Published in final edited form as:

J Fluid Mech. 2013 June 1; 724: 69–94. doi:10.1017/jfm.2013.152.

The Influence of Dielectric Decrement on Electrokinetics

Hui Zhao¹ and Shengjie Zhai

Department of Mechanical Engineering, University of Nevada, Las Vegas, NV, 89154

Abstract

We treat the dielectric decrement induced by excess ion polarization as a source of ion specificity and explore its impact on electrokinetics. We employ a modified Poisson-Nernst-Planck (PNP) equations accounting for the dielectric decrement. The dielectric decrement is determined by the excess ion polarization parameter α and when $\alpha = 0$ the standard PNP model is recovered. Our model shows that ions saturate at large zeta potentials (ζ). Because of ion saturation, a condensed counterion layer forms adjacent to the charged surface, introducing a new length scale, the thickness of the condensed layer (l_c). For the electro-osmotic mobility, the dielectric decrement weakens the electro-osmotic flow owing to the decrease of the dielectric permittivity. At large ζ , when $\alpha \rightarrow 0$, the electro-osmotic mobility is found to be proportional to ζ^2 , in contrast to ζ predicted by the standard PNP model. This is attributed to ion saturation at large ζ . In terms of the electrophoretic mobility M_e , we carry out both an asymptotic analysis in the thin-double-layer limit and solve the full modified PNP model to compute M_e . Our analysis reveals that the impact of the dielectric decrement is intriguing. At small and moderate ζ , the dielectric decrement decreases M_e with an increasing α . At large ζ , it is well known that the surface conduction becomes significant and plays an important role in determining M_e . It is observed that the dielectric decrement effectively reduces the surface conduction. Hence in stark contrast, M_e increases as α increases. Our predictions of the contrast dependence of the mobility on α at different zeta potentials qualitatively agree with experimental results on the dependence of the mobility among ions and provide a possible explanation for such ion specificity. Finally, the comparisons between the thin-double-layer asymptotic analysis and the full simulations of the modified PNP model suggest that at large ζ the validity of the thin-double-layer approximation is determined by l_c rather than the traditional Debye length.

Keywords

colloids; microfluidics; micro-/nano-fluidic dynamics

1. Introduction

Electrokinetic phenomena originate from the interaction between excess counterions inside a double layer near a charged surface and an applied electric field (Lyklema 1995). They find broad applications in lab-on-a-chip technologies (Stone *et al.* 2004; Squires & Quake 2005),

¹All correspondence should be directed to this author (hui.zhao@unlv.edu).

colloidal science (Russel *et al.* 1989), separation of DNA biomolecules (Viovy 2000), and DNA sequencing (Zwolak & Di Ventra 2005).

A charged surface attracts counterions and repels coions, forming an electrical double layer with a thickness of nanometers. An applied electric field drives ions to migrate. Inside the double layer, the imbalanced migration between counterions and coions drags water to move and induces an electrokinetic flow. When the double layer thickness is smaller than the size of other geometric features, the induced flow outside the double layer satisfies the famous Smoluchowski velocity assuming a constant permittivity and a constant viscosity (Lyklema 1995):

$$u_s = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}E_t. \quad (1.1)$$

In the above, ε is the relative dielectric permittivity of bulk water; ε_0 is the vacuum permittivity; η is the viscosity of the water; E_t is the component of the external electric field parallel to the surface; and ζ is the zeta potential of the surface. For stationary surfaces, the flow is termed electro-osmosis.

For a freely suspended charged particle, the particle's motion and the accompanied flow motion are known as electrophoresis. In contrast to electro-osmosis where the flow increases with an increasing ζ , the scenario of electrophoresis is much more complicated. At large ζ , the surface conduction becomes significant (Dukhin & Deryaguin 1974). The surface conduction effectively weakens the tangential electric field and creates concentration polarization. Both of them attempt to reduce the electrophoretic mobility, yielding the mobility to attain a maximum and then decrease as the zeta potential increases (O'Brien & White 1978; O'Brien 1983).

To understand electrokinetic phenomena, the vast majority of theoretical work uses the Poisson-Nernst-Planck (PNP) equations coupled with the Stokes equations. In the classical PNP model, ions are treated as point-like charges that only interact via the Coulomb forces (Lyklema 1995). Although the PNP model provides reasonable interpretation for some experimental results, the model has its own shortcomings and cannot capture certain important physics. For example, measured electrophoretic mobilities of latex particles showed ion specificity. With the same pH value and bulk concentration, the mobilities of particles suspended into different 1-1 symmetric electrolytes are different (Gallardo *et al.* 1993; Lopez-Leon *et al.* 2003; 2005; Salis *et al.* 2012). It was also observed that the dependence of the mobility on salts follows certain order (Lopez-Leon *et al.* 2003; 2005). Not surprisingly, the PNP model is unable to explain this salt-dependence of the mobility. Moreover, a large number of experiments in colloid, polymer and interface science also show that ion-specific effects are pronounced as classified by the famous Hofmeister series, which again cannot be predicted by the PNP model (Collins & Washabaugh 1985; Conway 1995; Cacace *et al.* 1997; Jungwirth & Tobias 2001; Manciu & Ruckenstein 2003; Ruckenstein & Manciu 2003; Kunz *et al.* 2004b 2004c; Kunz 2010; Lo Nostro & Ninham 2012).

The presence of excess ion polarization has been invoked to explain ion-specific effects (Netz 2000; 2001; 2004; Bostrom *et al.* 2001; Kunz *et al.* 2004a). Due to excess ion polarization, charged ions induce strong local electric fields which create hydration shells around solvated ions. Inside the hydration shell, the typical ion-induced local electric field is much stronger than the external electric field. Hence polar water molecules are forced to be aligned with the local ion-induced electric field rather than the external electric field. The corresponded response of water molecules to the external electric field is therefore lowered. Accordingly, the dielectric permittivity which characterizes the response of water molecules to an external electric field is decreased (Ben-Yaakov *et al.* 2009b; 2011; Holovko & Kapko 2009; Gavish & Promislow 2012). Figure 1 schematically depicts how water molecules around the hydration shell of solvated ions respond to an external electric field. Experiments confirmed that the dielectric permittivity of an electrolyte solution decreases as the salt concentration increases. This phenomenon is termed dielectric decrement (Hasted *et al.* 1948; Hasted 1973). The impact of excess ion polarization on the double layer capacitance was first investigated by Bikerman (1942). His model includes how excess ion polarization modifies the chemical potential of the ions. He discussed the possible influence of excess ion polarization on the dielectric permittivity as well but no detailed results were presented.

The dielectric permittivity was found to be linearly dependent on the salt concentration when the salt concentration is less than 2 M (Hasted *et al.* 1948; Glueckauf 1964; Wei & Sridhar 1990; 1992; Buchner *et al.* 1999; Chandra 2000; Levy *et al.* 2012; Gavish & Promislow 2012)

$$\varepsilon(C_{\pm}) = \varepsilon_w - \alpha(C_+ + C_-). \quad (1.2)$$

In the above, $\varepsilon(C_{\pm})$ is the relative concentration-dependent dielectric permittivity of the electrolyte solution; ε_w is the relative dielectric permittivity of pure water (80); $C_{\pm}$ are ion concentrations; and α is a phenomenological coefficient with a unit of M^{-1} , termed the excess ion polarization (Hasted *et al.* 1948; Ben-Yaakov *et al.* 2011; Hatlo *et al.* 2012). In (1.2), we assume that the dielectric permittivity of water ε_w is equal to its bulk value, which is valid for electric fields below 0.1 V/nm (Booth 1951; Danielewicz-Ferchmin & Ferchmin 2002; Gavryushov & Linse 2003; Joshi *et al.* 2004). $\alpha > 0$ corresponds to the dielectric decrement. α is salt-specific (Hasted *et al.* 1948; Glueckauf 1964; Wei & Sridhar 1990; 1992; Buchner *et al.* 1999; Chandra 2000).

To describe the dielectric decrement, we employ the mean-field approximation due to its mathematical convenience. Under the framework of the mean-field approximation, Ben-Yaakov *et al.* (2011) modifies the free energy by including the effect of ion concentrations on the local dielectric permittivity through the local variation of the concentrations in the relative dielectric permittivity $\varepsilon(C_{\pm})$. With this newly defined free energy, the modified Poisson-Boltzmann (PB) model describing equilibrium double layers is derived (Ben-Yaakov *et al.* 2009b; 2011). They found out that the dielectric decrement depletes ions inside the double layer adjacent to a charged surface and the osmotic pressure between two charged surfaces increases (Ben-Yaakov *et al.* 2011). Recently, Hatlo *et al.* (2012) applied the modified PB model to compute the differential double-layer capacitance, compared their

predictions with experiments, and obtained good agreements over a wide range of salt concentrations. Both studies indicated that the dielectric decrement influences the properties of the double layer under certain conditions and one may need to consider the impact of the dielectric decrement, in particular, when interpreting experiments showing ion specificity.

Recall that the electrophoretic mobility shows ion specificity. Given that the dielectric permittivity plays an important role in determining both the electrostatic ion-ion and ion-surface interactions, which directly influence the electrokinetic flows, it is worthwhile to explore the consequences of the dielectric decrement on electrokinetic phenomena, which is the central focus of our manuscript. We expect that our studies building on thermodynamics principles can provide a simple and physically-based analysis of the impact of the dielectric decrement to, at least, qualitatively explain ion specificity observed in electrokinetics.

