

Comparison of the Zeta Potential with the Diffuse Layer Potential from Charge Titration

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The hypernetted chain (HNC) theory is used to compare charge titration and zeta potential data for several colloids. It is found that the HNC diffuse layer potential is closer to the zeta potential than that calculated with the traditional Poisson–Boltzmann (PB) approximation, and hence the amount of counterion binding required to bring the two into conformity is reduced. Further improvement is obtained by using an effective PB diffuse layer potential, calculated from both the numerical HNC theory and the analytic extended PB approximation. The rationale for using the effective PB potential is that the conversion from the measured electrophoretic mobility to the zeta potential invokes the PB approximation. In the case of silver iodide quantitative agreement is obtained without any fitting parameters, which confirms that no counterion binding occurs. For the metal oxides analyzed (titanium dioxide, aluminum oxide, and silicon dioxide) the two measurements can only be reconciled by postulating counterion binding or surface charge mobility.

Introduction

The electric double layer plays a major role in diverse areas such as adhesion, self-assembly, filtration, wetting, electrokinetics, and it is perhaps the major determinant of colloidal interactions and colloid stability. Consequently the charge and potential of a range of surfaces and colloidal particles have been measured in order to quantify the electric double layer for various systems. Surface charge is determined by charge titration, whereas the so-called zeta potential is generally determined by electrokinetic techniques (e.g., electrophoresis, streaming potential, electroosmosis).^{1–3} The distinction between the surface potential and the zeta potential is that the latter applies at the plane of shear, which may be up to 2–3 water diameters away from the surface.^{4–6}

In the basic model of the electric double layer, the colloid particle is planar, spherical, or cylindrical in shape, with a smooth and uniformly charged surface, and the solvent is treated as a dielectric continuum. The double layer is divided into a compact part adjacent to the surface, and a diffuse part. In the diffuse part the ions are mobile and obey the laws of statistical mechanics: the counterions (i.e., those of opposite charge to the surface) are attracted toward the surface and the co-ions are repelled. This gives rise to an ion density profile that decays to the bulk concentration of the electrolyte far from the surface. Similarly the electrostatic potential profile decays to zero in the bulk. The rate of decay or screening length is taken to be the Debye length.

The compact part of the double layer can be defined by the inner and outer Helmholtz planes. The inner Helmholtz plane represents the plane of closest approach of nonhydrated ions to the surface, (≈ 0.1 – 0.2 nm from the

surface), where a physical (nonelectrostatic) adsorption may occur. The outer Helmholtz plane represents the closest approach of the hydrated ions, (≈ 0.6 nm from the surface). The relative dielectric permittivity of the region between the surface and the inner Helmholtz plane, (sometimes called the Stern layer), is taken to be $\epsilon_{r1} \approx 5$, and that between the two Helmholtz planes is $\epsilon_{r2} \approx 20$, which are significantly less than that of bulk water ($\epsilon_r = 78$) due to surface-induced structure.^{1–3} Apart from those adsorbed at the inner Helmholtz plane, ions are excluded from both inner regions of the double layer, so that there the potential consists of two linear regimes. The potential at the outer Helmholtz plane is called the diffuse layer potential. Insofar as the shear plane lies close to the outer Helmholtz plane,^{4–6} the diffuse layer potential may be identified with the zeta potential.

There is a degree of evidence to show that this model of the electric double layer, although grossly simplified in many respects (it ignores, for example, the discreteness of the surface charge and the molecular nature of water) is sufficient to encompass the essential features of reality. Conversely, although the compact region may appear somewhat artificial, it also appears necessary for the full description of the available data.^{1–3} Much of the evidence for the nature of the compact region comes from electrochemical measurements, (e.g., the capacitance of the mercury electrode). Additional evidence is obtained from the comparison of charge titration data with measured zeta potentials, which shows that the surface potential calculated from the former is much greater than the zeta potential. By including the adsorbed counterions and the capacitance of the compact region the two measurements may be made consistent.

Of course some theory is required to compare the model with measurement, and the earliest and still most widespread approach is that of Gouy and Chapman,^{7,8} (the above model is often called the Gouy–Chapman–Grahame–Stern or GCGS model). This theory invokes the Poisson–Boltzmann (PB) approximation, which is a mean field approach that equates the potential of mean

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force of an ion in the double layer to the mean electrostatic potential. As such PB neglects ionic correlations, which arise from the electrostatic interactions between the ions, and from excluded volume effects due to ion size. In recent years a variety of sophisticated statistical mechanical techniques have been applied to inhomogeneous fluids. These include simulations, integral equations, and density functional approaches; the results for the electric double layer have been reviewed.^{9,10} What has emerged from tests against these more exact approaches is that for a given model the PB approximation can be quantitatively in error, even for low electrolyte concentrations and moderate surface charges.⁹⁻¹⁴

In view of these tests it is questionable whether the PB approximation really provides a reliable justification for any particular model of the inner region of the double layer. It could well be argued that the values of any fitted parameters are just effective quantities that bring the two experimental techniques into conformity by compensating for the shortcomings of the PB approximation. The issue is quite important because much of the quantitative modeling of the surface chemistry of colloid particles (e.g., ion binding coefficients) is predicated upon the validity of the GCGS and more elaborate models of the double layer.

The obvious question then is whether the discrepancy between the charge titration and zeta potential measurements can be resolved, or at least reduced, if the diffuse layer potential is calculated using a more sophisticated theory. In this paper we reanalyze literature data for a selection of colloids using the hypernetted chain (HNC) integral equation, which accurately includes the excluded volume and electrostatic correlation effects neglected by the PB approximation. Applying Occam's razor we use the simplest model of the electric double layer, which has coincident Helmholtz planes and no specific (i.e., non-electrostatic) ion adsorption. The rationale for this approach is to see whether the experimental data can be reconciled by an accurate solution of the simplest model of the electric double layer. While undoubtedly there are many physical effects neglected in this model, the present procedure will allow an estimate of the extent to which these effects are negligible in practice. If one attributes any discrepancy that remains after the present analysis to specific counterion adsorption, then the present results should enable a more accurate quantitative estimate of the binding constants than was previously obtained with the PB approximation.

I. Electric Double Layer

A. The Basic Model. The most basic model of the electric double layer utilizes the so-called restricted primitive model of the electrolyte. Here the solvent is taken to be a dielectric continuum of relative permittivity ϵ_r . The ions are modeled as hard spheres all with diameter d , with a point charge $\pm q$ at their center. By electroneutrality, the concentrations of the cations and the anions are equal.

In the present case we shall consider the planar double layer, so that the colloid particle is modeled as a smooth planar wall (semi-infinite half-space) with uniform surface charge density σ . The wall is made of the same dielectric

material as the solvent (and so are the ions) so that image charges are neglected. The distance of closest approach of the ions to the wall is $d/2$, (coincident Helmholtz planes), and the part of the double layer between this plane and the wall is called the Stern layer.

Due to the planar geometry the functions describing the electric double layer vary in the z -direction normal to the wall. These include the mean electrostatic potential $\psi(z)$ and the ion number density profiles $\rho_{\pm}(z)$. We choose the coordinate system such that the plane of closest approach to the surface is at $z = 0$, so that the potential drop across the double layer is $\psi(0)$. This is also called the diffuse layer potential and is often denoted ψ_d . In the Stern layer, $-d/2 < z < 0$, the potential is given by $\psi(z) = \psi(0) - 4\pi\sigma z/\epsilon$, where $\epsilon = 4\pi\epsilon_0 \epsilon_r$, ϵ_0 being the permittivity of free space (SI units). Our sole concern here is with the potential in the diffuse part of the double layer. (It is possible to model the Stern layer with a dielectric constant different to that of the bulk, but this only affects the surface potential by modification of the above formula, not the diffuse layer potential itself.)

B. Theories. 1. *The Poisson–Boltzmann Approximation.* The Poisson–Boltzmann (PB) approximation was used by Gouy and Chapman^{7,8} to describe the above model of the electric double layer. The formally exact Poisson's equation relates the mean electrostatic potential to the ion density profiles

$$\frac{d^2\psi(z)}{dz^2} = \frac{-4\pi q}{\epsilon} [\rho_+(z) - \rho_-(z)] \quad (1)$$

This is combined with a Boltzmann-like expression for the density profiles,

$$\rho_{\pm}(z) = \rho e^{\mp q\psi(z)/k_B T} \quad (2)$$

where $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann's constant, T is the absolute temperature, and $\rho \equiv \rho_+ = \rho_-$ is the bulk number density (concentration) of the ions.

