

Generalization of a Classic Thin Double Layer Polarization Theory of Colloidal Suspensions to Electrolyte Solutions with Different Ion Valences

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The classic Dukhin–Shilov theory for the thin double layer polarization of colloidal suspensions in binary electrolyte solutions was developed for symmetric electrolytes: equal counterion and co-ion valences. A rigorous generalization of this theory to asymmetric electrolytes, such that the valence of counterions is double or half the valence of co-ions, is presented. This generalization is possible because analytical solutions of the intervening integrals exist for these two particular cases but do not exist in the general case of different counterion and co-ion valences, a result apparently overlooked or ignored in the past.

Introduction

The classic Dukhin–Shilov theory for the thin double layer polarization of colloidal suspensions in binary electrolyte solutions was developed considering that both ion species have the same valence.^{1,2} This requirement has a purely mathematical nature: analytic expressions for the intervening integrals do not exist for the general case $z^+ \neq z^-$ (z^\pm are the unsigned ion valences). Nevertheless, a generalization has been made,³ but it is based on approximate solutions for the equilibrium potential in the double layer.

In what follows, we show a result apparently overlooked since the development of the theory in the early 1970s: while it is true that there is no analytic solution in the general case $z^+ \neq z^-$, analytic results do exist in the all-important cases $z^+ = 2z^-$ and $z^- = 2z^+$ (this was already shown in 1953,⁴ mentioned in 1961,⁵ but apparently ignored in later works). We use these solutions to generalize the theory and obtain new expressions for the dipolar coefficient, conductivity increment, and electrophoretic mobility.

In doing this, and in view of the general lack of detail in the existing presentations of either the original Dukhin–Shilov theory or its extension to AC fields,^{1,2,6–8} we provide a full deduction, including all of the intermediate steps, assumptions, and justifications, that lead to the final solution. This might prove to be useful for future extensions of the theory intended to generalize the standard model.⁹

Equation Set

The classic Dukhin–Shilov counterion polarization theory is based on the *standard electrokinetic model*, the *thin double layer approximation*, and the principle of *local equilibrium*.

According to the *standard model*,¹⁰ a suspended particle is represented by an insulating sphere of radius a , with a uniform fixed surface charge density σ_0 . The surrounding electrolyte solution is characterized by its viscosity η_e , absolute permittivity ϵ_e , the unsigned valences of its ions z^\pm , their diffusion coefficients D^\pm , and their concentrations far from the particle $C^\pm(\infty)$.

Under steady state conditions, the ion concentrations $C^\pm(\vec{r})$, electric potential $\Phi(\vec{r})$, fluid velocity $\vec{V}(\vec{r})$, and pressure $P(\vec{r})$ are determined by the following set of equations:

(1) Nernst–Planck equations for the ion flows:

$$\vec{j}^\pm = -D^\pm \nabla C^\pm \mp C^\pm z^\pm D^\pm \nabla \Phi + C^\pm \vec{V} \quad (1)$$

where the symbol \sim denotes a dimensionless magnitude $\Phi = \Phi e / (kT)$.

(2) Continuity equations:

$$\nabla \cdot \vec{j}^\pm = 0 \quad (2)$$

(3) Poisson equation:

$$\nabla^2 \Phi = -(z^+ C^+ - z^- C^-) \frac{e}{\epsilon_e} \quad (3)$$

(4) Navier–Stokes equation:

$$\eta_e \nabla^2 \vec{V} - \nabla P = (z^+ C^+ - z^- C^-) e \nabla \Phi \quad (4)$$

(5) Condition of incompressible fluid:

$$\nabla \cdot \vec{V} = 0 \quad (5)$$

Equilibrium Equations

In equilibrium (lower index 0), both the ion and the fluid flows vanish, so that eq 1 reduces to

$$-\nabla C_0^\pm \mp C_0^\pm z^\pm \nabla \Phi_0 = 0$$

which can be integrated from a generic point to a point far from the particle, where the equilibrium potential is zero, to obtain

$$C_0^\pm = z^\mp N e^{\mp z^\pm \Phi_0} \quad (6)$$

In this expression, the concentration N is defined as

$$N = \frac{C^{\pm}(\infty)}{z^{\mp}} \quad (7)$$

in view of the condition of electroneutrality in the bulk far from the particle

$$z^+ C^+(\infty) - z^- C^-(\infty) = 0$$

In the most usual cases when at least one of the valences is equal to unity, the value of N coincides with the electrolyte concentration, as can be seen from eq 7.

Combining eq 6 with the equilibrium Poisson equation leads to the Poisson–Boltzmann equation for the electric potential:

$$\nabla^2 \tilde{\Phi}_0 = -\frac{z^+ z^- e^2 N}{\epsilon_s kT} (e^{-z^+ \tilde{\Phi}_0} - e^{z^- \tilde{\Phi}_0}) \quad (8)$$

Finally, the equilibrium Navier–Stokes equation reduces to

$$-\nabla P_0 = z^+ z^- N kT (e^{-z^+ \tilde{\Phi}_0} - e^{z^- \tilde{\Phi}_0}) \nabla \tilde{\Phi}_0$$

where eq 6 was used. Integrating this equation from a generic point to a point far from the particle, where the electric potential vanishes and the pressure reduces to a constant value $P(\infty)$, shows that

$$P_0 - P(\infty) = N kT (z^- e^{-z^+ \tilde{\Phi}_0} + z^+ e^{z^- \tilde{\Phi}_0} - z^+ - z^-) \quad (9)$$

Solution of the Poisson–Boltzmann Equation for a Flat Interface

While the Poisson–Boltzmann equation (eq 8) can only be solved analytically in spherical coordinates for low values of the electric potential, a general solution exists in the case of plane geometry. We so consider a flat charged surface and choose an orthogonal coordinate system with the x axis extending in the normal direction from the surface and toward the fluid. Under these conditions, eq 8 reduces to

$$\frac{d^2 \tilde{\Phi}_0}{dx^2} = \frac{z^+ z^- e^2 N}{\epsilon_s kT} (e^{-z^+ \tilde{\Phi}_0} - e^{-z^- \tilde{\Phi}_0})$$

which can be integrated one time from a generic point $(x, \tilde{\Phi}_0)$ to infinity $(x \rightarrow \infty, \tilde{\Phi}_0 = 0)$:

$$\frac{d\tilde{\Phi}_0}{dx} = -\text{sign}(\tilde{\Phi}_0) \kappa \sqrt{\frac{2}{z^+ + z^-} \left(\frac{e^{z^- \tilde{\Phi}_0} - 1}{z^-} + \frac{e^{-z^+ \tilde{\Phi}_0} - 1}{z^+} \right)} \quad (10)$$

where

$$\kappa = \sqrt{\frac{z^+ z^- (z^+ + z^-) e^2 N}{\epsilon_s kT}} \quad (11)$$

is the reciprocal Debye length.

Equation 10 can be integrated from the surface $(x = 0, \tilde{\Phi}_0 = \tilde{\zeta})$ to a generic point $(x, \tilde{\Phi}_0)$:

$$\int_{\tilde{\zeta}}^{\tilde{\Phi}_0} \frac{d\tilde{\Phi}_0}{\sqrt{\frac{2}{z^+ + z^-} \left(\frac{e^{z^- \tilde{\Phi}_0} - 1}{z^-} + \frac{e^{-z^+ \tilde{\Phi}_0} - 1}{z^+} \right)}} = -\text{sign}(\tilde{\zeta}) \kappa x$$

However, analytic results can only be obtained for $z^+ = z^- = z$, $z^+ = 2z^- = 2z$, and $2z^+ = z^- = 2z$. The solutions for these three cases, which we shall designate with the upper indices 11, 21, and 12, are

(11) For $z^+ = z^- = z$:

$$\frac{e^{z\tilde{\Phi}_0/2} - 1}{e^{z\tilde{\Phi}_0/2} + 1} = e^{-\kappa x} \frac{e^{z\tilde{\zeta}/2} - 1}{e^{z\tilde{\zeta}/2} + 1} \quad (12)$$

(21) For $z^+ = 2z^- = 2z$

$$\frac{\sqrt{2e^{z\tilde{\Phi}_0} + 1} - \sqrt{3}}{\sqrt{2e^{z\tilde{\Phi}_0} + 1} + \sqrt{3}} = e^{-\kappa x} \frac{\sqrt{2e^{z\tilde{\zeta}} + 1} - \sqrt{3}}{\sqrt{2e^{z\tilde{\zeta}} + 1} + \sqrt{3}} \quad (13)$$

(12) For $2z^+ = z^- = 2z$

$$\frac{\sqrt{1 + 2e^{-z\tilde{\Phi}_0}} - \sqrt{3}}{\sqrt{1 + 2e^{-z\tilde{\Phi}_0}} + \sqrt{3}} = e^{-\kappa x} \frac{\sqrt{1 + 2e^{-z\tilde{\zeta}}} - \sqrt{3}}{\sqrt{1 + 2e^{-z\tilde{\zeta}}} + \sqrt{3}} \quad (14)$$

It should be noted that eq 13 becomes identical to eq 14 if $-\tilde{\Phi}_0$ is substituted for $\tilde{\Phi}_0$ and $-\tilde{\zeta}$ for $\tilde{\zeta}$ in any one of them. This happens because when the sign of the charge of the particle is changed, counterions and co-ions exchange their roles. The dependence of the equilibrium potential on the ion valences, eqs 12–14, is represented in Figure 1, which also includes case 22: $z^+ = z^- = 2z$.

