# Extension of a Classic Thin Double Layer Polarization Theory of Colloidal Suspensions to Include the Stagnant Layer Conductivity

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ABSTRACT: A rigorous extension of the classic Dukhin—Shilov thin double layer polarization theory including the stagnant layer conductivity is presented. Precisely the same assumptions and approximations made in the original theory are maintained, and the same adsorption isotherms are used as in most of the existing numerical calculations. The obtained analytical results improve upon existing approximate extensions, mainly for low surface conductivities and high surface potentials and for high surface conductivities and low surface potentials. Moreover, they avoid the assumption that all the adsorbed ions in the stagnant layer must have a single sign. Finally, they present a very good agreement with numerical calculations specifically made using the same system parameters.
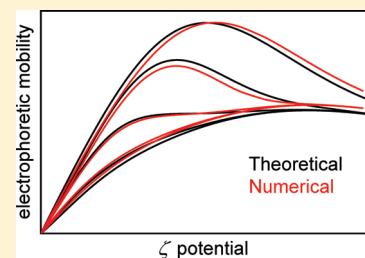
INTRODUCTION

The simplest, and still often used model for the interpretation of dielectric and electrokinetic phenomena in colloidal suspensions is the standard electrokinetic model.[1] It considers that the colloidal suspension is made of hard, insulating, perfectly smooth particles bearing a uniform fixed surface charge and immersed in the electrolyte solution solely characterized by its macroscopic properties. No specific interactions between ions in the electrolyte solution and the particle surface are considered so that the surface conductivity corresponds exclusively to the diffuse part of the electric double layer.

It was later realized, however, that this model can strongly oversimplify the system in the close vicinity of the solid—liquid interface.[2] Due to different factors such as surface roughness, gel-like surface properties, or specific behavior of water molecules in contact with a solid, a thin layer of immobilized water close to the surface can exist, forming the so-called "stagnant layer". On the contrary, ions in this layer can still move tangentially behind the surface of zero fluid velocity, originating the "anomalous", "Stern layer", or "stagnant layer" surface conductivity. Two main nonstandard models were formulated for the free ion density in the stagnant layer, which determines its conductivity value.[3−5] In the first, this density is simply considered to be equal to the diffuse ion density in the region between the particle surface and the zero fluid velocity surface. In the second, specific adsorption of ions to the particle surface is considered, so that the ion density in the stagnant layer is determined by ion adsorption isotherms and the ion density in the diffuse double layer just outside the slipping plane.

While the classic Dukhin—Shilov thin double layer polarization theory[6] was developed on the basis of the standard electrokinetic model, the first nonstandard model was considered in the theories of the electrophoretic mobility[7] and of the low frequency dielectric dispersion.[8,9]

As for the second nonstandard model, the effect of the stagnant layer conductivity of adsorbed ions on the dielectric and electrokinetic DC[10,11] and AC[12,13] properties was extensively studied numerically. However, no rigorous analytical studies are available to date. In ref 14 the thin double layer polarization theory[6] was extended without specifying any details about the structure of the double layer, only considering the movement of ions of a single sign in the stagnant layer, and totally disregarding convective effects in the whole system. In ref 15 the Fixman model[16] was extended to include the anomalous surface conductivity in an approximate fashion, neglecting the contribution of co-ions and without specifying any adsorption isotherms. Similarly, in ref 17 the Shilov—Dukhin low frequency dielectric dispersion theory[8] was extended, neglecting, furthermore, the existence of the capillary osmotic flow.

The purpose of the present work is to provide a rigorous extension of the classic Dukhin—Shilov thin double layer polarization theory[6] including the stagnant layer conductivity. We maintain precisely the same assumptions as in the original theory and use the same adsorption isotherms as in most of the existing numerical calculations.[11−13] We finally compare the obtained analytical results with existing approximate expressions[14,17] and with numerical data.[11]

EQUATION SET

We consider a suspended particle represented by an insulating sphere of radius a, with a uniform fixed surface charge density σ_0. The electrolyte solution is characterized by its viscosity η_e, absolute permittivity ε_e, the unsigned valences of its ions $z^{\pm} = z$, their diffusion coefficients $D^{\pm}$, and their concentrations far from the particle $C^{\pm}(\infty) = C(\infty)$. We furthermore consider that the particle is surrounded by a surface layer of adsorbed ions that can move tangentially with diffusion coefficients $D_s^{\pm}$ while the fluid remains immobile. Their equilibrium (lower index 0) surface densities are

determined by the following adsorption isotherms:

$$C_{s0}^{\pm} = \frac{N_s^{\pm} C_0^{\pm}(a)/K_s^{\pm}}{1 + C_0^{+}(a)/K_s^{+} + C_0^{-}(a)/K_s^{-}} \quad (1)$$

that were chosen in order to be able to compare the obtained results with numerical calculations[11] and with existing theories.[14,17] In this equation, $N_s^{\pm}$ are the maximum values of the surface concentrations of adsorbed ions, and $K_s^{\pm}$ are their dissociation constants.

The Dukhin—Shilov thin double layer polarization theory was reviewed in detail in ref 18, where an extension to different co-ion and counterion valences was presented. While, for sake of simplicity, this extension is not included in the present work, we will base our presentation on that reference in order to avoid unnecessary repetitions.