In this expression the potential of mean force of an ion is approximated by its charge times the mean electrostatic potential

$$\omega_{\pm}(z) = \pm q \psi(z) \quad (3)$$

What the approximation neglects is the correlations between the ions. For example, due to their size and their Coulombic interactions, each counterion in the double layer pushes aside other counterions, so that the local potential that it experiences is in general greater than the mean electrostatic potential. That is, correlations cause the counterions to be more strongly attracted to the surface than the Boltzmann approximation allows, and consequently the surface charge is actually screened more quickly, at least initially, than is predicted by the mean field PB approximation.

When the potential is low, the exponential may be linearized. The linear PB equation is

$$\frac{d^2\psi(z)}{dz^2} = \frac{8\pi q^2 \rho}{\epsilon k_B T} \psi(z) \quad (4)$$

with solution

$$\psi(z) = \psi(0) e^{-\kappa z} \quad (5)$$

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Here the Debye parameter

$$\kappa^2 \equiv \frac{8\pi q^2 \rho}{\epsilon k_B T} \quad (6)$$

sets the length scale of the double layer, which is the distance over which the surface charge is screened. From the electroneutrality of the double layer, the relationship between surface charge density and diffuse layer potential is given by

$$\begin{aligned} \sigma &= -q \int_0^\infty dz [\rho_+(z) - \rho_-(z)] \\ &= \int_0^\infty dz \frac{2q^2 \rho \psi(0)}{k_B T} e^{-\kappa z} \\ &= \frac{2q^2 \rho}{\kappa k_B T} \psi(0) \end{aligned} \quad (7)$$

or,

$$\psi(0) = \frac{4\pi\sigma}{\epsilon\kappa} \quad (8)$$

The nonlinear PB equation may also be solved. In this case the electrostatic potential is given by

$$\tanh \frac{q\psi(z)}{4k_B T} = \tanh \left[\frac{q\psi(0)}{4k_B T} \right] e^{-\kappa z} \quad (9)$$

The diffuse layer potential given by

$$\psi(0) = \frac{2k_B T}{q} \ln[s/2 + \sqrt{1 + s^2/4}] \quad (10)$$

where here and throughout we use a dimensionless surface charge

$$s \equiv \frac{4\pi q}{\epsilon k_B T \kappa} \sigma \quad (11)$$

As in the linear case, far from the surface the mean electrostatic potential decays exponentially to zero

$$\begin{aligned} \psi(z) &\approx \frac{4k_B T}{q} \tanh \left[\frac{q\psi(0)}{4k_B T} \right] e^{-\kappa z}, \quad z \rightarrow \infty \\ &\equiv \frac{\tilde{\sigma}_{\text{IPB}}}{4\pi\epsilon\kappa} e^{-\kappa z} \end{aligned} \quad (12)$$

The second equality defines an effective surface charge, which after some manipulation of eq 10 may be shown to be given by¹⁵

$$\tilde{\sigma}_{\text{IPB}} = \frac{-8}{s} (1 - \sqrt{1 + s^2/4}) \quad (13)$$

where again $\tilde{\sigma}_{\text{IPB}} = 4\pi q \tilde{\sigma}_{\text{IPB}} / \epsilon k_B T \kappa$. The point of this effective surface charge is that if this $\tilde{\sigma}_{\text{IPB}}$ were used instead of the actual σ in the linear PB approximation to give an effective diffuse layer potential, eq 8, then in the asymptotic regime the effective linear PB potential, eq 5, would be indistinguishable from the actual potential predicted by the nonlinear PB approximation with the actual surface charge, eqs 9 and 10. In other words, if the nonlinear PB

approximation were accurate and the mean electrostatic potential were measured far from the surface, then using the linear PB approximation to fit the results would give this effective surface charge, not the actual surface charge of the system. This point holds more generally and will be exploited extensively below.

Although our concern in this paper is with the electrostatic potential for an isolated double layer, it is worth mentioning that the value of the effective surface charge also holds for other properties of the double layer. For example, the pressure between two charge walls of separation h in the linear PB approximation is given by

$$P(h) = \frac{8\pi}{\epsilon} \sigma^2 e^{-\kappa h} \quad (14)$$

That given by the nonlinear PB approximation in the asymptotic regime is

$$\begin{aligned} P(h) &\approx \rho k_B T A^2 e^{-\kappa h}, \quad h \rightarrow \infty \\ &= \frac{8\pi}{\epsilon} \tilde{\sigma}_{\text{IPB}}^2 e^{-\kappa h} \end{aligned} \quad (15)$$

where $A \equiv 16[-1 + \sqrt{1 + s^2/4}]/s$. In other words, if one measured the force between two colloids in the asymptotic regime in a system accurately described by the nonlinear PB approximation, then the data would be well-fitted by the linear PB approximation with an effective surface charge. Since the value of this surface charge is the same as would have been obtained from a measurement of the mean electrostatic potential of an isolated colloid, there would be no contradiction between the two experiments and one would have no reason to believe that this was not the actual surface charge of the system.

2. Formally Exact Theory. The formally exact expression for the wall-ion potential of mean force is^{10,16}

$$\omega_\pm(z) = -k_B T [h_\pm(z) - \chi_\pm(z) + d_\pm(z)] \quad (16)$$

where, for the wall-ion pair, h is the total correlation function, χ is the short-range part of the direct correlation function, and d is the bridge function. The first two are related by the Ornstein-Zernike equation^{10,16}

$$\begin{aligned} h_\pm(z) - \chi_\pm(z) &= \pm q\psi(z)/k_B T + \\ &2\pi \sum_{\alpha=\pm} \int_0^\infty ds s \int_{-\infty}^\infty dz' \chi_{\pm,\alpha}(r) h_\alpha(z') \end{aligned} \quad (17)$$

where $r^2 = (z - z')^2 + s^2$, and $\chi_{\pm,\alpha}(r)$ is the short-range part of the bulk ion-ion direct correlation function. If both the wall-ion bridge function and the short-range part of the bulk ion-ion direct correlation function are neglected, the closure reduces to the nonlinear PB approximation.

Formally exact asymptotic analysis shows that the mean electrostatic potential behaves as^{10,16,17}

$$\psi(z) \approx \frac{-4\pi \tilde{\sigma}_{\text{IPB}}}{\epsilon \nu \tilde{\kappa}} e^{-\kappa z}, \quad z \rightarrow \infty \quad (18)$$

This has been deliberately cast in linear PB form. The

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effective surface charge $\tilde{\sigma}_{\text{IPB}}$ may be formally expressed in terms of χ_{\pm} ¹⁶

$$\tilde{\sigma}_{\text{IPB}} = \frac{1}{2}[\sigma + \tilde{q}\{\bar{\chi}_+(\tilde{\kappa}) - \bar{\chi}_-(\tilde{\kappa})\}] \quad (19)$$

and the factor v , the effective ion charge \tilde{q} , and the actual screening length $\tilde{\kappa}^{-1}$ may also be expressed in terms of the correlation functions of the bulk electrolyte.^{10,16,17}

In most cases of practical interest, to a very good approximation $v = 1$, $\tilde{q} = q$, and $\tilde{\kappa} = \kappa$. For example in monovalent electrolyte the departure is less than 3% at 0.1 M, and even smaller for lower concentrations.¹⁵ Hence the main concern is to obtain the effective surface charge. This is the charge that one would obtain by fitting the linear PB approximation to measured potential data. As discussed in the preceding section, this same effective surface charge appears in the formally exact asymptote for the pressure between two walls

$$P(h) \approx \frac{8\pi\tilde{\sigma}_{\text{IPB}}^2}{\epsilon v} e^{-\kappa h}, \quad h \rightarrow \infty \quad (20)$$

and so force measurements and potential measurements analyzed with the linear PB theory will be consistent with each other even though they do not yield the actual surface charge of the system. Fitting the nonlinear PB theory instead will yield the effective surface charge

$$\tilde{\sigma}_{\text{nl}} = \tilde{\sigma}_{\text{IPB}}/(1 - \tilde{\sigma}_{\text{IPB}}^2/16) \quad (21)$$

which follows from rearrangement of eq 13. (Here again, $\tilde{\sigma} = 4\pi q\tilde{\sigma}/\epsilon k_B T \kappa$).