The surface potential ζ is a function of the surface charge σ_0 and of the electrolyte solution concentration. The explicit form of this dependence is determined by the Gauss law at the surface:

$$\left. \frac{d\tilde{\Phi}_0}{dx} \right|_{x=0} = -\frac{e \sigma_0}{kT \epsilon_s} \quad (15)$$

Note that this expression implies that the electric field only exists in the electrolyte solution $(x \geq 0)$, which is justified in view of the electroneutrality of the double layer. Combining eq 15 with eqs 10 and 11 gives

$$\frac{z^- e^{-z^+ \tilde{\zeta}} + z^+ e^{z^- \tilde{\zeta}} - z^+ - z^-}{z^+ z^- (z^+ + z^-)} = \frac{1}{2} \left(\frac{\sigma_0 e}{\kappa \epsilon_s kT} \right)^2 \quad (16)$$

For the considered cases, this result reduces to the following quadratic or cubic equations from which explicit expressions of $\tilde{\zeta}$ as a function of σ_0 can be obtained:

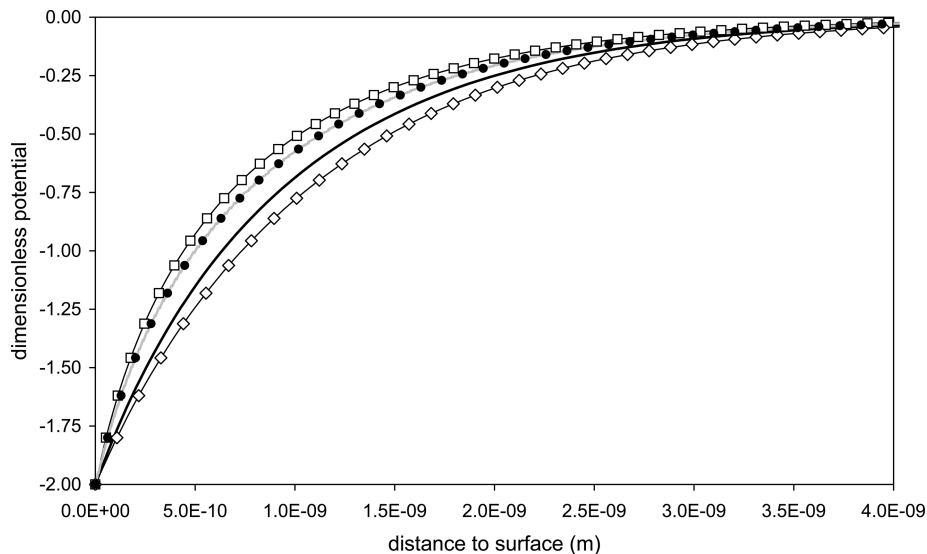


Figure 1. Equilibrium electric potential profiles calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

TABLE 1: System Parameters Used in All of the Figures, unless Specified Otherwise

particle radius	$a = 100 \times 10^{-9}$ m
electrolyte solution viscosity	$\eta_e = 8.90 \times 10^{-4}$ P
electrolyte solution absolute permittivity	$\epsilon_e = 78.54 \times \epsilon_0$
ion diffusion coefficients	$D^+ = D^- = 2 \times 10^{-8}$ m ² /s
ion concentrations such that	$\kappa a = 100$
dimensionless surface potential	$\tilde{\zeta} = -2$
temperature	298 K

(11) For $z^+ = z^- = z$

$$e^{2z\tilde{\zeta}} - \left[2 + \left(\frac{\sigma_0 z e}{\kappa \epsilon_e k T} \right)^2 \right] e^{z\tilde{\zeta}} + 1 = 0 \quad (17)$$

(21) For $z^+ = 2z^- = 2z$

$$2e^{3z\tilde{\zeta}} - 3 \left[1 + \left(\frac{\sigma_0 z e}{\kappa \epsilon_e k T} \right)^2 \right] e^{2z\tilde{\zeta}} + 1 = 0 \quad (18)$$

(12) For $2z^+ = z^- = 2z$

$$e^{3z\tilde{\zeta}} - 3 \left[1 + \left(\frac{\sigma_0 z e}{\kappa \epsilon_e k T} \right)^2 \right] e^{z\tilde{\zeta}} + 2 = 0 \quad (19)$$

As expected, the last two expressions become identical to one another if $-\tilde{\zeta}$ is substituted for $\tilde{\zeta}$ in any one of them.

The dependence of the surface potential on the surface charge for different values of the ion valences is represented in Figure 2. Note that the $\tilde{\zeta}^{21}$ and $\tilde{\zeta}^{12}$ curves are not antisymmetric with respect to the surface charge. As can be seen, the surface potential is determined almost exclusively by the charge of the counterions: $\tilde{\zeta}^{21} \approx \tilde{\zeta}^{11}$ and $\tilde{\zeta}^{12} \approx \tilde{\zeta}^{22}$ for positive particles, while $\tilde{\zeta}^{12} \approx \tilde{\zeta}^{11}$ and $\tilde{\zeta}^{21} \approx \tilde{\zeta}^{22}$ for negative ones. This is to be expected, since the number of counterions in the double layer is much higher than that of co-ions. Also, for a given surface charge, the surface potential strongly decreases with the counterion valence. This occurs because higher charged counterions are more strongly attracted by the surface charge and form, therefore, a thinner countercharge layer.

Solution with an Applied DC Electric Field

When a macroscopic DC electric field with amplitude E is applied to the system, eq 1 can be simplified writing the ion flows as

$$\vec{j}^\pm = -C^\pm D^\pm \nabla \tilde{\mu}^\pm + C^\pm \vec{V} \quad (20)$$

where $\tilde{\mu}^\pm = \mu^\pm/(kT)$ are the dimensionless electrochemical potentials:

$$\tilde{\mu}^\pm = \ln \frac{C^\pm}{z^\pm N} \pm z^\pm \Phi \quad (21)$$

These magnitudes have the important property that their gradient characterizes a departure from equilibrium, eq 20. Therefore, a system in equilibrium has constant values of the electrochemical potentials. This can be easily verified combining eqs 6 and 21, which show that $\tilde{\mu}_0^\pm = 0$ at all points of the electrolyte solution.

A further simplification consists of using the principle of *local equilibrium*. This principle, widely employed in nonequilibrium thermodynamics,^{11–13} states that every volume element of the system that is sufficiently small is in a state of equilibrium, even when different volume elements are not in equilibrium with one another. Accordingly, every volume element can be described using the same distribution function as for the whole system in equilibrium, except that the parameters involved vary now from one element to another.

In equilibrium, the system is characterized by its electric potential, Φ_0 ; ion concentrations, C_0^\pm ; and pressure, P_0 . Any volume element is in equilibrium with any other element. In particular, every volume element is in equilibrium with elements that are infinitely far away from the charged particle. These last elements are electroneutral and are characterized by their electric potential, $\Phi_0 = 0$; ion concentrations, $C_0^\pm = z^\mp N$; and pressure, $P_0 = P(\infty)$.

The equilibrium conditions, that is, the equations that relate the general values of the electric potential, ion concentrations, and pressure with the corresponding values far away from the particle, are given in eqs 6 and 9.

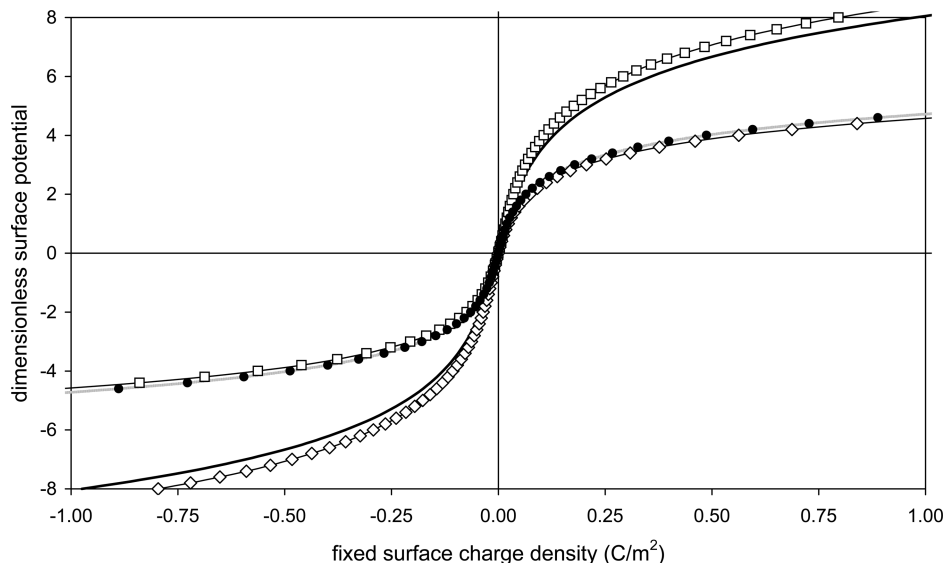


Figure 2. Equilibrium surface potential as a function of the fixed surface charge density, calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

Out of equilibrium, the system is characterized by its electric potential, Φ ; ion concentrations, C^\pm ; and pressure, P . Any volume element is assumed to be in a state of local equilibrium so that, in general, it is not in equilibrium with any other element of the system. However, its local equilibrium state can be expressed in terms of the parameters of a, so-called, *virtual system*. This system is defined by the conditions that each of its volume elements is in equilibrium with the corresponding element of the real system and, furthermore, by being electro-neutral in its entire volume. The virtual system is characterized by its electric potential, $\tilde{\varphi}$; ion concentrations, $c^\pm = z^\mp n$; and pressure, p , so that its electrochemical potential is

$$\tilde{\mu}^\pm = \ln \frac{n}{N} \pm z^\pm \tilde{\varphi} \quad (22)$$

The equations that relate the local equilibrium values of the electric potential, ion concentrations, and pressure of the real system with the corresponding values of the virtual system are given by expressions that are analogous to eqs 6 and 9:

$$C^\pm = z^\mp n e^{\mp z^\pm (\Phi - \tilde{\varphi})} \quad (23)$$

$$P - p = nkT [z^- e^{-z^+ (\Phi - \tilde{\varphi})} + z^+ e^{z^- (\Phi - \tilde{\varphi})} - z^+ - z^-] \quad (24)$$

Combining eqs 21 and 23 shows that the electrochemical potentials of the real and virtual systems have the same value, eq 22, so that at every point both systems are indeed in equilibrium with one another.

