

Ion Condensation in the Electric Double Layer and the Corresponding Poisson–Boltzmann Effective Surface Charge

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Received: April 17, 1995; In Final Form: June 23, 1995*

The effective surface charge obtained by fitting the Poisson–Boltzmann approximation to measured data is related to the actual surface charge. Evaluation of the formally exact expression, which depends upon the wall–ion direct correlation function, gives a precise measure of the amount of ion condensation in the planar double layer. Results are presented for 0.001, 0.01, and 0.1 M monovalent and divalent restricted primitive model electrolytes using the singlet hypernetted chain closure with the first bridge diagram. In general, the apparent surface charge is less than the actual surface charge, due to the influence of ion–ion correlations. Thus, the Poisson–Boltzmann approximation underestimates the actual surface charge and overestimates the amount of counterion binding. At high surface charge densities and apparent surface charge saturates, and there is a maximum surface charge density that a given electrolyte will appear to support. At surface charge densities beyond this and high concentrations (e.g. 0.1 M divalent, 75 Å² per unit surface charge), charge reversal occurs, due to overscreening by the counterions in the first layer adjacent to the surface.

Introduction

The charge on the surface of a particle is a key quantity in physical and colloid chemistry that determines the properties of the electric double layer in the adjacent electrolyte and the consequent behavior of the particles. The charge arises from the dissociation of surface chemical groups or from the chemical binding of electrolyte ions to the particle, and hence measurement of the surface charge can be used to deduce the binding constants for these reactions. Most frequently, the value of the surface charge is determined on the basis of the Poisson–Boltzmann theory, by fitting it to measured data. Examples include the electrophoretic mobility, the streaming potential, the differential capacitance of an electrode, and the force between charged surfaces.

The Poisson–Boltzmann approximation is a mean-field theory that neglects the effects of ion correlations. The latter arise from the interactions between the ions due to their charge and to their finite size and may be expected to have negligible effect at low electrolyte concentrations. However, at higher ionic strengths they become increasingly important, and in recent years more sophisticated numerical approaches to the electric double layer (simulation, integral equation, and density functional) have revealed deficiencies in the Poisson–Boltzmann approximation for physically realistic electrolyte concentrations and surface charge densities.^{1–3} Of course, these more accurate approaches are much more complicated than the mean-field theory, which is probably the reason that they are hardly ever used for the analysis of measured double-layer data.

The Poisson–Boltzmann approximation continues to be used because it is able to fit most data. Nevertheless, it must be recognized that the parameters that appear in the Poisson–Boltzmann theory represent effective rather than actual quantities and that their values compensate the quantitative errors in that approximation. For example, correlations between the ions decrease the electrostatic potential from its mean field value, and in order to fit this with the Poisson–Boltzmann approximation, one needs to use a value of the surface charge that is less than the actual surface charge. If this effective surface charge

were taken literally, then one would infer a certain counterion binding that has no basis in reality.

Using an effective surface charge to correct the Poisson–Boltzmann theory is an intuitively appealing notion. The validity of the concept is predicated upon the fact that the double-layer potential and ion profiles decay exponentially at a rate approximately equal to the Debye length, which is true to within experimental accuracy whenever the decay length is large enough to be measured.⁴ Consequently, the Poisson–Boltzmann approximation gives the qualitative behavior of the double layer, and the effective surface charge is defined as that quantity which makes the approximation exact or, equivalently, as that which is obtained by fitting the approximation to measured data. If the Poisson–Boltzmann approach is to be regarded as a quantitative theory for the double layer, one needs a prescription for the actual surface charge in terms of the effective surface charge.

That is the point of this paper. Numeric results are given that convert the effective or measured surface charge density to the actual surface charge density. The calculations are performed using the singlet hypernetted chain approximation with the first bridge diagram, which provides an accurate description of the planar electric double layer.^{1–3,8} The effective surface charge density depends upon an integral of the short-range part of the wall-ion direct correlation function, which is the result of a formally exact analysis of the asymptotic behavior of electrolytes and the double layer.⁹ This analysis confirmed that it is the bulk electrolyte decay length that determines the extent of the double layer and that it is close to the Debye length. Hence, for concentrations corresponding to the monotonic regime, the Poisson–Boltzmann approximation has the correct functional form, and the concept of an effective or fitted surface charge is well-defined. The analysis also shows that the effective surface charge is unique and that a single quantity characterizes the electrostatic potential, the magnitude of the ion profiles in the double layer, and also the interaction between two planar double layers. Consequently, the results given in this paper for converting the fitted surface charge density to the actual surface charge density can be used for a variety of measurement techniques, and they will allow the quantitative

* Abstract published in *Advance ACS Abstracts*, August 15, 1995.

determination of the surface charge density using measurements fitted on the basis of the Poisson–Boltzmann approximation.

