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Ionic size, permittivity, and viscosity-related effects on the electrophoretic mobility: A modified electrokinetic model

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A modified electrokinetic model is presented in which hydrated ions are represented as charged dielectric spheres so that the electrolyte solution becomes a nonhomogeneous fluid characterized by permittivity and viscosity values that are both functions of the local ionic concentrations. This modifies both the Poisson-Nernst-Planck and the Navier-Stokes equations and also introduces additional Born and dielectrophoretic forces acting on the ions. The model is numerically solved for a plane charged interface both in equilibrium and under the action of an applied tangential DC electric field, which makes it possible to determine the electrophoretic mobility of a suspended particle in the Smoluchowski limit. The obtained results show that the strong increase of the electrophoretic mobility due to steric and permittivity related effects is countered by the viscosity dependence on the ionic concentrations leading to values that are moderately higher than those predicted by the standard electrokinetic model. This behavior suggests that the proposed model may be used to improve the interpretation of experimental electrophoretic mobility data.

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I. INTRODUCTION

The dielectric and electrokinetic phenomena arising in colloidal particle suspensions in aqueous electrolyte solutions are classically described using the standard electrokinetic model (SEM). In this model, the electrolyte solution is treated as an incompressible fluid characterized by constant permittivity and viscosity values while ions are treated as point-like entities. These assumptions made it possible to calculate the equilibrium electric double layer structure at a solid-liquid interface [1,2], the electrophoretic mobility of spherical particles [3], and the suspension conductivity increment [4].

The numerous discrepancies among the theoretical predictions and the experimental determinations pointed, however, to the necessity to review the assumptions used in the SEM, mainly the point-like nature of the ions. Inclusion of their finite size is not trivial since it leads to many different consequences, the principal being

(1) Impossibility of the ionic charge to approach infinitely close to the charged interface.
(2) Impossibility of the ionic charge density to attain arbitrarily high values.
(3) Dependence of the solution permittivity on the ionic concentrations.
(4) Dependence of the solution viscosity on the ionic concentrations.

The finite value of the minimum approach distance of ions to the interface was first taken into account by Stern [5] and then presented as a modified Gouy-Chapman treatment in Ref. [6]. This

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aspect has an important bearing on the dependence of the surface potential on the surface charge at low surface charge values, and on the equilibrium double layer capacitance.

The influence of the second aspect was extensively studied by means of the introduction of steric interactions among ions [7–10]. It leads to the increment of the thickness of the equilibrium double layer further increasing the surface potential at any given surface charge. Out of equilibrium, the scarce existing works show an increment of the electrophoretic mobility at any given surface charge [11–17].

Another consequence of the finite ionic size is that the volume occupied by the ions can no longer be occupied by water molecules. The electrolyte solution should therefore behave as a mixture of nonpolar ions in a solvent made of polar water molecules. The resulting system has a lower permittivity value than pure water, this value being furthermore a variable dependent on the local ionic concentrations. This permittivity decrement has a direct bearing on the electric potential, increasing its value inside the double layer. Moreover, it also gives raise to two new forces acting on the ions: The Born force tending to move ions to regions of higher permittivity and the dielectrophoretic force tending to move ions toward regions of a weaker electric field (in view that their equivalent permittivity is lower than that of the surrounding medium). While the influence of these effects on the equilibrium properties of the system have been analyzed in several studies [18–25], we are aware of only a couple of works dealing with the out of equilibrium problem [26,27].

Finally, the presence of finite-size ions in the electrolyte solution should also increase its viscosity just as the presence of particles increases the viscosity of a suspension [28–31]. While all the above-mentioned aspects increase the electrophoretic mobility by moving the charged fluid away from the interface and the corresponding zero velocity plane, an increment of the viscosity should have an opposite effect decreasing the electrophoretic mobility. Other existing attempts to include the variation of viscosity in mobility calculations correspond to Refs. [32] and [33]. In the first work, the viscosity increase is considered to be due to electric saturation of water so that it is proportional to the square of the electric field strength in the double layer. A significant effect is obtained due to the use of the SEM for the calculation of the electric field while the finite size of ions is ignored. In the second, an analytic result for the electrophoretic mobility is deduced assuming “in a very crude attempt” that the quotient of the solution permittivity over viscosity has a linear dependence on the volume fraction of counterions in the double layer. This reduces the mobility to zero when the ionic concentration attains its steric limit.

In a previous work [20] we presented a modification of the SEM based on the representation of ions as dielectric spheres that takes into account the dependence of the electrolyte solution permittivity by means of the Maxwell mixture formula [34] and includes the corresponding Born and dielectrophoretic forces. Recently [25] we improved the model by means of the Boublik-Mansoori-Carnahan-Starling-Leland expression for the steric interactions [9,10], which allows for multiple ionic species having different ionic sizes.

In that work and the following one [35] we solved the model in equilibrium in order to analyze the double layer structure and differential capacitance for mixed electrolytes with different ionic sizes. Finally, in Ref. [16] we solved the out of equilibrium problem in order to obtain the mobility, permittivity, and conductivity spectra. However, in this last work we did not include the dependence of the electrolyte solution permittivity on the ionic concentrations and the corresponding Born and dielectrophoretic forces. The reason for this omission is that the used model was still incomplete: the presence of ions in the solution modifies its permittivity but does not alter its viscosity. This fact has no influence whatsoever on the equilibrium solution but is crucial for the system behavior out of equilibrium.