The main difference between eqs 23 and 24 and eqs 6–9 is that the parameters $\tilde{\varphi}$, n , and p of the virtual system depend on the position, while the equilibrium parameters have a constant value throughout the system. This position dependence of the virtual system parameters is a sufficient condition for nonequilibrium. Therefore, the irreversible thermodynamics equations (Nernst–Planck and Navier–Stokes equations) can only contain gradients of these parameters and cannot include gradients of quasiequilibrium distributions ($\tilde{\Phi} - \tilde{\varphi}$).

In order to be able to solve the problem, the equation set must first be linearized, writing all of the field-dependent magnitudes as an expansion in successive powers of the applied field strength:

$$\tilde{\Phi} = \tilde{\Phi}_0 + \delta\tilde{\Phi} + \dots$$

$$\tilde{\varphi} = \delta\tilde{\varphi} + \dots$$

$$n = N + \delta n + \dots$$

$$p = P(\infty) + \delta p + \dots$$

$$\tilde{V} = \delta\tilde{V} + \dots$$

$$\vec{j}^\pm = \delta\vec{j}^\pm + \dots$$

$$\tilde{\mu}^\pm = \delta\tilde{\mu}^\pm + \dots$$

where all of the magnitudes preceded by the δ character are linear in the applied field. These expansions are combined with the equation set, dropping all of the terms that are higher than first order in the applied field and making use of the equilibrium equations. This leads to

$$\delta\vec{j}^\pm = -C_0^\pm D^\pm \nabla \delta\tilde{\mu}^\pm + C_0^\pm \delta\vec{V} \quad (25)$$

$$\nabla \cdot \delta\vec{j}^\pm = 0 \quad (26)$$

$$\begin{aligned} \nabla^2 \delta\tilde{\Phi} = & [(z^+ z^+ C_0^+ + z^- z^- C_0^-) (\delta\tilde{\Phi} - \delta\tilde{\varphi}) - \\ & (z^+ C_0^+ - z^- C_0^-) \delta\tilde{n}] \frac{e^2}{\epsilon_e kT} \\ \eta_e \nabla^2 \delta\tilde{V} - \nabla \delta p = & kT (z^+ C_0^+ - z^- C_0^-) \nabla \delta\tilde{\varphi} + \\ & kT (C_0^+ - z^- N + C_0^- - z^+ N) \nabla \delta\tilde{n} \end{aligned} \quad (27)$$

$$\nabla \cdot \delta\vec{V} = 0 \quad (28)$$

where

$$\begin{aligned} \tilde{n} &= n/N \\ \delta\tilde{n} &= \delta n/N \\ \delta\tilde{\mu}^\pm &= \delta\tilde{n} \pm z^\pm \delta\tilde{\varphi} \end{aligned} \quad (29)$$

Combining eqs 25, 26, and 28 and using eqs 6 and 29 transforms the equation set into

$$\nabla^2 \delta \tilde{n} = z^+ z^- \left[\nabla \delta \tilde{\varphi} - \frac{D^- - D^+}{(z^+ + z^-) D^+ D^-} \delta \tilde{V} \right] \cdot \nabla \tilde{\Phi}_0$$

$$\nabla^2 \delta \tilde{\varphi} = \left[\nabla \delta \tilde{n} + (z^+ - z^-) \nabla \delta \tilde{\varphi} - \frac{z^+ D^- + z^- D^+}{(z^+ + z^-) D^+ D^-} \delta \tilde{V} \right] \cdot \nabla \tilde{\Phi}_0$$

$$\nabla^2 \delta \tilde{\Phi} = [(z^+ z^+ C_0^+ + z^- z^- C_0^-) (\delta \tilde{\Phi} - \delta \tilde{\varphi}) - (z^+ C_0^+ - z^- C_0^-) \delta \tilde{n}] \frac{e^2}{\epsilon_s kT}$$

$$\eta_c \nabla^2 \delta \tilde{V} - \nabla \delta p = kT (z^+ C_0^+ - z^- C_0^-) \nabla \delta \tilde{\varphi} + kT (C_0^+ - z^- N + C_0^- - z^+ N) \nabla \delta \tilde{n}$$

These equations greatly simplify in the electrolyte solution outside the boundary of the **equilibrium** double layer, where the equilibrium potential and the equilibrium charge density vanish ($\tilde{\Phi}_0 = 0$, $C_0^\pm = z^\mp N$):

$$\nabla^2 \delta \tilde{n} = 0$$

$$\nabla^2 \delta \tilde{\varphi} = 0$$

$$\nabla^2 \delta \tilde{\Phi} = \kappa^2 (\delta \tilde{\Phi} - \delta \tilde{\varphi})$$

$$\eta_c \nabla^2 \delta \tilde{V} = \nabla \delta p$$

The final simplification is achieved comparing the third expression with the Gauss equation:

$$\nabla^2 \delta \Phi = -\frac{\delta \rho}{\epsilon_c}$$

which shows that it is possible to define a dimensionless field-induced charge density:

$$\delta \tilde{\rho} = \frac{e}{\kappa^2 \epsilon_c kT} \delta \rho = -(\delta \tilde{\Phi} - \delta \tilde{\varphi})$$

This leads to the final equation set, valid outside the boundary of the equilibrium double layer:

$$\nabla^2 \delta \tilde{n} = 0$$

$$\nabla^2 \delta \tilde{\varphi} = 0$$

$$\nabla^2 \delta \tilde{\rho} = \kappa^2 \delta \tilde{\rho}$$

$$\eta_c \nabla^2 \delta \tilde{V} = \nabla \delta p$$

The appropriate solutions of the first two Laplace equations (the parts of the general solutions that do not diverge at infinity)

are

$$\delta \tilde{n} = \frac{K_c a^2}{r^2} \frac{e E a}{kT} \cos \theta \quad (30)$$

$$\delta \tilde{\varphi} = \left(\frac{K_d a^2}{r^2} - \frac{r}{a} \right) \frac{e E a}{kT} \cos \theta \quad (31)$$

where K_c and K_d are integration constants. The appropriate solution of the third Helmholtz equation can be written as

$$\delta \tilde{\rho} = K_\rho e^{\kappa(a-r)} \left(\frac{a}{r} \right)^2 \left(\frac{1 + \kappa r}{1 + \kappa a} \right) \frac{e E a}{kT} \cos \theta$$

where K_ρ is another integration constant. This expression shows that, in a DC field, the field-induced charge density decays exponentially on a length scale of the order of the double layer thickness. Finally,

$$\delta \tilde{\Phi} = \delta \tilde{\varphi} - \delta \tilde{\rho} = \left[\frac{K_d a^2}{r^2} - \frac{r}{a} - K_\rho e^{\kappa(a-r)} \left(\frac{a}{r} \right)^2 \left(\frac{1 + \kappa r}{1 + \kappa a} \right) \right] \times \frac{e E a}{kT} \cos \theta \quad (32)$$

showing that outside the double layer the potential satisfies the Laplace equation except for a rapidly decaying term.

Boundary Conditions

The constants K_c and K_d can be determined integrating the continuity equations written for the differences between the actual ion flows $\delta \vec{j}^\pm$, eq 25, and the flows $\delta \vec{j}_i^\pm$ calculated using expressions that are only valid outside the double layer:

$$\int_a^\infty \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 (\delta j_r^\pm - \delta j_{lr}^\pm)] + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta (\delta j_\theta^\pm - \delta j_{l\theta}^\pm)] \right\} dr = 0 \quad (33)$$

In these expressions, the long-range (lower index l) ion flows are

$$\delta \vec{j}_i^\pm = -z^\mp N D^\pm \nabla \delta \tilde{\mu}^\pm + z^\mp N \delta \tilde{V} \quad (34)$$

The integrals can be analytically evaluated in the case when the double layer is thin as compared to the radius of the particle:

$$\kappa a \gg 1 \quad (35)$$

The simplifications corresponding to this case, which were first used in refs 1 and 14 for stationary fields, which were presented in detail in refs 2 and 6 for periodic fields, and whose validity was numerically verified,¹⁵ are as follows:

- (a) The curvature of the surface is only taken into account in the solution of the equations corresponding to the electroneutral electrolyte solution, while the equations inside the thin double layer are solved **assuming a locally flat surface (thin double layer approximation)**.

- (b) Each portion of the double layer is considered to be in a state of local equilibrium, which means that **the electrochemical potentials, as well as their tangential derivative, do not change across the double layer** (they do change along it).

Outside the double layer, $\delta j_r^\pm = \delta j_r^\pm$, so that the integrand of eq 33 vanishes. Therefore, in view of eq 35, this equation reduces to

$$\frac{1}{a^2} \int_a^\infty \frac{\partial}{\partial r} [r^2 (\delta j_r^\pm - \delta j_{lr}^\pm)] dr + \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (\delta j_\theta^\pm - \delta j_{l\theta}^\pm) dr] = 0$$

The first integral further simplifies to

$$\frac{1}{a^2} \int_a^\infty \frac{\partial}{\partial r} [r^2 (\delta j_r^\pm - \delta j_{lr}^\pm)] dr = \frac{1}{a^2} [r^2 (\delta j_r^\pm - \delta j_{lr}^\pm)]_\infty - r^2 (\delta j_r^\pm - \delta j_{lr}^\pm)|_a = \delta j_{lr}^\pm|_a$$

since $\delta j_r^\pm|_a = 0$. Moreover, using eq 34

$$\delta j_{lr}^\pm|_a = (-z^\mp ND^\pm \nabla \delta \tilde{\mu}^\pm + z^\mp N \delta \vec{V})_r|_a = -z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a$$

since $\delta V_r|_a = 0$. This transforms eq 33 into

$$-z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a = -\frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (\delta j_\theta^\pm - \delta j_{l\theta}^\pm) dr]$$

The integrand is evaluated using eqs 25 and 34

$$\delta j_\theta^\pm = (-C_0^\pm D^\pm \nabla \delta \tilde{\mu}^\pm + C_0^\pm \delta \vec{V})_\theta = -C_0^\pm D^\pm \nabla_\theta \delta \tilde{\mu}^\pm + C_0^\pm \delta V_\theta$$

$$\delta j_{l\theta}^\pm = (-z^\mp ND^\pm \nabla \delta \tilde{\mu}^\pm + z^\mp N \delta \vec{V})_\theta = -z^\mp ND^\pm \nabla_\theta \delta \tilde{\mu}^\pm + z^\mp N \delta V_\theta$$

so that

$$(\delta j_\theta^\pm - \delta j_{l\theta}^\pm) = -(C_0^\pm - z^\mp N) D^\pm \nabla_\theta \delta \tilde{\mu}^\pm + (C_0^\pm - z^\mp N) \delta V_\theta$$