Method

The formulas used here to calculate the effective surface charge were derived in ref 9 and are based upon a formally exact asymptotic analysis of the Ornstein–Zernike equation. Somewhat earlier, a number of results for the decay length of the electric double layer had been obtained,^{5–7} and the decay length has been numerically calculated in hypernetted chain^{9,10} and in generalized mean spherical¹¹ approximations. Recent asymptotic analysis has emphasized the Poisson–Boltzmann form of the asymptote.^{12,13} Analytic results for the effective surface charge of the planar double layer have been obtained with the extended Poisson–Boltzmann approximation,¹⁴ and this approximation is tested below.

Closely related to the present work are the results obtained by Ennis¹⁵ for the effective surface charge. Those results were obtained with the inhomogeneous hypernetted chain approximation, from the short-range part of the ion profiles between two walls, whereas the present results are obtained from the asymptotic behavior of the singlet hypernetted chain approximation. The latter approach is computationally more tractable, even with the inclusion of bridge diagrams, and hence a greater number of concentrations have been able to be treated in the present study. (Ennis¹⁵ does treat excluded-volume effects in more detail than here.) For the case of an isolated wall the two approximations appear to be of comparable accuracy, according to the existing simulation evidence;^{1–3} far from the wall the singlet approach with bridge diagrams describes the bulk electrolyte more accurately than the inhomogeneous approach without bridge diagrams. Both Ennis¹⁵ and the present work deal with the restricted primitive model, and the results and conclusions are similar, as is discussed in more detail below. A comprehensive review of modern approaches to the double layer may be found in ref 3, which also contains a preliminary account of some of the results given here.

For an isolated planar wall with surface charge density σ , the effective surface charge density $\tilde{\sigma}$ is given by⁹

$$\tilde{\sigma} = [\sigma + \tilde{q}^T \chi(i\kappa)]/2 \quad (1)$$

(This result, which is the one used here, is in essence equivalent to a result given by Ennis¹⁵ that invokes a short-range part of the singlet ion density profiles.) The function on the right is a vector with elements that are the Fourier transform of the short-range part of the wall–ion direct correlation functions, evaluated at $k = i\kappa$. The decay length of the bulk electrolyte is κ^{-1} , which has the same form as the Debye length, κ_D^{-1} , but with effective ion charges,

$$\kappa^2 = (4\pi\beta/\epsilon) \sum_{\alpha} \tilde{q}_{\alpha} q_{\alpha} Q_{\alpha} \quad (2)$$

Here $\beta = 1/k_B T$ is the inverse temperature, $\epsilon = 4\pi\epsilon_0\epsilon_r$ is the total permittivity, Q_{α} is the concentration of species α , and the effective ion charges \tilde{q}_{α} are given in terms of the Fourier transform at $k = i\kappa$ of the short-range part of the bulk ion–ion direct correlation functions.^{9,12,15} In the bulk electrolyte the asymptotes of the ion–ion correlation functions are either monotonic or oscillatory, and this determines the type of decay in the double layer. In the monotonic regime the effective surface charge gives the magnitude of the asymptotes, which have Poisson–Boltzmann form, and it is only in this regime that the concept of a Poisson–Boltzmann effective surface

