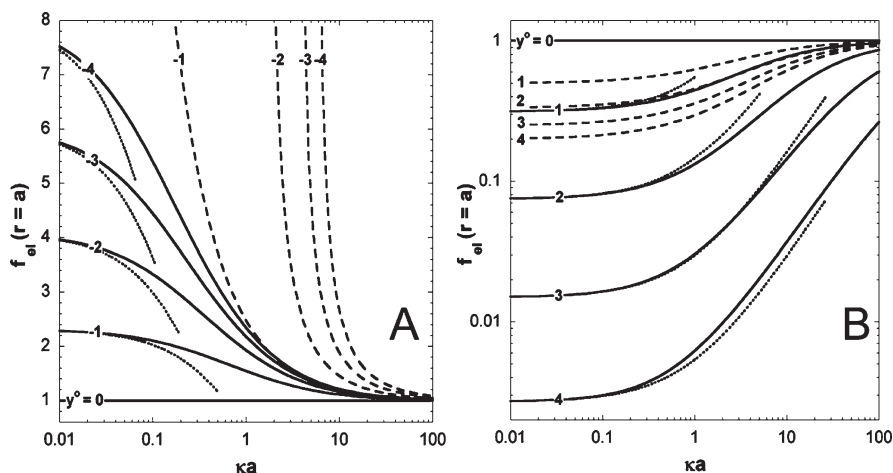


Figure 3. As in Figure 2 with  $|y_o| \geq 1$ .

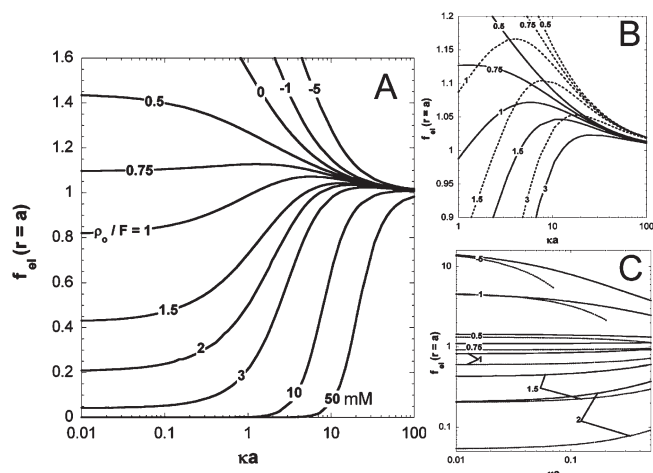


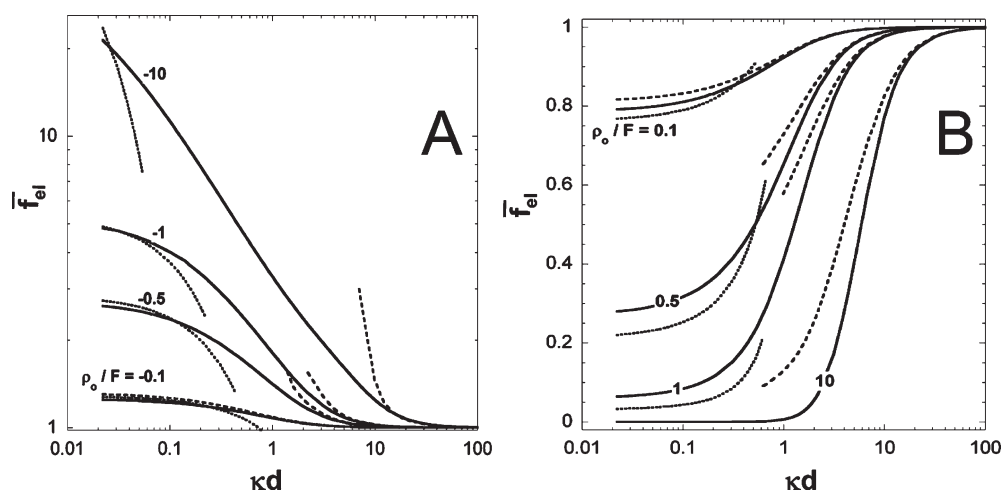
Figure 4. Electrostatic correction factor  $f_{el}$  at the position  $r = a$  for a soft particle of radius  $a = 40$  nm and shell thickness  $d = 20$  nm. Numerical results (solid lines) are reported as a function of dimensionless  $\kappa a$ . The potential at the core particle surface is  $y_o = -1$  and the volume charge density within the shell is  $\rho_o$ . Indicated are the equivalent molar concentrations of charges in the shell, i.e.,  $\rho_o/F$ . In inset (panel B), top, zoom on the maximum in  $f_{el}$  vs  $\kappa a$  curves. Dashed lines: estimations from eqs 18, 21, and 22 valid under Debye–Hückel condition ( $|y(r)| \ll 1$ ) (section 3.3.2). In the inset (panel C), down, zoom on  $f_{el}$  vs  $\kappa a$  curves in the low  $\kappa a$  regime. Short dotted lines: estimations from eqs 24, 28, and 29 valid under Debye–Hückel condition in the thick double layer limit ( $\kappa a \ll 1$ ) (section 3.3.3).