This transforms eq 33 into

$$-z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a = \frac{1}{a \sin \theta} \times \frac{\partial}{\partial \theta} [\theta \int_a^\infty (C_0^\pm - z^\mp N) D^\pm \nabla_\theta \delta \tilde{\mu}^\pm dr] - \frac{1}{a \sin \theta} \times \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (C_0^\pm - z^\mp N) \delta V_\theta dr]$$

The left-hand side of this expression represents the electrodiffusive flows of ions arriving to the outer boundary of the double layer. These flows spread out inside this layer in the form of surface ion flows (right-hand side). The first of these surface flows is electrodiffusive, while the second is convective. In the following sections, we shall evaluate these terms,

assuming that the tangential gradient of the electrochemical potential does not change across the double layer:

$$-z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a = \frac{D^\pm}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{\mu}^\pm|_a) \times \int_a^\infty (C_0^\pm - z^\mp N) dr - \frac{1}{a \sin \theta} \times \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (C_0^\pm - z^\mp N) \delta V_\theta dr] \quad (36)$$

Nonspecific Adsorption Coefficients

The first integrals in eq 36 represent the excess surface densities of counterions and co-ions, usually referred to as the nonspecific adsorption coefficients G_0^\pm :

$$G_0^\pm = \int_a^\infty (C_0^\pm - z^\mp N) dr = z^\mp N \int_0^\infty (e^{\mp z^\pm \tilde{\Phi}_0} - 1) dx$$

In writing the second equality, eq 6 was used and a locally flat double layer with the surface of the particle coinciding with the y, z plane of an orthogonal coordinate system was considered. The integral can be solved using the substitution

$$dx = \left(\frac{d\tilde{\Phi}_0}{dx} \right)^{-1} d\tilde{\Phi}_0 \quad (37)$$

with $d\tilde{\Phi}_0/dx$ obtained from the first integral of the Poisson–Boltzmann equation written for plane geometry, eq 10:

$$G_0^\pm = -\text{sign}(\tilde{\zeta}) \frac{z^\mp \kappa \epsilon_e kT}{e^{2\sqrt{2z^+ z^-} (z^+ + z^-)}} \times \int_{\tilde{\zeta}}^0 \frac{(e^{\mp z^\pm \tilde{\Phi}_0} - 1) d\tilde{\Phi}_0}{\sqrt{z^- e^{-z^+ \tilde{\Phi}_0} + z^+ e^{z^- \tilde{\Phi}_0} - z^+ - z^-}} \quad (38)$$

Analytic solutions only exist in the following cases:

- (11) For $z^+ = z^- = z$

$$G_0^{11\pm} = \frac{\kappa \epsilon_e kT}{z^2 e^2} (e^{\mp z \tilde{\zeta}/2} - 1) \quad (39)$$

- (21) For $z^+ = 2z^- = 2z$

$$G_0^{21\pm} = \frac{\kappa \epsilon_e kT}{z^\pm z e^2} \frac{e^{\mp z \tilde{\zeta}/2} \sqrt{e^{-z \tilde{\zeta}} + 2} - \sqrt{3}}{\sqrt{3}} \quad (40)$$

- (12) For $2z^+ = z^- = 2z$

$$G_0^{12\pm} = \frac{\kappa \epsilon_e kT}{z^\pm z e^2} \frac{e^{\mp z \tilde{\zeta}/2} \sqrt{e^{z \tilde{\zeta}} + 2} - \sqrt{3}}{\sqrt{3}} \quad (41)$$

The dependence of the nonspecific adsorption coefficients on the surface potential for different ion valences is represented in Figure 3. Note that the curves for positive and negative ions are not mirror images of one another in cases 21 and 12. The

adsorption coefficients for counterions are mainly determined by the dependence of the surface potential on the surface charge, Figure 2. For a given surface potential value, the surface charge strongly increases with the counterion valence, which leads to the corresponding increase of the adsorption coefficients. As for the co-ions, their adsorption coefficients decrease in modulus with the co-ion valence which leads to a stronger repulsion from the particle surface. Furthermore, since all of the figures correspond to a constant κ value, the total amount of co-ions in the electrolyte solution is highest in case 22 and lowest in case 11, eqs 7 and 11.

As expected, the condition of electroneutrality of the double layer:

$$z^+ G_0^+ - z^- G_0^- = \frac{-\sigma_0}{e} \quad (42)$$

is satisfied in all of the considered cases, as can be verified combining the obtained expressions 39–41 with eq 16. Moreover, condition 42 is satisfied in general, for any value of z^+ and z^- , as can be seen combining it with eq 38:

$$z^+ G_0^+ - z^- G_0^- = -\text{sign}(\tilde{\zeta}) \frac{z^+ z^- \kappa \epsilon_e k T}{e^2 \sqrt{2z^+ z^- (z^+ + z^-)}} \times \frac{2 \sqrt{z^- e^{-z^+ \tilde{\zeta}} + z^+ e^{z^- \tilde{\zeta}} - z^+ - z^-}}{z^+ z^-}$$

and then comparing this result with eq 16.

Electroosmosis and Capillary Osmosis

In order to solve the second integral in eq 36, the fluid velocity $\delta \vec{V}$ need only be calculated inside the double layer, since the factor multiplying $\delta \vec{V}$ in this equation vanishes outside of it. For a thin double layer, eq 35, the fluid velocity inside can be obtained solving eq 27 for a plane interface under the action of tangential gradients of the electric potential (electroosmosis) and of the electrolyte concentration (capillary osmosis). The local equilibrium across the thin double layer requires that the

parameters of the virtual system (φ , n , and p) do not change across the double layer. Therefore, the tangential components of the gradients of φ and n may be considered to have a constant value across the double layer.

As for the tangential component of the gradient of p , it can be neglected in view that the pressure gradient outside the double layer vanishes. This corresponds to a well-known feature of the electrophoretic motion.¹⁶ Another justification of this assumption can be obtained combining the equilibrium eqs 9 and 10 with eq 11:

$$P_0 - P(\infty) = \frac{\epsilon_e (kT)^2 \left(\frac{d\tilde{\Phi}_0}{dx} \right)^2}{2e^2}$$

At the surface of the particle, the normal component of the electric field is related to the surface charge density, eq 15, so that

$$P_0(0) - P(\infty) = \frac{\sigma_0^2}{2\epsilon_e}$$

This result shows that the surface pressure only depends on the surface charge (a constant), being independent of the concentration of the electrolyte solution. Therefore, the surface pressure should remain constant along the surface when the electrolyte concentration varies along the surface.

We so consider a flat charged surface and choose an orthogonal coordinate system with the x axis extending in the normal direction from the surface and toward the fluid. We assume that, at distances from the surface greater than the outer boundary of the double layer, the electric potential and the electrolyte concentration vary in the tangential y direction.

The Navier–Stokes equation (eq 27) written for the tangential component (parallel to the y axis) of the velocity is

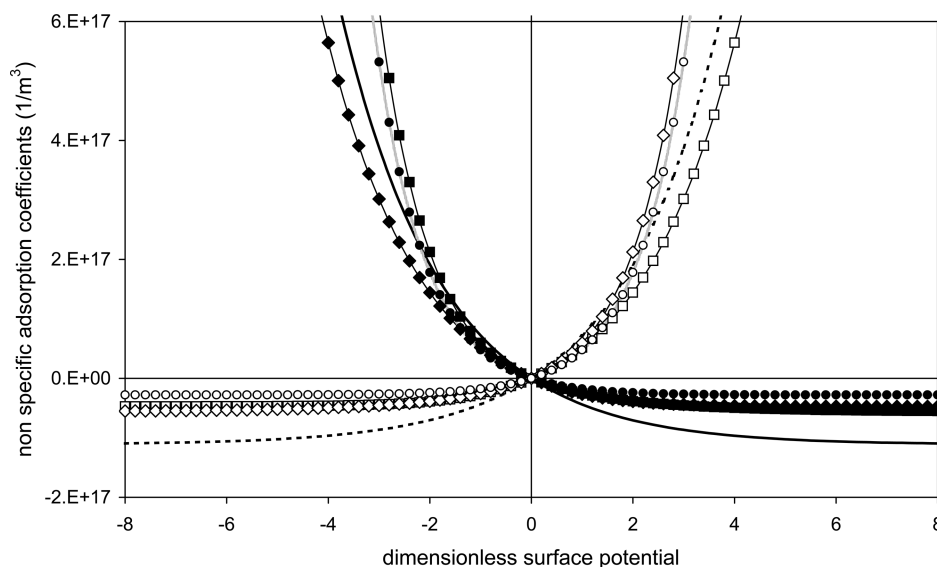


Figure 3. Nonspecific adsorption coefficients as a function of the surface potential, calculated for $z^+ = z^- = 1$ (black line G_0^{1+} , dotted line G_0^{1-}), $z^+ = 2z^- = 2$ (black squares G_0^{21+} , white squares G_0^{21-}), $z^{2+} = z^- = 2$ (black diamonds G_0^{12+} , white diamonds G_0^{12-}), and $z^+ = z^- = 2$ (gray line with black dots G_0^{22+} , gray line with white dots G_0^{22-}). Remaining parameters given in Table 1.

