

## Nonlinear effects in the electrophoresis of a spherical colloidal particle

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The reduced electrophoretic mobility-reduced zeta potential relationship for a charged macroparticle is shown to be nonuniversal and to be highly nonlinear. In agreement with experimental results, a mobility reversal due to the macroion's *charge inversion* and a nonlinear dependence of the mobility on salt concentration is obtained. [S1063-651X(99)50407-8]

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In the presence of a weak electrical field,  $\mathbf{E}$ , charged macroparticles in solution acquire a steady state velocity,  $\mathbf{U}$ , which is proportional to  $\mathbf{E}$ . This effect is known as electrophoresis [1,2]. The electrophoretic mobility is defined as  $\mu \equiv U/E$ . The determination of the electrophoretic mobility of a colloid particle and its relation to the particle's zeta potential  $\zeta$  (i.e., the electrostatic potential at the surface of slippage between the macroparticle and the electrolytic bathing solution), is most relevant for the experimental characterization of macroparticles and for a wide variety of concomitant scientific and practical problems [1,2]. The theoretical approach to study electrophoresis is (i) to obtain the ionic structure around the *nonmoving* macroparticle, commonly known as the electrical double layer (EDL) and (ii) to use this equilibrium EDL as an input of a hydrodynamical theory to calculate  $\mu$ . Since the pioneer work of Smoluchowski in 1903 [1,2], the development of a theoretical description of electrophoresis has been advanced by improving on the above two main aspects of the theory. In 1931, Henry [1,2] computed mobilities neglecting the relaxation effect; this is, he assumed that the spherically symmetric EDL around a macroparticle is not distorted when the external electric field, giving rise to the electrokinetic motion, is turned on. The recent state of the theory is represented by the well-known work of Wiersema *et al.* [3] and that of O'Brien and White [4], hereinafter referred to as the Wiersema, O'Brien, and White theory (WOWT). WOWT improved Henry's treatment by taking into account the deformation of the ionic cloud around the moving macroparticle, i.e., the relaxation effect. In WOWT the macroparticles are at infinite dilution and are taken to be hard spheres of radius  $R$ , with a uniform surface charge density  $\sigma$ . The ionic solution is represented by a *point ion* model (PIM); i.e., the ions "see" each other as point charges, immersed in a continuous medium of dielectric constant  $\epsilon$ . The structure of this EDL is calculated through the Poisson-Boltzmann (PB) equation. WOWT predicts that the dependence of  $\mu$  on  $\zeta$  is universal for symmetrical electrolytes, for a fixed value of  $\kappa A$ , and exhibit a nonmonotonical behavior for high  $\kappa A$  [4].  $A$  is the hydrodynamical radius of the macroparticle and  $\kappa$  is the inverse of the Debye length, which is defined by  $\kappa^2 = (4\pi\beta e^2/\epsilon)\sum_{i=1}^2\rho_i z_i^2$ . Here  $\beta = 1/(k_B T)$ ;  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\rho_i$  and  $z_i$  are the bulk concentration and valence of ions of species  $i$ , and  $e$  is the protonic charge. The exist-

tence of a maximum in the  $\mu$ - $\zeta$  curves is a characteristic feature of WOWT and its origin can be traced to the relaxation effect. Moreover, in the usual range of experimental conditions, this maximum seems to be confirmed allowing this theory to serve as the standard guidance for interpreting mobility measurements and relating them to the electrical properties (zeta potentials, surface charges, etc.) of the experimental systems under study. Although major disagreements have been reported between WOWT and experimental results [5], up to now only minor additions have been advocated to revise it [1,2].