The manuscript is organized as follows. In section 2, we introduce the modified PNP model accounting for the dielectric decrement and explicitly derive the ionic transport equations, suitable for dynamic problems. In section 3, we apply the modified PNP model to study electroosmotic flows. In section 4, we perform both a thin-double-layer analysis and a finite-doublelayer analysis to compute the electrophoretic mobility. The validity of the thin-double-layer asymptotical analysis is delineated as well. Section 5 concludes.

2. The Mathematical Model

Under the framework of the mean-field approximation, the free energy of a symmetric 1:1 electrolyte accounting for the dielectric decrement can be written as

$$F = \int d\vec{r} \left(-\frac{\varepsilon_0 \varepsilon(C_{\pm})}{2} |\nabla \psi|^2 + e(C_+ - C_-) \psi + kT(C_+ \ln C_+ + C_- \ln C_-) \right). \quad (2.1)$$

In the above, ψ is the electric potential; e is the elementary charge; kT is the thermal energy; $\varepsilon(C_{\pm})$ is given by (1.2). The last two terms are the entropic contribution to the free energy from cations and anions, respectively. (2.1) is similar to the regular Poisson-Boltzmann free energy except that the relative dielectric permittivity (ε) depends on the ion concentration now.

Applying the variational principle of the free energy, we can set $\delta F / \delta \psi$ equal to zero and obtain the governing equation for the electric potential ψ .

$$-\varepsilon_0 \varepsilon_w \nabla \cdot \left(\left(1 - \frac{\alpha}{\varepsilon_w} (C_+ + C_-) \right) \nabla \psi \right) = e(C_+ - C_-). \quad (2.2)$$

The chemical potential $\mu_{\pm}$ can be derived by

$$\mu_{\pm} = \frac{\delta F}{\delta C_{\pm}} = \frac{\varepsilon_0}{2} \alpha |\nabla \psi|^2 \pm e\psi + kT \ln(C_{\pm}), \quad (2.3)$$

given that $d\varepsilon/dC_{\pm} = -\alpha$. The gradient $\nabla\mu_{\pm}$ is ionic flux. The governing equations for ion concentrations can be postulated as (Kilic *et al.* 2007b):

$$\frac{\partial C_{\pm}}{\partial t} + \vec{u} \cdot \nabla C_{\pm} = \nabla \cdot \left(\frac{D_{\pm}}{kT} C_{\pm} \nabla \mu_{\pm} \right) = \nabla \cdot \left(D_{\pm} \nabla C_{\pm} \pm \frac{D_{\pm} e}{kT} C_{\pm} \nabla \psi + \frac{D_{\pm} \varepsilon_0 \alpha}{2kT} C_{\pm} \nabla (|\nabla \psi|^2) \right). \quad (2.4)$$

In the above, $\vec{u}$ is the fluid velocity. In contrast to the standard Nernst-Planck equations, (2.4) contains an extra term (the last term), representing the impact of the dielectric decrement on ionic transport. For simplification, thereafter, we assume that the ion diffusivity of cation is the same as that of anion ($D_+ = D_- = D$).

Consider that the Re number associated with electrokinetic flows is typically small. The velocities satisfy the Stokes equations:

$$\eta \nabla^2 \vec{u} - \nabla p - e(C_+ - C_-) \nabla \psi = 0, \quad (2.5)$$

in which p is the pressure. The fluid is incompressible:

$$\nabla \cdot \vec{u} = 0. \quad (2.6)$$

(2.2), (2.4), (2.5) and (2.6) formulate the modified Poisson-Nernst-Planck model accounting for the dielectric decrement. They can be solved to determine either the electro-osmotic flow near a charged surface or the electrophoretic motion of a charged particle.

Before we continue, first let us examine the structure of the equilibrium double layer. At equilibrium, the fluid is stationary ($\vec{u} \equiv 0$) and $\mu_{\pm}$ are constant throughout the system. By equating the chemical potentials with their bulk values, we can readily derive the ion concentrations:

$$C_{\pm} = C_0 e^{-\frac{\varepsilon_0 \alpha}{2kT} |\nabla \psi|^2 \mp \frac{e\psi}{kT}}, \quad (2.7)$$

where C_0 is the ion concentration far from the surface. Substituting (2.7) into (2.2), we have the modified Poisson-Boltzmann equation:

$$\varepsilon_0 \varepsilon_w \nabla \cdot \left(\left(1 - 2 \frac{\alpha}{\varepsilon_w} C_0 e^{-\frac{\varepsilon_0 \alpha}{2kT} |\nabla \psi|^2} \cosh \left(\frac{e\psi}{kT} \right) \right) \nabla \psi \right) = 2eC_0 e^{-\frac{\varepsilon_0 \alpha}{2kT} |\nabla \psi|^2} \sinh \left(\frac{e\psi}{kT} \right). \quad (2.8)$$

In the following, to simplify the analysis, we employ dimensionless variables. We select the thermal energy kT as the chemical potential scale; kTC_0 as the free energy scale; C_0 as the concentration scale; kT/e as the potential scale and the Debye length

($\lambda_D = \sqrt{\varepsilon_0 \varepsilon_w kT / 2e^2 C_0}$) as the length scale. With the aforementioned scales, (2.8) reduces to:

$$\nabla \cdot \left(\left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi|^2} \cosh(\varphi) \right) \nabla \varphi \right) = e^{-\hat{\alpha} |\nabla \varphi|^2} \sinh(\varphi), \quad (2.9)$$

where $\hat{\alpha} = \alpha C_0 / \varepsilon_w$ and ϕ is the dimensionless electric potential.

For a uniformly charged flat plate in contact with a binary 1-1 electrolyte, with a free energy defined in (2.1), remarkably, the following formula holds (Ben-Yaakov *et al.* 2009a):

$$\frac{1}{2} \left(\varepsilon + \sum_{\pm} \frac{\partial \varepsilon}{\partial C_i} C_i \right) \left(\frac{d\phi}{dy} \right)^2 + h - \sum_{\pm} C_i \frac{\partial h}{\partial C_i} = \text{constant}. \quad (2.10)$$

In the above, $\varepsilon = 1 - \hat{\alpha}(\hat{C}_+ + \hat{C}_-)$ and $h = C_+ \ln C_+ + C_- \ln C_-$ is the entropic contribution to the free energy. y is the coordinate perpendicular to the surface. Substituting (2.7) into (2.10), we can derive a relationship between $d\phi/dy$ and ϕ :

$$\left(1 - 4\hat{\alpha} e^{-\hat{\alpha} \left(\frac{d\phi}{dy} \right)^2} \cosh(\phi) \right) \left(\frac{d\phi}{dy} \right)^2 = 2e^{-\hat{\alpha} \left(\frac{d\phi}{dy} \right)^2} \cosh(\phi) - 2. \quad (2.11)$$

Unfortunately, (2.11) cannot be further integrated analytically to obtain the electric potential distribution except for low zeta potentials ($|\zeta| \ll 1$). When $|\zeta| \ll 1$, we can expand (2.11) in

terms of ϕ^2 and $\left(\frac{d\phi}{dy} \right)^2$ and only keep the leading order terms. After some algebra manipulations, we have:

$$\phi = \zeta e^{-\frac{y}{\sqrt{1-2\hat{\alpha}}}}. \quad (2.12)$$

3. The electro-osmotic mobility

Now let's consider an electro-osmotic flow near a uniformly charged flat surface in a binary symmetric electrolyte. An external electric field parallel to the surface ($\vec{E}_t$) drives excess counterions inside the double layer to migrate, which, in turn, drags the adjacent fluid to move, and induces an electro-osmotic flow with a velocity $U = M_{eo} \vec{E}_t$ outside the electric double layer (Lyklema 1995).

To compute the electro-osmotic mobility, we begin with the Stokes equation (2.5):

$$\frac{d^2 u}{dy^2} = -\frac{C_+ - C_-}{2} E_t, \quad (3.1)$$

In (3.1), the velocity is scaled by $\varepsilon_0 \varepsilon_w k^2 T^2 / (\eta e^2 \lambda_D)$. Substituting (2.2) into (3.1), we have

$$\frac{d^2 u}{dy^2} = \frac{d}{dy} \left((1 - \hat{\alpha}(C_+ + C_-)) \frac{d\phi}{dy} \right) E_t. \quad (3.2)$$

(3.2) can be integrated twice to obtain the velocity distribution:

$$u(y) = E_t \int_0^y \left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi|^2} \cosh(\varphi) \right) \frac{d\varphi}{ds} ds. \quad (3.3)$$

By letting $y \rightarrow \infty$, the electro-osmotic mobility M_{eo} can be deduced from (3.3):

$$M_{eo} = \int_0^\infty \left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi|^2} \cosh(\varphi) \right) \frac{d\varphi}{dy} dy. \quad (3.4)$$

Using (2.11), (3.4) becomes:

$$M_{eo} = \int_0^\infty \frac{2 - 4\hat{\alpha} + 2\hat{\alpha} \left(\frac{d\varphi}{dy} \right)^2}{2 + 4\hat{\alpha} \left(\frac{d\varphi}{dy} \right)^2} \frac{d\varphi}{dy} dy. \quad (3.5)$$

In the absence of the dielectric decrement ($\hat{\alpha} = 0$), the classical Helmholtz-Smoluchowski (HS) mobility ($M_{eo} = -\zeta$) is recovered.