TABLE 1: Properties of the Restricted Primitive Model Electrolyte Given by the Hypernetted Chain Approximation That Includes the First Bridge Diagram ($T = 298.15$ K, $\epsilon_r = 78.358$, $d = 4.25$ Å)

concn, M	κ_D^{-1} , Å	κ^{-1} , Å	\tilde{q}/q	ν
Monovalent				
0.001	96.11	96.14	1.00	1.00
0.01	30.39	30.36	1.00	1.00
0.1	9.61	9.32	1.06	1.00
Divalent				
0.001	48.06	50.64	0.90	1.00
0.01	15.20	17.21	0.78	1.01
0.02	10.75	12.33	0.76	1.02
0.05	6.80	7.81	0.76	1.04
0.07	5.74	6.55	0.77	1.06
0.1	4.81	5.40	0.79	1.09
0.15	3.92	4.27	0.85	1.14
0.2	3.40	3.56	0.91	1.21

charge is realistic. The mean electrostatic potential goes like^{9,15}

$$\psi(z) \sim \frac{4\pi\tilde{\sigma}}{\epsilon\nu\kappa} e^{-\kappa z}, \quad z \rightarrow \infty \quad (3)$$

where ν is a property of the bulk electrolyte that again depends upon the short-range part of the bulk ion–ion direct correlation functions. It is clear that this asymptote, which holds in the monotonic regime, has the same functional form as the linear Poisson–Boltzmann theory. More precisely, in the limit of low electrolyte concentrations, $\kappa \rightarrow \kappa_D$, $\nu \rightarrow 1$, and $\tilde{\sigma} \rightarrow \sigma$. For the cases in the monotonic regime that will be considered here, the screening length is relatively close to the Debye length and ν is almost unity (Table 1).

As mentioned above, a single effective surface charge describes all the asymptotic properties of the double layer. In particular, the wall–ion total correlation function, $h_{\alpha}(z) \equiv Q_{\alpha}(z)/Q_{\alpha} - 1$, goes like

$$h_{\alpha}(z) \sim -\beta\tilde{q}_{\alpha}\psi(z) \sim \frac{-4\pi\beta\tilde{q}_{\alpha}\tilde{\sigma}}{\epsilon\nu\kappa} e^{-\kappa z}, \quad z \rightarrow \infty \quad (4)$$

and again $\tilde{\sigma}$ determines the magnitude of the ion profiles. Also, the net pressure between two identical walls goes like^{9,15}

$$p(z) \sim \frac{8\pi\tilde{\sigma}^2}{\epsilon\nu} e^{-\kappa z}, \quad z \rightarrow \infty \quad (5)$$

which also reduces to the linear Poisson–Boltzmann result at low concentrations.

The properties and ion correlation functions of the restricted primitive model bulk electrolyte were computed using the hypernetted chain closure to the Ornstein–Zernike equation. From 2^{10} to 2^{14} grid points at a spacing of between 0.05 and 0.4 Å were used, depending upon the concentration. The first resummed bridge diagram was included and evaluated by expansion in on the order of 30 Legendre polynomials; the bridge function was recalculated up to three times in order to achieve self-consistency. For the double layer at a planar wall, the singlet Ornstein–Zernike equation with hypernetted chain closure and the first bridge diagram were solved as described previously,¹⁶ using similar numerical parameters to the above. The cycle of calculating the wall–ion bridge functions and the wall–ion total correlation functions was repeated up to 12 times in order to achieve self-consistency. After convergence, the effective surface charge was evaluated using eq 1.

Results

The concept of an effective surface charge that corrects the Poisson–Boltzmann approximation relies upon the fact that the

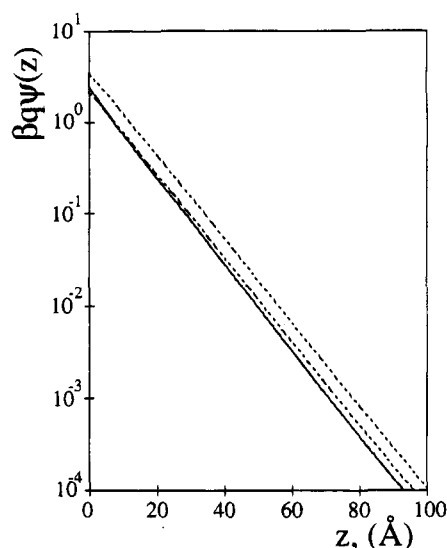


Figure 1. Mean electrostatic potential for a surface charge density of 0.064 C m^{-2} (250 Å^2 per unit charge) in a 0.1 M monovalent restricted primitive model electrolyte. The Debye length is 9.61 Å , the actual decay length is 9.31 Å , and $\nu = 1.0006$. Here and in all the figures $\epsilon_r = 78.358$, $T = 298.15 \text{ K}$, and $d = 4.25 \text{ Å}$. The linear Poisson-Boltzmann approximation (dotted curves) fits the hypernetted chain result (solid curve) with an effective surface charge equal to 401.8 Å^2 but overestimates the potential when the actual surface charge of 250 Å^2 is used.