On the other hand, the well established integral equations formalism [6] has been used in the past to study the EDL around a model spherical macroparticle [7–9]. The macroparticle is modeled as in WOWT. However, the ionic solution is modeled by the so-called restricted primitive model (RPM). In RPM the ions are taken to be hard spheres of diameter  $a$  and charge  $e z_i$ , embedded in a dielectric medium of dielectric constant  $\epsilon$ . The ionic size is commonly taken as that of a hydrated ion [6–10]. The hypernetted chain (HNC)–mean spherical approximation (MSA) is an integral equation that has been proven to be in good agreement with Monte Carlo data for the EDL of this model [8]. The HNC-MSA result for the EDL of a spherical macroparticle, immersed in a RPM electrolyte, has important quantitative and qualitative differences with that of the PB equation for a macroparticle immersed in a PIM electrolyte. Particularly, in RPM, a maximum in  $\zeta$  as a function of  $\sigma$  is predicted [7–9], whereas in PIM it is not upper bounded. In the colloid literature it is assumed that the location of the slipping surface of electrokinetic phenomena is at the distance of closest approach between the ion and the macroparticle, i.e., at  $r = R + a/2$ . Hence,  $\zeta = \psi^0(R + a/2)$  and the hydrodynamical radius  $A$  is equal to  $R + a/2$ . In general,  $\psi^0(r)$  is the mean electrostatic potential at the distance  $r$  from the center of the macroparticle [6,7]. The existence of a maximum in the  $\zeta$  vs  $\sigma$  curve must have important consequences for the  $\mu$ - $\zeta$  relation. For a weak applied  $\mathbf{E}$ , WOWT calculates  $\mu$  from the first-order hydrodynamical fields around the PIM-EDL. Thus, if a better description of the EDL is consistently incorporated into the hydrodynamical equations, corrections to the relaxation would be incorporated into the resulting  $\mu$ - $\zeta$  relationship. Here we carry out this program and report results for the mobility of a charged macroparticle immersed in a RPM electrolyte.

The ionic distribution, as a function of the distance  $r$  to the center of the macroparticle, gives the structure of the equilibrium EDL, and is expressed in terms of the concentration profiles,  $\rho_i^0(r) = \rho_i g_i(r)$ . Here  $g_i(r)$  is the ionic reduced concentration profile (RCP) of the ionic species  $i$ . The HNC-MSA integral equations for the RCPs are given by [6,7]  $g_i(r) = \exp\{-\beta u_{Mi}(r) + \sum_{m=1}^2 \rho_m \int c_{im}(s) [g_m(|\mathbf{r}+\mathbf{s}|) - 1] dV\}$ , where  $u_{Mi}(r)$  is the interaction potential between the macroparticle, represented by the subindex  $M$ , and an ion of species  $i$ ;  $c_{im}(s)$  is the MSA direct correlation function for ions of species  $i$  and  $m$ , distant by  $s$ ; and  $dV$  is the differential volume element around  $M$ . In the limiting case of  $a=0$ , this equation reduces to the integral equation form of the PB theory; i.e., for  $a=0$  we recover the EDL for the PIM. From the HNC-MSA equation, the equilibrium RCPs are numerically obtained and will be used as the *nonperturbed* distribution functions in a perturbation treatment of the hydrodynamical field equations for the calculation of the mobility. The corresponding governing equations for the hydrodynamical fields and ionic fluxes can be derived from general nonequilibrium arguments involving the conservation of momentum and fluid and ionic mass. In our derivation of the hydrodynamical equations we explicitly consider the *ionic size*, whereas the size of the solvent molecules is considered only through the hydrated ion size, since the solvent is the continuous supporting medium of the hydrodynamical field equations. From the Liouville equation and a general expression of the stress tensor, in terms of molecular variables [11], the momentum transfer equation (MTE) is found to be  $\eta \nabla^2 \mathbf{u}(\mathbf{r}) - \sum_{m=1}^2 \rho_m(\mathbf{r}) \nabla v_m(\mathbf{r}) - 1/\beta \sum_{m=1}^2 \nabla \rho_m(\mathbf{r}) - \sum_{m,l=1}^2 \int \rho_{ml}(\mathbf{r}, \mathbf{r}') \nabla u_{ml}(\mathbf{r}, \mathbf{r}') dV' = \mathbf{0}$ , where  $\eta$  is the viscosity of the fluid,  $\mathbf{u}(\mathbf{r})$  is the velocity of the electrolyte around the macroparticle,  $v_m(\mathbf{r})$  is the *total* electrostatic potential at  $\mathbf{r}$ , i.e.,  $v_m(\mathbf{r}) = ez_m [\psi(\mathbf{r}) - \mathbf{E} \cdot \mathbf{r}]$ ,  $\psi(\mathbf{r})$  is the non-equilibrium mean electrostatic potential due to all the particles in the system, and  $\rho_{ml}(\mathbf{r}, \mathbf{r}')$  and  $u_{ml}(\mathbf{r}, \mathbf{r}')$  are the two-particle correlation functions in the presence of the macroion, and the interaction potential for two ions of species  $m$  and  $l$ , respectively; i.e.,  $u_{ml}(\mathbf{r}, \mathbf{r}')$  is the *hard sphere* plus the *Coulomb* potentials. In MTE, the first term is the dissipative contribution, the second term is the external force tensor contribution due to interaction of the external fields with the particles, and the last two terms are the contributions of the kinetic and intermolecular interactions stress tensor components. From the generalized expression for the chemical potential of an inhomogeneous fluid [12], the gradient of the chemical potential of ions of species  $i$ ,  $\mu_i(\mathbf{r})$ , is given by  $\rho_i(\mathbf{r}) \nabla \mu_i(\mathbf{r}) = \rho_i(\mathbf{r}) \nabla v_i(\mathbf{r}) + 1/\beta \nabla \rho_i(\mathbf{r}) + \sum_{m=1}^2 \int \rho_{mi}(\mathbf{r}, \mathbf{r}') \nabla u_{mi}(\mathbf{r}, \mathbf{r}') dV'$ . This equation and the MTE are combined to get  $\eta \nabla^2 \mathbf{u}(\mathbf{r}) - \sum_{m=1,2} \rho_m(\mathbf{r}) \nabla \mu_m(\mathbf{r}) = \mathbf{0}$ . On the other hand, the diffusion equation for the ionic species is  $[\partial \rho_i(\mathbf{r}) / \partial t] = -\nabla \cdot \mathbf{J}_i(\mathbf{r})$ , such that the ionic fluxes are given by  $\mathbf{J}_i(\mathbf{r}) = \rho_i(\mathbf{r}) \mathbf{u}(\mathbf{r}) - [\rho_i(\mathbf{r}) / f_i] \nabla \mu_i(\mathbf{r})$ . Here  $f_i$  is the drag coefficient of an ion of species  $i$ . Thus, the stationary state ionic mass balance equation is  $\nabla \cdot [f_i \rho_i(\mathbf{r}) \mathbf{u}(\mathbf{r}) - \rho_i(\mathbf{r}) \nabla \mu_i(\mathbf{r})] = 0$ . If all of the involved quantities are written in the general form  $C = C^0 + \delta C$ , where  $C^0$  represents the quantity at equilibrium and  $\delta C$  is the assumed small nonequilibrium deviation, the resulting differential equations for the  $\delta C$ s, up to linear terms, are  $\eta \nabla^2 \mathbf{u}(\mathbf{r})$