In the present work we complete the modifications of the SEM modeling the electrolyte solution as a nonhomogeneous fluid with a viscosity that depends on the ionic concentrations. This further requires a modification of the Navier-Stokes and continuity equations. Finally, we solve the resulting model considering a DC applied electric field in order to calculate the electrophoretic mobility in the limit when the suspended particle radius is much bigger than the Debye screening length.

II. THEORETICAL MODEL

We consider a charged solid-liquid interface bearing a surface charge σ $(\mathrm{C/m^2})$ in equilibrium or under the action of an applied DC electric field. The aqueous electrolyte solution contains m ionic species characterized by their signed valences z_i and bulk molar concentrations $c_i^\infty(\mathrm{mol/m^3})$. The electrolyte solution is modeled as a nonhomogeneous fluid made of the hydrated ions represented as dielectric spheres with radii R_i and effective permittivities ε_i, suspended in the solvent with permittivity ε_s and viscosity η_s.

As in our previous works we estimate the solution permittivity ε by means of the Maxwell mixture formula [34], Fig. 1(a):

$$\frac{\varepsilon(\vec{r})-\varepsilon_s}{\varepsilon(\vec{r})+2\varepsilon_s}=\sum_{i=1}^{m}\phi_i(\vec{r})\frac{\varepsilon_i-\varepsilon_s}{\varepsilon_i+2\varepsilon_s}=\frac{4}{3}\pi N_A\sum_{i=1}^{m}R_i^3c_i(\vec{r})\frac{\varepsilon_i-\varepsilon_s}{\varepsilon_i+2\varepsilon_s}, \tag{1}$$

where N_A is the Avogadro number. The main reason for not using simpler linear functions as done in Refs. [26,27], is the limited range of validity of these functions that holds up to about 2 M [36–38]. However, the ionic concentrations close to charged interfaces easily surpass this value, Fig. 2(a), so that the use of a linear function could strongly underestimate the local solution permittivity value. As for the nonlinear function proposed in Ref. [38] we chose to use Eq. (1) because it only uses model parameters and is applicable to mixed electrolytes.

The viscosity η of a suspension of spherical particles is expected to be a continuous monotonously increasing function of the total volume fraction ϕ occupied by the particles. This function should reduce to the solvent viscosity in the low concentration limit: $\eta(0)=\eta_s$ and should reduce for low volume fractions to the rigorous Einstein [28,29] result

$$\eta(\vec{r})=\eta_s\left[1+\tfrac{5}{2}\phi(\vec{r})\right], \tag{2}$$

where

$$\phi(\vec{r})=\sum_{i=1}^{m}\phi_i(\vec{r})=\frac{4\pi}{3}N_A\sum_{i=1}^{m}R_i^3c_i(\vec{r}). \tag{3}$$

We are aware that Eq. (2) corresponds to a suspension of uncharged particles, which is not the case of electrolyte solutions where the particles are charged. However, existing studies of the viscosity of electrolyte solutions show that it can be expressed by an equation similar to Eq. (2) except for an additional term due to electric interactions that is proportional to the square root of the concentration. Nevertheless, this term is only important in the low concentration limit and completely irrelevant at the high concentrations encountered in the double layer [39–41]. A more complex equation was proposed in Ref. [39] and used to fit viscosity data of concentrated solutions obtained in that paper. We chose to use Eq. (2) mainly because it only uses model parameters and also because all the existing works dealing with electrolyte solutions always consider electroneutral systems so that they are hardly applicable to the case of electric double layers.

Furthermore, the viscosity is expected to diverge at the volume fraction value when particle close packing occurs, Fig. 1(b). The many works on this subject can be roughly divided into two groups [42]: one seeking to calculate additional terms to the linear expansion, (2) the other proposing equations that diverge at the close packing value. In this study we chose to follow the first of these two approaches because it should provide more precise viscosity values at low and medium volume fractions [42] and also because there is no general expression for the close packing volume fraction value in the general case of different particle sizes. We thus use the Batchelor-Green expression [30]:

$$\eta(\vec{r})=\eta_s[1+2.5\phi(\vec{r})+5.2\phi(\vec{r})^2], \tag{4}$$

realizing that Eq. (4) certainly underestimates the solution viscosity value Fig. 1(b). It should be noted, however, that the choice of the viscosity expression to be used in the calculations is less

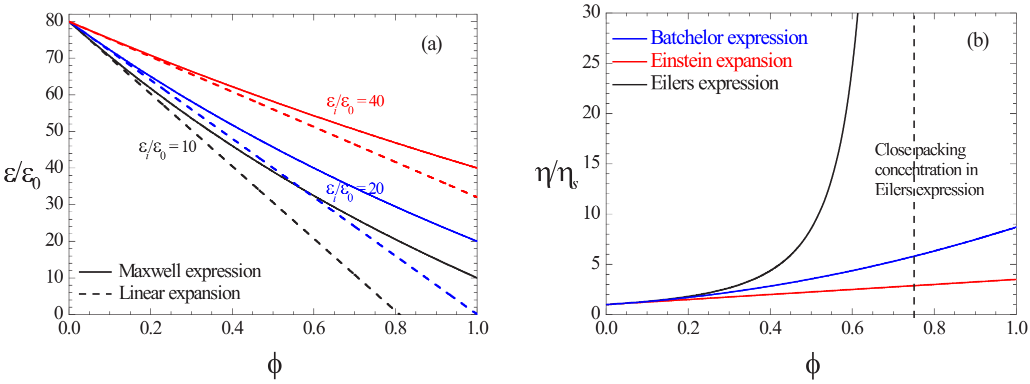

FIG. 1. Dependence of the electrolyte solution permittivity (a) and viscosity (b) on the total ionic volume fraction. Comparison of the Maxwell mixture formula with the linear expansion for the three indicated values of the equivalent ionic permittivity. Comparison of the Einstein linear expansion (2), the Batchelor-Green second order expansion (4), and the Eilers equation [31].