3. The Hypernetted Chain Approximation. The hypernetted chain (HNC) approximation consists of the neglect of the bridge function, $d_{\pm}(z) = 0$. Since the density profile may be written

$$\rho_{\pm}(z) = \rho[1 + h_{\pm}(z)] = \rho e^{-\omega_{\pm}(z)/k_B T} \quad (22)$$

and since the mean electrostatic potential may be written

$$\psi(z) = \frac{-4\pi q\rho}{\epsilon} \int_z^{\infty} dz' [h_+(z') - h_-(z')](z' - z) \quad (23)$$

one has two equations to solve for two unknown functions. (The bulk ion-ion direct correlation function may be assumed known; in practice it is often most convenient to obtain it by solving the HNC equation for the bulk electrolyte.) The HNC approximation has been extensively tested against simulations and is known to be accurate for both bulk electrolytes and for the electric double layer.^{9,10} There exist systematic methods for improving it by including bridge diagrams of increasing complexity,^{11,15,18} but this will not be done in the present analysis.

4. The Extended Poisson-Boltzmann Approximation. The HNC approximation just discussed is called a singlet theory, because it yields the single particle density profiles. An alternative approach to the statistical mechanics of the double layer is based upon the inhomogeneous Ornstein-Zernike equation

$$h_{\alpha,\beta}(\mathbf{r}, \mathbf{s}) = c_{\alpha,\beta}(\mathbf{r}, \mathbf{s}) + \sum_{\gamma} \int d\mathbf{t} \rho_{\gamma}(t_z) h_{\alpha,\gamma}(\mathbf{r}, \mathbf{t}) c_{\gamma,\beta}(\mathbf{t}, \mathbf{s}) \quad (24)$$

which, when coupled with a closure and a profile equation,

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yields the inhomogeneous pair correlation functions. Numerical results have been obtained for the electric double layer using the hypernetted chain closure.^{12,13,19}

An analytic solution to this equation has been obtained by Attard et al.^{20,21} in the case of the mean spherical closure for zero-sized ions

$$c_{\alpha,\beta}(\mathbf{r}, \mathbf{s}) = -u_{\alpha,\beta}^{\text{Coul}}(\mathbf{r}, \mathbf{s})/k_B T \quad (25)$$

To solve the inhomogeneous Ornstein-Zernike equation it was necessary to use the nonlinear PB ion profiles, rather than solving for them self-consistently. This approximation was justified by the variational formulation that was used.^{20,21} This theory for the double layer is called the extended Poisson-Boltzmann (EPB) approximation. When applied to the bulk electrolyte it is equivalent to including the electrostatic correlations at the level of the mean spherical model. Like that bulk theory the EPB approximation is expected to be an exact limiting law at lower electrolyte concentrations. Tests of the approximation confirm its accuracy at lower electrolyte couplings and surface charge densities.^{15,20,21} The EPB approximation is useful for isolating the effects of correlations due to electrostatics from those of ion size, since it includes the former but not the latter, and it gives the primary correction to the PB approximation at lower couplings.

The EPB approximation has been solved for the case when the walls are made of different dielectric material to the solvent (i.e., it includes the effects of image charges). However here we shall concentrate on the basic model where image charges are neglected. In this case the result for the effective surface charge required by the linear PB theory is a simple algebraic expression, namely^{15,21}

$$\tilde{\sigma}_{\text{IPB}} = \sigma \frac{A}{2s} \left[1 + \frac{\beta q^2 \kappa}{4\epsilon} \{2I + \ln 2\} \right]^{1/2} \quad (26)$$

where

$$A \equiv 16(-1 + \sqrt{1 + s^2/4})/s$$

the dimensionless surface charge again is $s \equiv 4\pi\beta q\sigma/\epsilon\kappa$, and I is given by²²

$$I = \frac{1}{2} \left(1 + \frac{2z^2 - 3}{(2z^2 - 1)^3} \right) \ln 2 + \frac{2 - 2z^3 + z}{2z(2z^2 - 1)^2} - \frac{\sqrt{z^2 - 1}}{z} \left(1 + \frac{2z^2 + 1}{(2z^2 - 1)^3} \right) \tan^{-1} \sqrt{\frac{z - 1}{z + 1}} - \frac{1}{2} \left(1 - \frac{2z^2 - 3}{(2z^2 - 1)^3} \right) \ln(z + z^2) \quad (27)$$

where $z \equiv (1 + s^2/4)^{1/2}$.

C. Effective Surface Charge. Figure 1 shows the mean electrostatic potential in the diffuse part of the double layer for a 1 mM monovalent electrolyte and a surface charge of $4 \mu\text{C cm}^{-2}$, (4 nm^2 per unit charge). The HNC result may be considered exact at this concentration. The hydrated diameter of cations such as sodium or potassium may be taken to be $d = 0.4 \text{ nm}$, and that of

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(21) Attard, P.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Phys.* **1988**, *89*, 4358.

(22) This is eq 3.23 of ref 21. Equation 3.20 from which it derives should have a factor of x multiplying δ_- in the denominator of the integrand. This is a typographical error only and none of the remaining results in the paper are affected.

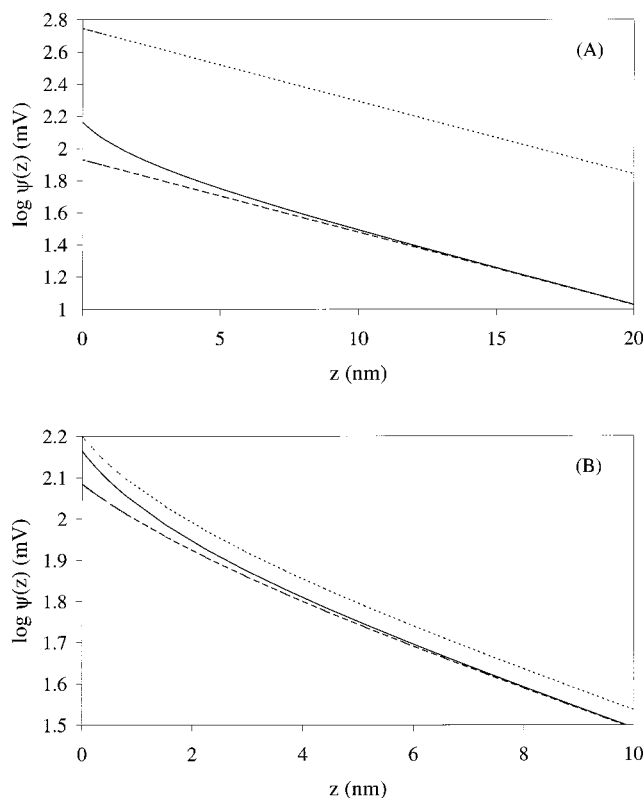


Figure 1. The logarithm of the electrostatic potential profile in the diffuse part of a double layer with surface charge density $\sigma = 4 \mu\text{C cm}^{-2}$ in 1 mM monovalent electrolyte. The solid curve is the HNC prediction ($d = 0.4$ nm), which gives as the diffuse layer potential $\psi(0) = 146$ mV. In (A), the dotted curve is the linear PB prediction using the actual surface charge, eqs 5 and 8, which gives $\psi(0) = 556$ mV. The dashed curve is also a linear PB prediction, eq 5, but with an effective surface charge $\tilde{\sigma}_{\text{IPB}} = 0.61 \mu\text{C cm}^{-2}$, eq 19, which gives $\psi(0) = 85$ mV, eq 8. In (B), the nonlinear PB approximation, eq 9, is used. The dotted curve uses the actual surface charge and gives $\psi(0) = 158$ mV, eq 10. The dashed curve uses an effective surface charge $\tilde{\sigma}_{\text{nl}} = 1.95 \mu\text{C cm}^{-2}$, eqs 19 and 21, which gives $\psi_{\text{nl}}(0) = 122$ mV, eq 10.

anions such as chloride or nitrate to be $d = 0.2$ nm. The present calculations are carried out for a symmetric electrolyte, but one expects the cations to dominate the properties of the double layer for negatively charged colloids and the anions to dominate for positively charged ones. The HNC gives a diffuse layer potential of $\psi(0) = 146$ mV when both ions have a diameter of 0.4 nm. This decreases by about 2% when both ions have a diameter of 0.2 nm. This is typical of the difference between the two; the larger diameter will be used for all the calculations reported here.