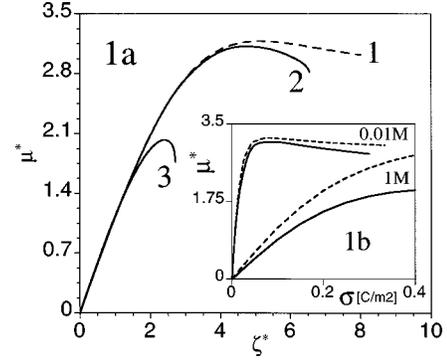


FIG. 1. (a) We show  $\mu^*$  as a function of  $\zeta^*$ ; curve 1 is the WOWT universal prediction for  $\kappa(R+a/2)=5$ ; curves 2 and 3 are the PME results for  $\rho_+ = \rho_- = 0.01$  M and  $R = 150.004$  Å and  $\rho_+ = \rho_- = 1$  M and  $R = 13.088$  Å, respectively. In (b) we plot  $\mu^*$  as a function of  $\sigma$ ; the upper curves are for  $\rho_+ = \rho_- = 0.01$  M and  $R = 150.004$  Å, whereas the lower curves are for  $\rho_+ = \rho_- = 1$  M and  $R = 13.088$  Å. The electrolyte is a 1:1 electrolyte ( $T = 298.16$  K,  $\epsilon = 78.54$ ,  $a = 4.25$  Å,  $f_+ = f_- = 2.212 \times 10^{-19}$  dynes sec  $\text{cm}^{-1}$ ,  $\eta = 0.008937$  poise). In all cases  $\kappa(R+a/2) = 5$ . The broken and solid lines are the WOWT and PME results, respectively.

$-\sum_{m=1,2} \rho_m^0(\mathbf{r}) \nabla \delta \mu_m(\mathbf{r}) = \mathbf{0}$  and  $\nabla \cdot [f_i \rho_i^0(\mathbf{r}) \mathbf{u}(\mathbf{r}) - \rho_i^0(\mathbf{r}) \nabla \delta \mu_i(\mathbf{r})] = \mathbf{0}$ . Here  $\delta \mu_i(\mathbf{r})$  is the deviation from the equilibrium chemical potential for an ion of species  $i$ . These last two equations are first order in our expansion around the unperturbed electrolyte's distribution functions  $[\rho_m^0(\mathbf{r})]$ , incorporate the hydrated ionic size, extend the equations employed by WOWT, and can be numerically solved by a method similar to that of O'Brien and White [4] to finally produce the electrophoretic mobility  $\mu$ . If  $a \neq 0$ , our theory incorporates ionic size effects in electrophoretic mobility calculations. Hereinafter we will refer to this theory as PME (primitive model electrophoresis). For  $a = 0$ , PME reduces to WOWT. Notice that  $\psi^0(\mathbf{r})$  can then be directly obtained from  $\rho_m^0(\mathbf{r})$  [7]. Therefore,  $\psi^0(\mathbf{r})$  is implicitly taken into account in our theory.

