

Surface Charge of Silver Iodide and Several Metal Oxides. Are All Surfaces Nernstian?

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Charge titration data for silver iodide, titanium dioxide, aluminum oxide, silica dioxide and ferric hydroxide are analyzed using a generic site binding model that has the Nernst equation as a limiting form. Both the hypernetted chain and the nonlinear Poisson–Boltzmann approximations are used to relate the diffuse double-layer potential to the surface charge, and a zeroth-order Stern layer is used to give the surface potential. In all cases it is shown that in the vicinity of the point of zero charge the Nernst equation accurately gives the surface charge. © 2000 Academic Press

Key Words: Nernst equation; charge titration; site binding; surface potential.

INTRODUCTION

Particles in aqueous electrolyte acquire a charge due to either chemical dissociation of surface groups, preferential physicochemical adsorption of electrolyte ions, or, in the case of an ionic crystal, preferential desorption or adsorption of ions. The charged surface of the particles and the associated diffuse electric double layer are the major determinants of the stability of colloidal dispersions, the transport properties of slurries, the self-assembly of amphiphiles, the adhesion of surfaces, and many other phenomena besides. Consequently the charging process of colloids has been widely studied (1, 2).

The ions involved in the charging process are called potential-determining ions; the surface charge of the colloid varies with the concentration of those ions. In addition there can be an indifferent background electrolyte, the ions of which do not themselves bind to the surface, but affect the surface charge indirectly via the diffuse layer potential. For example, for colloidal crystals of silver iodide the potential-determining ions are Ag^+ and I^- , whereas most other ions are indifferent. For common metal oxides such as TiO_2 , Al_2O_3 , SiO_2 , and FeOOH , H^+ is the potential-determining ion, and so the surface charge is a function of the pH. The concentration of the potential-determining ion at which the colloid has no net charge is called the point of

zero charge (pzc). In general the pzc is unchanged by varying the concentration of an indifferent electrolyte.

The three most important parameters involved in the study of charged particles are the surface charge density σ , the surface potential ψ_s , and the diffuse layer potential ψ_d . Gouy and Chapman (GC) (3, 4) used the Poisson–Boltzmann equation to obtain the diffuse layer potential, which in their model equals the surface potential. Stern (5) introduced a plane of closest approach to the surface for nonadsorbed ions. Within this ion-exclusion region the potential varies linearly with distance, and the water has a low dielectric permittivity due to surface-induced structure. Consequently the surface potential is greater than the diffuse layer potential. Grahame (6) refined the model by adding an inner Helmholtz plane at which unhydrated anions can adsorb, and an outer Helmholtz plane which represents the closest approach of hydrated cations. Measurements on electrodes such as mercury (6) and silver iodide (7) have provided strong electrochemical evidence for such a surface region; a typical value of the inner layer capacitance is $20 \mu\text{F cm}^{-2}$, which for a 2-Å-thick Stern layer would correspond to a relative dielectric permittivity of 4.5, substantially less than the 78.4 of bulk water. Accordingly, the so-called Gouy–Chapman–Stern–Grahame (GCSG) approach that includes a Stern layer is preferable to the GC approach.

Both the GC and the GCSG approaches invoke the Poisson–Boltzmann (PB) approximation for the diffuse layer potential of the electric double layer. This is a mean field approach that equates the potential of mean 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 more sophisticated statistical mechanical techniques have been applied to the electric double layer (for a review see (8, 9)), and these show that in certain circumstances the PB approximation can be quantitatively in error (8–16). Of these techniques, the singlet hypernetted chain (HNC) approximation (17), includes both ion size and ion correlations and it has the right combination of accuracy and tractability that allows the reliable analysis of experimental data in reasonable computer time (10, 15, 16).

In general the amount of bound ions, which give rise to the surface charge, increases as the bulk concentration of the

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potential-determining ion is increased. An equilibrium exists between the ions at the surface and the ions in the bulk such that following an increase in the bulk concentration, ions adsorb until the surface potential increases to the point where further adsorption is unfavorable. In addition to the effect of the surface potential, the surface activity or chemical potential of the ions is also affected by their surface density. The Nernst equation neglects the latter effect and predicts that the surface potential changes by 59.2 mV for each decade of concentration, which is an exceedingly simple and very general result. The prevailing wisdom is that silver iodide is a Nernstian surface, and that the metal oxides are definitely non-Nernstian (1, 2, 18). The common rationale for the former behavior is that the nonelectrical surface activity is independent of the surface charge for silver iodide, either because there are so many surface sites (1) or because the surface ions are in equilibrium with those in the bulk of the crystal (19). Conversely it is said that the metal oxides are non-Nernstian because neither of these circumstances prevails.

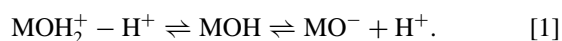
In this paper we model the acquisition of surface charge by colloidal particles, and in particular we revisit the question of the applicability of the Nernst equation. By direct comparison with experimental charge titration data, we shall show that *both* silver iodide and the metal oxides behave to a very good approximation as predicted by the Nernst equation, at least within several pH units of the pzc.

The site binding model that we analyze is in its essential features very similar to those developed by others (see, for example (1, 2, 18, 20), and references therein). We model the surface as having a fixed number of sites able to bind the potential-determining ions, and include the configurational entropy and the surface potential contributions to the surface chemical potential. The bulk chemical potential is taken to be purely configurational, namely it is the logarithm of the concentration. We include a zeroth-order Stern layer (coincident Helmholtz planes), which means that the surface potential differs significantly from the diffuse layer potential. In our work we model the potential-determining ions as being adsorbed *on* the surface, and hence the electrostatic contribution to the surface chemical potential depends upon the surface potential; others (e.g., (18)) use instead the diffuse layer potential (neglect the Stern layer, or GC model). The other significant improvement in the present work is that we use the HNC method to obtain the diffuse layer potential, whereas previously the PB approximation has been used.

I. MODEL AND ANALYSIS

A. Site Binding Models

1. *Metal oxides.* It is generally believed that the metal oxides acquire their charge by proton binding to terminal metal hydroxide groups that arise on the hydrated surface of the solid (1, 2). The generic chemical reactions may be represented as

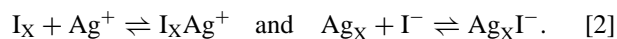


This shows the amphoteric nature of the surface; at high pH the surface is negatively charged, and at low pH it is positively charged. The MOH groups are thought to arise when an OH⁻ ion attacks the bond between an oxygen atom and one of the metal atoms that it bridges, giving rise to two terminal metal hydroxide groups.

While this is the charging mechanism commonly invoked for the metal oxides, there is evidence that other chargeable groups may be important, at least for TiO₂. The bonds of the bridging oxygens may remain intact and the oxygens themselves may be bound by a proton so that they become sites of positive charge. This was first suggested for the rutile form of TiO₂ on the basis of crystal structure modeling and TiO₂-gas infrared spectroscopy by Jones and Hockey (21). Quantum calculations for the TiO₂-gas interface confirm that it is favorable for a proton to bind to a bridging oxygen (22). Connor *et al.* (23) review the experimental evidence for both bridging and terminal hydroxyl groups at the TiO₂-gas interface, and they present infrared spectroscopy showing that both types of groups are present at the TiO₂-water interface. Yates (24) estimates that the number of available bridging hydroxide sites on rutile is equal to the number of terminal metal hydroxide sites.

We have modeled and analyzed TiO₂ when both types of groups, bridging and terminal, occur, but the results are indistinguishable from those obtained when only the reaction above (terminal hydroxyl groups only) is taken into account. In this work we shall only present results for this reaction scheme. We use the same formalism for all the metal oxides studied, the only difference between them being the values given for the site density and the binding constants.