critical than that of the permittivity. The reason is that the solution viscosity increases with the volume fraction, which agrees with Eq. (4) that is always positive. On the contrary, since $\varepsilon_i \approx 20\varepsilon_0$ is smaller than $\varepsilon_s \approx 80\varepsilon_0$, the solution permittivity decreases with the volume fraction so that a linear expansion could become negative for sufficiently high volume fraction values, Fig. 1(a).

In view of the spatial dependence of the electrolyte solution viscosity the usual form of the Navier-Stokes equation can no longer be used. The general expression for this case [43] is

$$\begin{aligned}
&-\eta(\vec{r})\nabla\times\nabla\times\vec{v}(\vec{r})+\nabla\eta(\vec{r})\cdot[\nabla\vec{v}(\vec{r})+\nabla\vec{v}^{T}(\vec{r})]+\nabla\big[\zeta(\vec{r})-\tfrac{2}{3}\eta(\vec{r})\big]\nabla\cdot\vec{v}(\vec{r})\\
&+\big[\zeta(\vec{r})+\tfrac{1}{3}\eta(\vec{r})\big]\nabla[\nabla\cdot\vec{v}(\vec{r})]=\nabla P(\vec{r})+\rho(\vec{r})[\vec{v}(\vec{r})\cdot\nabla]\vec{v}(\vec{r})+eN_A\sum_{i=1}^{m}z_i c_i(\vec{r})\nabla\Psi(\vec{r}), \qquad (5)
\end{aligned}$$

where $\zeta(\vec{r})$ is the second viscosity coefficient, $\nabla\vec{v}(\vec{r})$ is the gradient of the velocity vector, $\nabla\vec{v}^{T}(\vec{r})$ is the transposed gradient of the velocity vector, P is the pressure, Ψ is the electric potential, while

$$\rho(\vec{r})=\rho_s+\frac{4\pi}{3}N_A\sum_{i=1}^{m}R_i^3 c_i(\vec{r})(\rho_i-\rho_s), \qquad (6)$$

ρ_i, and ρ_s are the electrolyte solution, ionic, and solvent mass densities, respectively.

Moreover, the usual form of the continuity equation should also be modified because of the dependence of the electrolyte solution mass density on the ionic concentrations:

$$\nabla\cdot[\rho(\vec{r})\vec{v}(\vec{r})]=0. \qquad (7)$$

Equations (5) and (7) greatly simplify when the solvent and the ionic mass densities have the same value. In this simplest case they reduce to the final form used in this work for the modified Navier-Stokes and continuity equations:

$$\begin{aligned}
&-\eta(\vec{r})\nabla\times\nabla\times\vec{v}(\vec{r})+\nabla\eta(\vec{r})\cdot[\nabla\vec{v}(\vec{r})+\nabla\vec{v}^{T}(\vec{r})]\\
&=\nabla P(\vec{r})+\rho_s[\vec{v}(\vec{r})\cdot\nabla]\vec{v}(\vec{r})+eN_A\sum_{i=1}^{m}z_i c_i(\vec{r})\nabla\Psi(\vec{r}), \qquad (8)
\end{aligned}$$

$$\nabla\cdot\vec{v}(\vec{r})=0. \qquad (9)$$

Equations (1), (4), (8), and (9), together with the already deduced modified forms of the Nernst-Planck, continuity, and Poisson equations [25]

$$\vec{J}_i(\vec{r}) = -D_i(\vec{r})c_i(\vec{r})\left[\nabla\mu_i(\vec{r}) - \frac{g_i(\vec{r})}{kT}\nabla E^2(\vec{r})\right] + c_i(\vec{r})\vec{v}(\vec{r}), \tag{10}$$

$$\nabla\cdot[\vec{J}_i(\vec{r})] = 0, \tag{11}$$

$$\nabla\cdot[\varepsilon(\vec{r})\nabla\Psi(\vec{r})] = -eN_A\sum_{i=1}^{m} z_i c_i(\vec{r}), \tag{12}$$

constitute the modified electrokinetic model (MEM) proposed in this work. In the above equations

$$D_i(\vec{r}) = \frac{\eta_s}{\eta(\vec{r})}D_i^{\infty}, \tag{13}$$

$$\mu_i(\vec{r}) = \ln c_i(\vec{r}) + \mu_i^{ex}(\vec{r}) + \frac{z_i e}{kT}\Psi(\vec{r}) + \frac{{z_i}^2 e^2}{8\pi kTR_i\varepsilon_e(\vec{r})}, \tag{14}$$

$$g_i(\vec{r}) = 2\pi\varepsilon(\vec{r})R_i^3\frac{\varepsilon_i - \varepsilon(\vec{r})}{\varepsilon_i + 2\varepsilon(\vec{r})}, \tag{15}$$