Under steady state conditions, the ion concentrations $C^{\pm}(\vec{r})$, electric potential $\Phi(\vec{r})$, fluid velocity $\vec{V}(\vec{r})$, and pressure $P(\vec{r})$ outside the stagnant layer are determined by the usual set of Nernst—Planck, continuity, Poisson, Navier—Stokes, and incompressibility equations:

$$\vec{j}^{\pm} = -D^{\pm}\nabla C^{\pm} \mp C^{\pm} z D^{\pm} \nabla \tilde{\Phi} + C^{\pm} \vec{V} \quad (2)$$

$$\nabla \cdot \vec{j}^{\pm} = 0 \quad (3)$$

$$\nabla^2 \Phi = -(C^{+} - C^{-})\frac{ze}{\varepsilon_e} \quad (4)$$

$$\eta_e \nabla^2 \vec{V} - \nabla P = (C^{+} - C^{-})ze\nabla\Phi \quad (5)$$

$$\nabla \cdot \vec{V} = 0 \quad (6)$$

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

■ EQUILIBRIUM EQUATIONS

In equilibrium, both the ion and the fluid flows vanish, so that eqs 2 and 5 can be integrated to obtain

$$C_0^{\pm} = zNe^{\mp z\tilde{\Phi}_0} \quad (7)$$

$$P_0 - P(\infty) = zNkT(e^{-z\tilde{\Phi}_0} + e^{z\tilde{\Phi}_0} - 2) \quad (8)$$

where

$$N = C(\infty)/z$$

and $P(\infty)$ is the pressure far away from the particle. Combining eq 7 with the equilibrium Poisson equation leads to the Poisson—Boltzmann equation for the electric potential:

$$\nabla^2 \tilde{\Phi}_0 = -\frac{z^2 e^2 N}{\varepsilon_e kT}(e^{-z\tilde{\Phi}_0} - e^{z\tilde{\Phi}_0})$$

While this equation 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:

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

where x is the distance to the particle surface. This equation can be integrated one time from a generic point (x, Φ_0) to

infinity ($x \rightarrow \infty$, $\Phi_0 = 0$):

$$\frac{d\tilde{\Phi}_0}{dx} = -sign(\tilde{\Phi}_0)\frac{\kappa}{z}\sqrt{e^{z\tilde{\Phi}_0} + e^{-z\tilde{\Phi}_0} - 2} \quad (9)$$

and a second time from the surface ($x = 0$, $\tilde{\Phi}_0 = \tilde{\zeta}$) to a generic point ($x$, $\tilde{\Phi}$):

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

In this expression, $\tilde{\zeta}$ is the equilibrium surface potential, while

$$\kappa = \sqrt{\frac{2z^3 e^2 N}{\varepsilon_e kT}} \quad (10)$$

is the reciprocal Debye length. The equilibrium surface potential is a function of the fixed surface charge density σ_0, the stagnant layer surface charge density $\sigma_{s0}^{+} + \sigma_{s0}^{-}$, and the electrolyte concentration. The explicit form of this dependence can be obtained combining the Gauss law at the surface

$$\frac{d\tilde{\Phi}_0}{dx}\bigg|_{x=0} = -\frac{e}{kT}\frac{\sigma_0 + \sigma_{s0}^{+} + \sigma_{s0}^{-}}{\varepsilon_e} \quad (11)$$

with eqs 9 and 10, which leads to

$$\sigma_0 + \sigma_{s0}^{+} + \sigma_{s0}^{-} = \sqrt{2\varepsilon_e kT}\frac{(e^{z\tilde{\zeta}} - 1)\sqrt{zN}}{e^{z\tilde{\zeta}/2}} \quad (12)$$

where $\sigma_{s0}^{\pm} = \pm zeC_{s0}^{\pm}$

Figure 1 shows the dependence of the total (squares 0), cation (blue line 0), and anion (red line 0) excess surface densities of the diffuse double layer on the surface potential. Lines 1—4 show the corresponding dependences for the surface ion densities of the stagnant layer. The system parameters taken from ref 11 and used in this and all the following figures (except Figures 3 and 4) are given in Table 1. These parameters roughly correspond to a suspension of 100 nm particles in an aqueous 10 mM/L KCl solution, which leads to a $\kappa a = 32.9$ value. The maximum adsorbed ion concentrations $N_s^{\pm}$ correspond to a maximum surface charge density of 0.8 Cm^{-2}. The last two columns in Table 1 determine the dissociation constant values written as

$$K_s^{\pm} = 1000N_A 10^{-pK^{\pm}} \, m^{-3}$$

so that $K_s^{+} = 6.02 \times 10^{25} \, m^{-3}$ while $6.02 \times 10^{24} \, m^{-3} \leq K_s^{-} \leq 6.02 \times 10^{27} \, m^{-3}$.

As can be seen, for the chosen parameters, the total ion density of the stagnant layer (squares 1—4) is always higher than the total excess ion density of the diffuse layer (squares 0), except for extreme $\tilde{\zeta}$ potential values for which the stagnant layer fully saturates. Squares 3 are fully symmetrical with respect to positive and negative ions because their minimum, which corresponds to equal anion and cation densities, is located at $\tilde{\zeta} = 0$. For squares 2 (4), the dissociation constant of negative ions is higher (lower) than for positive ones so that the minimum is attained for a positive (negative) $\tilde{\zeta}$ potential value. The stagnant layer ion densities strongly differ from one another for positive $\tilde{\zeta}$ potentials because the chosen dissociation constants of counterions (anions) strongly differ. On the contrary, all the stagnant layer ion density lines converge to a single one for negative $\tilde{\zeta}$ potentials because the dissociation constants of counterions (cations) have then a single value.

Table 1. System Parameters Used All in the Figures except When Stated Otherwise

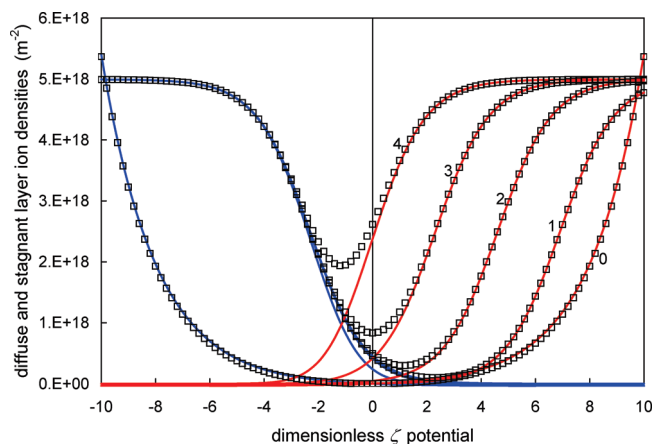|			
$T = 298.16$ K	$D^{\pm} = D_s^{\pm} = 2 \times 10^{-9}$ m^2 s^{-1}	1: $pK^{+} = 1$	1: $pK^{-} = -1$
$\varepsilon_e = 78.54\,\varepsilon_0$	$C(\infty) = 0.01 \times 1000\,N_A$ m^{-3}	2: $pK^{+} = 1$	2: $pK^{-} = 0$
$\eta_e = 8.904 \times 10^{-4}$ N s m^{-2}	$a = 10^{-7}$ m	3: $pK^{+} = 1$	3: $pK^{-} = 1$
$z = 1$	$N_s^{\pm} = 4.99 \times 10^{-18}$ m^{-2}	4: $pK^{+} = 1$	4: $pK^{-} = 2$