At low zeta potentials ($|\zeta| \ll 1$), by neglecting the higher order terms $\left(\frac{d\varphi}{dy} \right)^2$ in (3.5), we have

$$M_{eo} = -(1 - 2\hat{\alpha})\zeta. \quad (3.6)$$

On the contrary, at high zeta potentials $|\zeta| \gg 1$, since

$$\lim_{\left(\frac{d\varphi}{dy} \right)^2 \rightarrow \infty} \frac{2 - 4\hat{\alpha} + 2\hat{\alpha} \left(\frac{d\varphi}{dy} \right)^2}{2 + 4\hat{\alpha} \left(\frac{d\varphi}{dy} \right)^2} = \frac{1}{2}, \quad (3.7)$$

$M_{eo} \sim \zeta/2$. Interestingly, when $|\zeta| \gg 1$, the scaling relationship between the mobility and the zeta potential does not depend on $\hat{\alpha}$ any more as long as $\hat{\alpha} \neq 0$. In other words, for $|\zeta| \gg 1$, the electro-osmotic mobility can be at most roughly decreased by a factor of 2 compared to the classical Helmholtz-Smoluchowski mobility.

For an arbitrary ζ , to compute the electro-osmotic mobility, we have to numerically solve the modified Poisson-Boltzmann equation (2.9) to obtain ϕ and then integrate (3.5). Figure 2 plots the mobility $|M_{eo}|$ against the zeta potential $|\zeta|$ for different $\hat{\alpha}$. In figure 2a, the solid line is the HS mobility. Evidently, the dielectric decrement ($\hat{\alpha} \neq 0$) reduces the mobility.

To understand the role of the dielectric decrement in the mobility reduction, we plot the distribution of the charge density $\rho = C_+ - C_-$ within the double layer in figure 3. The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$ (in the absence of the dielectric decrement), $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$ when $\zeta = 3$. Figure 3 suggests that the dielectric decrement effectively depletes ions from the double

layer and therefore reduces the charge density, translating into a reduction of the induced flow, since the electro-osmotic flow is driven by the action of the applied electric field on excess counterions characterized by ρ inside the double layer.

Interestingly, we also can show that the charge density approaches to a limiting value ($1/(2\hat{\alpha})$) with an increasing ζ . When $|\zeta| \gg 1$, counterions are dominate inside the double layer. (2.11) suggests

$$|\rho| = \left| 2e^{-\hat{\alpha}\left(\frac{d\varphi}{dy}\right)^2} \sinh(\varphi) \right| \sim 2e^{-\hat{\alpha}\left(\frac{d\varphi}{dy}\right)^2} \frac{e^{|\varphi|}}{2} \sim 2e^{-\hat{\alpha}\left(\frac{d\varphi}{dy}\right)^2} \cosh(\varphi) = \lim_{\frac{d\varphi}{dy} \rightarrow \infty} 2 \frac{2 + \left(\frac{d\varphi}{dy}\right)^2}{2 + 4\hat{\alpha}\left(\frac{d\varphi}{dy}\right)^2} = \frac{1}{2\hat{\alpha}}. \quad (3.8)$$

(3.8) demonstrates that the dielectric decrement imposes a maximum on ion concentrations, preventing ions from exponentially increasing with ζ as predicted by the standard PB model. Notice that in contrast to steric effects where the saturation of counterions does not change the electro-osmotic mobility directly (Bazant *et al.* 2009), the dielectric decrement reduces the mobility since the local variation of the dielectric permittivity has direct consequences on ion-ion and ion-surface interactions in the presence of an external electric field which explicitly determine the mobility.

In addition, in order to understand the impact of the dielectric decrement on the local dielectric permittivity inside the double layer, figure 4 plots $\varepsilon = 1 - \hat{\alpha}(C_+ + C_-)$ against y . The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$ when $\zeta = 3$. Clearly, ε decreases as approaching the charged surface since counterion concentration increases with a decreasing y . The larger $\hat{\alpha}$; the smaller ε . In addition, because ion saturates at $1/(2\hat{\alpha})$, ε eventually approaches $1/2$ with an increasing ζ . In figure 4, the zeta potential is still considered to be modest. The local dielectric permittivity does not reach its limit. An increase of ζ will cause ε to saturate.

With the decrease of ε , according to (1.1), the electro-osmotic mobility is reduced since it reduces the dielectric permittivity. Furthermore, figure 2a supports our scaling analysis that the mobility is proportional to ζ^2 at large zeta potentials. In addition, although (3.6) is derived under the assumption $|\zeta| \ll 1$, figure 2b suggests that (3.6) has much broader applicability and indeed can accurately predict the mobility up to $|\zeta| \sim 2$.

For electro-osmosis near a charged dielectric surface, usually the surface charge rather than the zeta potential is fixed. Although the surface charge can be directly related to the zeta potential, it is still worthwhile to examine the impact of the dielectric decrement on the mobility in terms of the surface charge.

When $|\sigma| \ll 1$, from (2.12), one can obtain the surface charge density as a function of the zeta potential:

$$\sigma = -(1 - 2\hat{\alpha}) \frac{d\varphi(0)}{dy} = \sqrt{1 - 2\hat{\alpha}\zeta}. \quad (3.9)$$

(3.6) and (3.9) give rise to the relationship between the mobility and the surface charge density:

$$M_{eo} = -\sqrt{1-2\hat{\alpha}\sigma}. \quad (3.10)$$

Figure 5 depicts $|M_{eo}|$ against $|\sigma|$ for various $\hat{\alpha}$, in which solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. To understand the behavior in figure 5, figure 6 plots the zeta potential in terms of σ . The fact that the mobility increases with an increasing σ is attributed to its increasing

zeta potential. In addition, consider $\sigma = -\varepsilon \frac{d\varphi}{dn} \sim \varepsilon \frac{\zeta}{\lambda_D}$ or $\zeta \sim \frac{\sigma \lambda_D}{\varepsilon}$ and the local dielectric permittivity at the surface is smaller for a larger α . It is not surprising that the zeta potential of $\hat{\alpha} = 0.1$ is much larger than those of $\hat{\alpha} = 0.01$ and $\hat{\alpha} = 0.05$ as witnessed in figure 6, translating into a higher electro-osmotic mobility.

4. The electrophoretic mobility

In this section, we consider a uniformly charged spherical particle with a radius R suspended in a binary 1-1 electrolyte. An imposed electric field $\vec{E}$ drives the particle to migrate with a velocity $\vec{U} = M_e \vec{E}$. Charged particle's motion under the action of the electric field is well known as electrophoresis. M_e is the electrophoretic mobility. To describe the electrophoretic motion of the particle, we choose a reference frame moving with the particle. To calculate M_e , we use a regular perturbation expansion in terms of the applied electric field assuming that the external electric field only slightly disturbs the electric potential and the ions' concentrations of the equilibrium double layer, which is often the case commonly seen in practice (O'Brien & White 1978). M_e can be deduced from the first-order equations.

The zeroth order electric potential (equilibrium potential) $\phi^{(0)}$ can be obtained from solving (2.9) and the concentration $C_{\pm}^{(0)}$ obeys (2.7).

4.1. The first order approximation

The first order equations are linear in the perturbed quantities. It is convenient to decompose the first order problem into two sub problems in the moving reference frame: the **E** problem and the **U** problem (O'Brien & White 1978). The **E** problem consists of the same imposed electric field at infinity and zero velocity at infinity. The second problem has zero electric field and a uniform flow field at infinity. According to the linearity, the solutions of the first order problem can be written as a superposition:

$$X^{(1)} = X^{(1)E} + M_e X^{(1)U}, \quad (4.1)$$

where X stands for any of the dependent variables. M_e can be obtained by nullifying the net force acting on the particle.

Since all the equations (not all the boundary conditions) are the same for the **E** and **U** problems, henceforth we drop the superscripts **E** and **U**. The first order equations are:

$$\nabla \bullet \left((1 - \hat{\alpha}(C_+^{(0)} + C_-^{(0)}) \nabla \varphi^{(1)} - \hat{\alpha}(C_+^{(1)} + C_-^{(1)}) \nabla \varphi^{(0)}) \right) = -\frac{C_+^{(1)} - C_-^{(1)}}{2\hat{\lambda}_D^2}, \quad (4.2)$$

$$\nabla^2 \vec{u}^{(1)} - \nabla p^{(1)} - \frac{C_+^{(0)} - C_-^{(0)}}{2\hat{\lambda}_D^2} \nabla \varphi^{(1)} - \frac{C_+^{(1)} - C_-^{(1)}}{2\hat{\lambda}_D^2} \nabla \varphi^{(0)} = 0, \quad (4.3)$$

$$\nabla \bullet \vec{u}^{(1)} = 0, \quad (4.4)$$

and

$$\nabla \bullet \left(\nabla C_{\pm}^{(1)} \pm (C_{\pm}^{(0)} \nabla \varphi^{(1)} + C_{\pm}^{(1)} \nabla \varphi^{(0)}) + \hat{\lambda}_D^2 \hat{\alpha} C_{\pm}^{(1)} \nabla |\nabla \varphi^{(0)}|^2 + 2\hat{\lambda}_D^2 \hat{\alpha} C_{\pm}^{(0)} \nabla (\nabla \varphi^{(0)} \bullet \nabla \varphi^{(1)}) - m \vec{u}^{(1)} C_{\pm}^{(0)} \right) = 0 \quad (4.5)$$

In contrast to the equations in section 3, when studying electrophoresis, it is convenient to choose the particle radius R as the length scale, while the rest scales remain the same.