$$\eta_e \frac{d^2 \delta V_y}{dx^2} - \frac{d\delta p}{dy} = kT(z^+ C_0^+ - z^- C_0^-) \frac{d\delta \tilde{\varphi}}{dy} + kT(C_0^+ - z^- N + C_0^- - z^+ N) \frac{d\delta \tilde{n}}{dy} \quad (43)$$

where the tangential derivative of the pressure can be neglected, as shown above. It is preferable to separate the tangential fluid velocity into electroosmotic and capillary osmotic contributions:

$$\delta V_y = \delta V_y^{\text{eo}} + \delta V_y^{\text{co}}$$

and solve independently the corresponding equations:

$$\frac{d^2 \delta V_y^{\text{eo}}}{dx^2} = \frac{kT}{\eta_e} \frac{d\delta \tilde{\varphi}}{dy} (z^+ C_0^+ - z^- C_0^-)$$

$$\frac{d^2 \delta V_y^{\text{co}}}{dx^2} = \frac{kT}{\eta_e} \frac{d\delta \tilde{n}}{dy} (C_0^+ - z^- N + C_0^- - z^+ N)$$

The electroosmotic equation can be transformed using eq 6 and the equilibrium Poisson equation (eq 8):

$$\frac{d^2 \delta V_y^{\text{eo}}}{dx^2} = -\frac{\varepsilon_e (kT)^2}{\eta_e e} \frac{d\delta \tilde{\varphi}}{dy} \frac{d^2 \tilde{\Phi}_0}{dx^2}$$

This equation can be integrated two times with respect to the variable x . The first integration interval extends from a generic point inside the double layer to a point beyond its outer boundary, where $d\delta V_y^{\text{eo}}/dx = 0$ and $d\tilde{\Phi}_0/dx = 0$:

$$\frac{d\delta V_y^{\text{eo}}}{dx} = -\frac{\varepsilon_e (kT)^2}{\eta_e e} \frac{d\delta \tilde{\varphi}}{dy} \frac{d\tilde{\Phi}_0}{dx}$$

The second integration is performed from the surface, where $\delta V_y^{\text{eo}} = 0$ and $\tilde{\Phi}_0 = \tilde{\xi}$, to a generic point inside the double layer, leading to the final result:

$$\delta V_y^{\text{eo}} = \frac{\varepsilon_e (kT)^2}{\eta_e e} \frac{d\delta \tilde{\varphi}}{dy} (\tilde{\xi} - \tilde{\Phi}_0) \quad (44)$$

The electroosmotic velocity has the same direction as the tangential field for negative surface charges, while, for positive ones, its direction is opposite to that of the tangential field. Equation 44 shows that the electroosmotic velocity as a function of the potential is independent of the valences of the ions in the solution, and attains a single common value at the outer boundary of the double layer ($\tilde{\Phi}_0 = 0$). However, this velocity expressed as a function of the distance to the charged plane does depend on the ion valences, since the potential as a function of the distance depends on the valences, eqs 12–14. This dependence is shown in Figure 4. Close to the particle, the velocity is highest for cases 21 and 22, which correspond to divalent counterions, since they form a higher charge density near the surface.

As for the capillary osmotic equation, it is also combined with eq 6 and integrated from a generic point inside the double

layer to a point beyond its outer boundary, where $d\delta V_y^{\text{co}}/dx = 0$:

$$\int_x^\infty \frac{d}{dx} \frac{d\delta V_y^{\text{co}}}{dx} dx = \frac{NkT}{\eta_e} \frac{d\delta \tilde{n}}{dy} \int_x^\infty (z^- e^{-z^+ \tilde{\Phi}_0} + z^+ e^{z^- \tilde{\Phi}_0} - z^+ - z^-) dx$$

The right-hand-side integral is transformed using the substitution given in eq 37, which leads to

$$\frac{d\delta V_y^{\text{co}}}{dx} = \text{sign}(\tilde{\Phi}_0) \frac{\kappa \varepsilon_e}{\eta_e \sqrt{2z^+ z^- (z^+ + z^-)}} \left(\frac{kT}{e} \right)^2 \frac{d\delta \tilde{n}}{dy} \times \int_{\tilde{\Phi}_0}^0 \sqrt{z^- e^{-z^+ \tilde{\Phi}_0} + z^+ e^{z^- \tilde{\Phi}_0} - z^+ - z^-} d\tilde{\Phi}_0$$

The remaining integral can only be solved analytically in the following cases:

$$(11) \text{ For } z^+ = z^- = z$$

$$\frac{d\delta V_y^{\text{co11}}}{dx} = -\frac{\kappa \varepsilon_e (kT)^2}{\eta_e (ze)} \frac{d\delta \tilde{n}}{dy} e^{-z\tilde{\Phi}_0/2} (e^{z\tilde{\Phi}_0/2} - 1)^2$$

$$(21) \text{ For } z^+ = 2z^- = 2z$$

$$\frac{d\delta V_y^{\text{co21}}}{dx} = -\frac{\sqrt{3}\kappa \varepsilon_e (kT)^2}{6\eta_e (ze)} \frac{d\delta \tilde{n}}{dy} e^{-z\tilde{\Phi}_0} [(2e^{z\tilde{\Phi}_0} + 1)^{3/2} - 3\sqrt{3}e^{z\tilde{\Phi}_0}]$$

$$(12) \text{ For } 2z^+ = z^- = 2z$$

$$\frac{d\delta V_y^{\text{co12}}}{dx} = \frac{d\delta V_y^{\text{co21}}(-\tilde{\Phi}_0)}{dx}$$

The second integration is performed from the surface, where $\delta V_y^{\text{co}} = 0$ and $\tilde{\Phi}_0 = \tilde{\xi}$, to a generic point inside the double layer. The integral in the right-hand side is transformed again using the substitution given in eq 37. This leads to the following results for the three cases that can be analytically solved:

$$(11) \text{ For } z^+ = z^- = z, \text{ and using eq 11}$$

$$\delta V_y^{\text{co11}} = \frac{4\varepsilon_e (kT)^2}{\eta_e (ze)} \ln \left(\frac{e^{z\tilde{\Phi}_0/4} + e^{-z\tilde{\Phi}_0/4}}{e^{z\tilde{\xi}/4} + e^{-z\tilde{\xi}/4}} \right) \frac{d\delta \tilde{n}}{dy} \quad (45)$$

$$(21) \text{ For } z^+ = 2z^- = 2z, \text{ and using eq 11}$$

$$\delta V_y^{\text{co21}} = \frac{3\varepsilon_e (kT)^2}{2\eta_e (ze)} \times \ln \left[\frac{e^{2z\tilde{\Phi}_0/3} + e^{-z\tilde{\Phi}_0/3} (2 + \sqrt{6e^{z\tilde{\Phi}_0} + 3})}{e^{2z\tilde{\xi}/3} + e^{-z\tilde{\xi}/3} (2 + \sqrt{6e^{z\tilde{\xi}} + 3})} \right] \frac{d\delta \tilde{n}}{dy} \quad (46)$$

$$(12) \text{ For } 2z^+ = z^- = 2z, \text{ and using eq 11}$$

$$\delta V_y^{\text{co12}} = \delta V_y^{\text{co21}}(-\tilde{\Phi}_0, -\tilde{\xi}) \quad (47)$$

The origin of this velocity is the dependence of the equilibrium potential, eqs 12–14 and 17–19, on the electrolyte concentration. If this concentration changes in the y direction, then the potential also changes, leading to the appearance of a tangential electric field that leads to a tangential fluid flow following the Navier–Stokes equation (eq 43). For a negative (positive) surface charge, the potential gradient has the same (opposite) direction as the concentration gradient so that the direction of the corresponding fluid velocity is always in the opposite direction to the concentration gradient: from high to low concentration.

Figure 5 represents the capillary osmotic velocity profiles for different ion valences. Close to the particle, the capillary osmotic and the electroosmotic velocities have the same behavior: highest (in modulus) values for divalent counterions. However, the contrary occurs far from the particle because, for univalent counterions, a larger fraction of the double layer charge is further away from the surface, where the velocity is zero due to the adhesion condition.

Analytic expressions for the capillary osmotic velocity values in asymmetric electrolyte solutions (cases 21 and 12) were already obtained by Muller¹⁷ in 1978. However, these expressions only provide the limiting values outside the double layer (right-hand-side asymptotes in Figure 5), rather than the velocity profiles that are required in the forthcoming calculations. Nevertheless, they do coincide with eqs 46 and 47 written for $\tilde{\Phi}_0 = 0$, providing a confirmation for the validity of these equations.

Integration Coefficients

The second integrals in eq 36 can now be solved using for the tangential fluid velocity the sum of the electroosmotic and capillary osmotic contributions. In order to do this, we substitute δV_θ for δV_y and ∇_θ for d/dy in eqs 44–47. This leads to the following equations:

$$(11) \text{ For } z^+ = z^- = z$$

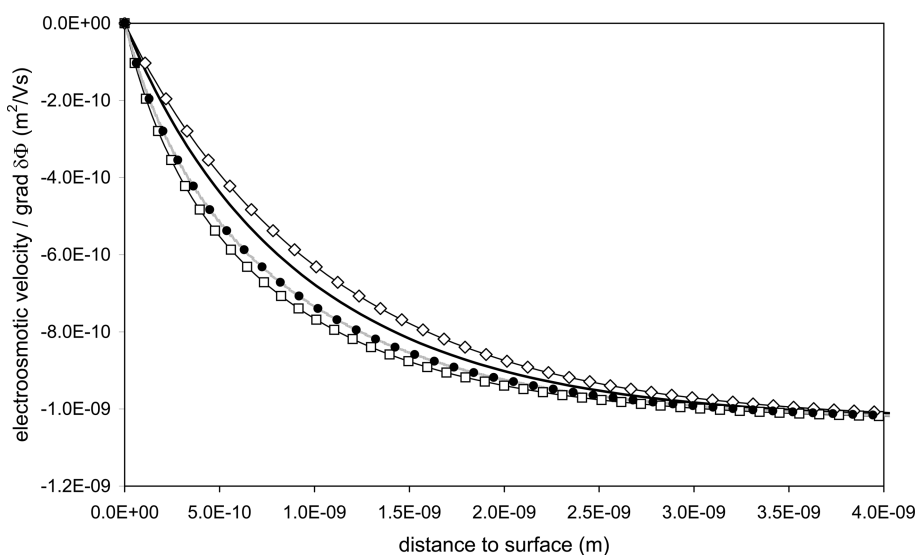


Figure 4. Electroosmotic velocity per unit tangential gradient of the electric potential profiles, calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