2. *Silver iodide.* We model the silver iodide crystal as consisting of silver binding sites, which are labeled I_X, and iodide binding sites, which are labeled Ag_X. The two relevant reactions are



We assume that there are equal numbers of each type of site, and that this is fixed. Although obviously a simplified picture of the surface of the ionic crystal, as in the case of TiO₂ the final results turn out to be insensitive to the details of the model.

3. *Indifferent electrolyte.* It is assumed that in addition to the potential-determining ions there is a background electrolyte that is indifferent, which means that its ions have no specific chemical affinity for the surface. (Of course the ions of the diffuse part of the double layer may be regarded as electrostatically bound to the surface.) In fact nonelectrostatic binding of the electrolyte ions to the surface is permissible provided that it occurs equally for the cations and anions (which defines “indifferent”), and that the number of sites available to the potential-determining ions is not significantly altered by such binding.

B. Statistical Mechanics

1. *Metal oxides.* Denote the total number of available metal hydroxide sites by N , which is fixed, and the number of neutral, positive, and negative sites by N_0 , N_+ , and N_- , respectively. For any configuration one has the constraint

$$N_0 + N_+ + N_- = N. \quad [3]$$

Later these will be taken to represent the number of sites per unit area. This equation holds for both equilibrium and nonequilibrium configurations. The equilibrium number of bound sites is obtained by maximizing the total constrained entropy, which in this case takes the form (25)

$$S(\tilde{N}_+, \tilde{N}_- | N, \mu, T) = S(\tilde{N}_+, \tilde{N}_-; N) - E(\tilde{N}_+, \tilde{N}_-)/T + (\tilde{N}_+ - \tilde{N}_-)\mu/T, \quad [4]$$

where the tilde signifies a nonequilibrium value. The first term on the right-hand side is the entropy of the surface in that particular macrostate, and the two remaining terms are the surface-dependent part of the reservoir entropy (25). The temperature T and the chemical potential μ are determined by the reservoir (bulk solution); the latter is taken to be just the logarithm of the proton concentration,

$$\mu = \mu_0 + k_B T \ln \rho_H. \quad [5]$$

The energy consists of a chemical part and an electrostatic part. The chemical contribution is

$$E_c = \tilde{N}_+ v_+ + \tilde{N}_- v_- + \tilde{N}_0 v_0 = \tilde{N}_+(v_+ - v_0) + \tilde{N}_-(v_- - v_0) + N v_0, \quad [6]$$

where the v_i are the binding energies for the different groups. The electrostatic contribution is

$$E_\psi = \int_0^{\tilde{\sigma}} \psi_s(\sigma') d\sigma', \quad [7]$$

where $\psi_s(\sigma)$ is the surface potential and the surface charge is $\tilde{\sigma} = q(\tilde{N}_+ - \tilde{N}_-)$, q being the charge on a proton. This expression assumes that the potential-determining ions adsorb at the plane of the surface charge, rather than at the Stern or inner Helmholtz plane where they would experience the diffuse layer potential. Furthermore, it also assumes that they feel the uniform surface potential rather than a local micropotential, which in reality would be the case for discrete ions (20).

The entropy of the surface is the number of distinct rearrangements of the three types of surface sites,

$$\begin{aligned} S(\tilde{N}_+, \tilde{N}_-; N)/k_B &= \ln \frac{\tilde{N}!}{\tilde{N}_+! \tilde{N}_-! \tilde{N}_0!} \\ &= N \ln N - \tilde{N}_+ \ln \tilde{N}_+ \\ &\quad - \tilde{N}_- \ln \tilde{N}_- - \tilde{N}_0 \ln \tilde{N}_0. \end{aligned} \quad [8]$$

Here Stirling's approximation has been used. This expression assumes that all configurations are equally likely, and it ignores any interactions between ions bound on adjacent sites (correlations). It is obviously the simplest approximation that takes into account the configurational contribution to the surface chemical potential, and it is expected to be valid when the surface density is low.

The equilibrium number of sites maximizes the total constrained entropy (25) and hence it satisfies

$$\begin{aligned} 0 &= \left. \frac{-T \partial S(\tilde{N}_+, \tilde{N}_- | N, \mu, T)}{\partial \tilde{N}_+} \right|_{N_+, N_-} \\ &= v_+ - v_0 + q \psi_s(\sigma) - \mu + k_B T \ln \frac{N_+}{N_0} \end{aligned} \quad [9]$$

and

$$\begin{aligned} 0 &= \left. \frac{-T \partial S(\tilde{N}_+, \tilde{N}_- | N, \mu, T)}{\partial \tilde{N}_-} \right|_{N_+, N_-} \\ &= v_- - v_0 - q \psi_s(\sigma) + \mu + k_B T \ln \frac{N_-}{N_0}, \end{aligned} \quad [10]$$

since $d\tilde{N}_0 = -d\tilde{N}_+ - d\tilde{N}_-$. Subtracting from these the respective expressions evaluated at the point of zero charge (pzc), one can eliminate the chemical potential and rewrite these as

$$\frac{N_+ N_0^{\text{pzc}}}{N_+^{\text{pzc}} N_0} = \frac{\rho_H}{\rho_H^{\text{pzc}}} e^{-\beta q \psi_s(\sigma)} \quad [11a]$$

and

$$\frac{N_- N_0^{\text{pzc}}}{N_-^{\text{pzc}} N_0} = \frac{\rho_H^{\text{pzc}}}{\rho_H} e^{\beta q \psi_s(\sigma)}, \quad [11b]$$

where $\beta = 1/k_B T$. These represent two nonlinear equations for the number of charge groups N_+ and N_- (recall that the right-hand side is also of function of these, since $\sigma = q(N_+ - N_-)$). Given the total number of groups N and the point of zero charge ρ_H^{pzc} there remains a single free parameter, N_0^{pzc} (equivalently $N_+^{\text{pzc}} = N_-^{\text{pzc}}$). This may be used as a fitting parameter. Specifying its value (and the point of zero charge) is equivalent to setting the binding energies. Note that the number of groups and the surface charge may now be taken per unit area.

Multiplying these two equations together one obtains

$$\frac{N_+ N_-}{(N_0)^2} = \frac{N_+^{\text{pzc}} N_-^{\text{pzc}}}{(N_0^{\text{pzc}})^2} = \text{const.} \quad [12]$$

This may be recognized as the familiar form for equilibrium constants.

2. *Nernst equation.* One may expand the equilibrium equations ([11a], [11b]) about the point of zero charge. With $N_i = N_i^{\text{pzc}} (1 + \delta_i)$ for $i = 0, +, \text{ or } -$, $\delta_+ + \delta_- + \delta_0 = 0$, the

surface potential may be written $\psi_s(\sigma) = qN_{\pm}^{\text{pzc}}(\delta_+ - \delta_-)/C_0$, where C_0 is the total capacitance at zero charge. In terms of the relative change in concentration, r , $\rho_{\text{H}} = \rho_{\text{H}}^{\text{pzc}}(1 + r)$, an expansion to linear order reveals that

$$\delta_+ = -\delta_- = \frac{r}{1 + 2\beta q^2 N_{\pm}^{\text{pzc}}/C_0}. \quad [13]$$

The total inverse capacitance is greater than the inner layer inverse capacitance, and typically $C \approx 20 \mu\text{F cm}^{-2}$. Also typically the number of charged sites at the pzc is $N_+^{\text{pzc}} = N_-^{\text{pzc}} \approx 4 \text{ nm}^{-2}$. Hence the denominator is of the order of 100 or greater, which means that the relative change in the number of charge groups is of the order of 2% of the change in the pH, $|\delta_{\pm}| \approx 0.02 |\text{pH} - \text{pH}^{\text{pzc}}|$. One may conclude that to a very good approximation one may neglect the variation in the binding with pH. This will be valid when the inverse capacitance is large and when the number of charged groups at the pzc is large.