In Fig. 1 we present WOWT and PME results for the reduced mobility,  $\mu^* \equiv (6\pi\eta e\beta/\epsilon)\mu$ , of a macroparticle in a 1:1 electrolytic solution. However, a Stern correction to WOWT has been made to consistently compare it with PME, i.e., when interacting with the macroparticle, the macroparticle-ion distance of maximum approach is  $R + a/2$ . In all of our calculations we have taken  $a = 4.25$  Å, which is the value commonly taken as the diameter of a hydrated ion [6–10]. The ionic concentrations and macroparticle radii were chosen to achieve  $\kappa(R+a/2) = 5$ . We investigated two combinations of concentration and radius:  $\rho_+ = \rho_- = 0.01$  M and  $R = 150.004$  Å, and  $\rho_+ = \rho_- = 1$  M and  $R = 13.088$  Å. In Fig. 1(a), we show  $\mu^*$  as a function of the reduced zeta potential,  $\zeta^* \equiv e\beta\zeta$ . For sufficiently low ionic concentration and surface charge density, PME agrees with WOWT. However, the relevant feature here is that, while WOWT is universal for every system where  $\kappa(R+a/2)$  is a constant, PME predicts very important quantitative and qualitative differences between the mobilities of the above two cases. This effect should have important consequences in the interpretation of mobility experiments. In Fig. 1(b),  $\mu^*$  is plotted as a function of  $\sigma$ . Now, WOWT does *not*

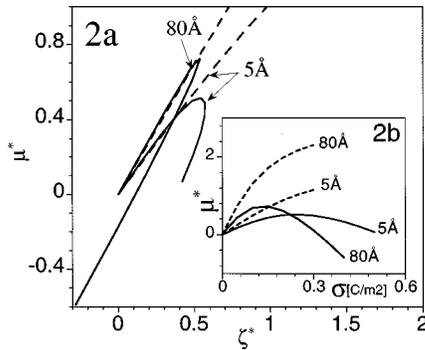


FIG. 2.  $\mu^*$  as a function of  $\zeta^*$  or  $\sigma$ , for a macroparticle immersed in a 2:2, 0.5-M electrolyte ( $f_+ = f_- = 4.424 \times 10^{-9}$  dynes sec cm).

predict a universal behavior for  $\mu^*$ , a fact which apparently had not been recognized before [13,14]. The results for 1:1 electrolytes included in Fig. 1 were computed in a range of conditions for which the HNC-MSA and the PB  $\zeta(\sigma)$  functions are both monotonic [7,8]. In Fig. 2 we consider the situation of a macroparticle moving in a 2:2 electrolyte of ionic concentrations  $\rho_+ = \rho_- = 0.5$  M. Since we have established the *nonexistence* of PME universal behavior of the  $\mu^*$ - $\zeta^*$  curves, for constant  $\kappa A$ , in Fig. 2 we compare WOWT and PME for the same values of all the physical parameters. Two cases of macroparticle's radii were studied,  $R = 5$  Å ( $\kappa A = 3.31$ ) and  $80$  Å ( $\kappa A = 38.19$ ). In Fig. 2(a) we plot  $\mu^*$  as a function of  $\zeta^*$ . Consistent with Fig. 1, the differences here between WOWT and PME are larger for higher valences and/or larger radius  $R$ . Note first that PME predicts two different mobilities for the same  $\zeta^*$  potential. For this divalent case, PME also allows the occurrence of negative electrophoretic mobilities and negative zeta potentials for our *positively* charged macroparticle. Experimental results seem to indicate that this last effect is real [5,15–17]. The origin of these novel characteristics of the  $\mu^*$ - $\zeta^*$  relationship can be found in the nonlinear behavior of  $\zeta$  predicted by the HNC-MSA theory of the EDL [7,10]. In Fig. 2(b) we have plotted  $\mu^*$  as a function of  $\sigma$ . The WOWT curves do not have a maximum, whereas PME curves do. This maximum implies that two macroparticles of the same size, but with different charges, can have the same electrophoretic mobility. The higher the macroparticle's surface charge density, the higher the electrical field drag force on it. On the other hand, the higher the macroparticle's surface charge density, the narrower the EDL and, hence, the lower the effective charge with which the particle travels. The combination of these two effects seems to explain the PME prediction of  $\mu^*$  as a function of  $\sigma$ . Most significantly, negative mobilities for positively charged macroparticles are predicted by PME. A 2:2, 0.5 M electrolyte, around a  $80$  Å,  $0.3$  C/m<sup>2</sup> macroparticle has an oscillatory counterion concentration profile (see Figs. 3, 11, and 12 of Ref. [7]). This is not the case for the  $5$  Å,  $0.3$  C/m<sup>2</sup> macroparticle [7]. Thus, if the particle moves along with just an inner part of its EDL, a negative electrophoretic mobility seems to be physically appealing, i.e., the macroparticle's effective charge “seen” by  $\mathbf{E}$  is negative. In Fig. 3 the PME and WOWT results for  $\mu^*$  of a  $R = 200$  Å,  $\sigma = -0.056$  C/m<sup>2</sup> macroparticle, immersed