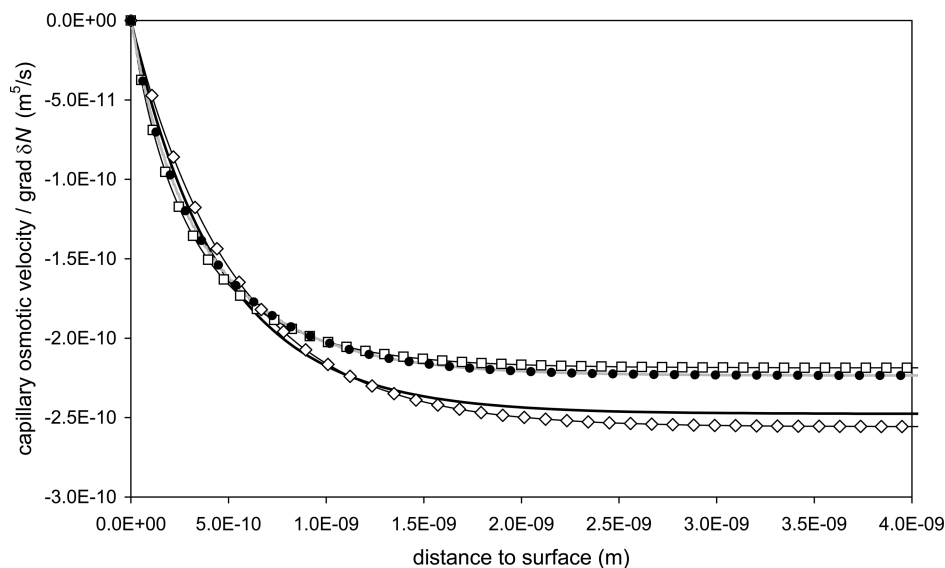


Figure 5. Capillary osmotic velocity per unit tangential gradient of the electrolyte concentration profiles, calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

$$\int_a^\infty (C_0^\pm - zN)\delta V_\theta dr = \frac{\epsilon_e (kT)^2}{\eta_e} \times \int_a^\infty (C_0^\pm - zN)(\tilde{\zeta} - \Phi_0)\nabla_\theta \delta \tilde{\varphi} dr + \frac{4\epsilon_e (kT)^2}{\eta_e (ze)} \times \int_a^\infty (C_0^\pm - zN) \ln \left(\frac{e^{z\tilde{\Phi}_0/4} + e^{-z\tilde{\Phi}_0/4}}{e^{z\tilde{\zeta}/4} + e^{-z\tilde{\zeta}/4}} \right) \nabla_\theta \delta \tilde{n} dr$$

(21) For $z^+ = 2z^- = 2z$

$$\int_a^\infty (C_0^\pm - z^\mp N)\delta V_\theta dr = \frac{\epsilon_e (kT)^2}{\eta_e} \int_a^\infty (C_0^\pm - z^\mp N)(\tilde{\zeta} - \Phi_0)\nabla_\theta \delta \tilde{\varphi} dr + \frac{3\epsilon_e (kT)^2}{2\eta_e (ze)} \int_a^\infty (C_0^\pm - z^\mp N) \times \ln \left[\frac{e^{2z\tilde{\Phi}_0/3} + e^{-z\tilde{\Phi}_0/3}(2 + \sqrt{6e^{z\tilde{\Phi}_0} + 3})}{e^{2z\tilde{\zeta}/3} + e^{-z\tilde{\zeta}/3}(2 + \sqrt{6e^{z\tilde{\zeta}} + 3})} \right] \nabla_\theta \delta \tilde{n} dr$$

(12) For $2z^+ = z^- = 2z$

$$\int_a^\infty (C_0^\pm - z^\mp N)\delta V_\theta dr = \frac{\epsilon_e (kT)^2}{\eta_e} \int_a^\infty (C_0^\pm - z^\mp N)(\tilde{\zeta} - \Phi_0)\nabla_\theta \delta \tilde{\varphi} dr + \frac{3\epsilon_e (kT)^2}{2\eta_e (ze)} \int_a^\infty (C_0^\pm - z^\mp N) \times \ln \left[\frac{e^{-2z\tilde{\Phi}_0/3} + e^{z\tilde{\Phi}_0/3}(2 + \sqrt{6e^{-z\tilde{\Phi}_0} + 3})}{e^{-2z\tilde{\zeta}/3} + e^{z\tilde{\zeta}/3}(2 + \sqrt{6e^{-z\tilde{\zeta}} + 3})} \right] \nabla_\theta \delta \tilde{n} dr$$

Earlier, we used the hypothesis that $\nabla_\theta \delta \tilde{\mu}^\pm$ does not change across the double layer. Combining this assumption with eq 29 shows that it implies that $\nabla_\theta \delta \tilde{\varphi}$ and $\nabla_\theta \delta \tilde{n}$ do not change either so that they can be removed from within the integral signs. Combining the resulting expressions with eq 6 and using the variable substitution given in eqs 10 and 37 leads to

$$\int_a^\infty (C_0^\pm - z^\mp N)\delta V_\theta dr = -\frac{\epsilon_e N (kT)^2}{\kappa \eta_e} (\nabla_\theta \delta \tilde{\varphi} I_{co}^\pm + \nabla_\theta \delta \tilde{n} I_{co}^\pm) \tag{48}$$

where

(11) For $z^+ = z^- = z$

$$I_{co}^{1\pm} = \pm 4(e^{\mp z\tilde{\zeta}/2} - 1) + 2z\tilde{\zeta}$$

$$I_{co}^{1\pm} = \frac{1}{z} \left[4(e^{\mp z\tilde{\zeta}/2} - 1) + (4 \pm 2)z\tilde{\zeta} - 16 \ln \left(\frac{1 + e^{z\tilde{\zeta}/2}}{2} \right) \right]$$

(21) For $z^+ = 2z^- = 2z$

$$I_{co}^{21\pm} = \frac{z^\mp}{z} \left[\pm \frac{z^\mp}{z} (e^{\mp z\tilde{\zeta}/2} \sqrt{3e^{-z\tilde{\zeta}} + 6} - 3) + 3z\tilde{\zeta} + \sqrt{3} \ln \left(\frac{1 + e^{z\tilde{\zeta}} + \sqrt{1 + 2e^{z\tilde{\zeta}}}}{(2 + \sqrt{3})e^{z\tilde{\zeta}}} \right) \right]$$

$$I_{co}^{21\pm} = \frac{z^\mp}{z^2} \left\{ \frac{z^\mp}{z^\pm} (e^{\mp z\tilde{\zeta}/2} \sqrt{3e^{-z\tilde{\zeta}} + 6} - 3) + \frac{z^\pm}{z^\mp} \left[3z\tilde{\zeta} + \sqrt{3} \ln \left(\frac{1 + e^{z\tilde{\zeta}} + \sqrt{1 + 2e^{z\tilde{\zeta}}}}{(2 + \sqrt{3})e^{z\tilde{\zeta}}} \right) \right] + 9 \ln \left(\frac{6}{2 + e^{z\tilde{\zeta}} + \sqrt{3 + 6e^{z\tilde{\zeta}}}} \right) \right\}$$

(12) For $2z^+ = z^- = 2z$

$$I_{co}^{12\pm} = \frac{z^\mp}{z} \left[\pm \frac{z^\mp}{z} (e^{\mp z\tilde{\zeta}/2} \sqrt{3e^{z\tilde{\zeta}} + 6} - 3) + 3z\tilde{\zeta} - \sqrt{3} \ln \left(\frac{1 + e^{-z\tilde{\zeta}} + \sqrt{1 + 2e^{-z\tilde{\zeta}}}}{(2 + \sqrt{3})e^{-z\tilde{\zeta}}} \right) \right]$$

$$I_{co}^{12\pm} = \frac{z^\mp}{z^2} \left\{ \frac{z^\mp}{z^\pm} (e^{\mp z\tilde{\zeta}/2} \sqrt{3e^{z\tilde{\zeta}} + 6} - 3) - \frac{z^\pm}{z^\mp} \left[3z\tilde{\zeta} - \sqrt{3} \ln \left(\frac{1 + e^{-z\tilde{\zeta}} + \sqrt{1 + 2e^{-z\tilde{\zeta}}}}{(2 + \sqrt{3})e^{-z\tilde{\zeta}}} \right) \right] + 9 \ln \left(\frac{6}{2 + e^{-z\tilde{\zeta}} + \sqrt{3 + 6e^{-z\tilde{\zeta}}}} \right) \right\}$$

These results, together with eqs 29, 30, 31, and 36, lead to the following expressions, from which the coefficients K_c and K_d can be obtained. We start with eq 36:

$$-z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a = \frac{D^\pm G_0^\pm}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{\mu}^\pm|_a) - \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (C_0^\pm - z^\mp N)\delta V_\theta dr]$$

and replace $\delta \tilde{\mu}^\pm$ in the right-hand side by means of eq 29

$$-z^\mp ND^\pm \nabla_r \delta \tilde{\mu}^\pm|_a = \frac{D^\pm G_0^\pm}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{n}|_a) \pm \frac{z^\pm D^\pm G_0^\pm}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{\varphi}|_a) - \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} [\sin \theta \int_a^\infty (C_0^\pm - z^\mp N)\delta V_\theta dr]$$

We then substitute the integral using eq 48

$$-\nabla_r \delta \tilde{\mu}^\pm|_a = \left(\frac{G_0^\pm}{z^\mp N} + \frac{z^\pm z^\pm}{2z^\mp \kappa} 3m^\pm I_{co}^\pm \right) \times \\ \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{n}|_a) + \left(\pm \frac{z^\pm G_0^\pm}{z^\mp N} + \right. \\ \left. \frac{z^\pm z^\pm}{2z^\mp \kappa} 3m^\pm I_{co}^\pm \right) \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{\varphi}|_a)$$

where

$$m^\pm = \frac{2\varepsilon_e}{3\eta_c D^\pm} \left(\frac{kT}{z^\pm e} \right)^2$$