$$\begin{aligned}\mu_i^{ex} = &-\left(1 - 12R_i^2\frac{\xi_2^2}{\xi_3^2} + 16R_i^3\frac{\xi_2^3}{\xi_3^3}\right)\ln(1-\xi_3) + \frac{2R_i\left(3\xi_2 + 6R_i\xi_1 + 4R_i^2\xi_0\right)}{1-\xi_3}\\ &+ \frac{12R_i^2\xi_2(\xi_2 + 2R_i\xi_1\xi_3)}{\xi_3(1-\xi_3)^2} - \frac{8R_i^3\xi_2^3\left(\xi_3^2 - 5\xi_3 + 2\right)}{\xi_3^2(1-\xi_3)^3},\end{aligned} \tag{16}$$

$$\xi_j(\vec{r}) = \frac{2^{j-1}\pi N_A}{3}\sum_{i=1}^{m} c_i(\vec{r})R_i^j \quad j\in\{0,1,2,3\}, \tag{17}$$

while $c_i(\vec{r})$, $\vec{v}_i(\vec{r})$, and $D_i(\vec{r})$ are the local ionic concentrations, velocities, and diffusion coefficients; k, T, and e are the Boltzmann constant, absolute temperature, and elementary charge; $E(\vec{r})$ is the local electric field amplitude, and D_i^{∞} is the diffusion coefficients at infinite dilution.

The MEM includes steric interactions among ions by means of the Boublik-Mansoori-Carnahan-Starling-Leland expression (16), and all the effects related to the representation of hydrated ions as dielectric spheres: dependence of the electrolyte solution permittivity (1), viscosity (4), and ionic diffusion coefficients (13) on the ionic concentrations, and appearance of the Born and the dielectrophoretic forces acting on the ions. Note that when all the ionic size related effects are neglected (limit of ionic radii tending to zero) the SEM is recovered.

III. RESULTS AND DISCUSSION

A. Equilibrium results

In equilibrium (upper index 0), without any externally applied perturbation, all velocities must vanish so that the MEM equations (10), (14), (12), and (8) become

$$\nabla\mu_i^0(\vec{r}) = \nabla\left\{\ln c_i^0(\vec{r}) + \mu_i^{ex,0}(\vec{r}) + \frac{z_i e}{kT}\Psi^0(\vec{r}) + \frac{1}{kT}\frac{{z_i}^2 e^2}{8\pi R_i\varepsilon^0(\vec{r})}\right\} = \frac{g_i^0(\vec{r})}{kT}\nabla[E^0(\vec{r})]^2, \tag{18}$$

$$\nabla\cdot[\varepsilon^0(\vec{r})\nabla\Psi^0(\vec{r})] = -eN_A\sum_{i=1}^{m} z_i c_i^0(\vec{r}), \tag{19}$$

$$\nabla P^0(\vec{r}) = -eN_A\sum_{i=1}^{m} z_i c_i^0(\vec{r})\nabla\Psi^0(\vec{r}). \tag{20}$$

TABLE I. Parameter values used in the numerical simulations.

$e = 1.602\times10^{-19}$ C	$\sigma = 0.3\,\mathrm{C/m^2}$	$c^{\infty}_{\mathrm{Na}^+} = 10$ mM	$c^{\infty}_{\mathrm{Cl}^-} = 10$ mM
$k = 1.381\times10^{-23}$ J/K	$\eta_s = 0.8904\times10^{-3}$ P	$D^{\infty}_{\mathrm{Na}^+} = 1.33\times10^{-9}\,\mathrm{m^2/s}$	$D^{\infty}_{\mathrm{Cl}^-} = 2.03\times10^{-9}\,\mathrm{m^2/s}$
$N_A = 6.022\times10^{23}\,\mathrm{mol}^{-1}$	$T = 298$ K	$R_{\mathrm{Na}^+} = 3.58$ Å	$R_{\mathrm{Cl}^-} = 3.32$ Å
$\varepsilon_0 = 8.854\times10^{-12}$ F/m	$\varepsilon_s = 80\times\varepsilon_0$	$\varepsilon_{\mathrm{Na}^+} = 20\times\varepsilon_0$	$\varepsilon_{\mathrm{Cl}^-} = 20\times\varepsilon_0$

Considering a flat double layer with the interface located on the *yz* plane, Eqs. (18)–(20) simplify to

$$\frac{d\mu_i^0}{dx} = \frac{g_i^0}{kT}\frac{d}{dx}(\vec{E}^0)^2, \tag{21}$$

$$\frac{d}{dx}\left(\varepsilon^0\frac{d\Psi^0}{dx}\right) = -eN_A\sum_{i=1}^{m} z_i c_i^0, \tag{22}$$

$$\frac{dP^0}{dx} = -eN_A\sum_{i=1}^{m} z_i c_i^0\frac{d\Psi^0}{dx}. \tag{23}$$

A numerical solution of this equation system using the surface charge density value as the boundary condition at the interface leads to the following results. They were obtained considering an aqueous NaCl electrolyte solution and literature values determined from mobility measurements [44] for the hydrated ionic radii and effective ionic permittivity values taken from Ref. [45]. All the system parameters are listed in Table I.

Figure 2(a) represents the equilibrium counterion concentration profiles calculated for the system parameters given in Table I. It clearly shows the effect of the considered modifications to the SEM. The repelling forces among ions due to steric interactions strongly increase the thickness of the double layer and simultaneously decrease the maximum counterion density. The dielectric effects related to the dependence of the solution permittivity on the ionic concentration further increment these trends. The double layer thickness increases and the maximum counterion concentration decreases mainly due to the dielectrophoretic force [46,47].