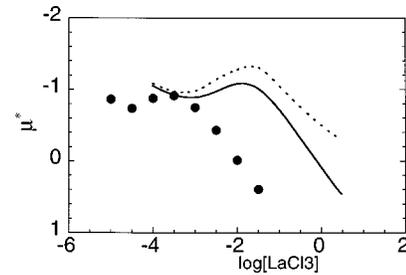


FIG. 3.  $\mu^*$  as a function of the  $\log_{10}$  of  $\text{LaCl}_3$  molar concentration ( $f_+ = 6.636 \times 10^{-9}$  and  $f_- = 2.212 \times 10^{-9}$  dynes sec cm<sup>-1</sup>). The black dots are the experimental data (Ref. [17]).

into a 1:3 electrolyte, such as  $\text{LaCl}_3$ , is plotted as a function of the logarithm of the molar ionic concentration. Larger values of  $R$  do not change significantly the mobility values. Experimental data for latex in  $\text{LaCl}_3$ , are also shown [17]. The qualitative agreement of both WOWT and PME with the experimental data is good; PME is better. The WOWT results were obtained *without* assuming universality, as shown in Fig. 1. As the concentration increases, WOWT mobility changes its increasing tendency and will not become positive, whereas PME does become positive and seems to be in better agreement with the linear increase of the mobility as the concentration increases in this logarithmic scale.

In the past, theoretical explanations for the maximum in the  $\mu^*$  vs concentration curve have been proposed by advocating surface conductance, *ad hoc* choices of  $\zeta^*$  potentials, surface roughness and “hairy” layers [5,13,14,18–20]. Here we show that, while these mechanisms could be present, they are not necessary to account for the mobility vs concentration maximum, which can be explained by simply not assuming universality in WOWT or, better, by taking into account the ionic size in the mobility theory. The PME concentration profiles around the macroparticle (not shown), for salt concentrations where a positive mobility is obtained, in Fig. 3, show a charge reversal, as proposed in the past [10] and observed in polymer experiments [21,22], whereas those from WOWT do not. A similar agreement to that in Fig. 3 is obtained when WOWT and PME are compared to experimental results for the mobility as a function of  $\text{CaCl}_2$  concentration [17]. The counterion and co-ion concentration profiles for salt concentrations, where the reversed mobility is obtained, have the same qualitative behavior (not shown here) as that in Fig. 21, for the 1 M case, from Ref. [10] where, to the best of our knowledge, the reversed mobility was first theoretically predicted. Our finite ion size theory (PME) extends the WOWT to include ionic size effects. PME has very important quantitative and qualitative differences with WOWT. In PME, no universality of the electrophoretic mobility is found and a highly nonlinear behavior of the electrophoretic mobility is predicted. For certain conditions, an inverted electrophoretic mobility is predicted. Experimental evidence of this inverted mobility has been reported in the past [5,15–17]. None of these effects are predicted by WOWT or any other transport theory. However, in the limit of zero ionic diameter, PME reduces to WOWT. A comparison with experimental data of WOWT (without assuming universality) and PME, for the mobility

vs electrolyte concentration, shows good qualitative agreement [5,17]. This mobility reversal, as predicted by PME, is related to the charge inversion phenomena observed in polymer studies [21,22].

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