Using eqs 30 and 31, the derivatives take the form

$$\frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{n}|_a) = -\frac{2}{a^2} K_c \frac{eEa}{kT} \cos \theta$$

$$\frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \nabla_\theta \delta \tilde{\varphi}|_a) = -\frac{2}{a^2} (K_d - 1) \frac{eEa}{kT} \cos \theta$$

while, using eq 29 together with eqs 30 and 31,

$$\nabla_r \delta \tilde{\mu}^\pm|_a = -\frac{2}{a} \left[K_c \pm z^\pm \left(K_d + \frac{1}{2} \right) \right] \frac{eEa}{kT} \cos \theta$$

Combining these results

$$a \left[K_c \pm z^\pm \left(K_d + \frac{1}{2} \right) \right] = - \left(\frac{G_0^\pm}{z^\mp N} + \frac{z^\pm z^\pm}{2z^\mp \kappa} 3m^\pm I_{co}^\pm \right) K_c - \\ \left(\pm \frac{z^\pm G_0^\pm}{z^\mp N} + \frac{z^\pm z^\pm}{2z^\mp \kappa} 3m^\pm I_{co}^\pm \right) (K_d - 1)$$

and factoring with respect to the coefficients leads to the final equations:

$$K_c (R^\pm + 2 - U^\pm) \pm z^\pm K_d (R^\pm + 2) = \pm z^\pm (R^\pm - 1) \quad (49)$$

where

$$R^\pm = \frac{2z^\pm (z^+ + z^-) e^2}{\kappa^2 a \varepsilon_e kT} G_0^\pm \pm \frac{3m^\pm z^\pm}{z^\mp \kappa a} I_{co}^\pm \\ U^\pm = \frac{3m^\pm z^\pm}{z^\mp \kappa a} (\pm I_{co}^\pm - z^\pm I_{co}^\pm)$$

As expected, these expressions reduce for $z^+ = z^- = z$ to the well-known results:

$$R^\pm = \frac{2G_0^\pm}{zaN} + 3m^\pm \left(\frac{2G_0^\pm}{zaN} \pm \frac{2z\tilde{\zeta}}{\kappa a} \right)$$

$$U^\pm = \frac{48m^\pm}{\kappa a} \ln \left[\cosh \left(\frac{z\tilde{\zeta}}{4} \right) \right]$$

The final expressions for the dipolar and concentration coefficients, obtained solving eq 49, are

$$K_d = \frac{z^+ (R^+ - 1)(R^- + 2 - U^-) + z^- (R^- - 1)(R^+ + 2 - U^+)}{z^+ (R^+ + 2)(R^- + 2 - U^-) + z^- (R^- + 2)(R^+ + 2 - U^+)} \quad (50)$$

$$K_c = \frac{3z^+ z^- (R^+ - R^-)}{z^+ (R^+ + 2)(R^- + 2 - U^-) + z^- (R^- + 2)(R^+ + 2 - U^+)} \quad (51)$$

The dependence of the dipolar coefficient K_d on the surface potential is represented in Figure 6 for different ion valences. Note that the curves are not symmetric with respect to the surface potential in cases 21 and 12. This asymmetry means that the derivative of these curves does not vanish for $\tilde{\zeta} = 0$ so that the series expansion of K_d in powers of $\tilde{\zeta}$ must have a nonvanishing linear term. Therefore, for asymmetric electrolytes with univalent counterion and divalent co-ion, the dipole coefficient attains values that are lower than $-1/2$.

Figure 6 shows a tremendous dependence of the dipolar coefficient on the ion valences: a very strong increase for divalent counterions and a slight decrease for univalent counterions and divalent co-ions. This dependence is reflected in similar changes in the conductivity increment ΔK defined by the following expression valid for dilute suspensions:

$$K = K_e (1 + \phi \Delta K) = K_e (1 + 3\phi K_d)$$

where K is the conductivity of the suspension, K_e the conductivity of the electrolyte solution, and ϕ the volume fraction occupied by the suspended particles.

The dependence of the concentration coefficient K_c on the surface potential is represented in Figure 7 for different ion valences. Note that the curves for cases 21 and 12 are not antisymmetric with respect to the surface potential. The limiting values of the dipolar and concentration coefficients calculated analytically, and using condition 35 with the obtained results, are

$$(11) \text{ For } z^+ = z^- = z$$

$$\lim_{\tilde{\zeta} \rightarrow -\infty} K_d^{11} = \frac{1}{4} \quad \lim_{\tilde{\zeta} \rightarrow \infty} K_d^{11} = \frac{1}{4} \\ \lim_{\tilde{\zeta} \rightarrow -\infty} K_c^{11} = \frac{3z}{4} \quad \lim_{\tilde{\zeta} \rightarrow \infty} K_c^{11} = -\frac{3z}{4}$$

$$(21) \text{ For } z^+ = 2z^- = 2z$$

$$\lim_{\tilde{\zeta} \rightarrow -\infty} K_d^{21} = \frac{1}{2} \quad \lim_{\tilde{\zeta} \rightarrow \infty} K_d^{21} = 0 \\ \lim_{\tilde{\zeta} \rightarrow -\infty} K_c^{21} = z \quad \lim_{\tilde{\zeta} \rightarrow \infty} K_c^{21} = -z$$

$$(12) \text{ For } 2z^+ = z^- = 2z$$

$$\lim_{\zeta \rightarrow -\infty} K_d^{12} = 0 \quad \lim_{\zeta \rightarrow \infty} K_d^{12} = \frac{1}{2}$$

$$\lim_{\zeta \rightarrow -\infty} K_c^{12} = z \quad \lim_{\zeta \rightarrow \infty} K_c^{12} = -z$$

The dipolar and concentration coefficient values determine the electrodiffusive part of the ion flows outside the double layer, which are proportional to the gradient of the electrochemical potentials. Using eqs 29, 30, and 31, these potentials can be written as

$$\delta\tilde{\mu}^\pm = \left[(K_c \pm z^\pm K_d) \frac{a^2}{r^2} \mp z^\pm \frac{r}{a} \right] \frac{eEa}{kT} \cos \theta$$

which reduce to the following limiting expressions for $\zeta \rightarrow \infty$:

(11) For $z^+ = z^- = z$

$$\delta\tilde{\mu}^{11+} = \left(-\frac{1}{2} \frac{a^2}{r^2} - \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

$$\delta\tilde{\mu}^{11-} = \left(-\frac{a^2}{r^2} + \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

(21) For $z^+ = 2z^- = 2z$

$$\delta\tilde{\mu}^{21+} = 2 \left(-\frac{1}{2} \frac{a^2}{r^2} - \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

$$\delta\tilde{\mu}^{21-} = \left(-\frac{a^2}{r^2} + \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

(12) For $2z^+ = z^- = 2z$

$$\delta\tilde{\mu}^{12+} = \left(-\frac{1}{2} \frac{a^2}{r^2} - \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

$$\delta\tilde{\mu}^{12-} = 2 \left(-\frac{a^2}{r^2} + \frac{r}{a} \right) \frac{zeEa}{kT} \cos \theta$$

These expressions show that, despite the strong dependence of the limiting values of K_d and K_c on the ion valences, the

electrodiffusive ion flow lines remain unchanged. The flow of counterions is similar to that of ions for a highly conductive particle in a low conductivity medium, while the flow of co-ions corresponds to an insulating particle in a conducting medium. The only dependence of the above expressions on the ion valences corresponds to the factor 2 appearing in the expressions for $\delta\tilde{\mu}^{21+}$ and $\delta\tilde{\mu}^{12-}$, which compensates for the differences in the bulk concentrations of univalent and divalent ions.

The electrophoretic mobility can now be calculated from the sum of the electroosmotic and capillary osmotic velocities on the particle equator just outside the double layer.¹⁸ These velocities can be obtained from eqs 44 and 45–47, setting in these equations $\tilde{\Phi}_0 = 0$ (outer boundary of the double layer). The tangential components of the electrolyte concentration and of the electric potential gradients appearing in the resulting expressions, evaluated on the particle equator using eqs 30 and 31 are

$$\nabla_\theta \delta\tilde{n}|_{r=a, \theta=\pi/2} = -K_c \frac{eE}{kT} \quad \nabla_\theta \delta\tilde{\varphi}|_{r=a, \theta=\pi/2} = -(K_d - 1) \frac{eE}{kT}$$

Therefore, the electrophoretic velocity of the particle is

$$v_p = \frac{2}{3} (\delta V_{co}|_{\theta=\pi/2} + \delta V_{co}|_{\theta=\pi/2})$$

so that the dimensionless electrophoretic mobility

$$\tilde{u} = \frac{3e\eta_e v_p}{2\varepsilon_c kTE}$$

is given by the following expressions:

(11) For $z^+ = z^- = z$

$$\tilde{u}^{11} = \zeta (1 - K_d^{11}) + \frac{4}{z^2} \ln \left(\frac{e^{z\zeta/4} + e^{-z\zeta/4}}{2} \right) K_c^{11}$$

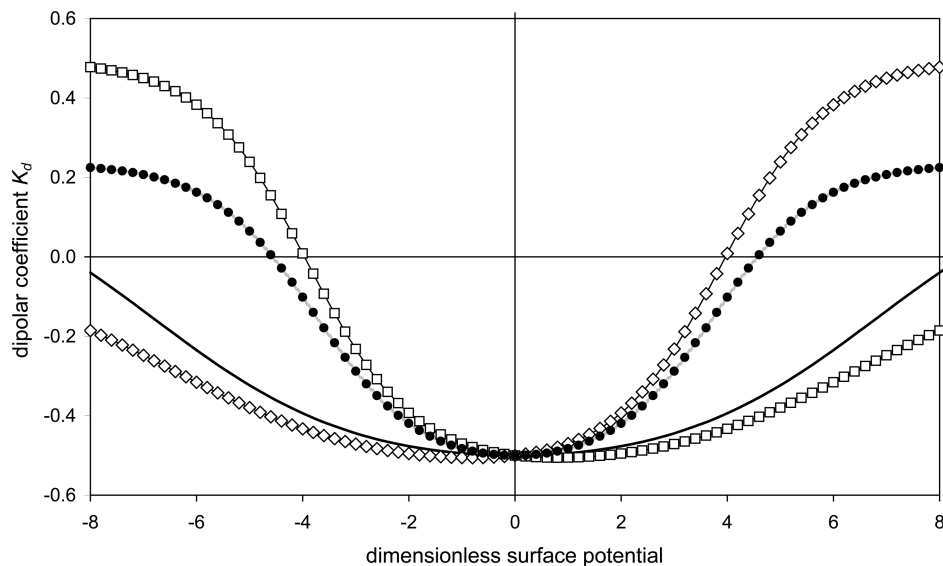


Figure 6. Dipolar coefficient K_d as a function of the surface potential, calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