The linear and the nonlinear PB approximation are tested in Figure 1. It is clear that in general this approximation overestimates the mean electrostatic potential of the double layer, with the linear approximation being the worse of the two. For the given surface charge ($4 \mu\text{C cm}^{-2}$) the linear PB gives a surface potential of 556 mV, and the nonlinear PB gives 158 mV, which are 280% and 8% too high, respectively. Using an effective surface charge density of $\tilde{\sigma}_{\text{IPB}} = 0.61 \mu\text{C cm}^{-2}$ in the linear case, and $\tilde{\sigma}_{\text{nl}} = 1.95 \mu\text{C cm}^{-2}$ in the nonlinear case, ensures that the mean electrostatic potential predicted by these two approximations agrees with the HNC result far from the surface. These are the surface charge densities that would be inferred by analyzing the experimental data with the PB approximation in the asymptotic regime. (In Figure 1, the Debye length $\kappa^{-1} = 9.60$ nm was used for the PB calculations, whereas the HNC screening length is $\tilde{\kappa}^{-1} =$

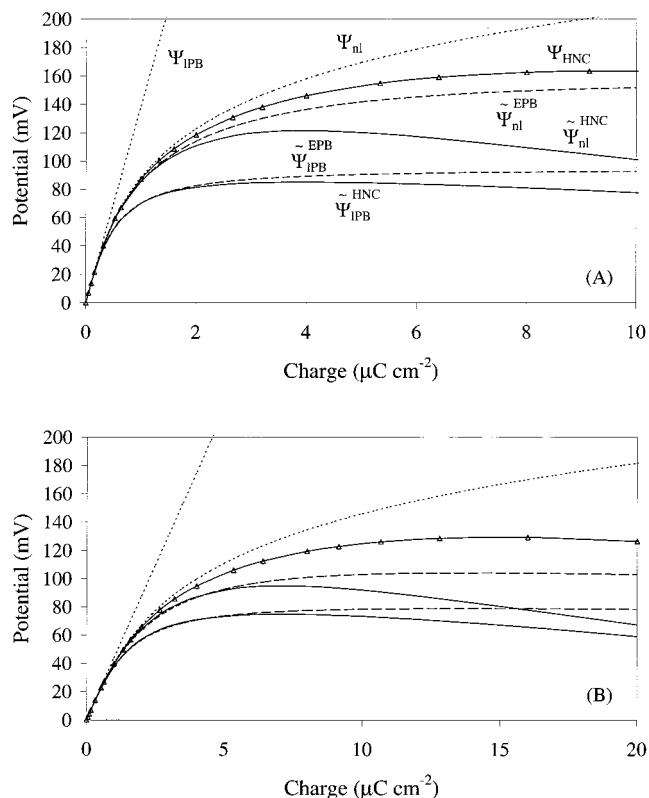


Figure 2. The actual and effective diffuse layer potential as a function of the actual surface charge in monovalent electrolyte. The solid curve with triangles is the HNC actual potential drop, the dotted curves are the PB actual potential drop, (eqs 8 and 10), the solid curves are the PB effective potential drop using the HNC, (eqs 8 and 19, and eqs 10, 19, and 21), and the dashed curves are the PB effective potential drop using the EPB, (eqs 8 and 25, and eqs 10, 25, and 21). In each case the nonlinear PB approximation lies closer to the HNC actual potential drop than does the corresponding linear PB approximation. Part A is for 1 mM, and part B is for 10 mM.

9.61 nm; the difference between two would not be experimentally measurable.) These effective surface charges correspond to effective diffuse layer potentials of $\tilde{\psi}_{\text{IPB}}(0) = 85$ mV and $\tilde{\psi}_{\text{nl}}(0) = 122$ mV, which underestimate the actual diffuse layer potential of $\psi(0) = 146$ mV. The conclusion to be drawn from Figure 1 is that using an effective diffuse layer potential makes the PB approximation exact in the asymptotic regime.

Figure 2A shows the actual and the effective diffuse layer potential as a function of the actual surface charge density in 1 mM monovalent electrolyte. The various potentials are defined in the figure caption and also in Table 1. At low surface charge densities the PB approximation is accurate, and the regime of validity of the nonlinear PB approximation is larger than that of the linear PB approximation. As the surface charge density is increased, the rate of increase of the actual diffuse layer potential given by the HNC theory decreases. This flattening also occurs in the nonlinear PB approximation, but nevertheless this approximation increasingly overestimates the actual diffuse layer potential. The effective diffuse layer potentials, which would be obtained by fitting the PB approximations to the exact results for the electrostatic potential profile in the asymptotic regime, are markedly less than the actual diffuse layer potential at higher surface charges. In fact, the effective potential drop required by the PB approximations decreases with increasing surface charge density at high enough surface charge densities. In the 1 mM electrolyte, at a surface

Table 1. The Diffuse Layer Potentials

symbol	name	equations
ψ_{IPB}	linear Poisson–Boltzmann	8
ψ_{nl}	nonlinear Poisson–Boltzmann	10
ψ_{HNC}	hypernetted chain	23
$\tilde{\psi}_{\text{IPB}}^{\text{HNC}}$	effective linear Poisson–Boltzmann using the hypernetted chain	8,19
$\tilde{\psi}_{\text{nl}}^{\text{HNC}}$	effective nonlinear Poisson–Boltzmann using the hypernetted chain	10,19,21
$\tilde{\psi}_{\text{IPB}}^{\text{EPB}}$	effective linear Poisson–Boltzmann using the extended Poisson–Boltzmann	8,25
$\tilde{\psi}_{\text{nl}}^{\text{EPB}}$	effective nonlinear Poisson–Boltzmann using the extended Poisson–Boltzmann	10,21,25

charge density of $\sigma = 4 \mu\text{C cm}^{-2}$, (4 nm^2 per unit surface charge), the actual diffuse layer potential is $\psi(0) = 146.1 \text{ mV}$, whereas the effective diffuse layer potentials are $\tilde{\psi}_{\text{IPB}}(0) = 85.17 \text{ mV}$ and $\tilde{\psi}_{\text{nl}}(0) = 121.65 \text{ mV}$. For an electrolyte with ions of diameter $d = 0.2 \text{ nm}$ the results are 85.11 mV and 121.44 mV , respectively. So at all surface charge densities Figure 2 confirms the result established in Figure 1, that the effective diffuse layer potential in both the linear and the nonlinear PB approximations underestimates the actual diffuse layer potential.

Figure 2A also compares the EPB approximation for the effective diffuse layer potentials with that given by the HNC theory. (Note that the EPB is *not* being compared to the actual diffuse layer potential.) It may be seen that the EPB is quite accurate for all surface charge densities in predicting the effective potential required by the linear PB approximation, and up to a surface charge density of about $\sigma = 2 \mu\text{C cm}^{-2}$ for the nonlinear PB approximation. Even beyond this it remains a useful approximation up to quite high surface charge densities. Hence as an analytic result it provides a useful complement to the effective potential derived from the HNC numerical approach. At $\sigma = 4 \mu\text{C cm}^{-2}$, the EPB result for the effective diffuse layer potentials are $\tilde{\psi}_{\text{IPB}}(0) = 89.30 \text{ mV}$ and $\tilde{\psi}_{\text{nl}}(0) = 136.48 \text{ mV}$.

Figure 2B shows a similar comparison at the higher monovalent electrolyte concentration of 10 mM . In this case the decrease in the HNC effective diffuse layer potential with increasing surface charge density is more marked, particularly for the nonlinear case. The fact that the HNC effective potential is nonmonotonic means that the charge cannot be unambiguously deduced from the measured potential without additional information. The EPB remains quantitatively accurate up to about $5 \mu\text{C cm}^{-2}$, and qualitatively confirms the HNC result that the effective diffuse layer potential is less than the actual diffuse layer potential for both the linear and the nonlinear PB approximations.

