An experimental/theoretical method to measure the capacitive compactness of an aqueous electrolyte surrounding a spherical charged colloid

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The capacitive compactness has been introduced very recently [G. I. Guerrero-García *et al.*, Phys. Chem. Chem. Phys. **20**, 262–275 (2018)] as a robust and accurate measure to quantify the thickness, or spatial extension, of the electrical double layer next to either an infinite charged electrode or a spherical macroion. We propose here an experimental/theoretical scheme to determine the capacitive compactness of a spherical electrical double layer that relies on the calculation of the electrokinetic charge and the associated mean electrostatic potential at the macroparticle's surface. This is achieved by numerically solving the non-linear Poisson-Boltzmann equation of point ions around a colloidal sphere and matching the corresponding theoretical mobility, predicted by the O'Brien and White theory [J. Chem. Soc., Faraday Trans. 2 **74**, 1607–1626 (1978)], with experimental measurements of the electrophoretic mobility under the same conditions. This novel method is used to calculate the capacitive compactness of NaCl and $CaCl_2$ electrolytes surrounding a negatively charged polystyrene particle as a function of the salt concentration. *Published by AIP Publishing.* https://doi.org/10.1063/1.5024553

I. INTRODUCTION

The electrical double layer is the ionic cloud existing around charged macroions or electrodes in electrolyte solutions. The thickness, or spatial extension, of this ionic cloud determines many of the thermodynamic and electrokinetic properties of charged colloids dissolved in Coulombic fluids.[1–16] In a very recent study, some of the present authors have proposed the concept of capacitive compactness to characterize the thickness of the electrical double layer.[17] The main idea is to consider that the diffuse ionic charge surrounding, for instance, a spherical charged colloid can be replaced by an infinitely thin spherical shell, defining an effective electrical double layer capacitor (see Fig. 1). The separation distance between the electrodes of this effective capacitor plus the radius of the spherical charged colloid defines the capacitive compactness τ_c. In order to determine τ_c, the electrostatic potential difference between the electrodes of the effective electrical double layer capacitor is equated to the mean electrostatic potential at the surface of the charged colloid.[17] This definition is general, and it has been theoretically supported by electrostatics and statistical mechanics arguments.[17,18] With the aim of providing the specific expression of the capacitive compactness in spherical geometry, let us consider a $z_- : z_+$ electrolyte dissolving a spherical macroion of radius R_M, valence z_M, and surface charge density $\sigma_0 = (e_0 z_M)/(4\pi R_M^2)$, where e_0 is the protonic charge. Ions can approach up to a closest approach instance b measured from the colloidal surface, and this distance defines the location of the so-called Helmholtz plane, as shown in Fig. 1. The capacitive compactness in spherical geometry can be explicitly written as[17,18]

$$\tau_c = \left(\frac{1}{R_M} - \frac{\varepsilon_0 \epsilon}{R_M^2 \sigma_0} \psi_0 \right)^{-1}, \qquad (1)$$

where ψ_0 is the mean electrostatic potential at the colloidal surface, ϵ is the dielectric constant everywhere, and ε_0 is the vacuum permittivity. Notice that the explicit dependence of the capacitive compactness on the microscopic structure can be obtained by replacing the definition of the mean electrostatic potential at the colloidal surface in terms of the corresponding ionic radial distribution functions in spherical coordinates, $g_i(r)$, viz.,

$$\psi_0 = \frac{e_0}{\varepsilon_0 \epsilon} \int_0^\infty \sum_i z_i \rho_i^{bulk} g_i(t) \left(t - \frac{t^2}{r} \right) dt, \qquad (2)$$