Figure 1. Total (squares 0), cation (blue line 0), and anion (red line 0) excess densities of the diffuse double layer and their dependence on the surface potential. Corresponding dependences of the stagnant layer ion densities: lines 1–4. System parameters given in Table 1.
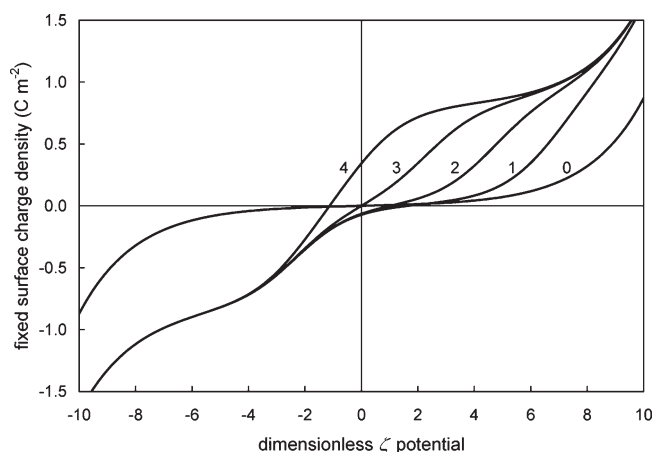
Figure 2. Fixed surface charge density σ_0 and its dependence on the surface potential. Without (0) and with the stagnant layer (1–4). System parameters given in Table 1.

Figure 2 shows the dependence of the fixed surface charge density σ_0 on the surface potential both without and with the stagnant layer (lines 0 and 1–4, respectively). As can be seen, the presence of the adsorbed ions, mostly counterions, strongly increases the fixed surface charge value needed to maintain a given value of the surface potential. Since line 3 is symmetrical with respect to the surface potential sign, the counterion and co-ion charge densities in the stagnant layer compensate each other for $\tilde{\zeta} = 0$ so that the corresponding value of the fixed surface charge is zero. On the contrary, for line 2 (4) the dissociation constant of negative ions is larger (smaller) than for positive ones

so that for $\tilde{\zeta} = 0$ the stagnant layer charge is positive (negative), which leads to a negative (positive) fixed surface charge.

■ SOLUTION WITH AN APPLIED DC ELECTRIC FIELD

When a macroscopic DC electric field with amplitude E is applied to the system, ion flows appear in the diffuse double layer, the surrounding electrolyte solution, and the stagnant layer. The former two are determined by electrodiffusion and convection, while the latter is determined only by electrodiffusion. The equation set 2–6, valid outside the stagnant layer, is first simplified writing the ion flows in terms of the dimensionless electrochemical potentials:

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

$$\tilde{\mu}^{\pm} = \ln\frac{C^{\pm}}{zN} \pm z\tilde{\Phi} \tag{13}$$

A further simplification consists in using the principle of local equilibrium and expressing the system parameters in terms of the parameters of a virtual system (defined by the conditions that each of its volume elements is in equilibrium with the corresponding element of the real system and by being electroneutral in its entire volume). The virtual system parameters are its electric potential $\tilde{\varphi}$, ion concentrations $c^{\pm} = zn$, and pressure p, so that its electrochemical potentials are

$$\tilde{\mu}^{\pm} = \ln\frac{n}{N} \pm z\tilde{\varphi} \tag{14}$$

Equating eqs 13 and 14 leads to

$$C^{\pm} = zne^{\mp z(\tilde{\Phi} - \tilde{\varphi})} \tag{15}$$

$$P - p = znkT\left[e^{-z(\tilde{\Phi} - \tilde{\varphi})} + e^{z(\tilde{\Phi} - \tilde{\varphi})} - 2\right]$$

which relate the local equilibrium values of the electric potential, ion concentrations, and pressure of the real and virtual systems, and are analogous to the equilibrium eqs 7 and 8.

The equation set is then linearized, writing all the field-dependent magnitudes as expansions in successive powers of the applied field strength:

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

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

and dropping all the terms that are higher than first order in the applied field while using the equilibrium equations. Finally, the ion flow, continuity, and incompressibility equations are combined, leading to

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

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

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

$$\eta_e \nabla^2 \delta\vec{V} - \nabla\delta p = kTz(C_0^+ - C_0^-)\nabla\delta\tilde{\varphi}$$
$$+ kT(C_0^+ + C_0^- - 2zN)\nabla\delta\tilde{n} \qquad (16)$$

where $\tilde{n} = n/N$ and $\delta\tilde{n} = \delta n/N$.

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

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

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

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

where

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

is the dimensionless field induced charge density. The solutions of these Laplace and Helmholtz equations are

$$\delta\tilde{n} = \frac{K_c a^2}{r^2}\frac{eEa}{kT}\cos\theta \qquad (17)$$

$$\delta\tilde{\varphi} = \left(\frac{K_d a^2}{r^2} - \frac{r}{a}\right)\frac{eEa}{kT}\cos\theta \qquad (18)$$

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

where K_c, K_d, and K_ρ are integration constants.

■ 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 $\delta\vec{j}^{\pm}$ and the long-range ion flows $\delta\vec{j}_l^{\pm}$ that are only valid outside the diffuse double layer:

$$\int_a^\infty \left\{\frac{1}{r^2}\frac{\partial}{\partial r}[r^2(\delta j_r^{\pm} - \delta j_{lr}^{\pm})] + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}[\sin\theta(\delta j_\theta^{\pm} - \delta j_{l\theta}^{\pm})]\right\}dr = 0$$
$$(19)$$

where

$$\delta\vec{j}^{\pm} = -C_0^{\pm}D^{\pm}\nabla\delta\tilde{\mu}^{\pm} + C_0^{\pm}\delta\vec{V} \qquad (20)$$

$$\delta\vec{j}_l^{\pm} = -zND^{\pm}\nabla\delta\tilde{\mu}^{\pm} + zN\delta\vec{V} \qquad (21)$$

$$\delta\tilde{\mu}^{\pm} = \delta\tilde{n} \pm z\delta\tilde{\varphi} \qquad (22)$$

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

$$\kappa a \gg 1 \qquad (23)$$

considering that (a) the curvature of the surface needs only be taken into account outside the double layer, while the equations inside it are solved assuming a locally flat surface,

and (b) each portion of the diffuse double layer is in a state of local equilibrium, so that the electrochemical potentials and their tangential derivatives do not change across its width.