In view of this analysis, the left-hand sides of the equilibrium equations ([11a], [11b]) may be set equal to unity, which allows them to be rewritten as

$$\psi_s^{\text{N}} = \frac{k_{\text{B}}T}{q} \ln \frac{\rho_{\text{H}}}{\rho_{\text{H}}^{\text{pzc}}}. \quad [14]$$

This is known as the Nernst equation for the surface potential. Since the latter is also a function of the surface charge, one may equivalently regard this as an equation for the surface charge. Given any approximation for the potential as a function of the surface charge (see below), it is straightforward to use the Nernst equation to calculate $\rho_{\text{H}}^{\text{N}}(\sigma)$, (i.e., $\sigma \Rightarrow \psi_s(\sigma) \Rightarrow \rho_{\text{H}}^{\text{N}}(\sigma)$). Explicitly, from Eq. [13], in terms of the pH distance from the from the pzc, $\Delta\text{pH} = -r/2.303$, the surface charge is

$$\begin{aligned} \sigma &= \frac{-4.606q N_{\pm}^{\text{pzc}} \Delta\text{pH}}{1 + 2\beta q^2 N_{\pm}^{\text{pzc}}/C_0} \\ &\approx -(2.303C_0/\beta q)\Delta\text{pH}. \end{aligned} \quad [15]$$

This is the explicit form of the Nernst equation for the surface charge in the vicinity of the pzc, and it may be used to calculate the slope of the surface charge–pH curve at the pzc.

Using the Nernst equation to *define* the nernst potential, ψ_s^{N} , one may eliminate the pH from the full equilibrium equations. Dividing the first of the equilibrium equations ([11a]) by the second ([11b]) one obtains

$$\frac{N_+}{N_-} = e^{2\beta q[\psi_s^{\text{N}} - \psi_s(\sigma)]}. \quad [16]$$

If $\text{pH} < \text{pH}^{\text{pzc}}$, then $\sigma > 0$, $\psi_s(\sigma) > 0$, and $N_+ > N_-$. Hence the left-hand side of this equation is greater than 1, which means that $\psi_s^{\text{N}} > \psi_s > 0$. Conversely, for $\text{pH} > \text{pH}^{\text{pzc}}$, one has $\psi_s^{\text{N}} < \psi_s < 0$. One concludes that in general the Nernst potential provides an

upper bound on the magnitude of the actual surface potential,

$$|\psi_s^{\text{N}}(\text{pH})| > |\psi_s(\text{pH})|. \quad [17]$$

In terms of the charge as the independent variable, when the potential increases monotonically with charge one has

$$|\sigma^{\text{N}}(\text{pH})| > |\sigma(\text{pH})|. \quad [18]$$

This is a formally exact result that does not rely upon the validity of the Nernst equation or upon being in the vicinity of the pzc. These conclusions however are obviously predicated upon the present site binding model. If, for example, the actual surface charge were found to be greater than the Nernstian prediction, then one would conclude that either the present approximations for the total constrained entropy of the site binding model had broken down, or else that the site binding model itself was inapplicable.

3. *Silver iodide.* For the case of a crystal of silver iodide we take there to be N I_{X} sites that bind Ag^+ and an equal number of Ag_{X} sites that bind I^- . The bound ions simply occupy available sites; they themselves do not become new binding sites for their counterions. This is obviously the simplest possible model of ion binding for AgI. It will turn out that in practice the predicted surface charge is insensitive to the precise model of the surface. Similarly to the case for metal oxides treated above, the total constrained entropy is

$$\begin{aligned} S(\tilde{N}_+, \tilde{N}_- | N, \mu, T) &= S(\tilde{N}_+, \tilde{N}_-; N) - E(\tilde{N}_+, \tilde{N}_-)/T \\ &\quad + \tilde{N}_+ \mu_{\text{Ag}}/T + \tilde{N}_- \mu_{\text{I}}/T. \end{aligned} \quad [19]$$

The chemical potentials are just the logarithm of the respective ion concentrations,

$$\mu_i = \mu_{0i} + k_{\text{B}}T \ln \rho_i, \quad [20]$$

where $i = \text{Ag}$ or I . The two concentrations are related by $\rho_{\text{Ag}}\rho_{\text{I}} = 10^{-16.2} \text{ M}^2$, or $\text{pAg} + \text{pI} = 16.2$. The chemical binding energy is

$$E_{\text{c}} = \tilde{N}_+ \nu_+ + \tilde{N}_- \nu_-, \quad [21]$$

and the electrostatic energy was given as Eq. [7] above. Finally, the entropy of the surface is

$$\begin{aligned} S(\tilde{N}_+, \tilde{N}_-; N)/k_{\text{B}} &= \ln \frac{N!}{\tilde{N}_+!(N - \tilde{N}_+)!} + \ln \frac{N!}{\tilde{N}_-!(N - \tilde{N}_-)!} \\ &= -\tilde{N}_+ \ln \frac{\tilde{N}_+}{N} - (N - \tilde{N}_+) \ln \frac{N - \tilde{N}_+}{N} \\ &\quad - \tilde{N}_- \ln \frac{\tilde{N}_-}{N} - (N - \tilde{N}_-) \ln \frac{N - \tilde{N}_-}{N}. \end{aligned} \quad [22]$$

Hence the equilibrium numbers of sites satisfy

$$0 = \frac{-T \partial S(\tilde{N}_+, \tilde{N}_- | N, \mu, T)}{\partial \tilde{N}_+} \Big|_{N_+, N_-} \\ = \nu_+ + q \psi_s(\sigma) - \mu_{\text{Ag}} + k_B T \ln \frac{N_+}{N - N_+} \quad [23]$$

and

$$0 = \frac{-T \partial S(\tilde{N}_+, \tilde{N}_- | N, \mu, T)}{\partial \tilde{N}_-} \Big|_{N_+, N_-} \\ = \nu_- - q \psi_s(\sigma) - \mu_{\text{I}} + k_B T \ln \frac{N_-}{N - N_-}, \quad [24]$$

which in terms of values at the pzc may be rewritten as

$$\frac{N_+}{N - N_+} \frac{N - N_+^{\text{pzc}}}{N_+^{\text{pzc}}} = \frac{\rho_{\text{Ag}}}{\rho_{\text{Ag}}^{\text{pzc}}} e^{-\beta q \psi_s(\sigma)} \quad [25a]$$

and

$$\frac{N_-}{N - N_-} \frac{N - N_-^{\text{pzc}}}{N_-^{\text{pzc}}} = \frac{\rho_{\text{I}}}{\rho_{\text{I}}^{\text{pzc}}} e^{\beta q \psi_s(\sigma)}. \quad [25b]$$

These represent two nonlinear equations for the equilibrium number of charge groups N_+ and N_- . Given the total number of available sites of each type N , and the point of zero charge $\rho_{\text{Ag}}^{\text{pzc}}$ (equivalently $\rho_{\text{I}}^{\text{pzc}}$), there remains a single free parameter, $N_+^{\text{pzc}} = N_-^{\text{pzc}}$. Specifying its value (and the point of zero charge) is equivalent to setting the binding energies.