electric double layer is exponentially decaying at a rate approximately equal to the Debye length. This is illustrated in Figure 1 for 0.1 M monovalent electrolyte, where the data rapidly becomes linear on the logarithmic scale. The Debye length is only 3% larger than the actual screening length in this case, and it can be seen that the linear Poisson-Boltzmann approximation is almost parallel to the hypernetted chain results. In order to distinguish the two experimentally, one would require extremely precise measurements covering several decades, which in general is impractical. Hence, even using the Debye length, one can obtain quite a good fit to the data with the linear Poisson-Boltzmann approximation using the effective surface charge density given by eq 1, namely 401.8 Å^2 per unit charge (0.040 C m^{-2}). If instead of the Debye length one used the actual decay length, then this effective surface charge density would give results in precise agreement with the actual potential over the whole asymptotic regime. One notes that a common experimental procedure is to deduce the electrolyte concentration from the measured decay length using the Debye formula, which would correspond to using κ instead of κ_D . In either case one would conclude that the linear Poisson-Boltzmann approximation was accurately describing the electric double layer and that one had measured a surface charge of 401.8 Å^2 . This is 65% less than the actual surface charge of 250 Å^2 (0.064 C m^{-2}), and one would no doubt conclude that a certain number of counterions had bound to the surface. In fact, however, there is no chemical binding in this model, and the counterion condensation is purely an artifact which compensates for the neglect of correlations in the Poisson-Boltzmann approximation.

The nonlinear Poisson-Boltzmann approximation is generally reckoned to improve upon the linear. It also decays exponentially in the asymptotic regime, and there is an equivalent effective surface charge. The relationship with the linear effective surface charge, eq 1, can be obtained by comparing the amplitudes of the two asymptotes, either for the electrostatic potential from an isolated surface or for the interaction between two surfaces, (cf. refs 14 and 15). The same expression results

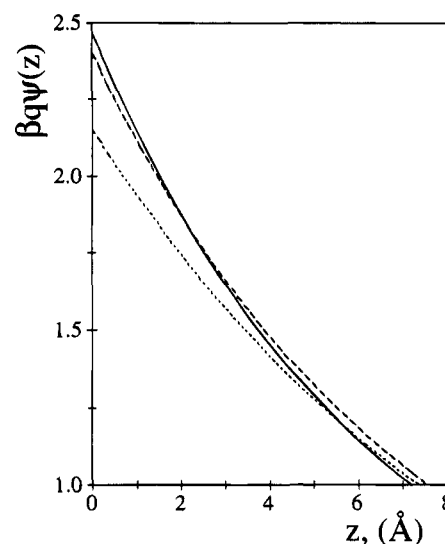


Figure 2. Electrostatic potential for the case of Figure 1 at small separations, where the nonlinear Poisson-Boltzmann approximation (dashed curve, 285.7 Å^2) is more accurate than the linear (dotted curve, 401.8 Å^2).

in both cases, namely

$$\tilde{s} = (8/\tilde{s}_{\text{nl}})[-1 + \sqrt{1 + \tilde{s}_{\text{nl}}^2/4}] \quad (6)$$

where $\tilde{s} \equiv 4\pi\beta q\tilde{\sigma}/\epsilon\kappa_D$ is the dimensionless surface charge fitted by the linear Poisson-Boltzmann approximation and $\tilde{s}_{\text{nl}} \equiv 4\pi\beta q\tilde{\sigma}_{\text{nl}}/\epsilon\kappa_D$ is that measured by fitting with the nonlinear approximation. Hence, the surface charge measured by fitting data with the nonlinear Poisson-Boltzmann approximation can be inserted into the right-hand side of this equation to obtain the equivalent linear Poisson-Boltzmann effective surface charge, which can then be used in conjunction with eq 1 and the data given below to deduce the actual surface charge. Alternatively, the relationship may be written