Outside the double layer, $\delta\vec{j}^{\pm} = \delta\vec{j}_l^{\pm}$ so that the integrand of eq 19 vanishes. Therefore, in view of eq 23, this equation reduces to

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

where the first integral further simplifies to

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

The first addend on the right-hand side of this equation (equal to zero in the classical formulation) corresponds to the radial ion flows entering the stagnant layer. As for the second addend (which corresponds to the radial ion flows leaving the diffuse double layer toward the solution), it can be transformed using eq 21 into

$$\delta j_{lr}^{\pm} = (-zND^{\pm}\nabla\delta\tilde{\mu}^{\pm} + zN\delta\vec{V})_r|_a = -zND^{\pm}\nabla_r\delta\tilde{\mu}^{\pm}|_a$$

since $\delta V_r|_a = 0$. Equation 19 so becomes
$$-\delta j_r^{\pm}(a) - zND^{\pm}\nabla_r\delta\tilde{\mu}^{\pm}|_a$$
$$= -\frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\int_a^\infty (\delta j_\theta^{\pm} - \delta j_{l\theta}^{\pm})\,dr\right] \qquad (24)$$

The integrand is evaluated using eqs 20—22:
$$\delta j_\theta^{\pm} - \delta j_{l\theta}^{\pm} = -(C_0^{\pm} - zN)D^{\pm}\nabla_\theta\delta\tilde{\mu}^{\pm} + (C_0^{\pm} - zN)\delta V_\theta$$

which transforms eq 24 into
$$-\delta j_r^{\pm}(a) - zND^{\pm}\nabla_r\delta\tilde{\mu}^{\pm}|_a$$
$$= \frac{D^{\pm}}{a\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\nabla_\theta\delta\tilde{\mu}^{\pm}|_a)\int_a^\infty (C_0^{\pm} - zN)\,dr$$
$$- \frac{1}{a\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\int_a^\infty (C_0^{\pm} - zN)\delta V_\theta\,dr\right] \qquad (25)$$

This equation coincides with the classical result (eq 36 in ref 18), except for the first addend in the left-hand side that depends on the presence of the stagnant layer.

Proceeding just as in the classical formulation, the right-hand side of this equation is evaluated considering a flat charged surface in contact with the electrolyte solution. The first integral is so replaced by the non specific adsorption coefficients: equilibrium surface ion densities in the diffuse double layer:

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

$$= \frac{\kappa\varepsilon_e kT}{z^2 e^2}(e^{\mp z\tilde{\zeta}/2} - 1) \qquad (26)$$

The second integral in eq 25 is evaluated considering that, outside the diffuse double layer, the electric potential and the electrolyte concentration vary in the tangential y direction, and solving the tangential component of the Navier—Stokes eq 16. The resulting expression is classically integrated,

neglecting the tangential derivative of the pressure in view of eqs 8, 9, and 11

$$P_0(0) - P(\infty) = \frac{(\sigma_0 + \sigma_{s0}^+ + \sigma_{s0}^-)^2}{2\varepsilon_e}$$

This equation shows that with no stagnant layer ($\sigma_{s0}^+ + \sigma_{s0}^- = 0$), the pressure has a constant value that does not depend on the electrolyte concentration and, therefore, on the y coordinate. In the considered case, however, the stagnant layer charge is not constant in the presence of a concentration gradient so that a tangential pressure gradient appears in the diffuse double layer:

$$\frac{dP(0)}{dy} = \frac{\sigma_0 + \sigma_{s0}^+ + \sigma_{s0}^-}{\varepsilon_e} \frac{d(\delta\sigma_s^+ + \delta\sigma_s^-)}{dy} \qquad (27)$$

On the other hand, combining eqs 9 and 11 and differentiating leads to

$$-ze(zNe^{-z\tilde{\zeta}} - zNe^{z\tilde{\zeta}})\frac{d\delta\Phi(0)}{dy}$$

$$= \frac{\sigma_0 + \sigma_{s0}^+ + \sigma_{s0}^-}{\varepsilon_e} \frac{d(\delta\sigma_s^+ + \delta\sigma_s^-)}{dy} \qquad (28)$$

Equations 27 and 28 show that the pressure gradient is equal to the equilibrium charge density multiplied by the tangential electric field, so that that the pressure and potential gradient terms in the Navier–Stokes equation exactly compensate each other. Therefore, the dependence of the total surface charge density on the y coordinate does not lead to any additional fluid flow (otherwise, a suspended particle with a nonuniform surface charge would spontaneously move).

In view of the above, the second integral in eq 25 can be calculated in terms of the electroosmotic and the capillary osmotic fluid velocities, just as in the classical formulation:

$$\delta V_\theta^{eo} = \frac{\varepsilon_e}{\eta_e}\left(\frac{kT}{e}\right)^2 (\tilde{\zeta} - \tilde{\Phi}_0)\nabla_\theta\delta\tilde{\varphi}|_a \qquad (29)$$

$$\delta V_\theta^{co} = \frac{4\varepsilon_e}{\eta_e}\left(\frac{kT}{ze}\right)^2 ln\left(\frac{e^{z\tilde{\Phi}_0/4} + e^{-z\tilde{\Phi}_0/4}}{e^{z\tilde{\zeta}/4} + e^{-z\tilde{\zeta}/4}}\right)\nabla_\theta\delta\tilde{n}|_a \qquad (30)$$

which lead to

$$\int_a^\infty (C_0^\pm - zN)\delta V_\theta dr = -\frac{\varepsilon_e N}{\kappa\eta_e}\left(\frac{kT}{e}\right)^2 (I_{eo}^\pm\nabla_\theta\delta\tilde{\varphi}|_a + I_{co}^\pm\nabla_\theta\delta\tilde{n}|_a)$$

where

$$I_{eo}^\pm = \pm 4(e^{\mp z\tilde{\zeta}/2} - 1) + 2z\tilde{\zeta} \qquad (31)$$

$$I_{co}^\pm = \frac{1}{z}\left[4(e^{\mp z\tilde{\zeta}/2} - 1) + (4 \pm 2)z\tilde{\zeta} - 16\,ln\left(\frac{1 + e^{z\tilde{\zeta}/2}}{2}\right)\right] \qquad (32)$$