$\hat{\lambda}_D = \lambda_D / R$ is the relative Debye length and $m = \frac{\varepsilon_0 \varepsilon_w k^2 T^2}{\eta e^2 D}$ is ion mobility.

To determine the particle's electrophoretic mobility M_e , we calculate the forces acting on the particle in both $\mathbf{E}$ and $\mathbf{U}$ problems and M_e is equal to $-F^{(1)E}/F^{(1)U}$ by nullifying the net force ($F^{(1)E} + M_e F^{(1)U} = 0$).

The aforementioned first-order equations with corresponding boundary conditions can be solved by the finite element software Comsol 3.5 (Comsol, Los Angle, USA). The computational domain consisted of a finite domain $1 \leq r \leq L$. Here we let $L = 10^4$ since an increase in L by a factor of 10 leads to variations smaller than 0.1%, indicating that L is large enough to render the computational results L -independent. In addition, to resolve the detailed structure of the double layer, non-uniform elements were employed with a dense mesh near the particle's surface and the elements' size gradually increased as the distance from the particle increased. The mesh was refined a few times to assure that the computational results are mesh-independent.

To verify the computational algorithm, we calculated the electrophoretic mobility in the absence of the dielectric decrement ($\hat{\alpha} = 0$) for various $\hat{\lambda}_D$ and obtained excellent agreements with the results reported in (O'Brien & White 1978). Moreover, our computed electrophoretic mobility agreed well with those predicted by the asymptotical analysis in the limit of thin double layers (see below).

4.2 Electrophoretic mobility for thin double layers

In the limit of thin double layers ($\hat{\lambda}_D \ll 1$), we can apply an asymptotic analysis to compute the electrophoretic mobility (Dukhin & Deryaguin 1974; Grosse & Shilov 1996; Khair & Squires 2009). Briefly, in the thin double layer limit, most of the electrolyte remains neutral

except for a thin and locally planar double layer close to the particle's surface. Conveniently, we can decompose the region into the double layer and the bulk regions.

At moderate or large zeta potentials, surface conduction is significant. Surface conduction withdraws ions from the bulk at one end of the particle and depletes ions into the bulk at the other end of the particle to maintain the current conservation. This ion-transport process creates a concentration gradient outside the double layer. The bulk concentration gradient creates an osmotic pressure which can drive a flow termed the diffusio-osmotic flow (Anderson 1989). Hence in this case, the flow velocity inside the double layer consists of both an electro-osmotic component and a diffusio-osmotic component.

When $\hat{\lambda}_D \ll 1$, the dominate fluid flow inside the double layer is parallel to the surface. Since the surface is assumed to be locally flat, for the double layer region, it is convenient to use the Debye length λ_D to rescale the radial coordinate ($y = (r-1)/\hat{\lambda}_D$). With this new coordinate, the electro-osmotic velocity component is readily given by (3.3):

$$\vec{u}_{\parallel}^{(1)E} = \vec{E}_{\parallel} \int_0^y \left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \cosh(\varphi^{(0)}) \right) \frac{d\varphi^{(0)}}{ds} ds, \quad (4.6)$$

where $\vec{E}_{\parallel}$ is the tangential electric field at the outer edge of the double layer.

To compute the diffusio-osmotic component, we need first to compute the osmotic pressure from the normal component of the Stokes equation:

$$\frac{dp^{(1)}}{dy} = \frac{1}{\hat{\lambda}_D^2} e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{dy} C^{(1)}. \quad (4.7)$$

Substituting (4.7) into the tangential component of the Stokes equation, we have

$$\frac{d^3 \vec{u}_{\parallel}^{(1)D}}{dy^3} = e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{dy} \nabla_s C^{(1)}. \quad (4.8)$$

(4.8) can be integrated three times with proper boundary conditions. The diffusio-osmotic velocity component becomes:

$$\vec{u}_{\parallel}^{(1)D} = \nabla_s C^{(1)} \left(-\frac{y^2}{2} \int_y^\infty \left(e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{ds} \right) ds + y \int_y^\infty \left(s e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{ds} \right) ds + \frac{1}{2} \int_0^y \left(s^2 e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{ds} \right) ds \right)$$

Finally, the slip velocity $\vec{u}_{\parallel}^{(1)s}$ at the outer edge of the double layer is given by letting $y \rightarrow \infty$:

$$\vec{u}_{\parallel}^{(1)s} = \vec{E}_{\parallel} \int_0^\infty \left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \cosh(\varphi^{(0)}) \right) \frac{d\varphi^{(0)}}{dy} dy + \frac{\nabla_s C^{(1)}}{2} \int_0^\infty \left(y^2 e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{dy} \right) dy. \quad (4.10)$$

In the limit of thin double layers, the mobility of the sphere can be calculated from $\vec{u}_{\parallel}^{(1)s}$ via the following formula (Anderson 1989):

$$M_e = -\frac{1}{4\pi} \oint_{r=1} \vec{u}_{\parallel}^{(1)s} \cdot \hat{E}_{\infty} dS, \quad (4.11)$$

where $\hat{E}_{\infty} = \vec{E}_{\infty}/|\vec{E}_{\infty}|$ is a unit vector tangential to the imposed electric field at infinity. To explicitly compute M_e , we still require the surface derivatives of the electric potential and bulk concentration at the double-layer-bulk interface ($r = 1$) that are determined by the solutions in the bulk.

In the bulk region, we switch back to the original coordinate using the particle's radius as the length scale. The bulk concentration $C^{(1)} = C_+^{(1)} = C_-^{(1)}$ obeys

$$\nabla^2 C^{(1)} = 0. \quad (4.12)$$

Due to charge neutrality in the bulk, the electric potential in the bulk satisfies the Laplace equation

$$\nabla^2 \varphi^{(1)} = 0. \quad (4.13)$$

(4.12) and (4.13) are readily integratable:

$$C^{(1)} = \frac{K}{r^2} \cos\theta, \quad (4.14)$$

and

$$\varphi^{(1)} = \left(-r + \frac{f}{r^2}\right) \cos\theta. \quad (4.15)$$

K and f are integral constants that need to be determined by the boundary conditions.

To derive the effective boundary conditions on the particle's surface, we invoke the quasi-equilibrium approximation where the bulk reaches a local equilibrium with the double layer (Dukhin & Deryaguin 1974; O'Brien 1983; Grosse & Shilov 1996). Under the quasi-equilibrium assumption, the perturbed chemical potentials are constant across the thin double layer. We can then write down the ion conservation equations in terms of the actual and far field variables, take the difference, and integrate the resulting equation in terms of the radial coordinate from $y = 0$ to infinity (throughout the double layer). Then we obtain the following boundary conditions in terms of chemical potentials ($\mu_{\pm}^{(1)} = C^{(1)} \pm \varphi^{(1)}$) at $r = 1$:

$$\left. \frac{\partial \mu_{\pm}^{(1)}}{\partial r} \right|_{r=1} = \pm 2R_{\pm} \varphi^{(1)}(1) + 2U_{\pm} C^{(1)}(1). \quad (4.16)$$

The detailed derivation of (4.16) can be found in Grosse & Shilov (1996) and Zhao (2010). In (4.16),

$$R_{\pm} = \hat{\lambda}_D \int_0^{\infty} \left((C_{\pm}^{(0)} - 1) \pm m(1 - C_{\pm}^{(0)}) u_{\parallel}^{(1)E} \right) dy, \quad (4.17)$$

and

$$U_{\pm} = \hat{\lambda}_D \int_0^{\infty} \left((C_{\pm}^{(0)} - 1) + m(1 - C_{\pm}^{(0)}) u_{\parallel}^{(1)D} \right) dy. \quad (4.18)$$

Substituting (4.14) and (4.15) into (4.16), we have

$$K = \frac{-3(R_+ - R_-)}{2((R_+ + R_- + 2) + (U_-(R_+ + 1) + U_+(R_- + 1)))}, \quad (4.19)$$

and

$$f = \frac{(2R_+ + 2R_- - 2) + (U_-(2R_+ - 1) + U_+(2R_- - 1))}{2((R_+ + R_- + 2) + (U_-(R_+ + 1) + U_+(R_- + 1)))}. \quad (4.20)$$

Finally, using (4.14) and (4.15) with (4.11) gives rise to the electrophoretic mobility:

$$M_e = \frac{2}{3}(-1 + f) \int_0^{\infty} \left(1 - 2\hat{\alpha} e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \cosh(\varphi^{(0)}) \right) \frac{d\varphi^{(0)}}{dy} dy + \frac{1}{3} K \int_0^{\infty} \left(y^2 e^{-\hat{\alpha} |\nabla \varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{dy} \right) dy. \quad (4.21)$$

When $|\zeta| \ll 1$, the surface conduction is negligible and there is almost no ion exchange across the double-layer-bulk interface. Hence there is no concentration polarization,

translating into no diffusio-osmotic flow ($\vec{u}_{\parallel}^{(1)D} = 0$) as well, and the electric field at the double-layer-bulk interface is parallel to the surface. The electrophoretic mobility is solely determined by the electro-osmotic flow inside the double layer. The dielectric decrement reduces the magnitude of the electro-osmotic flow by a factor of $1 - 2\hat{\alpha}$. Accordingly, the electrophoretic mobility should also decrease with the same ratio. Indeed, with $\vec{u}_{\parallel}^{(1)D} = 0$ and neglecting higher order terms, we can analytically integrate (4.21) and obtain

$$M_e = (1 - 2\hat{\alpha})\zeta, \quad (4.22)$$

consistent with our simple argument.