$$\tilde{s}_{\text{nl}} = 16\tilde{s}/(16 - \tilde{s}^2) \quad (7)$$

Figure 2 shows the mean electrostatic potential for the 0.1 M monovalent electrolyte on a linear scale at small separations. The linear Poisson-Boltzmann curve uses $|e/\tilde{\sigma}| = 401.8 \text{ Å}^2$, and the nonlinear Poisson-Boltzmann curve uses $|e/\tilde{\sigma}| = 285.7 \text{ Å}^2$. Thus, the nonlinear Poisson-Boltzmann approximation underestimates the surface charge density (250 Å^2) by about 15%, which is not as bad as the linear approximation. Both approximations for the potential would be coincident in the large distance asymptotic regime and would fit the hypernetted chain result. As these small separations, it can be seen that the linear Poisson-Boltzmann approximation does not increase rapidly enough, but for this particular concentration and surface charge density the nonlinear Poisson-Boltzmann approximation remains in good agreement with the more sophisticated approach. In other words, the applicable regime of the effective surface charge is greater in the nonlinear than in the linear approximation. Hence, if one performs a measurement that samples only the asymptotic regime, then one can just as well fit the data with the linear as the nonlinear Poisson-Boltzmann approximation. In the first case one may use the data below directly to deduce the actual surface charge density, and in the second case one should use that data and eq 6 to obtain the actual surface charge density. On the other hand, if the measurement relies upon the properties of the double layer in the vicinity of the surface, then one is probably best advised to use the nonlinear

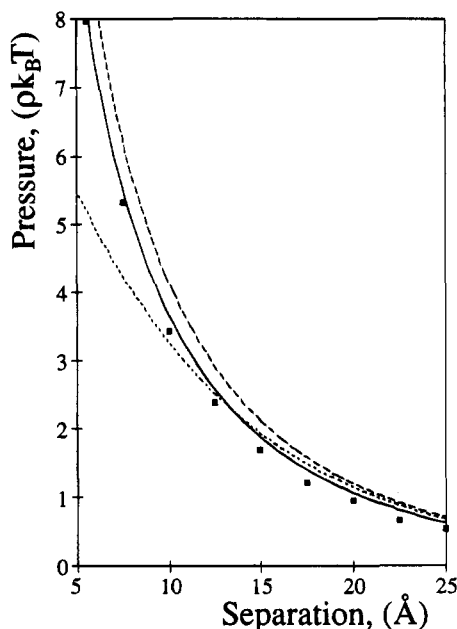


Figure 3. Double-layer pressure between the walls of Figure 2. The symbols represent inhomogeneous hypernetted chain data,¹⁷ and the solid and dashed curves are the nonlinear Poisson–Boltzmann approximation with the effective (285.7 Å²) and the actual (250 Å²) surface charge densities, respectively, and the dotted curve is the linear Poisson–Boltzmann approximation using 401.8 Å² per unit surface charge.

Poisson–Boltzmann approximation and to convert this fitted surface charge to the real surface charge using eq 6 and the data below.

A similar conclusion holds for the double-layer interaction. In Figure 3 it can be seen that the nonlinear Poisson–Boltzmann with the effective surface charge calculated for an *isolated* surface describes the pressure between *interacting* surfaces quite accurately. Using the actual surface charge in the Poisson–Boltzmann approximation gives too large a repulsion. At large separations both the linear and the nonlinear Poisson–Boltzmann approximations with their respective effective surface charges fit the hypernetted chain data. However, at small separations the linear Poisson–Boltzmann approximation does not increase rapidly enough, whereas the nonlinear approximation continues to describe the data quite reliably. Again, one concludes that the nonlinear version with effective surface charge has a larger range of validity than the linear version and is preferable if one is performing measurements in the nonasymptotic regime.