Although the difference between the Steric and the Steric+Dielectric curves shown in Fig. 2(a) is rather small, it is markedly magnified in Fig. 2(b) where the dimensionless potential, $y^0 = e\Psi^0/kT$,

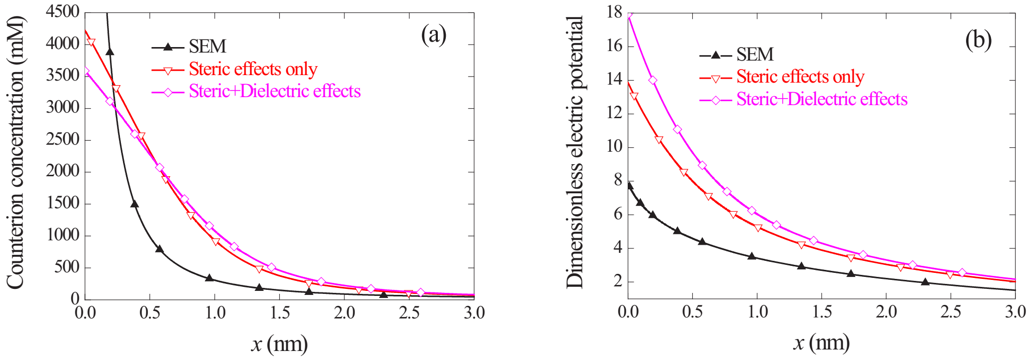

FIG. 2. (a) Equilibrium counterion concentration profiles corresponding to the SEM and its considered modifications. (b) Equilibrium dimensionless electric potential profiles corresponding to the SEM and its considered modifications. System parameters given in Table I.

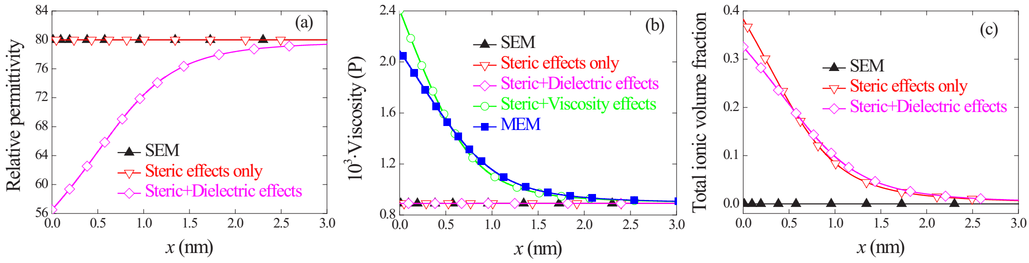

FIG. 3. (a) Equilibrium electrolyte solution permittivity profiles corresponding to the SEM and its considered modifications. (b) Equilibrium electrolyte solution viscosity profiles corresponding to the SEM and its considered modifications. (c) Total equilibrium ionic volume fraction profiles corresponding to the SEM and its considered modifications. System parameters given in Table I.

profiles are represented. This occurs because the electric potential is determined not only by the volume charge density but also by the permittivity value.

The electrolyte solution permittivity profiles calculated considering a value of $20\,\varepsilon_0$ for the equivalent ionic permittivities are represented in Fig. 3(a). As can be seen, a decrease of the order of 25 dielectric units close to the interface is obtained. This decrement determines the magnitude of all the dielectric effects. It should be noted that these effects would markedly increase if the dielectrophoretic force were calculated substituting $\varepsilon_s = 80\,\varepsilon_0$ for $\varepsilon(\vec{r})$ in Eq. (15) as done in Ref. [21].

Figure 3(b) represents the equilibrium viscosity profiles calculated for the considered models. It shows that this magnitude can increase by a factor of the order of 2 near the interface, which should have a strong bearing on the tangential fluid velocity and, therefore, the electrophoretic mobility. Figure 3(c) shows the total equilibrium ionic volume fraction profiles, Eq. (3), which is required for the calculation of the viscosity. As can be seen this value is lower than 0.4, which means that the use of the Batchelor expression (4), is fairly well justified.

Figure 4 shows the surface potential as function of the surface charge for the considered models. As can be seen, this dependence strongly varies with the chosen model. For example, a surface

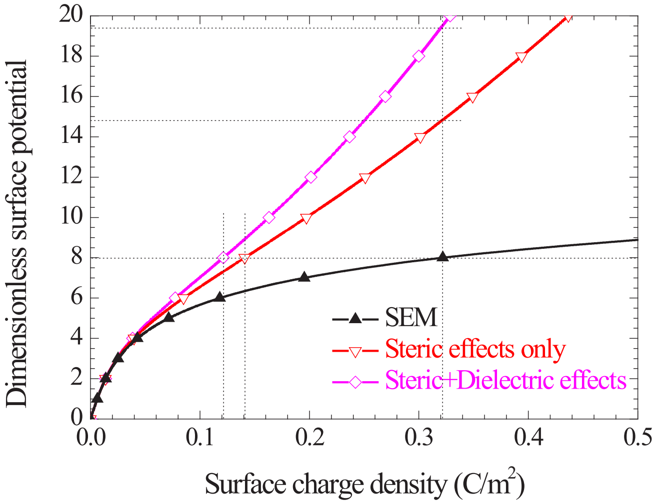

FIG. 4. Dimensionless surface potential dependence on the surface charge density for the SEM and its considered modifications. System parameters given in Table I.

potential value of 8 corresponds to a surface charge value of $0.32\,\mathrm{C/m^2}$ according to the SEM, 0.14 for the model that only includes steric interactions, and to 0.12 for the model that also includes dielectric effects. Analogously, a surface charge value of $0.32\,\mathrm{C/m^2}$ corresponds to a surface potential of 8 according to the SEM, 14.4 for the model that only includes steric interactions, and 18.7 for the model that also includes dielectric effects. This shows that even for reasonable surface charge values, huge surface potentials that are physically impossible for the SEM are normal for the MEM. It also shows that the choice of the independent variable used in a plot such as Fig. 6 becomes crucial in order to obtain a meaningful representation.