where z_i and ρ_i^{bulk} are the valence and bulk concentration of species i of the supporting electrolyte, respectively. In the classical linear Poisson-Boltzmann or Debye-Hückel theory of point ions, the capacitive compactness *measured from the*
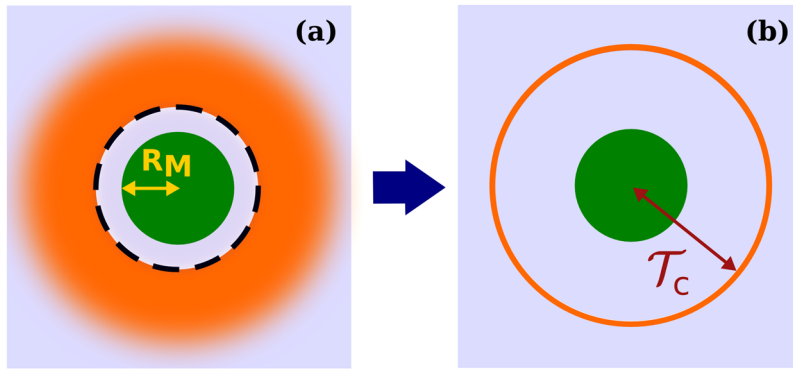
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FIG. 1. (a) Spherical electrical double layer and (b) the associated capacitive compactness τ_c, which is defined as the sum of the separation distance between the two electrodes of the corresponding effective capacitor plus the radius of the spherical charged colloid. The closest approach distance between point ions and the colloidal surface, specifying the Helmholtz plane, is drawn with a black dashed line in panel (a).

Helmholtz plane reduces to the Debye length in spherical and planar geometries.[19] In such a scenario, the thickness of the electrical double layer is independent of the colloidal charge. One major limitation of the Debye-Hückel theory is that it is valid only in the limit of very weakly charged surfaces neutralized by point ions. As the non-linear Poisson-Boltzmann theory is valid even at larger colloidal charges than the Debye-Hückel description, this full Poisson-Boltzmann approach is more appealing as a way to calculate the capacitive compactness via Eq. (1). In this defining equation of τ_c, it is necessary to know the colloidal charge and the mean electrostatic potential at the colloidal surface in order to obtain the capacitive compactness. Aiming for a practical determination of τ_c, the colloidal charge is available from chemical titration experiments. However, until very recently, it had been thought that it was impossible to measure directly the mean electrostatic potential of charged electrodes by experiments.[20,21] Fortunately, this limitation has been lately overcome via sophisticated X-ray photoelectron spectroscopy experiments[22] which are able to measure directly the mean electrostatic potential at the colloidal surface. In any case, even if this technique is very promising, nowadays only very few research groups are able to use it (see, e.g., Refs. 23–29).

Therefore, and in view of such a difficulty, we would like to propose here an alternative experimental/theoretical approach to calculate the electrokinetic colloidal charge and the corresponding mean electrostatic potential at the colloidal surface, with the ultimate objective of determining the capacitive compactness τ_c of the electrical double layer. This method is based on standard electrophoresis experiments to measure the mobility of charged particles and on the theoretical calculation of the electrophoretic mobility through the widely used O'Brien and White approach.[30]

II. THEORETICAL AND EXPERIMENTAL METHODS

According to the well-known O'Brien and White prescription, the theoretical electrophoretic mobility of a charged spherical colloid, including hydrodynamic retardation and relaxation effects due to the electrolyte, can be obtained from a perturbation approach as follows. In the O'Brien and White theory, under the influence of an external electrical field $\vec{E}_0$ and for low-Reynolds numbers, the stationary motion of an incompressible and Newtonian electrolytic fluid around a

fixed spherical colloid is governed by the non-equilibrium equations

$$\eta \, \nabla^2 \vec{u}(\vec{r}) - \nabla p(\vec{r}) = \rho_c(\vec{r}) \, \nabla \psi(\vec{r}) \tag{3}$$

and

$$\nabla \cdot \vec{u}(\vec{r}) = 0. \tag{4}$$

In the above equations, η is the dynamic viscosity of the medium and $\vec{u}(\vec{r})$, $p(\vec{r})$, $\rho_c(\vec{r})$, and $\psi(\vec{r})$ are, respectively, the velocity, pressure, volume charge density, and mean electrostatic potential at position $\vec{r}$ inside the fluid. Due to the presence of $\psi(\vec{r})$ in Eq. (3), the previous equations must be complemented with the corresponding Poisson equation, viz.,

$$\nabla^2 \psi(\vec{r}) = -\frac{1}{\varepsilon_0 \epsilon} \rho_c(\vec{r}), \tag{5}$$

where

$$\rho_c(\vec{r}) = \sum_{i=+,-} e_0 \, z_i \, \rho_i(\vec{r}). \tag{6}$$

In turn, to determine the stationary ionic densities $\rho_i(\vec{r})$, the following ion conservation equations are required:

$$\nabla \cdot \left[k_B T \, \nabla \rho_i(\vec{r}) + e_0 z_i \rho_i(\vec{r}) \nabla \psi(\vec{r}) - \lambda_i \rho_i(\vec{r}) \vec{u}(\vec{r}) \right] = 0, \tag{7}$$

with k_B, T, and λ_i being the Boltzmann constant, the temperature, and the ionic drag coefficients, respectively; $i = +, -$, and

$$\rho_i(\vec{r}) = \rho_i^{bulk} g_i(\vec{r}). \tag{8}$$

As indicated previously, in the O'Brien and White description, the reference system is located at the center of the colloid; therefore, the resolution of Eqs. (3)–(7) yields the velocity of the fluid at infinite. Clearly, the negative value of such a velocity should be equivalent to the velocity of the macroparticle moving in a quiescent electrolytic environment and, then the colloidal electrophoretic mobility (velocity per unit electrical field) is a final result of this hydrodynamical theory.

At this point, it is important to notice that all the functions involved in the above equations are non-equilibrium quantities. Hence, to proceed with the solution, any of the non-equilibrium functions, $A(\vec{r})$, is written in the general perturbative form

$$A(\vec{r}) = A^{eq}(r) + \delta A(\vec{r}), \tag{9}$$

where $A^{eq}(r)$ is the corresponding radially symmetric quantity at *equilibrium* (i.e., when $\vec{E}_0 = \vec{0}$), and $\delta A(\vec{r})$ stands for the

deviation from equilibrium due to the presence of the external force. In a perturbation scheme, the reference functions $A^{eq}(r)$ are supposed to be known and, in our particular case, we have, for example, that

$$\psi^{eq}(r) = -\frac{k_B T}{z_i e_0} \ln g_i^{eq}(r), \quad (10)$$

with $i = +$ or $-$, indistinctly, and $g_i^{eq}(r)$ being the Poisson-Boltzmann ionic distributions for a point-ion spherical double layer at equilibrium, *corresponding to a given colloidal surface charge density σ_0*. Substituting all the hydrodynamical fields, in the form given by Eq. (9), in Eqs. (3)–(7) leads to the following first-order system of partial differential equations for the supposedly small perturbations $\delta A(\vec{r})$:

$$\eta \nabla^2 \delta \vec{u}(\vec{r}) - \nabla \delta p(\vec{r}) - \rho_c^{eq}(r) \nabla \delta \psi(\vec{r}) - \delta \rho_c(\vec{r}) \nabla \psi^{eq}(r) = \vec{0}, \quad (11)$$

$$\nabla \cdot \delta \vec{u}(\vec{r}) = 0, \quad (12)$$

$$\nabla^2 \delta \psi(\vec{r}) = -\frac{1}{\varepsilon_0 \epsilon} \delta \rho_c(\vec{r}), \quad (13)$$

and

$$\nabla \cdot \left[k_B T \nabla \delta \rho_i(\vec{r}) + e_0 z_i \rho_i^{eq}(r) \nabla \delta \psi(\vec{r}) \right.$$
$$\left. + e_0 z_i \delta \rho_i(\vec{r}) \nabla \psi^{eq}(r) - \lambda_i \rho_i^{eq}(r) \vec{u}(\vec{r}) \right] = 0. \quad (14)$$

By symmetry arguments,[30] the perturbation terms can be expressed in polar coordinates as

$$\delta A(\vec{r}) = A_r(r) A_\theta(\cos \theta). \quad (15)$$

The usage of the previous variable-separated forms in Eqs. (11)–(14) produces a system of ordinary differential equations for the radial functions $A_r(r)$, which can be straightforwardly integrated in a numerical way (e.g., via a Runge-Kutta method). The implementation of the full O'Brien and White theory of electrophoresis was carried out here by means of a fast and accurate Fortran code of our own.[31–33] This program provides the electrophoretic mobility for a given set of parameters of the system and a fixed boundary condition, e.g., at a constant surface charge density σ_0 at the colloidal surface.