The fact that the surface charge density fitted by the Poisson–Boltzmann approximation was less than the actual surface charge density in the above case occurs quite generally. This can be seen in Figure 4, which shows the effective surface charge for monovalent electrolyte at 10^{−3}, 10^{−2}, and 10^{−1} M concentrations. At low surface charge densities the effective and actual surface charges coincide (on the scale of the figure), but as the surface charge density is increased, the effective surface charge becomes noticeably less than the actual surface charge. At intermediate surface charge densities the curves for the three different concentrations agree with each other for the departure from the actual surface charge, which indicates that the dimensionless parameter $s \equiv 4\pi\beta q\sigma/\epsilon\kappa_D$ is here appropriate. At higher surface charge densities the curves begin to separate, and the discrepancy between the actual and the effective surface charge increases with increasing electrolyte concentration. Similar behavior was obtained by Ennis¹⁵ for 0.05 and 0.5 M

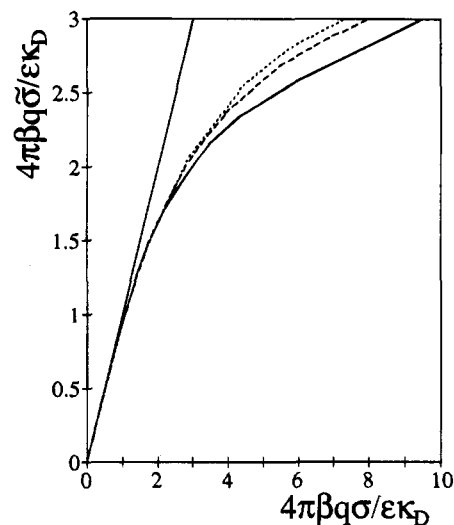


Figure 4. Effective or fitted surface charge density, $\bar{\sigma}$, as a function of the actual surface charge density, σ , for a restricted primitive model monovalent electrolyte. From bottom to top the curves are for concentrations of 0.1, 0.01, and 0.001 M, and the straight line is a guide to the eye.

monovalent electrolytes; in addition, he found that the saturated effective surface charge increased slightly with the ion diameter.

That the effective surface charge density is less than the actual surface charge density is due to ion correlations. In one sense this is a trite and obvious statement, since by definition the effective surface charge compensates the neglect of correlations in the mean field Poisson–Boltzmann approximation. The tautology does, however, indicate the physical origin of the decrease in the surface charge density. An ion in the double layer sees not the mean electrostatic potential but a local potential. A single counterion in the double layer repels other counterions from its vicinity, which *increases* the magnitude of the local electrostatic potential above its average value in the absence of the ion. This enhances the adsorption excess of counterions in the double layer compared to the mean-field prediction. (It is sufficient to focus upon the counterions since there are more of these than co-ions; the co-ions show a reduced expulsion from the double layer compared to the mean field prediction because their surrounding cloud of counterions *decreases* the local potential). The dominance of the counterions means that there is a rapid screening of the actual surface charge (i.e., more rapid than predicted by the mean field prediction), which means that a reduced effective surface charge is apparent some distance from the surface.

Figure 5 shows the ion distributions for the same case as Figure 1. It can be seen that the mean field approximations do indeed underestimate the number of counterions close to the surface. The effect is quite marked in the linear version, mostly due to the fact that the potential drop is relatively large ($\beta q\psi(0) = 2.5$), and linearizing the exponential is not such a good approximation. However, as discussed above, the nonlinear approximation predicts fewer counterions in the double layer in the vicinity of the surface than in reality because the mean field theory neglects the correlations between the ions. It is this enhanced counterion condensation that decreases the effective surface charge from its bare value.

One of the earliest indications that the effective surface charge required to correct the Poisson–Boltzmann approximation was less than the actual surface charge was given by Stillinger and Kirkwood,⁵ who used a moment expansion to obtain a correction to the Debye length due to electrostatic and finite size correlation effects. By insisting upon electroneutrality and enforcing the

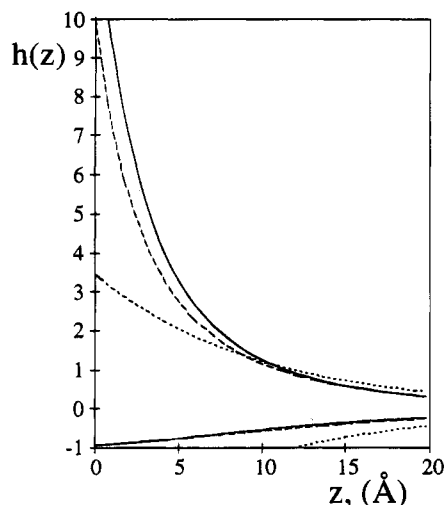


Figure 5. Wall-counterion (upper) and wall-co-ion (lower) total correlation function, as given by the hypernetted chain (solid curve), nonlinear Poisson-Boltzmann (dashed curve), and linear Poisson-Boltzmann (dotted curve) approximations. This is for the same case as Figure 1 (0.1 M monovalent electrolyte), and all the approximations used the bare surface charge density (250 Å^2).