B. DC results

When an external perturbation is applied to the system, all the system variables X modify their values with respect to their equilibrium X^0 state:

$$X = X^0 + \delta X, \tag{24}$$

where δX is the perturbation dependent variable change. For sufficiently weak perturbations, only linear terms in the perturbation need to be considered. This allows us to write the MEM nonequilibrium equations as

$$\delta\vec{J}_i = D_i^0 c_i^0\left[-\nabla\delta\mu_i + \frac{\delta\vec{v}}{D_i^0} + \frac{g_i^0}{kT}\nabla\delta E^2 + \frac{\delta g_i^0}{kT}\nabla(E^0)^2\right], \tag{25}$$

$$\nabla\cdot\delta\vec{J}_i = 0, \tag{26}$$

$$\varepsilon^0\nabla^2\delta\Psi + \delta\varepsilon\nabla^2\Psi^0 + \nabla\varepsilon^0\cdot\nabla\delta\Psi + \nabla\delta\varepsilon\cdot\nabla\Psi^0 = -eN_A\sum_{i=1}^{m} z_i\delta c_i, \tag{27}$$

$$-\eta^0\nabla\times\nabla\times\delta\vec{v} + \nabla\eta^0\cdot[\nabla\delta\vec{v} + \nabla\delta\vec{v}^T] - \nabla\delta P = eN_A\sum_{i=1}^{m} z_i c_i^0\nabla\delta\Psi + eN_A\sum_{i=1}^{m} z_i\delta c_i\nabla\Psi^0. \tag{28}$$

We now consider that the interface is flat and that the perturbation consists in a uniform tangential electric field applied along the y axis:

$$\delta\vec{E} = E_a\hat{u}_y. \tag{29}$$

Since the plane extends to infinity it follows that

$$\delta c_i = \delta\mu_i^{ex} = \delta\varepsilon = \delta P = 0, \tag{30}$$

$$\delta\vec{v}_i = v_i(x)\hat{u}_y, \tag{31}$$

$$\delta\vec{v} = v(x)\hat{u}_y, \tag{32}$$

which transforms the Navier-Stokes equation (28) into

$$\eta^0\frac{d^2v}{dx^2} + \frac{d\eta^0}{dx}\frac{dv}{dx} = \frac{d}{dx}\left(\eta^0\frac{dv}{dx}\right) = -eN_A\sum_{i=1}^{m} z_i c_i^0 E_a. \tag{33}$$

Using the equilibrium Poisson equation (22) makes it possible to rewrite Eq. (33) as

$$\frac{d}{dx}\left(\eta^0\frac{dv}{dx}\right) = \frac{d}{dx}\left(\varepsilon^0\frac{d\Psi^0}{dx}\right)E_a. \tag{34}$$

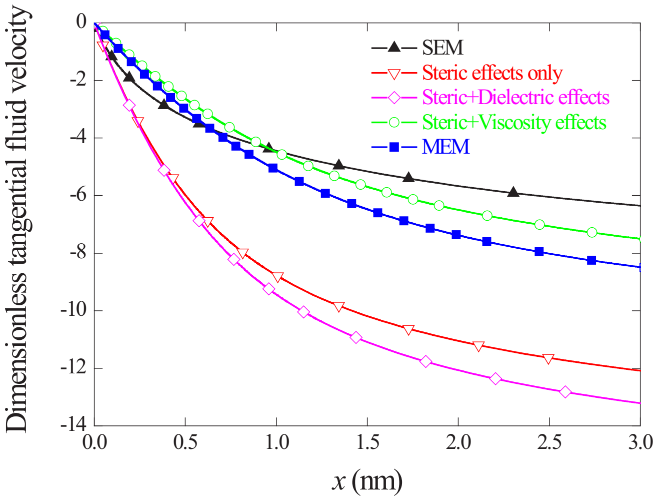

FIG. 5. Dimensionless tangential electrolyte solution velocity profiles corresponding to the SEM and its considered modifications. System parameters given in Table I.

Integrating this equation from 0 to x leads to following expression for the electrolyte solution velocity:

$$v(x) = E_a \int_0^x \frac{\varepsilon^0(x)}{\eta^0(x)} \frac{d\Psi^0}{dx} dx, \tag{35}$$

which reduces to

$$v(x) = E_a \frac{\varepsilon_s}{\eta_s} [\Psi^0(x) - \Psi^0(0)] \tag{36}$$

for constant solution permittivity ($\varepsilon^0(x) = \varepsilon_s$) and viscosity ($\eta^0(x) = \eta_s$) values.