Following the same analysis as for the metal oxides, the relative variation in the number of charge groups with pAg is given by

$$\delta_{\text{Ag}} = -\delta_{\text{I}} = \frac{r}{N/(N - N_{\pm}^{\text{pzc}}) + 2\beta q^2 N_{\pm}^{\text{pzc}}/C_0}, \quad [26]$$

where $\rho_{\text{Ag}} = \rho_{\text{Ag}}^{\text{pzc}}(1 + r)$, and $N_{\text{Ag}} = N_{\text{Ag}}^{\text{pzc}}(1 + \delta_{\text{Ag}})$. Hence if almost all the available sites are bound at the pzc, $N_{\pm}^{\text{pzc}} \rightarrow N$, or if the capacitance is small, then the change in the relative number of bound groups with pAg is negligible. That is to say the contribution of the configurational entropy may be neglected and the left-hand sides of the equilibrium equations ([25a], [25b]) may be set equal to unity, giving once more the Nernst equation ([14]). Since the Nernstian nature of the AgI crystal surface is independent of this configurational entropy, any other site binding model of the surface will also yield the Nernst equation when the equivalent simplification is made.

C. Electric Charge and Potential

1. Stern layer. The relationship between the surface charge density and the surface potential is now required. We use a model of the electric double layer that includes a zeroth-order Stern

layer, which is of thickness $d/2$ and has relative dielectric permittivity ϵ' . In the language of colloid science this model has coincident inner and outer Helmholtz planes with no specific (i.e., chemical) ion binding at the inner plane; in the language of statistical mechanics the Stern layer represents the plane of closest approach to the surface of the electrolyte ions, the smallest of which has diameter d . The Stern layer is in addition meant to account for, at least approximately, the structuring of the water by the surface, and so its value is taken to be somewhat less than the permittivity of the bulk aqueous electrolyte, $\epsilon' < \epsilon = 78.4$. Within the Stern layer the electrostatic potential is a linear function of distance, and the surface potential ψ_s is related to the diffuse layer potential ψ_d by

$$\psi_s = \psi_d + \frac{4\pi\sigma d/2}{4\pi\epsilon_0\epsilon'} \equiv \psi_d + \frac{\sigma}{C}, \quad [27]$$

where C is the inner layer capacitance per unit area. For low electrolyte concentrations, the diffuse layer capacitance is smaller than the inner layer capacitance and it therefore dominates the total capacitance (whose inverse equals the sum of the inverse capacitances). Conversely the inner layer dominates at high electrolyte concentrations. In this work we take the inner-layer capacitance to be fixed independent of the surface charge and electrolyte concentration, although its value may depend upon the specific colloid.

2. Poisson–Boltzmann approximation. The traditional theory for the diffuse layer potential in colloid science utilizes the Poisson–Boltzmann (PB) approximation. In this theory the diffuse layer potential is given by

$$\psi_d = \frac{2k_B T}{q} \ln \left[\frac{s}{2} + \sqrt{1 + \frac{s^2}{4}} \right], \quad [28]$$

where the dimensionless surface charge is

$$s = \frac{4\pi q \sigma}{4\pi\epsilon_0\epsilon k_B T \kappa}. \quad [29]$$

The Debye length is

$$\kappa^{-1} = \sqrt{\frac{4\pi\epsilon_0\epsilon k_B T}{8\pi q^2 \rho}}, \quad [30]$$

where ρ is the concentration of the background electrolyte. Note that this expression assumes a monovalent binary electrolyte. Strictly one should add to this the contribution from the pH or the pAg. However, except at low electrolyte concentrations and far from the point of zero charge, this contribution is negligible. The PB approximation applied to the planar double is called the Gouy–Chapman (GC) approximation when the Stern layer is neglected, in which case $\psi_s = \psi_d$. It is called the Gouy–Chapman–Stern–Grahame (GCSG) approximation when the Stern layer is included.

3. *Hypernetted chain approximation.* The Poisson–Boltzmann approximation is a mean-field theory that neglects the correlations between the ions. Such correlations arise from the Coulombic and excluded volume (nonzero diameter) interactions of the ions. In recent years a number of sophisticated statistical mechanical techniques have been developed to incorporate these effects including simulations, integral equations, and density functional techniques (8, 9). For the present purpose the singlet hypernetted chain (HNC) approximation represents the best compromise between accuracy and tractability. Tests have shown it to be a relatively robust approximation that gives reliable results in reasonable computer time, and as such it is suited for the quantitative analysis of experimental data. We have used the HNC method to calculate the diffuse layer potential for a range of surface charge densities and electrolyte concentrations. The restricted primitive model is used for the electrolyte, with the anions and cations both having diameter $d = 0.4$ nm, a relative permittivity of $\epsilon = 78.4$, and a temperature of $T = 298$ K. Using an algorithm previously described (15, 16), the HNC diffuse layer potential was computed, and the results were fitted to an empirical function,

$$\psi_d(\sigma) = A[f \tanh a\sigma + (1 - f) \tanh b\sigma]. \quad [31]$$

This is odd in the charge as required for the restricted primitive model. The fitting parameters for three different electrolyte concentrations are given in Table 1. The error in the fitted potential compared to the actual potential is of the order of 1% for surface charge densities up to about $10 \mu\text{C cm}^{-2}$ in 1 mM electrolyte, and up to $40 \mu\text{C cm}^{-2}$ in 1 M electrolyte. The most noticeable difference between the HNC and PB approximations is the saturation of the former at high surface charges. The consequence of this is that the PB approximation tends to underestimate the charge that develops on the colloid surface far from the point of zero charge. Alternatively, it may be said that the PB approximation overestimates the diffuse layer potential for a given surface charge density, as we have discussed in our recent paper on the zeta potential (26).

D. Numerical Algorithm

There are four parameters that need to be specified for each type of colloid: the number of sites per unit area available for

binding N , the number of bound sites at the point of zero charge $N_+^{\text{pzc}} = N_-^{\text{pzc}}$, the pzc $\rho_{\text{H}}^{\text{pzc}}$ (or $\rho_{\text{Ag}}^{\text{pzc}}$), and the inner-layer capacitance C . Of these N and the pzc are known or measured parameters. The remaining two parameters are regarded as free parameters that may be varied to secure the best agreement with the charge titration data. It turns out that the calculated charge is rather insensitive to the values of N and $N_+^{\text{pzc}} = N_-^{\text{pzc}}$ (which is another way of saying that the Nernst equation is very good), but that it is quite sensitive to the value of the inner-layer capacitance, particularly at higher electrolyte concentrations. Hence the latter may be obtained with some accuracy by fitting the charge titration data. In this work we did not allow the values of the parameters to vary with the concentration of the background electrolyte.

The numerical solution of the nonlinear equations, for given values of the four parameters and the current concentrations of the potential determining ions and background electrolyte, begins with a guess for N_+ and N_- . From this the surface charge follows and thence the HNC diffuse layer potential, $\psi_d(\sigma)$. The initial guess is now varied (essentially using a Newton–Raphson technique), until the equilibrium equations ([11a], [11b] or [25a], [25b]) are satisfied (i.e., until the left- and right-hand sides are equal). Typically three- or four-figure convergence was regarded as satisfactory. The charge versus pH (or pAg) was calculated and compared to the experimental charge titration data. The values of the adjustable parameters were then changed to improve the fit to the experimental charge data.

The Nernst equation as written gives the surface potential as a function of the pH (or pAg). It is therefore an implicit equation for the surface charge. Turning this around, one may specify the surface charge σ , and using either the GC, GCSG, or HNC theories obtain the diffuse layer potential $\psi_d(\sigma)$, and thence the surface potential $\psi_s(\sigma)$. The Nernst equation is then invoked to give the corresponding concentration of the potential-determining ion explicitly, $\rho_{\text{H}}(\sigma)$ or $\rho_{\text{Ag}}(\sigma)$.