II. Analysis

A. Experimental Techniques. 1. Charge Titration.

Charge titration consists of adding a known amount of the potential determining ions to a solution of known colloid volume fraction.^{1–3} Measurement of the free concentration of ions yields the amount of ions adsorbed to the colloid. Provided that one knows the surface area of the colloids, which in some cases can be problematic,^{3,23} this gives a relative measure of the surface charge density.

To obtain the absolute surface charge density measurements are carried out at several background concentrations of indifferent (i.e., nonbinding) electrolyte. The unique point of intersection of the titration curves corresponds to the point of zero charge. For the silver iodide colloids analyzed below the charge is measured as a function of the concentration of silver ions in a background

of KNO_3 or NaNO_3 . For the metal oxides the pH determines the potential and the typical indifferent electrolyte is KNO_3 or NaCl .

2. Electrophoresis. Colloid particles in a dilute dispersion move in response to an applied electric field. This phenomenon is known as electrophoresis, and measurement of the mobility (the velocity divided by the field strength) gives the zeta potential, which is believed to be related to the diffuse layer potential.^{1–3}

Consider a single spherical colloid of radius a and central point charge Q , which is equivalent to a uniform surface charge density of $\sigma = Q/4\pi a^2$. The force acting on it due to an external electric field of magnitude E is $F_E = QE$. For a steady velocity v this is balanced by the Stokes drag $F_\eta = 6\pi\eta av$, where η is the shear viscosity of water. Hence the electrophoretic mobility is

$$\mu_E \equiv \frac{v}{E} = \frac{Q}{6\pi\eta a} \quad (28)$$

Taking the zeta potential to be equal to the surface potential, Coulomb's law gives $\zeta \approx \psi(a) = Q/\epsilon a$, (recall that $\epsilon = 4\pi\epsilon_0\epsilon_r$). Hence one sees that the mobility is proportional to the zeta potential

$$\mu_E = \frac{\epsilon\zeta}{6\pi\eta} \quad (29)$$

This is known as the Hückel–Onsager equation.

The above neglected the double layer completely. For the case of a spherical charged colloid, the linear PB approximation gives the surface potential as $\psi(a) = Q/\epsilon a(1 + \kappa a)$, so that the above becomes

$$\mu_E = \frac{\epsilon\zeta}{6\pi\eta}(1 + \kappa a) \quad (30)$$

The Hückel–Onsager equation is therefore expected to be valid for low potentials, low electrolyte concentrations ($\kappa \rightarrow 0$), and small particles ($a \rightarrow 0$).

The opposite to this last limit is a planar wall, and we now consider a slit comprising two parallel planar walls of surface charge density σ , separated by h , and of breadth $B \gg h$, and length $L \gg h$. For convenience it is easier to imagine that the walls are fixed and that the counterions and water flow in response to an applied electric field, (the phenomenon known as electroosmosis), but it ought to be evident that in the limit $h \rightarrow \infty$ this relative motion of fluid and wall ought to be the same as the electrophoretic motion of a large particle. With the ion profiles in the z direction normal to the surfaces, and the applied field and velocities in the x direction parallel to the surfaces, the water velocity profile may be denoted $v(z)$. The tangential force per unit volume acting on the water due to shear is

$$F_\eta = \eta \frac{\partial^2 v(z)}{\partial z^2} \quad (31)$$

(23) Overbeek, J. Th. G. In *Colloid Science*; Krut, H. R., Ed.; Elsevier: Amsterdam, 1952; Vol. 1, p 115.

The forces acting on the ions comprise the electric force due to the applied field, and the force due to the Stokes drag, which arises from the motion of the ions relative to the water

$$F_{\pm} = \pm q\rho_{\pm}(z)E - 6\pi\eta a_{\pm}\rho_{\pm}(z)[v_{\pm}(z) - v(z)] \quad (32)$$

where $\rho_{\pm}(z)$ and $v_{\pm}(z)$ are the density and velocity profiles of the ions. Note that this formula is PB-like in the sense that only electrostatics and drag contribute to the potential of mean force; ion correlations are neglected. Further, it is the bare applied field that enters here rather than the mean field; ion rearrangement and induced streaming potentials, which would decrease the motive force, are also neglected.

In the steady state the force on the ion vanishes, which gives the Stokes drag in terms of the applied field. The drag force on the ion is equal and opposite to the force exerted by the ions on the water, so that the total force on the water is

$$F = \eta \frac{\partial^2 v(z)}{\partial z^2} + 6\pi\eta \{ a_+ \rho_+(z) [v_+(z) - v(z)] + a_- \rho_-(z) [v_-(z) - v(z)] \} = \eta \frac{\partial^2 v(z)}{\partial z^2} + q[\rho_+(z) - \rho_-(z)]E \quad (33)$$

This also vanishes in the steady state, and using Poisson's equation gives

$$\eta \frac{\partial^2 v(z)}{\partial z^2} = \frac{\epsilon E}{4\pi} \frac{\partial^2 \psi(z)}{\partial z^2} \quad (34)$$

Integrating twice, one has

$$\psi(z) = \frac{4\pi\eta}{\epsilon E} v(z) + c_1 z + c_0 \quad (35)$$

The coefficient of the linear term vanishes (for a symmetric system). This may be evaluated at the midplane (where for $h \gg \kappa^{-1}$ the potential is zero and the water velocity may be denoted v) and at the shear plane (where the water velocity vanishes, and where the potential is called the zeta potential). Subtracting the two to eliminate c_0 one obtains

$$\mu \equiv \frac{v}{E} = \frac{\epsilon \zeta}{4\pi\eta} \quad (36)$$

This is known as the Helmholtz–Smoluchowski equation. The plane of shear is expected to be close to the outer Helmholtz plane, and so one expects the zeta potential to be approximately equal to the diffuse layer potential.

The zeta potential deduced from the mobility using the Helmholtz–Smoluchowski equation is two-thirds that deduced from the Hückel–Onsager equation. There has been a history of refinements to the Hückel–Onsager approximation for spherical colloids, beginning with the work of Henry²⁴ and including the more recent and relatively sophisticated works of Overbeek and Wiersema^{25,26} O'Brien and White,²⁷ and Dukhin.²⁸ (For discussion

of these and other approaches, see refs 1–3, 28.) In general these approaches express the electrophoretic mobility as

$$\mu = \frac{\epsilon \zeta}{6\pi\eta} f(\kappa a) \quad (37)$$

where $f(\kappa a) \rightarrow 1$, $\kappa a \rightarrow 0$, which is the Hückel–Onsager limit, and $f(\kappa a) \rightarrow 3/2$, $\kappa a \rightarrow \infty$, which is the Helmholtz–Smoluchowski limit. At intermediate values of κa , the value of $f(\kappa a)$ differs between the different approaches.

While the experimentally determined quantity is the mobility, it is the zeta potential that is usually reported, and the above shows that this depends on the particular approximation used to relate the two. In turn this determines the specific comparison that is to be made with the charge titration data. If the relationship between the mobility and the zeta potential were exact, then one should compare the zeta potential with the double layer potential calculated exactly from the titrated surface charge. Normally however the relationship is based upon the PB approximation, and it therefore follows that the appropriate comparison is with the double layer potential calculated from the effective surface charge. In turn, the effective surface charge will depend on whether the expression for the electrophoretic mobility has used the linear or the nonlinear PB approximation.

Henry²⁴ used the linear PB approximation in deriving his formula for the zeta potential, so arguably in this case the linear PB effective double layer potential is the appropriate point of comparison. The nonlinear PB approximation, (among other simplifying approximations), was used in the later analyses,^{25–28} and so in these cases the nonlinear PB effective double layer potential should arguably be used. The situation is not completely clear because of these additional approximations, and also because the contribution from the asymptotic regime to the final formula is not necessarily dominant.

B. Comparison. This section presents measured and predicted zeta potentials for several colloids. As far as possible the titration and electrophoretic data taken from the literature emanates from the same laboratory in each case. This restriction was observed because it is known that the surface properties of colloidal particles can be sensitive to the mode of preparation and history of the sample, and by ensuring that the two types of measurements are performed on identical samples one can have some confidence in comparing the two.