Finally, the first addend in eq 25 can be expressed in terms of the stagnant layer parameters using the continuity equation:

$$\nabla_\theta \cdot \delta j_s^\pm + \delta j_r^\pm(a)\,cos\,\theta = 0$$

where

$$\delta j_s^\pm = \frac{D_s^\pm C_{s0}^\pm}{a}\left[\frac{\delta C_s^\pm}{C_{s0}^\pm} \pm z\delta\tilde{\Phi}(a)\right]sin\,\theta$$

so that

$$\delta j_r^\pm(a) = -\frac{2D_s^\pm C_{s0}^\pm}{a^2}\left[\frac{\delta C_s^\pm}{C_{s0}^\pm} \pm z\delta\tilde{\Phi}(a)\right]$$

Combining these results and using eq 22 transforms eq 25 into

$$-zND^\pm\nabla_r\delta\tilde{\mu}^\pm|_a = -\frac{2D^\pm G_0^\pm}{a^2}[\delta\tilde{n}(a) \pm z\delta\tilde{\varphi}(a)]$$

$$-\frac{2D_s^\pm C_{s0}^\pm}{a^2}\left[\frac{\delta C_s^\pm}{C_{s0}^\pm} \pm z\delta\tilde{\Phi}(a)\right]$$

$$+\frac{\varepsilon_e N}{\kappa\eta_e}\left(\frac{kT}{e}\right)^2 \frac{1}{a\,sin\,\theta}\frac{\partial}{\partial\theta}[sin\,\theta(I_{eo}^\pm\nabla_\theta\delta\tilde{\varphi}|_a + I_{co}^\pm\nabla_\theta\delta\tilde{n}|_a)]$$

$$(33)$$

As can be seen, the diffuse and the stagnant layer electrodiffusive flow terms have exactly the same form except for the electrochemical potentials involved.

In order to proceed, it is necessary to determine the expression for the field-induced changes of the stagnant layer ion concentrations $\delta C_s^\pm$. Just as in ref 11, we assume that the equilibrium adsorption isotherms (eq 1) are also valid out of equilibrium:

$$C_s^\pm = \frac{N_s^\pm C^\pm(a)/K_s^\pm}{1 + C^+(a)/K_s^+ + C^-(a)/K_s^-}$$

so that

$$\frac{\delta C_s^\pm}{C_{s0}^\pm} = \frac{\delta C^\pm(a)}{C_0^\pm(a)} - \frac{C_{s0}^+\delta C^+(a)}{N_s^+ C_0^+(a)} - \frac{C_{s0}^-\delta C^-(a)}{N_s^- C_0^-(a)}$$

where the field-induced ion concentration changes at the inner boundary of the diffuse double layer $\delta C^\pm(a)$ are determined by the local equilibrium condition, eq 15:

$$\frac{\delta C^\pm(a)}{C_0^\pm(a)} = \delta\tilde{n}(a) \mp z[\delta\tilde{\Phi}(a) - \delta\tilde{\varphi}(a)]$$

The stagnant layer electrochemical potentials in eq 33 so become:

$$\frac{\delta C_s^\pm}{C_{s0}^\pm} \pm z\delta\tilde{\Phi}(a) = \left(1 - \frac{C_{s0}^+}{N_s^+} - \frac{C_{s0}^-}{N_s^-}\right)\delta\tilde{n}(a)$$

$$\pm\left(1 \mp \frac{C_{s0}^+}{N_s^+} \pm \frac{C_{s0}^-}{N_s^-}\right)z\delta\tilde{\varphi}(a) + \left(\frac{C_{s0}^+}{N_s^+} - \frac{C_{s0}^-}{N_s^-}\right)z\delta\tilde{\Phi}(a)$$

Next, an expression for the field-induced potential change at the inner boundary of the diffuse double layer $\delta\tilde{\Phi}(a)$ is needed. Note that inside the diffuse double layer $\delta\tilde{\Phi}$ depends on the distance to the particle, unlike $\delta\tilde{\varphi}$ and $\delta\tilde{n}$ that are classically considered to remain constant across the thin double layer in view of the local equilibrium condition. The potential change $\delta\tilde{\Phi}(a)$ can be expressed as the sum of $\delta\tilde{\varphi}(a)$ plus a contribution dependent on the concentration change.

This contribution can be determined combining eqs 1, 7, and 12:

$$\sigma_0 + ze \frac{N_s^+ zN e^{-z\tilde\zeta}/K_s^+ - N_s^- zN e^{+z\tilde\zeta}/K_s^-}{1 + zN e^{-z\tilde\zeta}/K_s^+ + zN e^{+z\tilde\zeta}/K_s^-}$$

$$= \sqrt{2\varepsilon_e kT} \frac{(e^{z\tilde\zeta}-1)\sqrt{zN}}{e^{z\tilde\zeta/2}}$$

which leads to

$$z\delta\tilde\Phi(a) = z\delta\tilde\varphi(a)$$
$$-\left\{\left[\frac{\sqrt{2\varepsilon_e kT}\sqrt{zN}}{2e^{z\tilde\zeta/2}}(e^{z\tilde\zeta}-1) - ze(C_{s0}^+ - C_{s0}^-)\left(1 - \frac{C_{s0}^+}{N_s^+} - \frac{C_{s0}^-}{N_s^-}\right)\right]\right.$$
$$\left/\left[\frac{\sqrt{2\varepsilon_e kT}\sqrt{zN}}{2e^{z\tilde\zeta/2}}(e^{z\tilde\zeta}+1) + zeC_{s0}^+\left(1 - \frac{C_{s0}^+}{N_s^+} + \frac{C_{s0}^-}{N_s^-}\right)\right.\right.$$
$$\left.\left.\left. + zeC_{s0}^-\left(1 + \frac{C_{s0}^+}{N_s^+} - \frac{C_{s0}^-}{N_s^-}\right)\right]\right\}\frac{\delta N}{N}\right.$$