II. RESULTS AND DISCUSSION

We now compare the measured charge for several colloids with the various theoretical predictions. The theory labeled HNC is the present site binding model, Eqs. [11a], [11b] or Eqs. [25a], [25b], with the diffuse layer potential calculated from the surface charge using the hypernetted chain theory, Eq. [31], and the surface potential from the inner-layer capacitance, Eq. [27]. The three remaining theories are the various versions of the Nernst equation ([14]), which use either the HNC, Eq. [31], or the PB, Eq. [28], approximations to relate the surface charge to the diffuse layer potential. The HNC and the GCSG include the Stern layer, Eq. [27], whereas for GC, $\psi_s = \psi_d$.

A. Silver Iodide

Figure 1 compares the measured charge on AgI (27) with the various theoretical predictions. In this case the point of zero

TABLE 1
Parameters for the Fit to the Hypernetted Chain Diffuse Layer Potential

Concn (M)	A (mV)	f	a (cm ² /μC)	b (cm ² /μC)
10 ⁻³	163.6	0.5992	0.2974	1.5403
10 ⁻²	128.9	0.7024	0.1835	0.7017
10 ⁻¹	99.96	0.7812	0.0955	0.2867
10 ⁰	65.23	0.9558	0.0487	0.1445

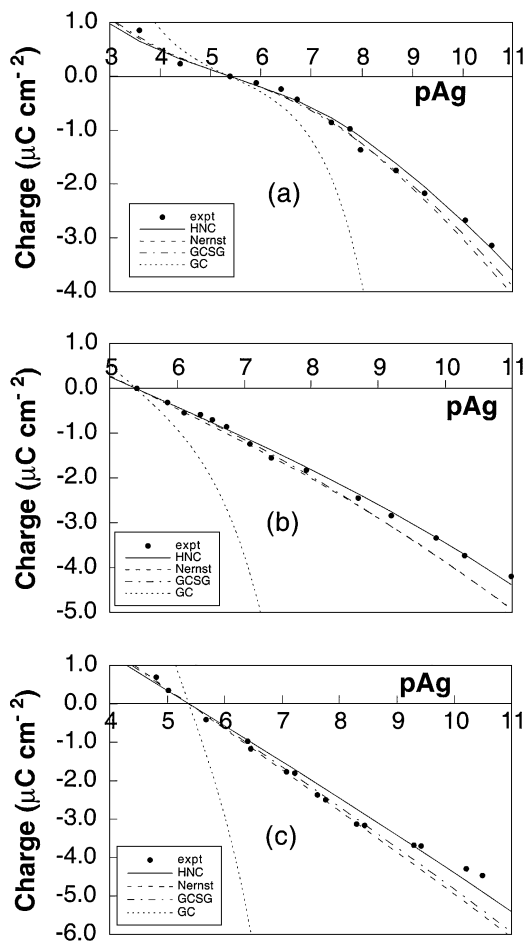


FIG. 1. Surface charge on AgI as a function of pAg for various concentrations of KNO_3 . The symbols are the measured titrated charge reported by Overbeek (27), and the curves are the various theoretical predictions using $\text{pAg}^{\text{pzc}} = 5.38$ and $C = 22.1 \mu\text{F cm}^{-2}$. The solid curve labeled “HNC” is the full site binding model with HNC using $N = 5 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 1 \text{ nm}^{-2}$, and the three remaining curves are the Nernst equation using GC, GCSG, and HNC. The latter is labeled simply “Nernst,” and in some cases it is virtually coincident with the GCSG curve. Concentrations: (a) 1 mM, (b) 12 mM, and (c) 100 mM.

charge is $\text{pAg}^{\text{pzc}} = 5.38$ (27), and the fitted inner-layer capacitance was $C = 22.1 \mu\text{F cm}^{-2}$ (discussed below). These are the only parameters that enter the Nernst theory. The two additional parameters of the full site binding model (HNC) were $N = 5 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 1 \text{ nm}^{-2}$. The former was fixed and would correspond to a distance between the ions of the crystal of $\approx 0.3 \text{ nm}$ if every ion on the surface were a binding site; the latter was treated as a fitting parameter and corresponds to 20% of the available sites being bound at the pzc. The values of these parameters should not be taken too literally, given the simplified nature of the model of the AgI crystal and its binding sites, and the relative insensitivity of the predicted surface charge to these two parameters. The relatively small departure of the HNC curve from the Nernst–HNC curve in Fig. 1 is a consequence of this insensitivity. The fact that the magnitude of latter exceeds that of the former confirms Eq. [18].

As expected, the charge is odd about the pzc, being increasingly positive as the concentration of Ag^+ is increased. The fact that $\text{pAg}^{\text{pzc}} = 5.38$ is less than $\text{pI}^{\text{pzc}} = 16.2 - 5.38 = 10.82$ (i.e., at the pzc the concentration of silver ions in the bulk is greater than that of iodide ions) indicates that the binding energy of iodide is less than that of silver (i.e., I^- is preferentially adsorbed to the surface of the crystal, or, equivalently, Ag^+ is preferentially solvated). As the electrolyte concentration is increased, the charge–pAg relationship becomes more linear (Fig. 1c). This is due to the fact that, for a given surface charge density, the dimensionless surface charge s decreases with increasing Debye parameter, Eq. [29], and the diffuse layer potential is a linear function of s for small s . In this regime, then, the surface potential is a strictly linear function of the surface charge density (because the contribution from the inner-layer is always linear), and hence according to the Nernst equation ([14]), the surface charge density must be a linear function of pAg.

From Fig. 1 one can conclude that it is essential to include a Stern layer, since this is neglected in the Nernst–GC theory, which clearly does not fit the data. The remaining theories give reasonable fits to the data, with the full site binding HNC model being slightly better, as may be expected since it has an extra fitting parameter. There is little difference between the PB approximation and the HNC approximations for the diffuse layer potential. In general the PB is valid and the two will agree when the ions are far apart, which means low electrolyte concentrations and low surface charge densities. In Fig. 1a one can begin to see a difference between the Nernst–HNC and the Nernst–GCSG theories at the most negative surface charge densities, and in Fig. 1c the discrepancy is noticeable over the whole regime due to the higher electrolyte concentration. Although the full HNC site binding model is slightly better, the simple Nernst equation is nevertheless adequate. One can conclude from the data in Fig. 1 that to a good approximation silver iodide is a Nernstian surface within a neighborhood of almost 5 pAg units of the pzc.

Figure 2 shows the measured electromotive force (EMF) for AgI electrodes as a function of the surface charge density (28). The EMF should be directly comparable to the surface potential, and the HNC and GCSG predictions for this are also shown. Although the data do not test the site binding model *per se*, it does test the HNC and PB approximations, and the model of the diffuse and inner-layers. The same fixed value of the inner-layer capacitance as in Fig. 1 was used, $C = 22.1 \mu\text{F cm}^{-2}$. In the HNC picture, the Stern layer is one-half an ion diameter thick, which in this case corresponds to 0.2 nm thick. Hence this value of the inner-layer capacitance corresponds to a relative permittivity of $\epsilon' = 5$, which is substantially less than that of bulk water. This value, which is slightly less than the dielectric saturation value of bulk water ($\epsilon' \approx 6$), scales linearly with the thickness of the Stern layer. We have chosen not to increase the latter and use throughout a fixed value equal to half the crystallographic ionic radius. The value of the inner-layer capacitance fitted here is consistent with the range of measured and fitted values for AgI