The zeta potential in general was taken as given by the authors of the original papers. The conversion from the measured mobility obviously depends on the particular approximation used by the original authors. In most cases this was that of Wiersema and Overbeek^{25,26} or that of O'Brien and White.²⁷ In some cases the Helmholtz–Smoluchowski formula, eq 36, and the Henry formula²⁴ were used. These experimental zeta potentials are compared with various theoretical potentials as a function of concentration of the potential determining ion. The surface charge density used in the theoretical calculations was obtained from a smooth interpolation of the charge titration data. In some cases this involved extrapolation beyond the range of the measured data to enable comparison with the full mobility data, and a degree of caution should be exercised in these regimes.

The theoretical potentials that are shown are the HNC and PB diffuse layer potentials, and the PB effective diffuse layer potentials calculated with the HNC theory. For the

(24) Henry, D. C. *Proc. R. Soc. (London) Ser. A* **1931**, 133, 106.

(25) Wiersema P. H.; Loeb, A. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1966**, 22, 78.

(26) Overbeek, J. Th. G.; Wiersema P. H. In *Electrophoresis*; Bier, M., Ed.; Academic: New York, 1967; Vol. 2, Ch. 1.

(27) O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday II* **1978**, 74, 1607.

(28) Dukhin, S. S.; Derjaguin, B. V. In *Surface and Colloid Science*; Matijevic, E., Ed.; Wiley: New York, 1974; Vol. 7, pp 52–72.

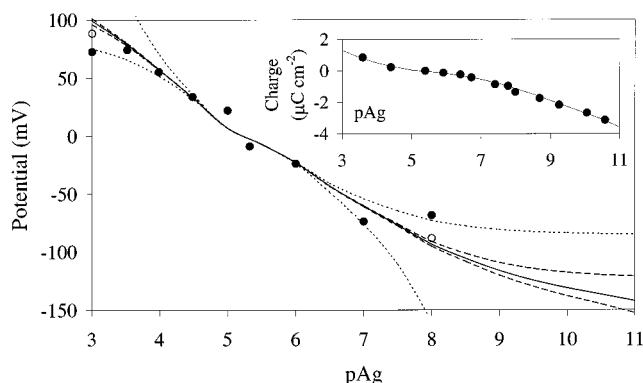


Figure 3. The zeta potential measured for AgI in 1 mM KNO₃ compared to the diffuse layer potential calculated from the titrated charge. The circles are measured data from Osseo-Asara et al.³⁰ (solid circles Henry formula; open circles O'Brien-White formula¹). The solid curve is the HNC, the dashed curves are the nonlinear PB, and the dotted curves are the linear PB. In the case of the PB both the actual and the effective diffuse layer potential is shown, which have larger and smaller magnitudes than the HNC, respectively. The HNC theory is used to calculate the effective potentials. The inset shows the measured titrated charge (circles, ref 23) and the smooth fit giving the surface charge used in the theoretical calculations.

actual and effective PB quantities, both the linear and the nonlinear approximations were examined. As shown by Figure 2, the effective PB diffuse layer potential calculated with the EPB approximation is quite close to the HNC result for this quantity, except at higher surface charges. The EPB curves would in most cases overlap with the HNC effective potential curves in the following figures, and for this reason the EPB results are not shown.

1. Silver Iodide. Silver iodide (AgI) is perhaps the colloid that has been studied quantitatively for the longest period of time, and for this reason is quite well characterized. It has a point of zero charge at pAg = 5.44, (pI = 10.56), and, in addition to the electrokinetic measurements analyzed here, various electrochemical measurements that utilize its conductivity have been made.²⁹ Figure 3 shows the zeta potential of AgI in 1 mM KNO₃. In this case the zeta potential data and the charge titration data are from two different sources,^{23,30} but as an ionic crystal in equilibrium with the electrolyte in this case one expects little variation between data from different laboratories. The surface charge density obtained from the titrations depends on the total surface area of the colloid, and there is some uncertainty in the estimation of this quantity.^{3,23}

It may be seen from Figure 3 that at low potentials all the theoretical curves coincide with each other and with the measured zeta potential. At higher potentials the linear PB approximation greatly overestimates the diffuse layer potential, since the HNC result may be regarded as the exact diffuse layer potential for this particular model. The experimental zeta potential was obtained with the Henry approximation,³⁰ and this is compared with the O'Brien-White prediction at the extremities,¹ where the discrepancy between the two is the greatest. For the case of the Henry approximation, which invokes the linear PB approximation, the zeta potential lies close to both the HNC diffuse layer potential, and also the effective linear PB diffuse layer potential. In view of the experimental scatter it is difficult to say with full confidence which of

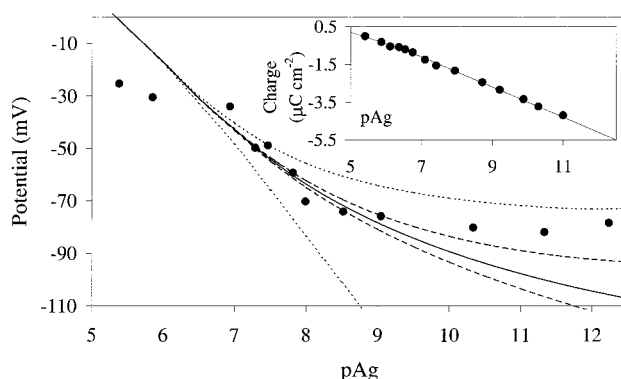


Figure 4. Silver iodide in 12 mM KNO₃, (all curves as in Figure 3). The measured zeta potential is from Troelstra and Kruyt³¹ and the titrated charge is from Overbeek²³ at an electrolyte concentration of 10 mM.

the two the measured zeta potential actually corresponds to, but focusing on the two extreme points, (pAg = 3 and pAg = 8), suggests that it is the effective linear PB diffuse layer potential.

For the nonlinear PB approximation, the effective potential lies closer to the HNC diffuse layer potential than in the linear case. Using the O'Brien-White formula shifts the zeta potential in the same direction, which reinforces the idea that the zeta potential gives the effective PB diffuse layer potential.

Figure 4 shows the potential results for AgI in 12 mM KNO₃. (The charge used for the theoretical calculations comes from titration data for 10 mM KNO₃, as shown in the inset.) The zeta potential was derived from the measured mobility using the Helmholtz-Smoluchowski equation.^{23,31} Again at low potentials all the theoretical potentials coincide, (the measured mobility has a relatively large error in this regime), and at this higher concentration they diverge at higher potentials somewhat more markedly than in Figure 3. At intermediate potentials the zeta potential is closer to the HNC diffuse layer potential than the effective linear PB potential, while the converse holds at higher potentials. The qualitative saturation of both the zeta potential and the effective potentials, which does not occur to nearly the same extent for the HNC diffuse layer potential, again suggests that it is the effective potential that should be compared to the zeta potential.

It should be stressed that no fitting parameters have been used here in comparing the theoretical and experimental potentials. The quantity used in the HNC and PB calculations is the titrated charge. In the literature the zeta potential is usually compared with the diffuse layer potential calculated from the CGCS model and the PB approximation using a calculated surface charge. The latter is obtained from the Nernst expression, which involves several fitting parameters. In the case of AgI where it is not necessary to invoke counterion binding, only one parameter is used, and this is the capacitance of the Stern layer.¹⁻³

2. Titanium Dioxide. Titanium dioxide, TiO₂, is the first of the metal oxides that we shall analyze. In these cases the surface charge arises from the protonation and deprotonation of the metal hydroxyl group



(29) Lyklema, J.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1961**, *16*, 595.

(30) Osseo-Assare, K. A. M. Sc. Thesis, University of California, Berkeley, 1972.; Osseo-Assare, K. A.; Fuerstenau, D. W.; Ottewill, R. H. *Am. Chem. Soc. Symposium No. 8*, **1978**, p 63.

In general increasing the pH deprotonates the surface causing a negative surface charge, whereas lowering the

(31) Troelstra, S. A.; Kruyt, H. R. *Kolloid Z.* **1942**, *101*, 182.