Writing this equation as

$$z\delta\tilde\Phi(a) = z\delta\tilde\varphi(a) - S\delta\tilde n \qquad (34)$$

transforms the expression for the stagnant layer electrochemical potential appearing in eq 33 into

$$\frac{\delta C_s^\pm}{C_{s0}^\pm} \pm z\delta\tilde\Phi(a) = M\delta\tilde n(a) \pm z\delta\tilde\varphi(a)$$

where

$$M = 1 - \frac{C_{s0}^+}{N_s^+}(1+S) - \frac{C_{s0}^-}{N_s^-}(1-S)$$

Thus eq 33 becomes

$$a\nabla_r\delta\tilde\mu^\pm|_a = \frac{2G_0^\pm}{zNa}[\delta\tilde n(a) \pm z\delta\tilde\varphi(a)] + \frac{2D_s^\pm C_{s0}^\pm}{D^\pm zNa}[M\delta\tilde n(a)$$
$$\pm z\delta\tilde\varphi(a)] + \frac{3m^\pm}{\kappa a}[I_{eo}^\pm z\delta\tilde\varphi(a) + zI_{co}^\pm\delta\tilde n(a)]$$

where

$$m^\pm = \frac{2\varepsilon_e}{3\eta_e D^\pm}\left(\frac{kT}{ze}\right)^2$$

Using eqs 17, 18, and 22 and factoring with respect to the coefficients, leads to the final equations:

$$K_c(R^\pm + R_s^\pm M - U^\pm + 2) \pm zK_d(R^\pm + R_s^\pm + 2)$$

$$= \pm z(R^\pm + R_s^\pm - 1)$$

where

$$R^\pm = \frac{2G_0^\pm}{zNa} \pm \frac{3m^\pm}{\kappa a}I_{eo}^\pm \qquad (35)$$

$$R_s^\pm = \frac{2D_s^\pm C_{s0}^\pm}{D^\pm zNa} \qquad (36)$$

$$U^\pm = \frac{3m^\pm}{\kappa a}(\pm I_{eo}^\pm - zI_{co}^\pm)$$

The resulting expressions for the dipolar and concentration coefficients are

$$K_d = \frac{\begin{bmatrix}(R^+ + R_s^+ - 1)(R^- + R_s^- M + 2 - U^-)\\ +(R^- + R_s^- - 1)(R^+ + R_s^+ M + 2 - U^+)\end{bmatrix}}{\begin{bmatrix}(R^+ + R_s^+ + 2)(R^- + R_s^- M + 2 - U^-)\\ +(R^- + R_s^- + 2)(R^+ + R_s^+ M + 2 - U^+)\end{bmatrix}} \qquad (37)$$

$$K_c = \frac{3z(R^+ + R_s^+ - R^- - R_s^-)}{\begin{bmatrix}(R^+ + R_s^+ + 2)(R^- + R_s^- M + 2 - U^-)\\ +(R^- + R_s^- + 2)(R^+ + R_s^+ M + 2 - U^+)\end{bmatrix}} \qquad (38)$$

It should be noted that the form of these equations is not trivial: the stagnant layer surface conductivities (proportional to $R_s^\pm$) are not simply added to the corresponding diffuse double layer surface conductivities (proportional to $R^\pm$) since in some instances, but not always, they are multiplied by the coefficient M.

■ DISCUSSION

Figures 3 and 4 show a comparison of the obtained results with existing approximate extensions of the classic theory. Extension[14] incorporates the stagnant layer conductivity but neglects all convective effects and assumes, furthermore, that the stagnant layer contains ions of a single sign. In the case that these ions are negative, the obtained results are

$$K_d = \frac{(R_{nc}^+ - 1)(R_{nc}^- + R_s^- + 2) + (R_{nc}^- + R_s^- - 1)(R_{nc}^+ + 2)}{2(R_{nc}^+ + 2)(R_{nc}^- + R_s^- + 2)} \qquad (39)$$

$$K_c = \frac{3z(R_{nc}^+ - R_{nc}^- - R_s^-)}{2(R_{nc}^+ + 2)(R_{nc}^- + R_s^- + 2)} \qquad (40)$$

where the diffuse double layer surface conductivity coefficients with no convection are

$$R_{nc}^\pm = \frac{2G_0^\pm}{zNa} \qquad (41)$$

The extension[17] of the classic theory incorporates the stagnant layer conductivity but neglects all the contribution of co-ions and of the capillary osmosis and assumes, furthermore, that the stagnant layer only contains counterions. In the case that the counterions are negative, the obtained results are:

$$K_d = \frac{R^- + R_s^- - 4}{4(R^- + R_s^- + 2)} \qquad (42)$$

$$K_c = \frac{-3z(R^- + R_s^-)}{4(R^- + R_s^- + 2)} \qquad (43)$$

Figure 3 represents the dipolar coefficient K_d as a function of the $\tilde\zeta$ potential. The black line 0 corresponds to the classic solution with no stagnant layer, while black lines 1−4 correspond to different values of the stagnant layer parameters (eq 37). The blue lines correspond to the existing extension[14]
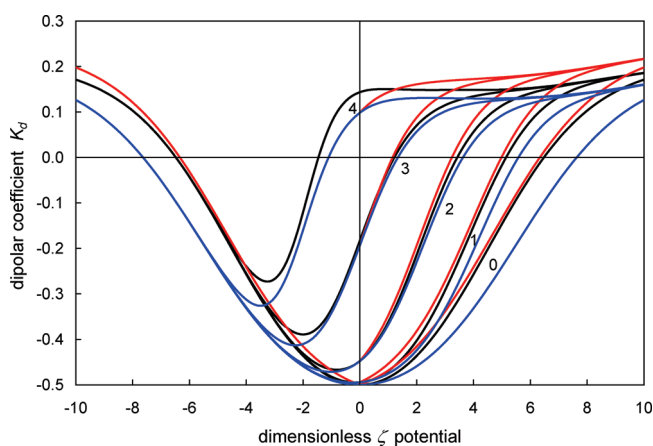
Figure 3. Dipolar coefficient K_d and its dependence on the surface potential. Present theory: eq 37, black lines. Existing approximate theories: eq 39, blue lines; eq 42, red lines. System parameters given in Table 1 except for $N_s^+ = 0$.
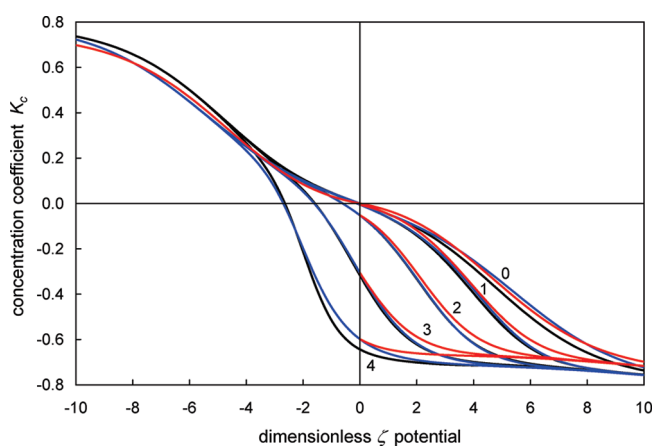
Figure 4. Concentration coefficient K_c and its dependence on the surface potential. Present theory: eq 38, black lines. Existing approximate theories: eq 40, blue lines; eq 43, red lines. System parameters given in Table 1 except for $N_s^+ = 0$.

eq 39, while the red lines correspond to the existing extension[17] eq 42. In order to satisfy the above-mentioned hypothesis of the existing extensions regarding the sign of the ions in the stagnant layer, eq 37 was evaluated considering that $N_s^+ = 0$ in eq 1. This implies that the blue 1—4 lines are no longer present in Figure 1 so that the squares coincide with the red lines.

Figure 3 shows that eq 42 generally works better than eq 39 because the influence of co-ions in the diffuse double layer is much smaller than that of convection (except for very small $|\tilde{\zeta}|$ values). This behavior is clearly seen in lines 0 that do not include any stagnant layer conductivity. For increasing stagnant layer conductivity values, the agreement between the three expressions improves since the relative contribution of the diffuse double layer conductivity to the total surface conductivity diminishes. Note that the results of both existing extensions coincide for $\tilde{\zeta} = 0$ since, in this case, there is no convection ($I_{eo}^{\pm} = I_{co}^{\pm} = 0$, eqs 31 and 32) and no nonspecific adsorption ($G_0^{\pm} = 0$, eq 26, so that the surface conductivity of the diffuse double layer vanishes ($R^{\pm} = R_{nc}^{\pm} = 0$, eqs 35,41)).

Equations 39,42 and 40,43 therefore become

$$K_d|_{\tilde{\zeta}=0} = \frac{R_s^- - 4}{4(R_s^- + 2)}$$

$$K_c|_{\tilde{\zeta}=0} = \frac{-3zR_s^-}{4(R_s^- + 2)}$$

However, these expressions do not coincide with the corresponding results of the present theory since, under these conditions, eqs 37 and 38 reduce to

$$K_d|_{\tilde{\zeta}=0, R_s^+=0} = \frac{R_s^-(2 - M) - 4}{2R_s^-(1 + M) + 8}$$

$$K_c|_{\tilde{\zeta}=0, R_s^+=0} = \frac{-3zR_s^-}{2R_s^-(1 + M) + 8}$$

The presence of the coefficient M in the above equations is responsible for the strong discrepancy between the present theory and the existing ones for the highest stagnant layer conductivity: lines 4 in Figure 3 ($M = 0.728$ for $\tilde{\zeta} = 0$).

Figure 4 represents the concentration coefficient K_c as a function of the $\tilde{\zeta}$ potential. The black lines correspond to the present theory, eq 38 with $N_s^+ = 0$ in eq 1, while the blue and red lines represent the existing approximate results (eqs 40 and 43, respectively). As can be seen for $\tilde{\zeta} > 0$, the presence of the stagnant layer made of counterions strongly increases the concentration polarization: the 1—4 lines are always lower than the 0 lines. This happens because the counterions in the stagnant layer increase the difference between the counterion and co-ion transfer numbers of the whole double layer. Note that even for $\tilde{\zeta} = 0$ the concentration polarization persists due entirely to the stagnant layer conductivity. For $\tilde{\zeta} < 0$, an unusual behavior is apparent since the surface conductivity due to co-ions in the stagnant layer surpasses the counterion conductivity in the diffuse double layer, leading to negative values of the concentration coefficient (2—4 lines). Only for sufficiently small $\tilde{\zeta}$ potential values the diffuse double layer conductivity surpasses the stagnant layer conductivity and the concentration polarization becomes positive as usual for a negative $\tilde{\zeta}$ potential. As in Figure 3, the agreement between the present and the existing results is fairly good except for very high stagnant layer conductivity values: lines 4 and small $|\tilde{\zeta}|$ values.

Figure 5 represents the conductivity increment $\Delta K = 3K_d$ as a function of the $\tilde{\zeta}$ potential. As before, the black lines correspond to the present theory, but considering now that N_s^+ have the values given in Table 1 (blue 1—4 lines in Figure 1). However, the red lines correspond now to numerical results calculated using the Mangelsdorf—White[11] program. As can be seen, the theoretical results of the present work are in very good agreement with the numerical ones, except for high $|\tilde{\zeta}|$ values. However, these deviations appear to originate in the classical (no stagnant layer) model, as can be seen comparing the 0 black and red lines. While this behavior is well-known,[19] the reason why the classical model predicts lower conductivity increment values than numerical calculations at high $|\tilde{\zeta}|$, even when the requirement $\kappa a \gg 1$ is fulfilled, is still unclear. At low $|\tilde{\zeta}|$ values, the agreement between the theoretical and numerical results is quite good and it should be noted that for the highest stagnant layer conductivity (lines 4), the theoretical maximum is solely due to the presence of the coefficient M in eq 37.