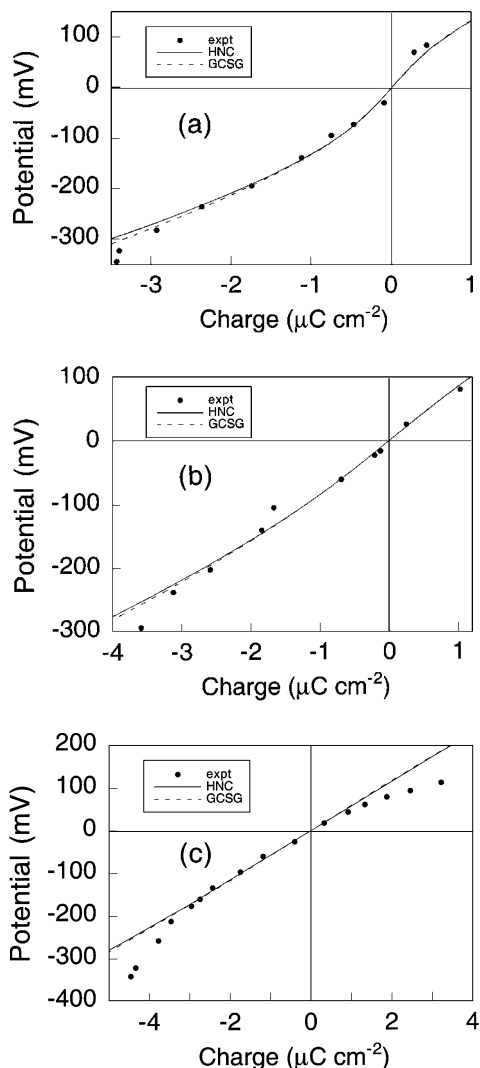


FIG. 2. Surface potential as a function of $p\text{Ag}$ for various concentrations of KF . The symbols are the measured electromotive force reported by Lyklema and Overbeek (28), the solid curve is the HNC prediction, and the dashed curve is the GCSG prediction, both using the inner-layer capacitance of Fig. 1. Concentrations: (a) 1 mM, (b) 10 mM, and (c) 100 mM.

reported in the literature (28–30). At low electrolyte concentrations the HNC and the GCSG are in agreement because of the validity of the PB in this regime, and at high electrolyte concentrations they agree because of the dominance of the inner-layer capacitance.

Since the inner-layer capacitance dominates the total capacitance at high electrolyte concentrations, the curvature in Fig. 2c indicates that the inner-layer capacitance varies with surface charge density, perhaps a form of electrostriction. Alternatively, Lyklema and Overbeek (28) show that the capacitance depends upon the nature of the counterion, and follows the lyotropic order, as is known to be the case for the mercury electrode (6). This may be interpreted as counterion binding to the surface, or it may suggest that the GC and the HNC models and treatments of the diffuse part of the double layer are inadequate at high

concentrations. We have not attempted to include any of these possible effects in our calculations, and for each surface we use a constant inner-layer capacitance throughout.

B. Titanium Dioxide

Figure 3 shows the titrated surface charge data for the rutile form of TiO_2 obtained by Yates (24), and compares it to the present theories. As in the case of AgI , the Nernst–GC theory fails badly, which again indicates the necessity of including a Stern layer. The inner-layer capacitance used for the remaining theories was $C = 97.4 \mu\text{F cm}^{-2}$, which for $d = 0.4 \text{ nm}$ corresponds to a relative dielectric permittivity of the inner layer of $\epsilon' = 22$. This capacitance is 4 times larger than for AgI , which may be interpreted as indicating that the perturbation of the vicinal water is less severe in the case of the TiO_2 surface. On the basis of Fig. 3, one cannot choose between the full HNC site binding model and the Nernst–HNC model. The two are almost coincident because the fitted number of sites at the pzc, $N_+^{\text{pzc}} = N_-^{\text{pzc}} = 3 \text{ nm}^{-2}$, is almost the maximum allowed; the number of available metal hydroxyl sites on rutile has been given by Yates as 6.12 nm^{-2} (24). Yates estimates that half of these sites are terminal metal hydroxyl sites and half are bridging hydroxyl sites, and the present calculations treat these as equivalent. We have developed and solved the model for the two distinct types of sites and find negligible departure from the present calculations. This is expected given the coincidence in Fig. 3 of the HNC and the Nernst–HNC curves; the latter is independent of the particular model of the surface.

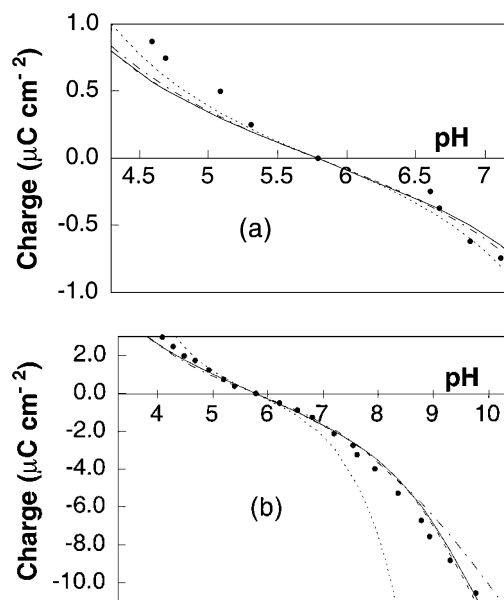


FIG. 3. Surface charge on the rutile form of TiO_2 as a function of pH for various concentrations of KNO_3 . The symbols are the measured titrated charge reported by Yates (24), and the various theoretical curves are as in Fig. 1 and use $\text{pH}^{\text{pzc}} = 5.8$ and $C = 97.4 \mu\text{F cm}^{-2}$. The HNC site binding model (full curve) uses $N = 6.12 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 3.00 \text{ nm}^{-2}$. Concentrations: (a) 1 mM and (b) 10 mM.

The reason that in this case the HNC and the Nernst–HNC curves coincide is that in the former almost all of the sites are bound at the pzc, which is the condition for the validity of the Nernst equation. Using a smaller number of bound sites would decrease the magnitude of the HNC fitted charge (recall that the Nernst equation provides an upper bound), but unlike AgI, the TiO_2 data tend to lie marginally on the high charge side of the Nernst curve. This is most evident for the 1 mM case, Fig. 3a, at low pH, and indicates perhaps the beginning of a breakdown in the site binding model, or else systematic experimental error. (The good agreement of the Nernst–GC theory here is most likely fortuitous.) Despite this, over the measured range of about 4 pH units of the pzc, one must conclude from Fig. 3 that to a very good approximation rutile is a Nernstian surface.

C. Aluminum Oxide

Figure 4 shows charge titration data from Sprycha (31) for $\gamma\text{-Al}_2\text{O}_3$ in NaCl. The pzc was at $\text{pH}^{\text{pzc}} = 8.1$ (31) and the number of available hydroxyl sites was 8 nm^{-2} (31–33). The inner-layer capacitance $C = 88.5 \mu\text{F cm}^{-2}$ corresponds to a relative dielectric permittivity of $\epsilon' = 20$ for the 0.2-nm-thick inner layer. There is little difference between HNC and Nernst–HNC because of the relatively large value of $N_+^{\text{pzc}} = N_-^{\text{pzc}} = 3.5 \text{ nm}^{-2}$ used. On the high pH side of the pzc, the magnitude of the experimental data is systematically higher than the Nernst equation for all four electrolyte concentrations. Since Nernst provides an upper bound for the charge in the present site binding model, this suggests that the model is inapplicable for negative surface charges. The asymmetry about the pzc evident in this case may arise from

the Na^+ counterion. Although it is difficult to reconcile this idea with the constancy of the pzc, it suggests that NaCl may not be indifferent for Al_2O_3 .

When the pH is less than pH^{pzc} , the Nernst equation quite accurately predicts the surface charge that is acquired by $\gamma\text{-Al}_2\text{O}_3$ over the 4 orders of magnitude in concentration displayed in Fig. 4. One can conclude that for positive surface charges, aluminum oxide is Nernstian over a range of at least 3 pH units below the pzc.