4.3 Results for thin double layers

Figure 7 plots the mobility M_e against ζ for various $\hat{\alpha}$ when $\hat{\lambda}_D = 0.01$. The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. In figure 7b, we compare the electrophoretic mobility to the

analytical solution (4.22) derived under the limit of low zeta potentials ($|\zeta| \ll 1$). Similar to the electro-osmotic mobility in section 3, despite that (4.22) is strictly derived with $|\zeta| \ll 1$, (4.22) can still be applied to predict the mobility when $\zeta < 2$.

With the increase of the zeta potential, surface conduction becomes increasingly important. Since the surface conduction, in general, weakens the tangential electric field acting on the double layer to maintain the current conservation, the larger the surface conduction; the smaller the tangential electric field, resulting in a smaller mobility. On the other hand, the higher zeta potential; the more excess counterions harbored inside the double layer, leading to a higher mobility. Hence, the competition between the weaker tangential electric field and the increase of excess counterions inside the double layer with the increasing ζ results in a local maximum mobility in terms of ζ as shown in figure 7.

Even more interestingly, figure 7 indicates that at large zeta potentials, the higher the influence of the dielectric increment (larger $\hat{\alpha}$); the larger the mobility. In addition, the maximum mobility is shifted to the right. To understand this behavior, we plot the Dukhin number Du versus ζ when $\hat{\lambda}_D = 0.01$ in figure 8. The Du number is a measure of the importance of surface conduction, defined as $Du = \sigma_s/(\sigma_b R)$ which compares the surface conduction σ_s to the bulk conductivity σ_b . Du number can be written as (Lyklema 1995):

$$Du = \frac{\hat{\lambda}_D}{2} \left(\int_0^\infty (C_+^{(0)} + C_-^{(0)} - 2) dy + m \int_0^\infty (C_+^{(0)} - C_-^{(0)}) u^{(1)E} dy \right) \quad (4.23)$$

The first and second terms in (4.23) are, respectively, the migration and convection contributions to the Du number.

At large ζ , the dominant counterions inside the double layer are saturated at $1/2\hat{\alpha}$. The larger $\hat{\alpha}$; the smaller the saturated counterion concentration, mitigating the surface conduction. The surface conduction reduces the mobility M_e . In other words, the smaller Du is; the larger M_e is. Hence M_e increases with the increasing $\hat{\alpha}$ at high zeta potentials. In addition, consider that the Du number grows much slowly with ζ at large $\hat{\alpha}$, deferring the influence of the surface conduction to a higher ζ . It is not surprising that the maximum mobility shifts to the right when $\hat{\alpha}$ increases.

Next we examine the impact of the dielectric decrement on the electrophoretic mobility in terms of the surface charge as well. When $|\sigma| \ll 1$, neglecting the surface conduction, the electrophoretic mobility is the same as the electro-osmotic mobility:

$$M_e = \sqrt{1 - 2\hat{\alpha}\sigma}. \quad (4.24)$$

Figure 9 depicts the mobility M_e against σ for various $\hat{\alpha}$ when $\hat{\lambda}_D = 0.01$. Here we do not show the results for $\hat{\alpha} = 0$ since the curve is very similar to the one in figure 7. In (a), the solid line, the dashed line, and the dotted-dashed line correspond, respectively, to $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. In (b) the mobilities are compared to (4.24) derived under the low-surface-charge assumption.

In Lyklema (1994), the electrokinetic charge from which the mobility can be deduced was plotted against the surface charge density for different typed particles submerged into different salt concentrations. For example, for goethite particles, at low surface charges, the mobility in 10 mM salt is smaller than the mobility in 1 mM salt. In contrast, the mobility in 10 mM is larger than that in 1 mM at high surface charges. Consider that $\hat{a}$ ($\hat{a} \equiv aC_0/\epsilon_w$) is proportional to the salt concentration and $\hat{a}$ in 10 mM is larger than that in 1 mM. This experimentally observed qualitative difference at different surface charges is consistent with figure 9 and qualitatively confirms our predictions. Our model attributes this contrast dependence of the mobility on salt concentrations between low surface charges and high surface charges to the different impact of the dielectric decrement on the electrophoretic mobility.

In addition, figure 9 suggests that the mobility first increases, attains a local maximum, then decreases, and finally increases again as σ increases. In contrast, for $\hat{a} = 0$, the mobility eventually decreases to a limiting value after attaining its maximum. As suggested by figure 6, the increase of the mobility with an increasing σ at high σ is attributed to the high zeta potential.

To understand the increase of the mobility at large ζ , figure 10 plots the mobility scaled by the zeta potential as a function of ζ , in which the solid line, the dashed line, and the dotted-dashed line, correspond, respectively, to $\hat{a} = 0.01$, $\hat{a} = 0.05$, and $\hat{a} = 0.1$. Clearly, figure 10 suggests that $M_e \sim \zeta$ when $\zeta \gg 1$. This linear scaling relationship can be readily understood. At high zeta potentials, due to the dielectric decrement, a condensed charged layer with a density $1/2\hat{a}$ forms near the oppositely charged surface. The thickness of this condensed layer l_c grows with ζ . Indeed, one can show that l_c grows like $\zeta^{1/2}$. For the detailed derivation of this scaling relation between l_c and ζ , interested readers are referred to Khair & Squires (2009) and Zhao (2010).

At large ζ , the dominant contribution of the mobility comes from the condensed layer l_c with $C_- \sim 1/2\hat{a}$ and $C_+ \sim 0$. Consider $u_{\parallel}^{(1)E} \sim \zeta$ and $l_c \sim \zeta^{1/2}$.

$$R_{\pm} - \hat{\lambda}_D \int_0^{\infty} \left((C_{\pm}^{(0)} - 1) \pm m(1 - C_{\pm}^{(0)})u_{\parallel}^{(1)E} \right) dy \sim \zeta^{3/2}. \quad (4.25)$$

Similarly,

$$U_{\pm} = \hat{\lambda}_D \int_0^{\infty} \left((C_{\pm}^{(0)} - 1) + m(1 - C_{\pm}^{(0)})u_{\parallel}^{(1)D} \right) dy \sim \zeta^{5/2} \quad (4.26)$$

since (4.9) indicates that $u_{\parallel}^{(1)D} \sim \zeta^2$. In addition, because of the sign difference in the terms associated with $u_{\parallel}^{(1)E}$ in $R_{\pm}$ ((4.25)), one can easily show that the leading order terms in $U_+R_- + U_-R_+$ cancel out, yielding to

$$U_+R_- + U_-R_+ \sim \zeta^{5/2} \quad (4.27)$$

With the scaling relations with ζ of different terms, one can show

$$f \sim 1, \quad (4.28)$$

and

$$K \sim \zeta^{-1}. \quad (4.29)$$

Notice that

$$U_E = \int_0^\infty \left(1 - 2\hat{\alpha} e^{-\hat{\alpha}|\nabla\varphi^{(0)}|^2} \cosh(\varphi^{(0)}) \right) \frac{d\varphi^{(0)}}{dy} dy \sim \zeta, \quad (4.30)$$

and

$$U_C = \int_0^\infty \left(y^2 e^{-\hat{\alpha}|\nabla\varphi^{(0)}|^2} \sinh(\varphi^{(0)}) \frac{d\varphi^{(0)}}{dy} \right) dy \sim \zeta^2. \quad (4.31)$$

Finally, the linear scaling relationship between the mobility and the zeta potential is demonstrated:

$$M_e = \frac{2}{3}(-1+f)U_E + \frac{1}{3}KU_C \sim \zeta. \quad (4.32)$$

4.3 Electrophoretic mobility for finite double layers

For finite double layers, (4.21) under the assumption of thin double layers is not valid any more. Instead, we have to solve the first order equations (4.2)–(4.5) to numerically compute the mobility. First, we compare our numerical results to the predictions by (4.21) under the thin double layer approximation for various $\hat{\alpha}$ in figure 11. Evidently, direct numerical results generally agree well with (4.21). In turn, figure 11 validates our numerical algorithm.

Figure 11 suggests that at large zeta potentials the agreement deteriorates as $\hat{\alpha}$ increases. This is readily explained: due to the dielectric decrement, a condensed charged layer with a density $1/2\hat{\alpha}$ forms near the oppositely charged surface. The thickness of this condensed layer l_c grows with ζ as evidenced in figure 12. When deriving (4.21), we require $\hat{\lambda}_D \ll 1$. However, at large ζ , l_c becomes comparable or even larger than $\hat{\lambda}_D$ and l_c turns to be the correct double layer length. Hence in figure 11, it is not surprising that the numerical results do not agree well with (4.21) at large ζ and large $\hat{\alpha}$. Figure 11 reminds us to be cautious when using the thin-double-layer analysis, in particular, at high ζ .