qualitatively predict the existence of a maximum in  $f_{el}(r = a)$  with  $\kappa a$  (Figure 4B), in agreement with numerical results, they fail to reproduce the position and magnitude of that maximum. This is because the chosen electrostatic properties of the particle are not compatible with the conditions underlying the validity of eqs 18, 21, and 22. Interestingly, the low  $\kappa a$  expression quantitatively matches the asymptotic behavior of  $f_{el}(r = a)$  at sufficiently low  $\kappa a$  for core potential and shell charge that are of the same sign (Figure 4C). Important discrepancies, however, show up upon increasing the shell charge. In general, the appropriateness of eqs 24, 28, and 29 is subject to the accuracy in both (i) linearizing the Poisson–Boltzmann equation (eq 17, section 3.3.1) and

(ii) linearizing the so-obtained potential distribution with respect to position (eq 27, section 3.3.3).

**4.3. Porous Particle Limit.** In our modeling procedure, the completely porous particle case is retrieved for a virtually absent core, i.e., for  $a/d \rightarrow 0$ . The particle charge is randomly distributed over the particle body (i.e.,  $\alpha \rightarrow 0$ , sharp shell/medium interface, section 3.1, eq 7) and characterized by the immobile space charge density  $\rho_o$ . In this case the numerical computations of the conductive contribution should be expressed by  $\bar{f}_{el}$ , which is an integral form of  $f_{el}(r)$ , as outlined in section 3.2. Figure 5 shows some sets of results for  $\bar{f}_{el}$  as a function of  $\kappa d$  for  $d = 30$  nm and various values of the molar charge density  $\rho_o/F$  (mol m<sup>-3</sup>). It is immediately clear that charge densities may have a drastic impact on the rate of supply of ions from the medium, especially so in the small particle/thick double layer domain ( $\kappa d$  below unity). The feature will be quite important for nanoparticles in low ionic strength media. For example, for the 30 nm particle of Figure 5 with a 10 mM negative charge density dispersed in an aqueous medium with 0.1 mM ionic strength, the average acceleration of divalent counterions will be as high as a factor of about 5, whereas the retardation of divalent co-ions will be reduced by an even much larger factor (Figure 5A,B, respectively). This asymmetry is of the same nature as the one discussed in section 4.1 above (Figures 2 and 3). Under the conditions of Figure 5, the expression derived for  $\bar{f}_{el}$  (or equivalently  $f_{el}(0 < r < d)$ ) in the large  $\kappa a$  regime is of limited use for quantitatively reproducing the numerically obtained  $\bar{f}_{el}$  for  $\kappa d > 1$ . The thick double layer/small particle approach (section 3.3.3) satisfactorily reproduces the rigorous result in the very small  $\kappa d$  regime. Upon an increase of the particle charge, the agreement is met for smaller  $\kappa d$ . At fixed  $\kappa d$ , such an increase in particle charge density is indeed accompanied by an increase in the magnitude of the local potential, which in turn magnifies the inaccuracy of the expressions derived in section 3.3.3. Lower  $\kappa d$  values are then required to recover the basic Coulombic Debye regime to strengthen the impact of the extra-particulate field on M ion diffusion and diminish that of the field inside the particle, both effects being in line with a better fulfilling of the conditions underlying the validity of eqs 24, 28, and 29.





**Figure 5.** Electrostatic correction factor  $\bar{f}_{el}$  (eq 13) for a porous particle devoid of core ( $a \rightarrow 0$ ,  $d = 30$  nm) at various values of  $\rho_o/F$  (panel A,  $\rho_o/F < 0$ ; panel B,  $\rho_o/F > 0$ ). Numerical results (solid lines) are reported as a function of dimensionless  $\kappa d$ . Dashed lines: evaluation from eqs 18, 21, and 22 valid under Debye–Hückel condition ( $|y(r)| \ll 1$ ) (section 3.3.2). Short dotted lines: estimations from eqs 24, 28, and 29 valid under Debye–Hückel condition in the thick double layer limit ( $\kappa d \ll 1$ ) (section 3.3.3).