D. Silicon Dioxide

Silica is probably the most studied of the oxides, and its unusual colloidal behavior is well documented (34). One interesting feature of silica is that the surface charge density can increase to values higher than those allowed by the surface density of silanol groups, which creates particular challenges for the modeling of its double layer. We follow the common practice of modeling silica with a hydroxyl site density of 5 nm^{-2} (18, 24, 35). For the fully deprotonated case this would give a surface charge density of $-80 \mu\text{C cm}^{-2}$. As can be seen in Fig. 5, the titrated charge density can reach values more than twice as great as this (36). A porous gel layer model has been proposed to account for this discrepancy (36); in essence it says that there are more charge sites available than exist on the surface of the SiO_2 crystal, because the surface is porous, or because poly-silacic tendrils extend out from the surface. Obviously such extreme charge densities cannot be accounted for in any site binding model that ignores such possibilities, including the present one, and the real interest is whether the simpler models can account for the acquired charge at low and intermediate pH.

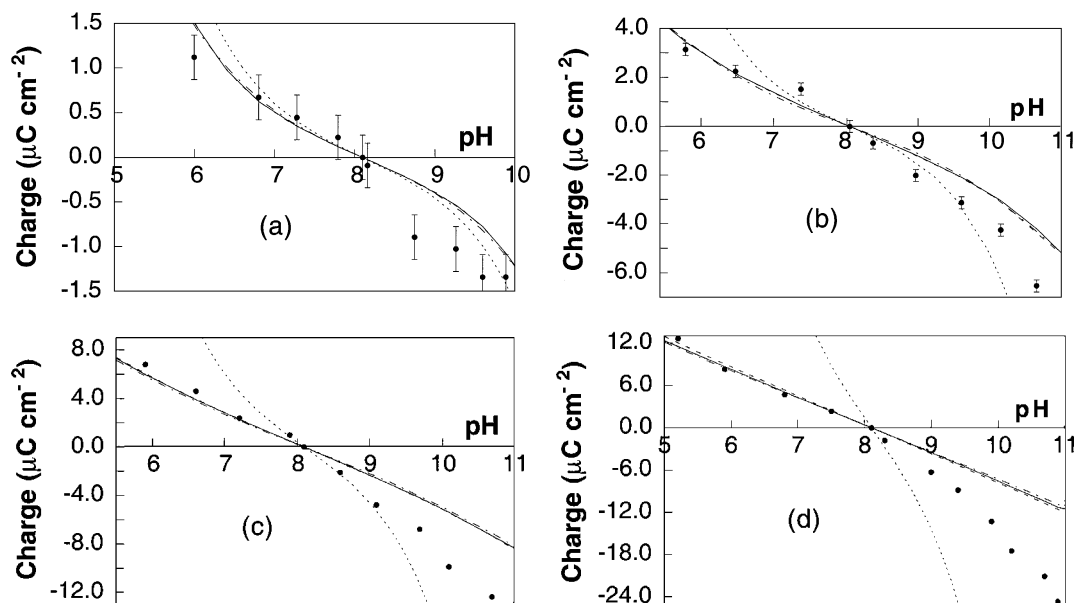


FIG. 4. Charge acquired by $\gamma\text{-Al}_2\text{O}_3$ in NaCl as a function of pH (all curves as in Fig. 1). The symbols represent data from Sprycha (31) with the error bars corresponding to the radius of the circles used to plot the original data; the experimental error is unknown. The theoretical curves use $\text{pH}^{\text{pzc}} = 8.1$ and $C = 88.5 \mu\text{F cm}^{-2}$. The HNC site binding model uses $N = 8 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 3.5 \text{ nm}^{-2}$. Concentrations: (a) 1 mM, (b) 10 mM, (c) 0.1 M, and (d) 1 M.

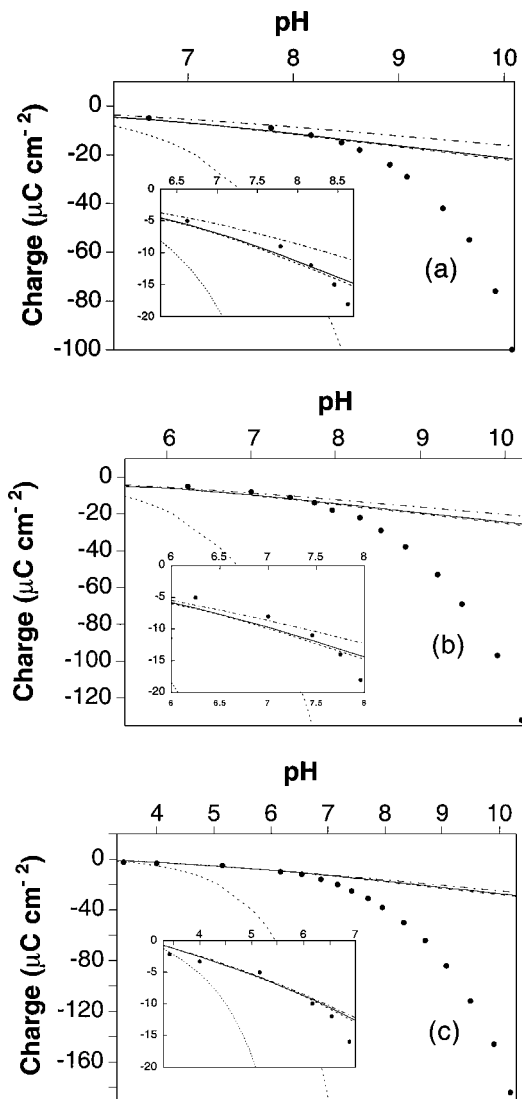


FIG. 5. Surface charge of SiO_2 in KCl as a function of pH (all curves as in Fig. 1). The experimental data (symbols) are from Tadros and Lyklema (36), and the theoretical curves are as in Fig. 1 and use $\text{pH}^{\text{pzc}} = 3.0$ and $C = 88.5 \mu\text{F cm}^{-2}$. The HNC site binding model uses $N = 5 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 2.49 \text{ nm}^{-2}$. Concentrations: (a) 1 mM, (b) 10 mM, and (c) 100 mM.

The pzc of silica is generally thought to be between pH 1 and 3.7. In the present work we have fixed its value at $\text{pH}^{\text{pzc}} = 3$ (36). The fact that this is at one extreme of the pH scale makes it possible to perform measurements 7 or 8 pH units away from the pzc. For comparison, the TiO_2 and Al_2O_3 measurements discussed above were limited to 3.5 and 3 pH units away from the points of zero charge, respectively. Hence it is unclear whether the gel layer occurs on silica and not on other metal oxides simply because silica can be extremely far from its pzc. In any case, again the appropriate test of the validity of the present site binding model and the Nernst equation is within 3–4 pH units of the pzc, or up to about pH 7.

Figure 5 shows experimental surface charge data for BDH precipitated silica as a function of pH (36). The GC theory clearly

does not fit the data, which once more confirms that a Stern layer is essential. In this case we used a value of $C = 88.4 \mu\text{F cm}^{-2}$ ($\epsilon' = 20$, thickness 0.2 nm). The HNC and the Nernst–HNC are in agreement with each other when the maximal value of $N_+^{\text{pzc}} = N_-^{\text{pzc}} = 2.5$ is used; a smaller value causes the HNC to move to smaller magnitudes of charge. In general the Nernst–GCSG is in agreement with the Nernst–HNC, except at the lowest concentrations of KCl (Figs. 5a and 5b). In this case the PB overestimates the diffuse layer potential for a given charge compared to the HNC, which gives a larger pH from the Nernst equation (i.e., the GCSG curve is shifted to higher pH). As the electrolyte concentration is increased the dimensionless surface charge decreases, in which regime the GCSG agrees with the HNC.