In our actual numerical calculations, the physical parameters used are the following: a negatively charged spherical particle of radius $R_M = 8000$ Å is immersed in an aqueous electrolyte solution with dielectric constant $\epsilon = 78.5$, at a temperature $T = 298$ K, with a solvent ionic friction $\eta = 0.008\,937$ P. For the 1:1 electrolyte, $\lambda_+ = \lambda_- = 2.212 \times 10^{-19}$ dyn s cm^{-1}. For the 2:1 salt, $\lambda_+ = 4.424 \times 10^{-19}$ dyn s cm^{-1} and $\lambda_- = 2.212 \times 10^{-19}$ dyn s cm^{-1}. The Helmholtz plane, or the closest approach distance between point ions and the colloidal surface, is $b = 2.5$ Å. As usual, the Debye length of the supporting electrolyte in bulk is defined as $\lambda_D = 1/\kappa_D$, where

$$\kappa_D = \left(\frac{\sum_i \rho_i^{bulk} z_i^2 e_0^2}{\varepsilon_0 \epsilon k_B T} \right)^{\frac{1}{2}}. \quad (16)$$

In order to calculate the capacitive compactness, it is necessary to know both the colloidal charge σ_0 and the associated

mean electrostatic potential at the colloidal surface ψ_0, which is a function of σ_0, i.e., $\psi_0(\sigma_0)$. This can be done by numerically solving the equilibrium non-linear Poisson-Boltzmann equation for point ions

$$\nabla^2 \psi^{eq}(r) = -\frac{1}{\varepsilon_0 \epsilon} \sum_{i=+,-} \rho_i^{bulk} z_i e_0 \exp \left(-\frac{\psi^{eq}(r) z_i e_0}{k_B T} \right), \quad (17)$$

which is valid even at non-weak colloidal charges under the same conditions used in the experiments. Next, and with the purpose of matching the experimental and the theoretical electrophoretic mobilities, we proceed as follows. First, we solve the integral equation version of the non-linear Poisson-Boltzmann equation (by employing an accurate and efficient finite element scheme) for a very small surface charge density σ_0^{trial} at a fixed ionic concentration.[34] This allows us to know the corresponding ionic profiles and the associated mean electrostatic potential at the colloidal surface $\psi_0(\sigma_0^{trial})$. Subsequently, the electrophoretic mobility can be numerically determined from these ionic profiles via the O'Brian and White theory. If the theoretical electrophoretic mobility is equal to the experimental one, the electrokinetic colloidal charge is then $\sigma_0 = \sigma_0^{trial}$ and the capacitive compactness can be calculated from Eq. (1). On the other hand, if the theoretical electrophoretic mobility is lower than the experimental one, σ_0^{trial} is gradually increased until both the theoretical and the experimental mobilities match each other.