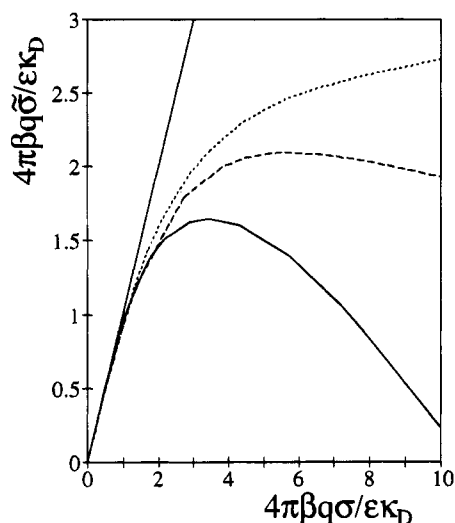


Figure 6. Effective surface charge density for, from bottom to top, 0.1, 0.01, and 0.001 M divalent electrolyte.

asymptote everywhere beyond the wall, they showed that the mean electrostatic potential was less than that predicted by the Poisson-Boltzmann approximation, increasingly so at higher electrolyte concentrations. That the mean field theory overestimates the potential drop across the isolated double layer has been shown by various approaches, including Monte Carlo, hypernetted chain, and modified Poisson-Boltzmann.¹ In more recent times investigations of interacting double layers have confirmed that the Poisson-Boltzmann approximation tends to overestimate the repulsion.¹⁸ In particular, Attard et al. [14] showed that ion correlations gave an attractive contribution and that asymptotically the double layer interaction had Poisson-Boltzmann form but with an effective surface charge (see below). The effect has been quantified numerically using the inhomogeneous hypernetted chain approximation.¹⁵

The above argument for the decrease in the effective surface charge density was based on electrostatic correlations, which suggests that the effect should be even larger in divalent electrolytes. This is indeed the case, as can be seen in Figure 6. (Similar results were obtained by Ennis¹⁵ for 0.125 and 0.3 M electrolyte.) Again, it is apparent that at intermediate surface

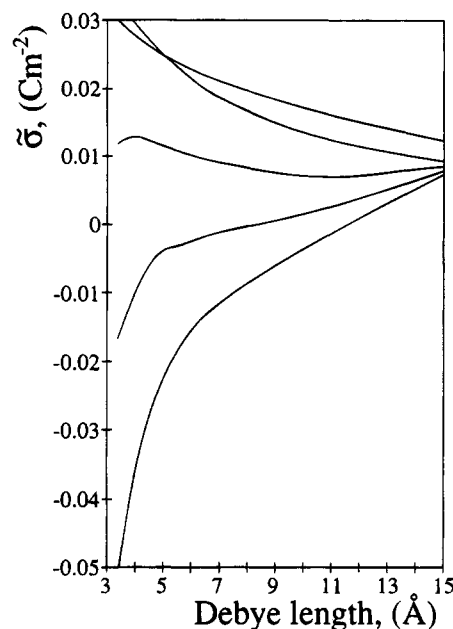


Figure 7. Effective surface charge density as a function of the Debye length of divalent electrolyte (0.01–0.2 M), at surface charge densities of (from bottom to top) $\sigma = 0.27, 0.21, 0.16, 0.11$, and 0.032 C m^{-2} ($|e/\sigma| = 60, 75, 100, 150$, and 500 Å^2).