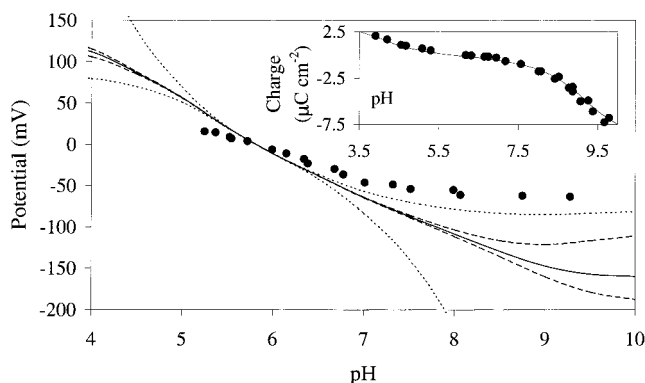


Figure 5. Titanium dioxide in 1 mM KNO_3 , (all curves as in Figure 3). The electrophoresis data is from Wiese³² and the titration data is from Yates.³³

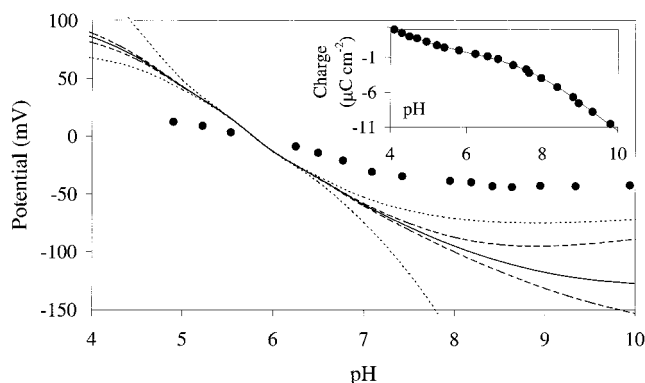


Figure 6. Titanium dioxide in 10 mM KNO_3 , (all curves as in Figure 3, and the experimental data is from the same sources as in Figure 5).

pH gives a positive surface charge. The point of zero charge for these particular samples of TiO_2 occurs at a pH of 5.8.^{32,33} These surfaces carry a higher surface charge than does AgI.

Figure 5 shows that the zeta potential lies closer to the effective diffuse layer potential than it does to the actual diffuse layer potential. The linear effective potential is in better agreement than is the nonlinear effective potential, even though the zeta potential was obtained using the formula of Wiersema and Overbeek,^{25,26} which in part utilizes the nonlinear PB approximation.

In Figure 6 the concentration of indifferent electrolyte has been increased to 10 mM, which again magnifies the discrepancy between the various approaches. Strangely enough, at small potentials where one expects the theories to be most accurate the experimental zeta potential appears to have a different slope to the theoretical curves. It is again the case that the zeta potential lies closer to the linear rather than the nonlinear PB effective potential.

3. Aluminum Oxide. Figure 7 shows zeta potential measurements for $\gamma\text{-Al}_2\text{O}_3$ from two laboratories,^{34,35} and one can see that apart from a small discrepancy in the point of zero charge (8.1 vs 8.5), there is good agreement between the two methods. The discrepancy for the titrated surface charge is a little greater, (not shown), and we have chosen to use the data of Sprycha³⁴ for the theoretical calculations. This does not greatly affect the results

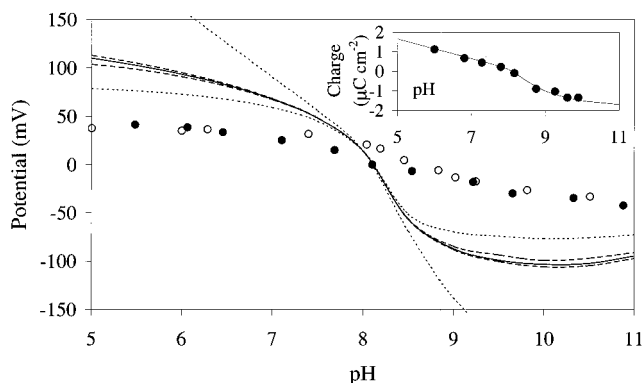


Figure 7. Aluminum oxide in 1 mM NaCl , (all curves as in Figure 3). The solid circles represent data from Sprycha³⁴ and the open circles are from Huang.³⁵

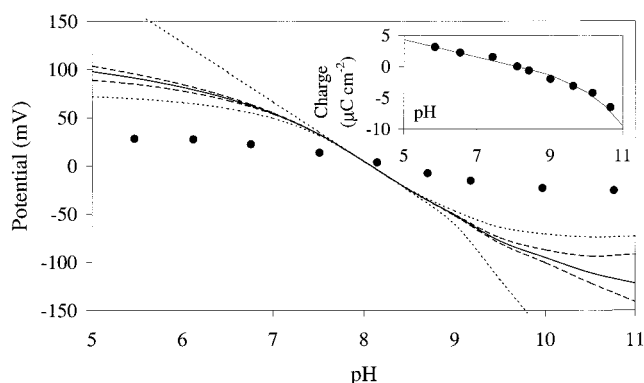


Figure 8. Aluminum oxide in 10 mM NaCl , (all curves as in Figure 3). The experimental data is from Sprycha.³⁴

because the calculated potential is not a sensitive function of the surface charge density at higher surface charge densities.

For the relatively low surface charge densities that develop in this case, there is little difference between the calculated potentials, particularly in the case of the nonlinear PB approximation. The zeta potential, derived from the measured mobility using the formula of Wiersema,²⁵ is most closely given by the linear PB effective diffuse layer potential.

At the higher concentration of background electrolyte, (10 mM NaCl , Figure 8), the surface charge density is higher, but the same conclusion holds, namely that the zeta potential probably corresponds to the linear PB effective diffuse layer potential rather than either the exact diffuse layer potential or the nonlinear PB effective diffuse layer potential. Overall, the agreement is less convincing for aluminum oxide than it was for titanium dioxide or silver iodide.

4. Silicon Dioxide. The final colloid that we have analyzed is silicon dioxide (Figures 9 and 10). Characterization of SiO_2 has historically been important, in part because it is so widespread in the terrestrial sphere. There is a great deal of evidence that the surface properties of SiO_2 are sensitive to the preparation and cleaning procedure,¹ and so in this case it was considered important to use mobility and titration data from the same source, even though this restricted the amount of data that we could analyze. In the case of 10 mM background electrolyte (Figure 9) there is a relatively high surface charge density at higher pH and a correspondingly large separation between the various theories. Of all the theories, the zeta potential corresponds most closely to the effective diffuse layer potential in the linear PB approximation.

(32) Wiese, G. R. Ph.D. Thesis, University of Melbourne, 1973. Wiese, G. R.; Healy, T. W. *J. Colloid Interface Sci.* **1975**, *51*, 427.

(33) Yates, D. E. Ph.D. Thesis, University of Melbourne, 1975. Yates, D. E.; Healy, T. W. *J. Chem. Soc., Faraday I* **1980**, *76*, 9.

(34) Sprycha, R. *J. Colloid Interface Sci.* **1989**, *127*, 1.

(35) Huang, C. P. Ph.D. Thesis, Harvard University, 1971. Huang, C. P.; Stumm, W. *J. Colloid Interface Sci.* **1973**, *43*, 409.

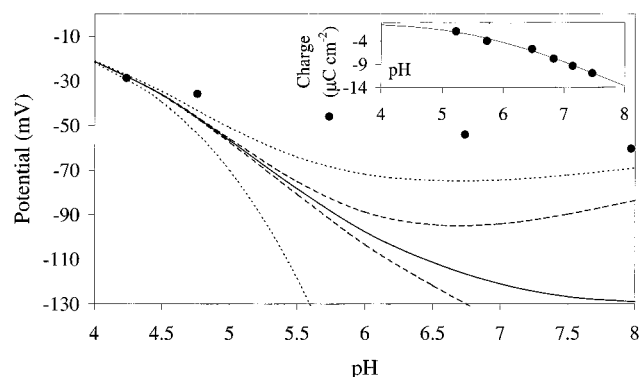


Figure 9. Silicon dioxide in 10 mM monovalent electrolyte, (all curves as in Figure 3). The experimental data is from James.³⁶

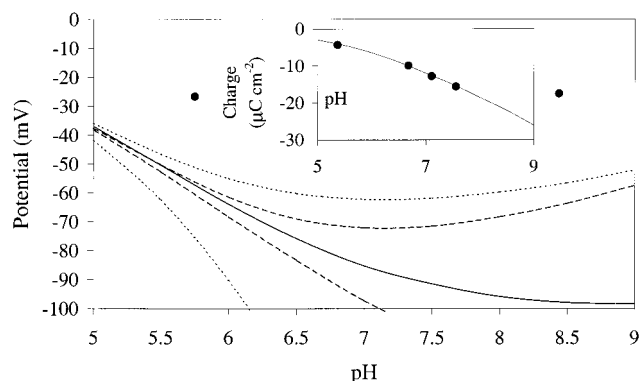


Figure 10. Silicon dioxide in 100 mM monovalent electrolyte, (all curves as in Figure 3; experimental data as in the preceding figure).