Next, we compare the computed mobility M_e to that predicted by (4.21) in terms of $\hat{\lambda}_D$. Figure 13 indicates that when $\hat{\lambda}_D > 0.05$, the computed mobility deviates from (4.21) for $\zeta = 6$. Hence for nanosize particles, we must resort to directly solve the full first-order equations to accurately predict the mobility. In addition, figure 13 suggests that as the double layer thickness increases, the mobility decreases, which is consistent with the case of the electrophoretic mobility in the absence of the dielectric decrement ($\alpha = 0$) (O'Brien & White 1978). In other words, the dielectric decrement does not change the dependence of the mobility on $\hat{\lambda}_D$ qualitatively.

In Lopez-Leon *et al.* (2003), experiments suggested a contrast dependence of mobility on salts for different charged particles. For a positively charged AMJ10 latex particle, experiments showed that the electrophoretic mobility follows the order $\text{NaCl} > \text{NH}_4\text{NO}_3 > \text{NaNO}_3 > \text{NaSCN}$. In stark contrast, for a negatively charged ABJ2 latex particle, the mobility follows the reverse order $\text{NaSCN} > \text{NH}_4\text{NO}_3 > \text{NaCl}$. In addition, the mobilities' difference among salts for the positively charged AMJ10 particle is much more significant than that of the negatively charged ABJ2 particle among salts. It is recognized that the reported magnitude of the surface charge density of the AMJ 10 latex particle is about twice larger than that of the ABJ2 particle.

To understand this different salt dependence, we plot the dimensional electrophoretic mobility M_e (m^2/Vs) as a function of the bulk concentration C_0 (mM) in figure 14. For colloidal particles, the surface charge is fixed for a range of salt concentrations. Hence here we set the surface charge density as a constant value of $8 \mu\text{C}/\text{cm}^2$ (a) and $3 \mu\text{C}/\text{cm}^2$ (b). The particle radius is assumed to be 100 nm. The solid line and the dashed line correspond, respectively, to $\alpha = 0$ and $\alpha = 40 \text{ M}^{-1}$. Here we focus on the high salt concentration range in which the impact of the dielectric decrement is prominent. Figure 14 suggests that the different salt dependence of mobility may be attributed to the different surface charge density. At small surface charges, the surface conduction is negligible. Since the dielectric decrement decreases the local permittivity, the mobility is accordingly reduced. At high surface charges, the dielectric decrement effectively mitigates the surface conduction, resulting in a higher mobility. Moreover, figure 14 also indicates that the mobilities' difference among salts associated with the high surface charge density is much larger than that with the low surface charge density, consistent with experimental results. In addition, the decrease of the mobility with the increase of the salt concentration observed in figure 14 agrees with experimental results as well. However, because of possible different specific ion absorptions on the surface which can change the zeta potential, favorable quantitative comparisons are not obtained. Nonetheless, qualitative agreements are already impressive.

5. Conclusion

Recently, a modified Poisson-Nernst-Planck model accounting for the dielectric decrement was developed (Ben-Yaakov *et al.* 2011; Hatlo *et al.* 2012). In this article, we extended this model to study electrokinetics. More specifically, we derived ionic transport equations. With ionic equations, we further coupled the model with the Stokes equations to explore the

influence of the dielectric decrement on electrokinetic phenomena including both electro-osmosis and electrophoresis.

First we explored the role of the dielectric decrement in determining the equilibrium double layer structure. We revealed that the dielectric decrement leads to ion saturation with an increasing zeta potential, preventing ion concentrations from exponentially growing to infinity as predicted by the classical Poisson-Boltzmann model. When the counterions saturate, a charged condensed layer begins to form adjacent to the surface and the thickness of the condensed layer grows like $\sqrt{\epsilon}$, effectively extending the double layer thickness beyond the traditional Debye length, which has a direct impact on the thin-double-layer asymptotic analysis.

Next we investigated the electro-osmotic flow near a flat homogeneously charged surface in the presence of the dielectric decrement. Not surprisingly, due to the decrease of the dielectric permittivity, the magnitude of the electro-osmotic flow is reduced. In addition, we discovered that at large zeta potentials the magnitude of the flow is proportional to ζ^2 as long as $\alpha \rightarrow 0$.

We also examined the impact of the dielectric decrement on the electrophoretic mobility. We first conducted an asymptotical analysis in the limit of thin double layers. We derived the bulk governing equations and effective boundary conditions. They can be solved to compute the electrophoretic mobility. Interestingly, in contrast to the impact of the dielectric decrement on the electro-osmosis which always weakens the flow, the consequence on the electrophoretic mobility is more intriguing. At low and moderate zeta potentials, the mobility decreases as α increases. On the contrary, at large zeta potentials, the mobility increases as α increases. We attributed this qualitative difference to the influence of the surface conduction at large zeta potentials since the dielectric decrement can effectively suppress the surface conduction. Our predictions of the contrast salt dependence for mobilities at different zeta potentials are qualitatively consistent with experimental results and provide a possible explanation of certain ion specificity observed in experiments.

Our asymptotical analysis is derived under the assumption of the thin double layer ($\lambda_D \ll 1$). However, at large enough zeta potentials, the thickness of the condensed layer l_c becomes much larger than the Debye length and is the correct double layer length scale. In other words, the thin-double-layer assumption requires $l_c \ll 1$ as well. We solved the full linearized modified PNP model to compute the electrophoretic mobility and our numerical solutions validate our argument that the thin-double-layer analysis is valid when both $\lambda_D \ll 1$ and $l_c \ll 1$.

In our analysis, we used (1.2) to describe the impact of the salt concentration on the dielectric permittivity. It is recognized that the dependence of the dielectric permittivity on the salt concentration deviates from the linear relationship when the concentration is larger than 2 M. Experiments revealed that the dielectric permittivity saturates at high salt concentrations (Hasted *et al.* 1948; Glueckauf 1964; Wei & Sridhar 1990; 1992; Buchner *et al.* 1999; Chandra 2000; Levy *et al.* 2012; Gavish & Promislow 2012). In our model, ions are predicted to saturate at $1/2\alpha$ with high zeta potentials. If the saturated ion concentration

near the surface is below 2 M, the linear relationship between ε and α holds. When $\alpha = 20 \text{ M}^{-1}$, the saturated concentration is estimated to be 2 M. In other words, when $\alpha > 20 \text{ M}^{-1}$, our model is applicable for any zeta potential. On the other hand, when $\alpha < 20 \text{ M}^{-1}$, ions saturate at a value higher than 2 M. Although our model is still applicable for low and moderate zeta potentials, for higher zeta potentials or concentrated solutions where ions may saturate near the charged surface, our model seems to overestimate the impact of the dielectric decrement since (1.2) predicts a lower dielectric permittivity compared to the one observed in experiments. Recently, Gavish & Promislow proposed a new functional dependence of dielectric permittivity on salt concentration involving a Langevin function which provides a remarkable accurate prediction up to 15 M (Gavish & Promislow 2012) with only one fitting parameter. Clearly, the incorporation of this new dependence of the dielectric permittivity into our model by replacing $\varepsilon(C_{\pm})$ in (2.1) with this new function will lead to new physics. This extension will be left for future investigations.

In electrokinetics, the concept of the Stern layer was introduced to circumvent the unrealistic capacitance predicted by the standard Poisson-Boltzmann model at large surface potentials. The Stern layer, accounting for steric repulsion between ions and the surface, acts like a linear capacitor in series with the diffuse layer. With the Stern layer, the zeta potential ζ , which is defined at the plane of shear, the interface between the Stern layer and the diffuse layer (Lyklema 1995), can be related to the surface potential ϕ_s by $\zeta = \phi_s / (1 + C_{diff}/C_{Stern})$. Here C_{diff} and C_{Stern} are, respectively, the capacitances of the diffuse layer and Stern layer. Consistent with our analysis, accounting for the Stern layer will only change the boundary condition of the electric potential from the surface potential ϕ_s to ζ at the plane of shear. All other derivation and analysis remain the same. Evidently, since $\zeta < \phi_s$, inclusion of the Stern layer would decrease the mobility predicted without considering the Stern layer.

We must emphasize that the dielectric decrement is just one source of ion specificity. Ion-specific effects originate from the interplays between ion-ion, ion-solvent, and ion-surface interactions including hydration, dispersion, (Ben-Yaakov et al. 2011), non-electrostatic ion-ion interaction (Zhao 2012) *et al.* There are experimental evidences that certain electrokinetic phenomena are ion-specific (Bazant *et al.* 2009). Our analysis in this manuscript suggested that the influence of ions on the dielectric permittivity needs to be considered in electrokinetics, in particular, at high salt concentrations and high zeta potentials.

In addition, steric effects have also been included to modify the PNP model accounting for the impact of finite ion size (Bikerman 1942; Borukhov *et al.* 1997; Kilic *et al.* 2007a; 2007b; Bazant *et al.* 2009). This modified PNP model has been applied to explain the alternating-current electro-osmotic flow reversal at high frequencies observed in experiments (Storey *et al.* 2008). Khair & Squires (2009) extensively studied steric effects on electrophoretic mobility. At large zeta potentials, the saturation of ions induced by steric effects mitigates the surface conduction and leads to a larger mobility compared to the one in the absence of steric effects. At large zeta potentials, the influence of steric effects is similar to the case that we studied here since both of them cause ion saturation.