III. RESULTS AND DISCUSSION

With the goal of illustrating the experimental/theoretical approach proposed here to calculate the capacitive compactness τ_c of aqueous electrolytes, we have performed electrophoresis experiments of charged colloids in the presence of monovalent and divalent counterions with added salt. A Zetameter 3.0 was used to measure the experimental electrophoretic mobilities (Zetameter, Inc.). In order to prepare the particle suspension, negatively charged polystyrene particles (≈ 1.6 μm of diameter, Invitrogen) were diluted in a buffer solution at pH 7 (NaH$_2$PO$_4$ buffer at low ionic strength), whereas the concentration of macroparticles was fixed at $\Phi_m = 0.0005\%$. Afterwards, the polystyrene particles were dissolved in aqueous NaCl and CaCl$_2$ electrolytes at different salt concentrations that ranged from 1 mM up to 200 mM. For these systems, the experimentally measured electrophoretic mobilities of polystyrene particles are plotted in Fig. 2 as a function of the ionic concentration. At a concentration of 1 mM, the electrophoretic mobilities of the charged polystyrene particles immersed in NaCl and CaCl$_2$ electrolytes are -6.96×10^{-8} and -3.93×10^{-8} m^2/(V s), respectively. According to the O'Brien and White theory, the electrokinetic surface charge densities σ_0 associated with these mobilities are -0.0138 and -0.0157 C/m^2 in the presence of NaCl and CaCl$_2$ salts, respectively. In addition, the mean electrostatic potentials at the colloidal surface $\psi_0(\sigma_0)$ associated with these surface charge densities are -108.62 and -60.89 mV, respectively. Once σ_0 and $\psi_0(\sigma_0)$ have been determined for all experimental concentrations, it is then possible to calculate the thickness of the electrical double layer via the capacitive compactness τ_c
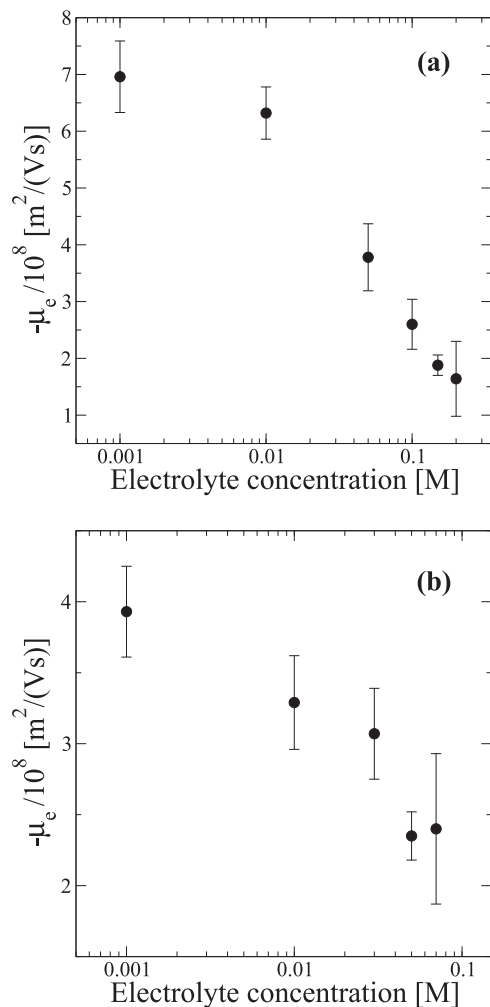
FIG. 2. Experimental electrophoretic mobilities of polystyrene particles ($\approx 1.6\,\mu$m of diameter) in the presence of (a) NaCl and (b) CaCl$_2$ electrolytes at different salt concentrations.
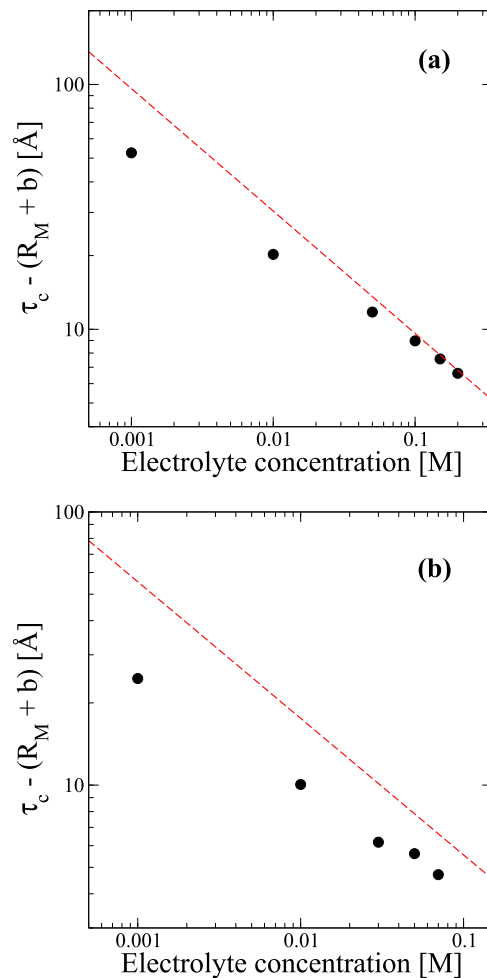

FIG. 3. Experimentally derived capacitive compactness τ_c (solid black dots) measured from the Helmholtz plane as a function of the ionic concentration of (a) NaCl and (b) CaCl$_2$ electrolytes, in the presence of a charged colloidal particle of radius $R_M = 8000$ Å. For comparison purposes, the corresponding Debye length of each supporting bulk electrolyte is displayed as a red dashed line.

by using Eq. (1). If the spherical colloid has an infinite radius, the capacitive compactness in the planar limit[17] can be written as $\tau_c = \varepsilon_0 \epsilon \frac{\psi_0}{\sigma_0}$. This equation provides the same results that Eq. (1) with an error of less than 1% for the parameters used in this study.