Figure 6 represents the dimensionless electrophoretic mobility as a function of the $\tilde{\zeta}$ potential. As in Figure 5, the black lines
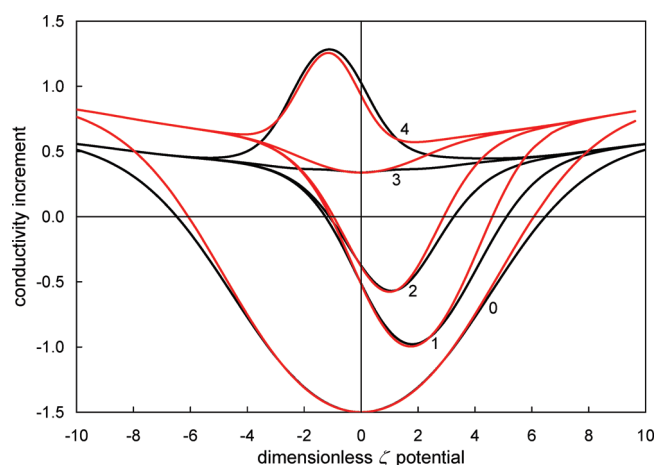
Figure 5. Conductivity increment $\Delta K = 3K_d$ and its dependence on the surface potential. Present theory: black lines; numerical results:[11] red lines. System parameters given in Table 1.
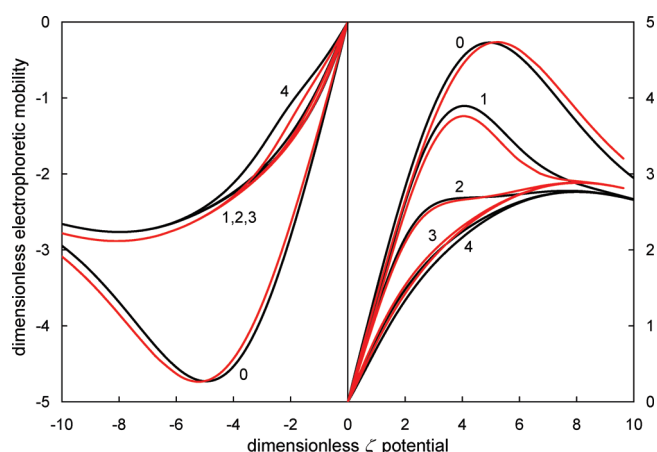
Figure 6. Electrophoretic mobility and its dependence on the surface potential. Present theory, eqs 37, 38, and 44: black lines; numerical results:[11] red lines. System parameters given in Table 1.

correspond to the present theory, while the red lines correspond to numerical results calculated using the Mangelsdorf−White[11] program. In order to better visualize the different results, the mobility values corresponding to negative (positive) $\tilde{\zeta}$ potentials are given on the left (right) ordinate axis. The theoretical values were calculated from the sum of the electroosmotic and the capillary osmotic velocities on the particle equator just outside the diffuse double layer.[20] These velocities can be obtained from eqs 29 and 30 setting $\tilde{\Phi}_0 = 0$ (outer boundary of the diffuse double layer) and using eqs 17 and 18 to evaluate the tangential components of the electrolyte concentration and of the electric potential gradients. The resulting dimensionless electrophoretic mobility expression is

$$\tilde{u} = \tilde{\zeta}(1 - K_d) + \frac{4}{z^2} ln\left(\frac{e^{z\tilde{\zeta}/4} + e^{-z\tilde{\zeta}/4}}{2}\right)K_c \qquad (44)$$

As can be seen, the theoretical results are in good agreement with the numerical results obtained using the program of ref 11 over the whole $\tilde{\zeta}$ potential range.

■ CONCLUSION

This work presents a rigorous extension of the classic Dukhin−Shilov double layer polarization theory to include the stagnant layer conductivity. This was made maintaining all the assumptions and approximations of the original theory and without any additional simplifications, such as neglecting the contribution of co-ions to the conductivity of the double layer or neglecting the diffusive ion flow inside the surface layer.

The stagnant layer properties were characterized by the adsorption isotherms usually used in numerical calculations.[11,12] However, the use of other isotherms is possible, since it only requires the recalculation of a single coefficient S (eq 34).

The obtained expressions for the dipolar and concentration coefficients are not trivial for the following reasons. First, the electrodiffusive ion flows in the diffuse double layer are determined by the electrochemical potentials that are assumed to be constant across the double layer in the classical theory. On the contrary, the conductive flows in the stagnant layer are determined by the tangential electric field at the particle surface, while the tangential concentration gradients inside the stagnant layer determine the diffusive flows. These magnitudes depend not only on the dipolar and concentration coefficients but also on the adsorption isotherm parameters. The end result is that the expressions for the dipolar and concentration coefficients can not be written in terms of the sum of the surface conductivities of the diffuse and the stagnant layers.

A comparison of the obtained results with those corresponding to existing approximate theories,[14,17] while using adsorption isotherms compatible with the hypothesis used in these theories, shows a fairly good agreement except for two extreme cases: (a) no surface conductivity and high $|\tilde{\zeta}|$, when the omission of all convective effects in[14] leads to dipolar coefficient values that are too small, and (b) high surface conductivity and low $|\tilde{\zeta}|$, when both approximate theories lead to large deviations due to the absence of the coefficient M in their results. Therefore, existing approximate theories might be useful for the interpretation of experimental data, but only in those cases when there is reason to believe that the stagnant layer conductivity is only due to ions of a single sign. In the general case, however, the influence of the adsorbed ions can not be described by means of a single parameter, the stagnant layer conductivity, so that full theoretical results as those presented here should be used.

A comparison of the obtained conductivity increment and electrophoretic mobility results with numerical calculations performed using the Mangelsdorf−While computer program[11] and precisely the same system parameters shows a very good agreement, at least for low or moderate $|\tilde{\zeta}|$ values. At extreme surface potentials, the classical theory leads to dipolar coefficient values that are systematically lower than those obtained numerically. The extended results maintain these same deviations, which do not seem to be affected by the inclusion of the stagnant layer conductivity.

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