The dimensionless tangential electrolyte solution velocity, $u(x) = e\eta^\infty v(x)/kT\varepsilon^\infty E_a$, under the action of an applied tangential electric field is represented in Fig. 5. As can be seen, the field induced tangential velocity greatly increases with respect to the SEM result when the steric interactions are taken into account, and even more when dielectric effects are also considered. This increment is mainly due to the increased thickness of the electric double layer, Fig. 2(a), which shifts the charged fluid further away from the interface and, therefore, from the zero velocity boundary condition plane. As shown in previous works [11–17] this results in electrophoretic mobility values that can be much higher than the SEM predictions [3]. As for the MEM predictions, the corresponding curve lies in between the above discussed ones. The velocity increment that results from the increased double layer thickness is partially compensated for by the increased fluid viscosity, Fig. 3(b). This last effect is particularly strong close to the interface where the viscosity value is highest leading to velocity values that are lower than the SEM predictions.

The obtained results make it possible to calculate the electrophoretic mobility in its simplest form corresponding to the Smoluchowski [48] approximation: the double layer is sufficiently thin as compared to the suspended particle radius while the surface charge or potential is sufficiently low so that the induced dipole moment of the particle is $m = -2\pi\varepsilon^\infty a^3 E_a$ and the value of the tangential electric field along the particle surface is $3/2E_a$. Using the dimensionless electrophoretic mobility expression

$$E = -\frac{3}{2} \frac{e\eta^\infty}{kT\varepsilon^\infty} \frac{v^\infty}{E_a} \tag{37}$$

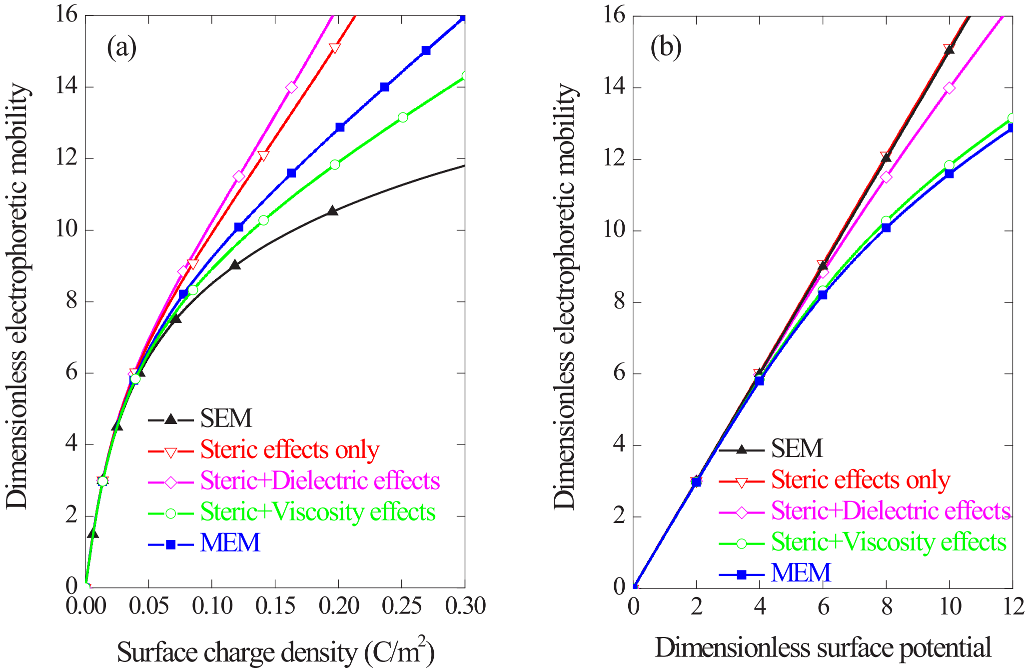

FIG. 6. Dimensionless electrophoretic mobility dependence on the surface charge density (a) and the dimensionless surface electric potential (b) for the SEM and its considered modifications. System parameters given in Table I.

(where the upper index ∞ denotes points far away from the particle) together with Eqs. (35) and (36) leads to the final expressions for the MEM and the SEM, respectively,

$$v^{\infty} = E_a \int_0^{\infty} \frac{\varepsilon^0(x)}{\eta^0(x)} \frac{d\Psi^0}{dx} dx \Rightarrow E = -\frac{3}{2} \frac{e\eta^{\infty}}{kT\varepsilon^{\infty}} \int_0^{\infty} \frac{\varepsilon^0(x)}{\eta^0(x)} \frac{d\Psi^0}{dx} dx, \tag{38}$$

$$v^{\infty} = -E_a \frac{\varepsilon_s}{\eta_s} \Psi^0(0) \Rightarrow E = \frac{3}{2} \frac{\eta^{\infty}}{\varepsilon^{\infty}} \frac{\varepsilon_s}{\eta_s} \frac{e\Psi^0(0)}{kT}. \tag{39}$$

Figure 6(a) shows the Smoluchowski electrophoretic mobility for the considered models as functions of the surface charge density. As can be seen, for any given particle charge the mobility strongly increases with respect to the SEM result when steric interactions are taken into account and this change is further increased when the dielectric effects are included. As for the MEM, Fig. 6(a) shows that the increment of the viscosity with the ionic concentration lowers the mobility values as expected. All these comments are in full agreement with those following Fig. 5.