Therefore, the capacitive compactness τ_c associated with NaCl and CaCl$_2$ electrolytes, surrounding a negatively charged spherical particle of radius $R_M = 8000$ Å, is plotted in Fig. 3. A distinctive common feature observed in both electrolytes is that the capacitive compactness τ_c decreases monotonically as a function of the salt concentration. In particular, in Fig. 3(a), it is evident that, in the presence of monovalent counterions, the capacitive compactness τ_c [obtained from Eq. (1)] is significantly lower than the associated bulk Debye length at low salt concentrations. As the capacitive compactness in the non-linear Poisson-Boltzmann theory reduces to the bulk Debye length in the limit of zero colloidal charge, the previous behavior suggests that the electrokinetic colloidal charge is significantly different from zero. This is consistent with the magnitude of the experimental electrophoretic mobility displayed in Fig. 2 in the presence of NaCl at the lowest ionic concentration. When the ionic concentration of NaCl increases, the difference between τ_c and the Debye length decreases and

both quantities approach to each other. Note that the convergence observed at high salt concentrations in Fig. 3(a) does not necessarily imply that, in general, the capacitive compactness reduces to the Debye length in concentrated electrolytes. In fact, we believe that this behavior at low colloidal charges is rather a coincidence for this particular univalent system. In this respect, a recent non-linear Poisson-Boltzmann calculation for a 1:1 electrical double layer displays a monotonic decreasing of the capacitive compactness as a function of the colloidal charge at salt concentrations as large as 1M.[19] This means that, if the supporting electrolyte is concentrated, τ_c is expected to have a different value regarding the Debye length in the regime of large colloidal charges, where the Debye-Hückel equation breaks down. In addition, a significant difference between τ_c and the Debye length (larger than that seen in the presence of monovalent counterions) can be observed at low salt concentrations of CaCl$_2$, as shown in Fig. 3(b). This difference decreases when the salt concentration increases, but this time τ_c clearly does not approach to the Debye length value as occurred in the presence of NaCl for the concentrations displayed.

IV. CONCLUDING REMARKS

In this report, we have proposed an experimental/theoretical method to calculate the capacitive compactness τ_c associated with a $z_- : z_+$ electrolyte in the presence of a spherical charged colloid. The propounded method relies on standard experimental electrophoresis measurements of charged particles in aqueous electrolytes, as well as on the O'Brien and White theory that provides the electrophoretic mobility associated with these charged colloids. When the experimental and the theoretical electrophoretic mobilities are equated, the electrokinetic surface charge density σ_0 and the mean electrostatic potential at the colloidal surface $\psi_0(\sigma_0)$ can be estimated without the necessity of very sophisticated X-ray photoelectron spectroscopy experiments,[22–29] in order to measure directly the mean electrostatic potential at the colloidal surface. Once σ_0 and $\psi_0(\sigma_0)$ are determined, the associated capacitive compactness τ_c can be calculated. This quantity is a robust and accurate measure of the spatial extension or thickness of the diffuse electrical double layer of ionic fluids.[17,19]

It is worth mentioning that even though the non-linear Poisson-Boltzmann does not include inter-ionic correlations and ionic exclusion volume effects, we would expect similar trends at dilute ionic concentrations and very low colloidal charges regarding more sophisticated approaches. In the opposite regime, however, very interesting phenomena could be expected. This includes a transition from a shrinking to an expansion of the electrical double layer as a function of the colloidal charge and the ionic concentration in the presence of multivalent coions.[17] On the other hand, we foresee that the present method can also be used if the experimental measurements of the electrophoretic mobility are replaced by the corresponding simulation results. As simulations are performed on a particular physical model, the theoretical approach selected has to be able to incorporate the same physical features in order to provide consistent results. In this manner, it would be possible to isolate the influence of different effects on the magnitude of the capacitive compactness, such as ion-correlations, ionic excluded volume effects, image charges, van der Waals interactions, etc. Work along these lines is currently in progress and will be published elsewhere.

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