Since the local-density mean-field model built on thermodynamics presented here is based on free energy and can be readily extended to account for other physical effects including steric effects and non-electrostatic interactions to better interpret experiments. One straightforward extension is to incorporate steric effects into our model. If the maximum concentration set by steric effects is much larger than that set by the dielectric decrement, the influence of steric effects is negligible. In contrast, if the saturated concentration due to steric effects is smaller than the one predicted by the dielectric decrement, we would expect that steric effects complicate the impact of the dielectric decrement by preventing the dielectric permittivity from reaching its limiting value set by the dielectric decrement. Rather, the dielectric permittivity reaches the value constrained by steric effects. In this case, steric effects shall have a consequence on electrokinetics. Since at large zeta potentials, both the dielectric decrement and steric effects reduce the surface conduction, both of them attempt to increase the mobility. Inclusion of steric effects may yield new findings, in particular, when the contribution from steric effects to ion saturation is comparable to or even larger than that from the dielectric decrement. These extensions are in order for future consideration.

The surface charge at a negatively charged silica surface is regulated by the availability of potential determining ions (Hunter 1981). Ions allow the surface to acquire charge through electrochemical reaction. Recently, surface charge regulation has been proposed to successfully explain overlimiting current witnessed in ion-exchange membranes (Andersen *et al.* 2012). Typically, H^+ is the one regulating the surface charge for the common pH values of interest. The surface charge is decreased by the presence of proton (H^+) at the surface. A negatively charged surface attracts protons due to electrostatic interactions and protons near the surface may effectively decrease the surface charge. Hence inclusion of the surface charge regulation may change the electrophoretic mobility due to the reduction of the surface charge. Detailed impact of surface charge regulation still deserves further investigation.

Electrostatic correlations are another source of ion specificity. Short-range correlations are crucial in concentrated solutions and systems with multivalent ions (Attard 1996; Vlachy 1999). They usually lead to over-screening: the first layer near the charged surface over-compensates the surface charge, leads to a second layer with opposite net charge which again induces another oppositely charged layer, and so on till the charge neutrality reaches in the bulk. The fluid in the bulk feels the impact of the charged layer adjacent to it. In this case, the adjacent layer may be oppositely charged compared to the surface charge. Bazant *et al.* developed a simple mean-field Landau-Ginzburg-type phenomenological theory accounting for non-local electrostatic correlations of interacting effective charges (Bazant *et al.* 2011). The model predicts the decrease of electro-osmotic flow and even the reversal of the electro-osmotic flow at certain conditions (Storey & Bazant 2012). Clearly, the influence of electrostatic correlations on the electrophoretic mobility deserves further attention.

Acknowledgments

The work was, in part, supported by NIH Grant No. 1R03HG006562-01.

References

- ANDERSON JL. Colloid transport by interfacial forces. *Annu Rev Fluid Mech.* 1989; 21:61–99.
- ANDERSON MB, VAN SOESTBERGEN M, MANI A, BRUUS H, BIESHEUVEL PM, BAZANT MZ. Current-induced membrane discharge. *Phys Rev Lett.* 2012; 109:108301. [PubMed: 23005334]
- ATTARD P. Electrolytes and the electrical double layer. *Adv Chem Phys.* 1996; 92:1–159.
- BAZANT MZ, KILIC MS, STOREY BD, AJDARI A. Towards an understanding of nonlinear electrokinetics at large applied voltages in concentrated solutions. *Adv Colloid Interface Sci.* 2009; 152:48–88. [PubMed: 19879552]
- BAZANT MZ, STOREY BD, KORNYSHEV AA. Double layer in ionic liquids: overscreening versus crowding. *Phys Rev Lett.* 2012; 106:046102. [PubMed: 21405339]
- BEN-YAAKOV D, ANDELMAN D, HARRIES D, PODGORNIK R. Ions in mixed dielectric solvents: Density profiles and osmotic pressure between charged interfaces. *J Phys Chem B.* 2009a; 113:6001–6011. [PubMed: 19338312]
- BEN-YAAKOV D, ANDELMAN D, HARRIES D, PODGORNIK R. Beyond standard Poisson-Boltzmann theory: ion-specific interactions in aqueous solutions. *J Phys Condens Matter.* 2009b; 21:424106. [PubMed: 21715841]
- BEN-YAAKOV D, ANDELMAN D, PODGORNIK R. Dielectric decrement as a source of ion-specific effects. *J Chem Phys.* 2011; 134:074705. [PubMed: 21341867]
- BIKERMAN JJ. Structure and capacity of the electric double layer. *Phil Mag.* 1942; 33:384–397.
- BORUKHOV I, ANDELMAN D, ORLAND H. Steric effects in electrolytes: a modified Poisson-Boltzmann equation. *Phys Rev Lett.* 1997; 79:435–438.
- BOSTROM M, WILLIAMS DRM, NINHAM BW. Specific ion effects: why DLVO theory fails for biology and colloid systems. *Phys Rev Lett.* 2001; 87:168103. [PubMed: 11690249]
- BOOTH F. The dielectric constant of water and the saturation effect. *J Chem Phys.* 1951; 19:391–394.
- BUCHNER R, HEFTER GT, MAY PM. Dielectric relaxation of aqueous NaCl solutions. *J Phys Chem A.* 1999; 103:1–9.
- CACACE MG, LANDAU EM, RAMSDEN JJ. The Hofmeister series: salt and solvent effects on interfacial phenomena. *Quart Rev Biophys.* 1997; 30:241–277.
- CHANDRA A. Static dielectric constant of aqueous electrolyte solutions: is there any dynamic contribution? *J Chem Phys.* 2000; 113:903–905.
- COLLINS KD, WASHABAUGH MW. The Hofmeister effect and the behaviour of water at interfaces. *Q Rev Biophys.* 1985; 18:323–422. [PubMed: 3916340]
- CONWAY BE. The solvation factor in specificity of ion adsorption at electrodes. *Electrochim Acta.* 1995; 40:1501–1512.
- DANIELEWICZ-FERCHMIN I, FERCHMIN AR. A phase transition in H₂O due to a high electric field close to an electrode. *Chem Phys Lett.* 2002; 351:397–402.
- DUKHIN, SS.; DERYAGUIN, BV. *Surface and Colloid Science.* Vol. 7. Wiley; 1974. Electrokinetic phenomena.
- GALLARDO V, SALCEDO J, VERA P, DELGADO AV. Electric and adsorption properties of pharmaceutical polymers. Part I: electrokinetics of aquacoat. *Colloid & Polym Sci.* 1993; 271:967–973.
- GAVISH, N.; PROMISLOW, K. Dependence of the dielectric constant of electrolyte solution on ionic concentration. 2012. arXiv:1208.5169v1
- GAVRYUSHOV S, LINSE P. Polarization deficiency and excess free energy of ion hydration in electric fields. *J Phys Chem B.* 2003; 107:7135–7142.
- GLUECKAUF E. Bulk dielectric constant of aqueous electrolyte solutions. *Trans Faraday Soc.* 1964; 60:1637–1645.
- GROSSE C, SHILOV VN. Theory of the low-frequency electrorotation of polystyrene particles in electrolyte solutions. *J Phys Chem.* 1996; 100:1771–1778.
- HASTED, JB. *Aqueous Dielectrics.* Chapman and Hall; 1973.
- HASTED JB, RITSON DM, COLLIE CH. Dielectric properties of aqueous ionic solutions. Parts I and II. *J Chem Phys.* 1948; 16:1–21.