(21) For $z^+ = 2z^- = 2z$

$$\tilde{u}^{21} = \tilde{\zeta}(1 - K_d^{21}) + \frac{3}{z^2} \ln \left[\frac{e^{-z\tilde{\zeta}/3} (\sqrt{2 + e^{-z\tilde{\zeta}}} + \sqrt{3e^{-z\tilde{\zeta}}})}{2\sqrt{3}} \right] K_c^{21}$$

(12) For $2z^+ = z^- = 2z$

$$\tilde{u}^{12} = \tilde{\zeta}(1 - K_d^{12}) + \frac{3}{z^2} \ln \left[\frac{e^{-z\tilde{\zeta}/3} (\sqrt{2 + e^{z\tilde{\zeta}}} + \sqrt{3e^{z\tilde{\zeta}}})}{2\sqrt{3}} \right] K_c^{12}$$

The expression for \tilde{u}^{11} as a function of K_d^{11} and K_c^{11} coincides with the equation used in 1970 by Dukhin and Semikhin to obtain the first analytic expression of the electrophoretic mobility based on the same counterion polarization model as used in the present work and limited, therefore, to the symmetric 11 case.¹⁹ Nevertheless, the final results (expressed as functions of $\tilde{\zeta}$) are slightly different, apparently due to the removal of

terms in ref 19 based on the condition $\kappa a \gg 1$. The final expressions for \tilde{u}^{21} and \tilde{u}^{12} are similar but not identical to the approximate results (valid for $\kappa a \gg 1$) obtained in 2005 by Ohshima.²⁰ While this treatment includes general electrolytes with any number of ion species and any valence values, analytic expressions are only presented for the same cases as in the present work: 21 and 12. Moreover, these expressions that should be valid for any value of the surface potential only include convection (proportional to m) terms for counterions.

The dimensionless mobilities as functions of the surface potential are represented in Figure 8 for different ion valences. Note that in this figure the curves corresponding to cases 21 and 12 are not antisymmetric with respect to the surface potential. Figure 8 shows that the electrophoretic mobility, unlike the conductivity increment, does not depend on the ion valences, at least for low values of the surface potential. On the contrary, for high $\tilde{\zeta}$ values, the electrophoretic mobility strongly depends on the counterion valence, decreasing when the valence of counterions increases. The limiting values for high and low surface potentials are

(11) For $z^+ = z^- = z$

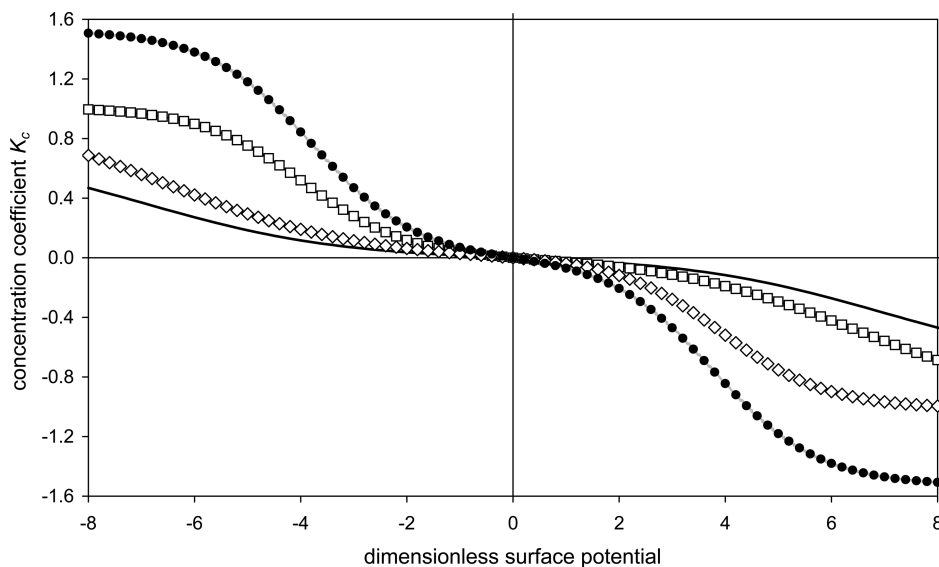


Figure 7. Electrolyte concentration coefficient K_c as a function of the surface potential calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

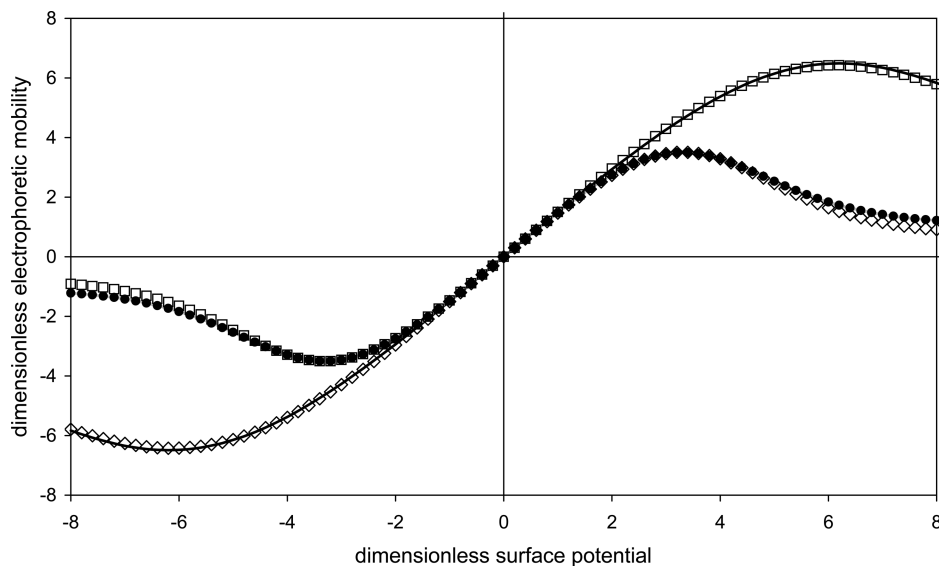


Figure 8. Dimensionless electrophoretic mobility as a function of the surface potential, calculated for $z^+ = z^- = 1$ (black line), $z^+ = 2z^- = 2$ (squares), $2z^+ = z^- = 2$ (diamonds), and $z^+ = z^- = 2$ (gray line with dots). Remaining parameters given in Table 1.

$$\lim_{\xi \rightarrow -\infty} \bar{u}^{11} = -\frac{3}{z} \ln(2) \quad \lim_{\xi \rightarrow \infty} \bar{u}^{11} = \frac{3}{z} \ln(2)$$

$$(21) \text{ For } z^+ = 2z^- = 2z$$

$$\lim_{\xi \rightarrow -\infty} \bar{u}^{21} = -\frac{3}{z} \ln\left(\frac{2\sqrt{3}}{1 + \sqrt{3}}\right) \quad \lim_{\xi \rightarrow \infty} \bar{u}^{21} = \frac{3}{z} \ln(\sqrt{6})$$

$$(12) \text{ For } 2z^+ = z^- = 2z$$

$$\lim_{\xi \rightarrow -\infty} \bar{u}^{12} = -\frac{3}{z} \ln(\sqrt{6}) \quad \lim_{\xi \rightarrow \infty} \bar{u}^{12} = \frac{3}{z} \ln\left(\frac{2\sqrt{3}}{1 + \sqrt{3}}\right)$$

These results coincide with eqs 36–38 in ref 21. They show that the limiting electrophoretic mobility values strongly depend on both the co-ion and counterion valences, increasing when the valence of co-ions increases and decreasing when the valence of counterions increases.

Conclusion

We generalized the classic Dukhin–Shilov thin double layer polarization theory, originally developed for symmetrical electrolytes, to the cases when the valence of counterions is double or half the valence of co-ions. This rigorous and purely analytic generalization was possible because the intervening expressions can be integrated in these two particular cases, a fact apparently overlooked in the past.

Our main qualitative conclusion is that the predicted behavior of suspensions of colloidal particles in asymmetric electrolyte solutions does not reduce to the symmetric case with the same counterion valence, even in the high surface potential limit. The limiting value of the dipolar coefficient for symmetric electrolytes is $K_d^{11} \rightarrow 1/4$, independently of the ion valence. On the contrary, for asymmetric electrolytes, this value reduces to $K_d^{21} \rightarrow 0$ when the counterion valence is half that of co-ions and increases to $K_d^{12} \rightarrow 1/2$ when the counterion valence is double that of co-ions. Obviously, this dependence on the ion valences also applies to the conductivity increment.

As for the electrophoretic mobility, it is mainly determined by the valence of counterions ($\bar{u}^{21} \approx \bar{u}^{11}$ and $\bar{u}^{12} \approx \bar{u}^{22}$ for positive particles and $\bar{u}^{12} \approx \bar{u}^{11}$ and $\bar{u}^{21} \approx \bar{u}^{22}$ for negative ones, Figure 8), decreasing when the counterion valence increases. However, for extreme surface potential values, the mobility becomes also dependent on the co-ion valence, increasing when the valence of co-ions increases.

The presentation was made providing all the intermediate steps, assumptions, and justifications that lead to the final solution, in view of the general lack of detail in the existing outlines of the theory. It was limited, however, to the DC case in order to shorten the already considerable length of the manuscript. Nevertheless, an extension to the AC case is relatively straightforward, since all of the intervening integrals remain unchanged.

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