Table 2. The Zeta Potential Compared to the Actual and Effective Linear PB Diffuse Layer Potentials at the Extremities Where They Appear to Saturate

colloid	conc (mM)	ζ (mV)	$\psi(0)$ (mV)	$\tilde{\psi}_{\text{IPB}}^{\text{HNC}}(0)$ (mV)	$\tilde{\psi}_{\text{IPB}}^{\text{EPB}}(0)$ (mV)
AgI	1	72	100	75	76
		-68	-140	-85	-88
TiO ₂	12	-80	-105	-72	-75
	1	-65	-160	-80	-92
Al ₂ O ₃	10	-42	-125	-74	-79
	1	40	110	80	80
		-40	-100	-75	-76
	10	28	100	70	72
SiO ₂		-25	-130	-74	-77
	10	-60	-130	-70	-79
	100	-26	-100	-57	-48

This conclusion is reinforced by the data for 100 mM background electrolyte, (Figure 10). Unfortunately there are only two experimental data points for the zeta potential in this case, and the most that one can conclude is that for this very high surface charge density, the zeta potential has more or less saturated at 26 mV.³⁶ Of all the theoretical quantities only the effective diffuse layer potentials show a comparable saturation. One concludes that at least qualitatively the zeta potential is given by the effective PB diffuse layer potentials.

III. Discussion and Conclusion

At high surface charge densities, (high concentrations of the potential determining ion), the predicted potentials tend to saturate, as does the measured zeta potential. In Table 2 the saturated value of the zeta potential is compared to the HNC diffuse layer potential and to the

effective linear PB potential at the extremities. It can be seen that the HNC diffuse layer potential overestimates the zeta potential by a factor of 2–4. (From the figures, the bare PB diffuse layer potentials are in obviously worse agreement with the zeta potential.) There is fairly good agreement between the HNC and the EPB values for the effective linear PB potential, which confirms the value of this analytic approximation. The effective potential is generally within a factor of 2 of the zeta potential, and in the case of silver iodide the agreement may be called quantitative. Two questions arise: why is the effective linear PB potential the most appropriate one to compare to the zeta potential, and why is the agreement in the case of silver iodide so much better than for the metal oxides.

As mentioned in the text, the conversion from the measured mobility to the zeta potential requires some theory, and all theory to date has invoked the PB approximation. Tests of the PB approximation have shown that in general it overestimates the mean electrostatic potential, but that using an effective surface charge, (equivalently an effective diffuse layer potential), secures agreement in the asymptotic regime (Figure 1). The required effective charge (potential) is a well-defined function of the actual surface charge, (Figure 2), and so one expects that the theories for the zeta potential will yield the exact mobility provided that the effective surface charge is used. To put it another way, the zeta potential is the effective potential that corresponds to the measured mobility, and its value depends on the approximation that is invoked.

Most of the theories for the zeta potential invoke the nonlinear PB approximation, and so it is surprising that it is the effective linear PB potential that is the one closest to the measured zeta potential. This could well be coincidental because quite generally the linear PB effective potential always has a lower magnitude than the nonlinear PB effective potential. Hence the good agreement obtained for the linear PB could be compensating for the simplified nature of the basic model. Any physical effect neglected in the model that tended to decrease the diffuse layer potential would partially compensate for the errors in the linear PB approximation.

One such possibility is counterion binding inside the shear plane. It has been proposed that a gel or porous layer containing counterions exists on the surface of some metal oxides,³⁷ so that the titratable charge is greater than the net charge that contributes to the zeta potential.^{38–40} There is evidence both for and against such a gel layer, and there are conflicting views on its existence.^{1–3}

A simpler possibility is embodied in the GCGS model, which allows for counterions to adsorb at the inner Helmholtz plane.^{41–43} Originally proposed on the basis of the PB approximation, the explanation would obviously work equally well, (if not better due to the lower amount of binding required), for the present HNC calculations. One could conclude that a degree of such binding must be occurring for the metal oxides, and it is this that causes the magnitude of the zeta potential to be less than the effective diffuse layer potential. Conversely, in the case

(37) Lyklema, J. *Croatica. Chem. Acta* **1971**, 43, 249.

(38) Lyklema, J. *J. Electroanal. Chem.* **1968**, 18, 341.

(39) Wright, H. J. L.; Hunter, R. J. *Aust. J. Chem.* **1973**, 26, 1191.

(40) Perram, J. W. *J. Chem. Soc., Faraday II* **1973**, 7, 993.

(41) Levine, S.; Smith, A. L. *Discuss. Faraday Soc.* **1971**, 52, 290.

(42) Perram, J. W.; Hunter, R. J.; Wright, H. J. L. *Aust. J. Chem.* **1974**, 27, 461.

(43) Yates, D. E.; Levine, S.; Healy, T. W. *J. Chem. Soc., Faraday I*, **1974**, 70, 1807.

(36) James, R. O. *Adv. Ceram.* **1987**, 21, 349.

of silver iodide one could conclude that no such counterion binding occurs.

This explanation in terms of counterion binding is certainly the conventional one,¹⁻³ but there are significant problems with it. One difficulty with the ion binding picture is that an indifferent electrolyte is used in the experiments, and by definition these ions cannot have a specific interaction with the surface. If they did, then the mobility or titration curves for different electrolyte concentrations would not all intersect at a unique point, (the point of zero charge for titration, and the coincident isoelectric point for electrokinetics). Furthermore, the viscosity of water confined between molecularly smooth surfaces shows it to have the same value as in bulk for separations as small as 1 nm,⁴⁻⁶ and the fact that one can actually bring such surfaces into intimate molecular contact indicates that the water *cannot* be immobilized. In other words, the evidence is against *both* adsorption and immobilization of counterions.

The present analysis may suggest an alternative explanation for the lower than expected zeta potential. The fact that for silver iodide the zeta potential is equal to the effective potential, whereas for the metal oxides it is significantly less than the effective potential, suggests that it is the nature of the surface charge that is important. Silver iodide is an ionic crystal, and the surface charge arises from an excess of the ionically bonded constituent ions. The surface charge for the metal oxides arises from the hydrolysis of the metal atom to M-OH, and the consequent binding or dissolution of H⁺ ions. We suggest that whereas for AgI the surface charges are immobilized by the strong ionic bond, for the metal oxides the surface

charges may have a degree of mobility along the surface. The fact that chemical equilibrium is established for the surface groups shows that the charges cannot be completely fixed, and no doubt there is a relationship between their mobility and their binding constants. It follows that an externally applied field would cause the surface charges to move relative to the solid, which would reduce the mobility of the colloid compared to the fixed surface charge case. (This putative surface charge mobility is distinct from the conductivity of the solid, and also from the so-called surface conductivity, which is in fact the conductivity of the diffuse part of the double layer.¹⁻³)

Obviously the present results do not on their own resolve the discrepancy between the diffuse layer potential calculated from the titrated charge and the zeta potential for the metal oxides. It is also possible that the theory relating the zeta potentials to the measured mobility needs further refinement. Detailed modeling of the compact region of the double layer, (charge and counterion adsorption, capacitance, etc.), would be required for a more definitive picture, and the present HNC approach provides a sound quantitative basis for such analysis. The present results already indicate that in the case of silver iodide no counterion binding occurs, and in the case of the metal oxides if counterion binding does occur, then it is much less than has been previously thought on the basis of the PB approximation. In the future we intend to model the dependence of the surface charge density upon the concentration of the potential determining ions, which we hope will further clarify the issue.

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