- HATLO MM, VAN ROIJ R, LUE L. The electric double layer at high surface potentials: The influence of excess ion polarizability. *Europhys Lett.* 2012; 97:28010.
- HOLOVKO M, KAPKO V. Ion association phenomena and static dielectric properties in electrolyte solution: application of the effective men spherical approximation – mass action law approach. *Acta Chim Slov.* 2009; 56:203–208.
- HUNTER, RJ. *Zeta Potential in Colloid Science.* Academic Press; 1981.
- JOSHI RP, QIAN J, SCHOENBACH KH, SCHAMILOGLU E. Microscopic analysis for water stressed by high electric fields in the prebreakdown regime. *J Appl Phys.* 2004; 96:3617–3625.
- JUNGWIRTH P, TOBIAS D. Molecular structure of salt solutions: a new view of the interface with implications for heterogeneous atmospheric chemistry. *J Phys Chem B.* 2001; 105:10468–10472.
- KHAIR AS, SQUIRES TM. Ion steric effects on electrophoresis of a colloidal particle. *J Fluid Mech.* 2009; 640:343–356.
- KILIC MS, BAZANT MZ, AJDARI A. Steric effects in the dynamics of electrolytes at large applied voltages I. Double-layer charging. *Phys Rev E.* 2007a; 75:021502.
- KILIC MS, BAZANT MZ, AJDARI A. Steric effects in the dynamics of electrolytes at large applied voltages II. Modified Poisson-Nernst-Planck equations. *Phys Rev E.* 2007b; 75:021503.
- KUNZ W. Specific ion effects in colloidal and biological systems. *Curr Opin Colloid Interface Sci.* 2010; 15:34–39.
- KUNZ W, BELLONI L, BERNARD O, NONHAM BW. Osmotic coefficients and surface tensions of aqueous electrolyte solutions: role of dispersion forces. *J Chem Phys B.* 2004a; 108:2398–2404.
- KUNZ W, HENLE J, NINHAM BW. ‘Zur Lehre von der Wirkung der Salze’ (about the science of the effect of salts): Franz Hofmeister’s historical papers. *Curr Opin Colloid Interface Sci.* 2004b; 9:19–37.
- KUNZ W, LO NOSTRO P, NINHAM BW. The present state of affairs with Hofmeister effects. *Curr Opin Colloid Interface Sci.* 2004c; 9:1–18.
- LEVY A, ANDELMAN D, ORLAND H. Dielectric constant of ionic solutions: a field-theory approach. *Phys Rev Lett.* 2012; 108:227801. [PubMed: 23003654]
- LO NOSTRO P, NINHAM BW. Hofmeister phenomena: an update on ion specificity in biology. *Chem Rev.* 2012; 112:2286–2322. [PubMed: 22251403]
- LOPEZ-LEON T, JODAR-REYES AB, BASTOS-GONZALEZ D, ORTEGA-VINUESA JL. Hofmeister effects in the stability and electrophoretic mobility of polystyrene latex particles. *J Phys Chem B.* 2003; 107:5696–5708.
- LOPEZ-LEON T, JODAR-REYES AB, ORTEGA-VINUESA JL, BASTOS-GONZALEZ D. Hofmeister effects on the colloidal stability of an IgG-coated polystyrene latex. *J Colloid Interface Sci.* 2005; 284:139–148. [PubMed: 15752795]
- LYKLEMA J. On the slip process in electrokinetics. *Colloids and Surfaces A.* 1994; 92:41–49.
- LYKLEMA, J. *Fundamentals of Interface and Colloid Science. Volume II: Solid-Liquid Interfaces.* Academic Press; 1995.
- MANCIU M, RUCKENSTEIN E. Specific ion effects via ion hydration: I. Surface tension. *Adv Colloid Interface Sci.* 2003; 105:63–101. [PubMed: 12969642]
- NETZ RR. Debye-Huckel theory for slab geometries. *Eur Phys J E.* 2000; 3:131–141.
- NETZ RR. Static van der Waals interactions in electrolytes. *Eur Phys J E.* 2001; 5:189–205.
- NETZ RR. Water and ions at interfaces. *Curr Opin Colloid Interface Sci.* 2004; 9:192–197.
- O’BRIEN RW. The solution of the electrokinetic equations for colloidal particles with thin double layers. *J Colloid Interface Sci.* 1983; 92:204–216.
- O’BRIEN RW, WHITE LR. Electrophoretic mobility of a spherical colloidal particle. *J Chem Soc Faraday Trans II.* 1978; 74:1607–1626.
- RUCKENSTEIN E, MANCIU M. Specific ion effects via ion hydration: II. Double layer interaction. *Adv Colloid Interface Sci.* 2003; 105:177–200. [PubMed: 12969645]
- RUSSEL, WB.; SAVILLE, DA.; SCHOWALTER, WR. *Colloidal Dispersions.* Cambridge University Press; 1989.

- SALIS A, CUGIA F, PARSONS DF, NINHAM BW, MONDUZZI M. Hofmeister series reversal for lysozyme by change in pH and salt concentrations: insights from electrophoretic mobility measurements. *Phys Chem Chem Phys*. 2012; 14:4343–4346. [PubMed: 22373665]
- SQUIRES TM, QUAKE SR. Microfluidics: fluid physics on the nanoliter scale. *Rev Mod Phys*. 2005; 77:977–1026.
- STONE H, STROOCK A, AJDARI A. Engineering flows in small devices: microfluidics toward a lab-on-a-chip. *Annu Rev Fluid Mech*. 2004; 36:381–411.
- STOREY B, BAZANT MZ. Effects of electrostatic correlations on electrokinetic phenomena. *Phys Rev E*. 2012; 75:021503.
- STOREY BD, EDWARDS LR, KILIC MS, BAZANT MZ. Steric effects on ac electro-osmosis in dilute electrolytes. *Phys Rev E*. 2008; 77:036317.
- VIOVY JL. Electrophoresis of DNA and other polyelectrolytes: physical mechanisms. *Rev Mod Phys*. 2000; 72:813–872.
- VLACHY Y. Ionic effects beyond Poisson-Boltzmann theory. *Annu Rev Phys Chem*. 1999; 50:145–165. [PubMed: 15012409]
- WEI YZ, SRIDHAR S. Dielectric spectroscopy up to 20 GHz of LiCl/H₂O solutions. *J Chem Phys*. 1990; 92:923–928.
- WEI YZ, SRIDHAR S. Ion size effects on the dynamic and static dielectric properties of aqueous alkali solutions. *J Chem Phys*. 1992; 96:4569–4573.
- ZHAO H. On the influence of ion excluded volume (steric) effects on the double layer polarization of a non-conducting nano particle in an AC field. *J Phys Chem C*. 2010; 18:8389–8397.
- ZHAO H. The influence of nonelectrostatic ion-ion interactions on double layer capacitance. *Phys Rev E*. 2012; 86:051502.
- ZWOLAK M, DI VENTRA M. Colloquium: physical approaches to DNA sequencing and detection. *Rev Mod Phys*. 2005; 80:141–165.

FIGURE 1. the schematics of ions adjacent to a charged surface and the schematics of water molecules around ions forming a hydration shell in response to an external electric field. Arrows represent the orientations of polar water molecules.

FIGURE 2.

The magnitude of the electro-osmotic mobility $|M_{eo}|$ as a function of the magnitude of the zeta potential $|\zeta|$ for different α . In (a), the solid line denotes the Helmholtz-Smoluchowski mobility ($M_{eo} = -\zeta$). (b) Comparisons between the prediction (3.6) under the limit of low zeta potentials (lines) and numerically computed mobilities (symbols). The squares and circles correspond, respectively, to $\alpha = 0.01$ and $\alpha = 0.1$.

FIGURE 3.

the charge density $\rho = C_+ - C_-$ as a function of y . The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$ when $\zeta = 3$.

FIGURE 4.

the local dielectric permittivity $\varepsilon = 1 - \hat{a}(\hat{C}_+ + C_-)$ as a function of y . The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{a} = 0$, $\hat{a} = 0.01$, $\hat{a} = 0.05$, and $\hat{a} = 0.1$ when $\zeta = 3$.

FIGURE 5.

The magnitude of the electro-osmotic mobility $|M_{eo}|$ as a function of the magnitude of the surface charge density $|\sigma|$ for different α . The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$.

FIGURE 6.

The zeta potential ζ as a function of σ for various $\hat{\alpha}$. The solid line, the dashed line, the dotted-dashed line, and the dotted line correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$.

FIGURE 7.

Mobility M_e as a function of ζ for various $\hat{\alpha}$ and $\hat{\lambda}_D = 0.01$. In (a), the solid line, the dashed line, the dotted-dashed line, and the dotted line, correspond, respectively, to $\hat{\alpha} = 0$, $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. (b) shows the mobilities (symbols) compared to the low-zeta-potential analytical formula (4.22).

FIGURE 8.

The Dukhin number Du as a function of ζ for various $\hat{\alpha}$ and $\hat{\lambda}_D=0.01$. The solid line, the dashed line, the dotted-dashed line, and the dotted line, correspond, respectively, to $\hat{\alpha}=0$, $\hat{\alpha}=0.01$, $\hat{\alpha}=0.05$, and $\hat{\alpha}=0.1$.

FIGURE 9.

Mobility M_e as a function of the surface charge density σ for various $\hat{\alpha}$ and $\hat{\lambda}_D = 0.01$. In (a), the solid line, the dashed line, and the dotted-dashed line, correspond, respectively, to $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. (b) shows the mobilities (symbols) compared to the low-surface-charge analytical formula (4.24).

FIGURE 10.

M_e/ζ as a function of the zeta potential ζ for various $\hat{\alpha}$ and $\hat{\lambda}_D=0.01$. The solid line, the dashed line, and the dotted-dashed line, correspond, respectively, to $\hat{\alpha} = 0.01$, $\hat{\alpha} = 0.05$, and $\hat{\alpha} = 0.1$. Inset shows M_e/ζ at large ζ .

FIGURE 11.

Mobility M_e versus ζ when $\hat{\lambda}_D=0.01$. The solid line, the dashed line, and the dotted-dashed line corresponds, respectively, to $\hat{\alpha}=0$, $\hat{\alpha}=0.01$, and $\hat{\alpha}=0.1$. The lines and symbols denote, respectively, the predictions from the thin double layer approximation (4.21) and those from directly solving the first-order equations.

FIGURE 12.

The charge density $\rho^{(0)}$ profile near the charged particle surface when $\hat{\alpha} = 0.1$. The solid line, the dashed line and the dotted-dashed line correspond, respectively, to $\zeta = 3$, $\zeta = 6$, and $\zeta = 9$.

FIGURE 13.

The electrophoretic mobility M_e as a function of $\hat{\lambda}_D$ when $\hat{\alpha} = 0.1$ and $\zeta = 6$. The line and the symbols correspond, respectively, to predictions from (4.21) and by direct numerical simulations.

FIGURE 14.

The dimensional electrophoretic mobility M_e (m^2/Vs) as a function of the bulk concentration C_0 (mM) when the particle radius is 100 nm with the surface charge density of $8 \mu\text{C}/\text{cm}^2$ (a) and $3 \mu\text{C}/\text{cm}^2$ (b). The solid line and the dashed line correspond, respectively, to $\alpha = 0$ and $\alpha = 40 \text{ M}^{-1}$.