The HNC-based models are seen to fit the data up to a surface charge of approximately $-18 \mu\text{C cm}^{-2}$, or pH 7–8. As shown in the insets to Fig. 5, within 3–4 pH units of the pzc the Nernst equation describes the nature of silica with relative accuracy. One can conclude two things from this. First, since the data exceed the Nernst prediction at extreme pH, then they cannot be

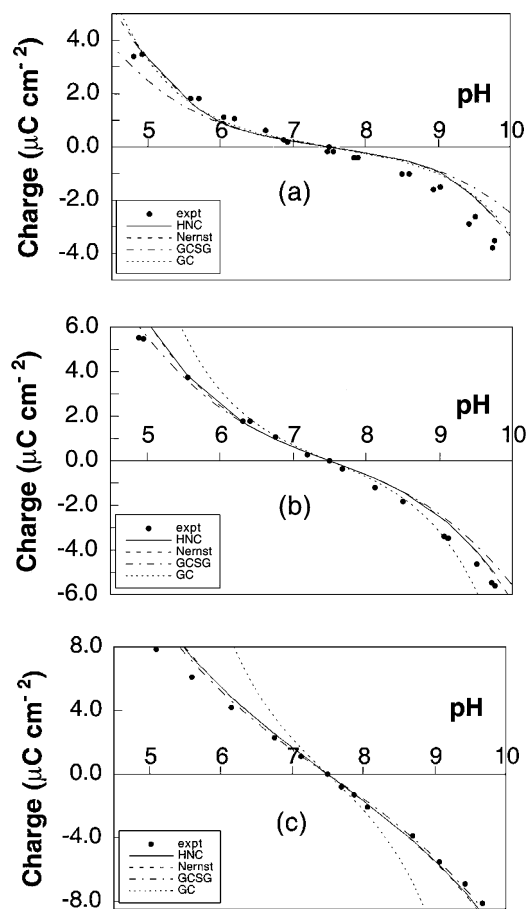


FIG. 6. Surface charge of FeOOH in KNO_3 as a function of pH (all curves as in Fig. 1). The experimental data (symbols) are from Yates (24), and the theoretical curves are as in Fig. 1 and use $\text{pH}^{\text{pzc}} = 7.5$ and $C = 177 \mu\text{F cm}^{-2}$. The HNC site binding model uses $N = 16 \text{ nm}^{-2}$ and $N_+^{\text{pzc}} = 4 \text{ nm}^{-2}$. Concentrations: (a) 1 mM, (b) 10 mM, and (c) 100 mM.

described by *any* simple site binding model; one has to invoke some sort of gel layer here. Second, and conversely, the fact that the Nernst equation does work at low and intermediate pH indicates that the simple site binding picture is valid in this regime. In other words, it appears as if the gel layer itself does not exist at low and intermediate values of the pH. Beyond these two conclusions one can also say on the basis of the insets to Fig. 5 that silica is a Nernstian surface within 3–4 pH units of the pzc.

E. Ferric Hydroxide

Figure 6 shows the titrated charge on α -FeOOH in KNO_3 (24). The pzc was at $\text{pH}^{\text{pzc}} = 7.5$ (24) and the number of available hydroxyl sites was $N = 16 \text{ nm}^{-2}$ (24). The inner-layer capacitance $C = 177 \mu\text{F cm}^{-2}$ corresponds to a relative dielectric permittivity of $\epsilon' = 40$ for the 0.2-nm-thick inner layer. There is little difference between HNC and Nernst–HNC because half the available sites were bound at the pzc, $N_+^{\text{pzc}} = N_-^{\text{pzc}} = 4 \text{ nm}^{-2}$. Compared to the Nernst–HNC, the Nernst–GCSG predicts that the charge is slightly smaller in magnitude, most noticeable at intermediate electrolyte concentrations and far from the pzc. This is probably due to the overestimation by the PB approximation of the diffuse layer potential at higher surface charge densities. In any case, the Nernst equation is very good and quite accurately predicts the surface charge that is acquired by FeOOH over the 5 pH units and 3 orders of magnitude in background electrolyte concentration displayed in Fig. 6. One can conclude that ferric hydroxide is Nernstian within at least 3 pH units of the pzc.

CONCLUSION

In this work we have explored the simplest model for the acquisition of surface charge by colloidal particles. We used a fixed number of sites and assigned a chemical binding constant to the potential-determining ions. We used a zeroth-order Stern layer, with fixed capacitance, and used either the Poisson–Boltzmann or the hypernetted chain approximations to describe the diffuse part of the electrical double layer. The aim was to see how well such a basic model would describe measured charge titration data. We found that for silver iodide, for titanium dioxide (rutile), and for ferric hydroxide a quantitative description was possible. For γ -aluminum oxide and for silica the description was similarly quantitative, albeit over restricted ranges.

We showed that the classic Nernst equation emerged as a limiting form of the present model in the vicinity of the point of zero charge. The validity of this limit increased for small capacitances and fully occupied sites at the point of zero charge. We also showed in general that the Nernst equation provides an upper bound on the charge given by any site binding model of the above type. The Nernst equation provides an exceedingly simple description of the colloidal charge and potential. It is independent of the detailed site binding model of the surface, and requires just two parameters: the point of zero charge and the

inner-layer capacitance. By direct comparison with the charge titration data, in all of the above cases the Nernst equation was shown to be essentially as accurate as the full site binding theories. That is, with the exception of negatively charged Al_2O_3 , within the vicinity of the point of zero charge (i.e., 3–4 pH units), all the surfaces that we studied are Nernstian.

This conclusion is significant because of the simplicity and the universality of the Nernst equation, and it is surprising that there is the wide-spread belief that the scope of the Nernst equation is quite limited. Of course silver iodide is well-known as a Nernstian surface (1, 2). Conversely it has been equally widely asserted that the metal oxides are non-Nernstian (1, 2, 18). The reason for this belief, which obviously contradicts the present conclusions, appears to be twofold. First, there appears to be a misunderstanding about what conditions are required for the Nernst equation to be valid. It relies not upon any equilibrium between the surface and the interior of a crystal, nor upon a large number of available binding sites *per se*, but rather upon the constancy of the surface configurational entropy (surface chemical activity). Such can be the case when the change in bound groups as the surface charge develops is relatively small, Eq. [13]. This in turn is ensured by a small value of the capacitance, a condition which can be met by the metal oxides just as well as by silver iodide.

Second, and perhaps more importantly, previous authors have used the Nernst equation for the potential, but instead of the surface potential, Eq. [14], they have interpreted it as an equation for the diffuse layer potential (1, 2, 18). Accordingly, they have compared the Nernst prediction with zeta potentials obtained from electrophoretic mobility or other electrokinetic measurements. We have recently shown that the zeta potential underestimates the diffuse layer potential (25); in any case the diffuse layer potential is in general much less than the surface potential. Hence the conclusion that metal oxides are non-Nernstian appears to stem from the erroneous comparison of the measured zeta potential with the Nernst prediction, when it is the surface potential that should be compared.

This point is worth emphasizing. Only the surface potential ψ_s obeys the Nernst equation. Neither the diffuse layer potential ψ_d obtained from force measurement (e.g., atomic force microscope or surface forces apparatus), nor the zeta potential obtained from electrokinetic measurement (e.g., electrophoresis or streaming potential), obeys the Nernst equation.

The present site binding calculations utilize the surface potential, and they establish the validity of the Nernst equation, at least in the neighborhood of the point of zero charge. Extrapolating from the present results for silver iodide and the metal oxides, it is reasonable to infer that the Nernst equation will perform equally well for other colloid particles, surfaces, and macromolecules.

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