Figure 6(b) shows the Smoluchowski electrophoretic mobility for the considered models as functions of the dimensionless surface potential. As can be seen, the SEM results reproduce the familiar linear behavior of the mobility. However, and rather surprisingly, the model that only includes steric interactions appears now to lead to results that are indistinguishable from those of the SEM. Actually, this behavior is rigorous and applies to all the possible steric interaction equations as can be seen from Eq. (39): the electrophoretic mobility is proportional to the surface potential with a proportionality coefficient that does not depend on the steric interactions. However, this conclusion should not be interpreted in the sense that the electrophoretic mobility in the Smoluchowski approximation is independent from the steric interactions. On the contrary, this dependence exists but is hidden in Fig. 6(b): the mobility of a particle with a given surface charge value corresponds to a point on the straight line in Fig. 6(b) according to the SEM but to a different point over the same line according to the model that only includes steric interactions. This occurs because the dependence of the surface potential on the surface charge is model dependent, Fig. 4.

Figures 6(a) and 6(b) suggest that the classic representation of the electrophoretic mobility as function of the surface potential for different κa values (where κ is the reciprocal Debye length and a is the suspended particle radius) [3] is better replaced by the electrophoretic mobility as function of the surface charge when modifications to the SEM are considered, Fig. 6(a). Moreover, such a representation seems to be advantageous from the experimental standpoint since the surface charge is a better controllable parameter than the surface potential when dealing with colloidal dispersions. It should finally be noted that this is not the only change to be taken into account since the value of κa ceases to fully characterize the system under study due to the appearance of additional characteristic lengths (the ionic radii) besides $1/\kappa$ and a (this matter is discussed in detail in Ref. [49], while its implications relative to the electrophoretic mobility are commented in Ref. [11]). Therefore, a plot of the electrophoretic mobility as function of the surface charge at different κa values should also specify whether these values were obtained keeping constant the electrolyte solution concentration or the particle radius.

IV. CONCLUSION

In this work we present a modification of the SEM removing the assumption that ions behave as point-like entities and apply the resulting equation system to the calculation of the electrophoretic mobility. This leads to the first out of equilibrium calculation performed taking into account all permittivity related effects with a finite ionic size: electrolyte solution permittivity dependence on the ionic concentrations and the inclusion of the Born and the dielectrophoretic forces acting on the ions. Furthermore, the finite size of the ions causes the electrolyte solution to behave as a nonhomogeneous fluid with variable viscosity that depends on the ionic concentrations. This effect is also included in the mobility calculation.

It should be noted that the presented MEM is formulated for a general electrolyte solution (any number of ionic species with different valences, radii, effective permittivity values), which requires the use of the Boublik-Mansoori-Carnahan-Starling-Leland expression (16) for the steric interactions rather than the much simpler Carnahan-Starling [8] or Bikerman [7] equations applicable for single size ions. Furthermore, the electrolyte solution permittivity dependence on the ionic concentrations is calculated using the Maxwell mixture formula (1) rather than the usually used linear functions, Fig. 1(a). Finally, unlike all previous works on this subject, the dependence of the electrolyte solution viscosity on the ionic concentrations is taken into account, and this is done using a second order expansion (4) rather than the simple linear dependence (2), Fig. 1(b).

It is well known that a major shortcoming of the SEM is that it generally fails to provide a simultaneous interpretation of electrokinetic and dielectric data: electrophoretic mobility and conductivity increment, for example. The surface potential values deduced from these two measurements do not coincide [50–52]. The most widely used solution to this problem is to generalize the SEM by introducing the Stern layer surface conductivity, see Refs. [53,54], and references therein. This modification always reduces the electrophoretic mobility so that a higher surface potential value is required in order to fit the electrokinetic data. By adjusting the Stern layer surface conductivity parameters a satisfactory simultaneous experimental data interpretation can be often achieved [55]. On the other hand, Fig. 6(b) shows that the MEM leads to a qualitatively similar behavior as the SEM together with the Stern layer surface conductivity: a lower electrophoretic mobility value for any given surface potential. Therefore, the MEM should improve upon the SEM in the simultaneous interpretation of electrokinetic and dielectric data without using any adjustable parameter. This does not signify that the Stern layer surface conductivity hypothesis is no longer necessary. It just suggests that its influence must be reduced. It should finally be noted that the MEM improves on both the SEM modifications that add steric interactions only or steric interactions plus permittivity related effects: in the first case because there is no lowering of the electrophoretic mobility at any given surface potential, Fig. 6(b) and, in the second, because the electrophoretic mobility becomes far too large at reasonable surface charge values, Fig. 6(a) [12,15].

We further show that while, according to the SEM, the system properties of a colloidal suspension can be characterized by the product κa and either the surface potential or the surface charge values, this no longer holds for model extensions taking into account finite ionic sizes. When this is done, the surface potential vs surface charge relationship becomes model dependent, Fig. 4, and a κa change obtained at constant κ or a leads to two different electrokinetic behaviors. This makes it advisable to replace the familiar O'Brien-White [3] representation of the mobility vs surface potential at constant κa by a mobility vs surface charge representation at constant a, Fig. 6(a). This avoids possible erroneous interpretations such as the apparent independence of the electrophoretic mobility on the steric interactions or the apparent decrement of the electrophoretic mobility with the permittivity related effects, Fig. 6(b), when these effects actually increment the mobility value, Fig. 6(a).

We should finally note that in view of the complexity of the MEM equations, the electrophoretic mobility was calculated in the present work using the Smoluchowski [48] approximation that ignores any particle polarization. Nevertheless, the qualitative trends obtained will be certainly maintained in forthcoming calculations performed using the thin double layer approximation and hopefully in the general case without any restrictions on the double layer thickness.

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