## 5. CONCLUSION AND OUTLOOK

Starting from Debye’s classical analysis of collisions between dispersed particles by conductive diffusion,<sup>4</sup> we developed a generalized theory for rates of reactions between ions and nanoparticles/colloids. It utilizes the nonlinear Poisson–Boltzmann equation, which is applicable to any electrostatic configuration and incorporates Debye’s Coulombic approach as a specific limiting case. A numerical procedure was developed for evaluating the electrostatic potential profile at the interphase between a spherical core/shell particle and an aqueous electrolyte solution. The profile is crucial because it represents the electric force exerted on ions that are diffusing toward the particle body. An integration procedure eventually yields the rigorous numerical solution of the conductive diffusion flux that governs the rate of reactions between ions and nanoparticles/colloids. Semianalytical solutions of the problem were found for extreme values of the ratio between particle radius and Debye screening length. Computations for a few example cases (core/shell, core only (“hard”) and shell only (“porous or soft”)) confirm the limitations in the applicability of all nonrigorous approaches.

With the current results at hand, it will be most interesting and challenging to confront the newly developed theory with experimental rate data on ion binding by nanoparticles/colloids. At the same time, it will be desirable to further expand the theoretical framework so as to include other geometries of particles and conductive diffusion fields and account for differentiated physical properties of the particle shell and core (e.g., permittivity, conductivity, viscosity, charge distribution). In addition, the coupling of core and shell charges to medium conditions should be given some attention, in particular the dependence on pH of core/shell charges and the distinction between colloidal constant potential and constant charge conditions. Limitations of shell ion permeabilities could play a central role too in the composition of the interphasial electric double layer developed around/within given types of biological particles. Finally, the coupling of ionic reactions with relaxation of the interphasial electric field (transient electrodynamics) is expected to be of utmost importance in situations where there is no excess of background

electrolyte or where Boltzmann relaxation for minor ions with high charge is involved.

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## LIST OF MAIN SYMBOLS AND ABBREVIATIONS

$a$	radius of the particle core
$A$	integration constant defined by eq 15
$B$	integration constant defined by eq 16
$c_M^*$	bulk concentration of metal ions M
$c^*$	bulk concentration of background electrolyte
$d$	thickness of the particle shell
$\bar{f}_{el}$	average conductive-diffusion correction factor for the diffusive flux of an ion to a porous particle
$f_{el}(X)$	local conductive-diffusion correction factor for the flux of an ion diffusing from/to a position $X$ in the particle shell
$D_P$	diffusion coefficient of a soft particle
$D_M$	diffusion coefficient of a metal ion M
$E_{\pm}(x)$	tabulated exponential integral functions
$g_{\alpha}(r)$	function defining the radial distribution of fixed immobile sites across the particle shell
$J_M^*$	steady state diffusion flux of an ion M from/toward a ligand colloidal particle
$k_B T$	thermal energy
$l_B = z_p z_M e^2 / (4\pi\epsilon_o \epsilon_r k_B T)$	Bjerrum length
M	metal ion
$r$	radial position
$r_M$	radius of a metal ion M
$r_p$	radius of a soft particle ( $r_p = a + d$ )

$U(r)$	local electrostatic interaction energy
$\omega_+$	constant defined in section 3.3.2
$\omega_-$	constant defined in section 3.3.2
$\omega_o$	constant defined in section 3.3.2
$X$	dimensionless space variable
$y(r)$	local dimensionless electrostatic potential
$y_o$	dimensionless potential at the particle core surface
$z$	valence of the symmetrical background electrolyte considered in the study
$z_M$	valence of the metal ion M
$z_p$	valence of the particle when viewed as a point-like charge
$\alpha$	characteristic length reflecting the soft material density gradient within the particle shell component
$\sigma_o$	charge density at the particle core surface
$\bar{\sigma}_o$	dimensionless charge density at the particle core surface
$\psi(r)$	local electrostatic potential at the soft particle/aqueous medium interphase
$\psi_o$	potential at the particle core surface
$\kappa^{-1}$	Debye length
$\rho_o$	space charge density in the particle shell
$\bar{\rho}_o$	dimensionless space charge density in the particle shell
$\varepsilon = \varepsilon_o \varepsilon_r$	dielectric permittivity of the medium outside and within the particle shell
$\nu$	collision frequency between two ions or particles

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