charge densities s is the appropriate dimensionless parameter. (The data for monovalents would coincide with this data for divalents in this regime.³) At higher surface charge densities the curves diverge from each other. In fact, the 0.01 and 0.1 M cases actually show a maximum effective surface charge, which then decreases as the actual surface charge increases. The experimental consequence of this behavior is that there will appear to be a maximum surface charge density that a given electrolyte can support. One would ascribe the decrease in the apparent surface charge to ion binding, even though in reality no chemical binding is taking place. The nonmonotonic behavior of the effective surface charge density is rather unexpected and is reminiscent of the hypernetted chain prediction that the potential drop across the double layer decreases with increasing surface charge at high surface charge densities.¹ This negative differential capacitance is unusual, but it does not violate any fundamental requirements.^{19,20} In the present case it is the effective surface charge density that goes through a maximum, at least in the case of divalent electrolytes at higher concentrations. When this occurs, there will be an ambiguity in deducing the actual surface charge density from the fitted density, and one may need additional information (such as a measurement in the nonasymptotic regime) to resolve the issue. Note that the bulk electrolyte quantity ν has not been included in Figure 6. For comparison with fitted surface charge densities, one should use $\tilde{\sigma}/\nu$ (or $\tilde{\sigma}/\sqrt{\nu}$ for interactions), which will make about a 20% difference for the 0.1 M divalent electrolyte (see Table 1).

The variation in the effective surface charge density with divalent electrolyte concentration is shown in Figure 7. At low electrolyte concentrations (large Debye lengths) the effective surface charge densities are almost independent of the actual surface charge density. There is almost an order of magnitude variation in the latter quantity in Figure 7, but only a 25% change in the effective surface charge density. This is a manifestation of the saturation effect at large s shown for the monovalent electrolyte in Figure 4 and for the 0.001 and 0.01 M divalent electrolyte shown in Figure 6. At high electrolyte concentrations in Figure 7, the effective surface charge density

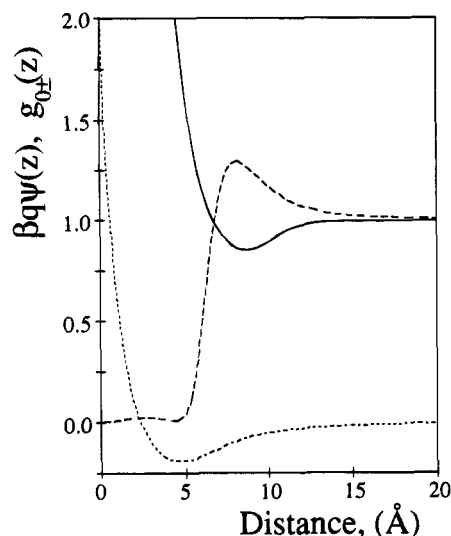


Figure 8. Mean electrostatic potential $\beta q\psi(z)$, dotted curve, and the counterion and co-ion distributions $g_{0\pm}(z)$, solid and dashed curves, respectively, for the 0.1 M divalent electrolyte with $|e/\sigma| = 75 \text{ \AA}^2$.

decreases with increasing surface charge density, which is a consequence of the maximum that appears in the preceding figure. In fact, the crossover of the two curves with the lowest surface charge density at high electrolyte concentrations indicates that the curve for 100 \AA^2 per unit surface charge lies on the low side of the maximum. When the actual surface charge density is low (upper curves, Figure 7), the effective surface charge density is markedly less than the actual surface charge density at low electrolyte concentrations but increases toward the actual value as the concentration is increased. (This is the same as decreasing the parameter s because κ_D appears in the denominator.) A transition occurs at about $80\text{--}90 \text{ \AA}^2$ per unit surface charge, and at higher surface charge densities than this the effective surface charge density decreases as the electrolyte concentration is increased (lower two curves, Figure 7). The effective surface charge density decreases to zero and eventually turns negative at high enough electrolyte concentrations and actual surface charge densities. Similar behavior has been noted by Ennis¹⁵ and others (see below). In particular, Ennis¹⁵ estimates reversal at $s = 4.39$ (101 \AA^2) for 0.125 M divalent 4.6 \AA ions; here it is found that, for 4.25 \AA divalent ions, reversal occurs at $s \approx 10.8$ (80 \AA^2) and $s \approx 7.8$ (90 \AA^2) for 0.1 and 0.15 M, respectively. A negative effective surface charge means that the particle or surface will appear to have the opposite charge to what it actually has in reality.

Physically, this charge reversal originates from the structure of the double layer. A layer of counterions forms at the wall with essentially close-packed density, excluding the co-ions, and at the same time overneutralizing the surface charge. Charge reversal occurs due to a combination of ion size and valence, and it also depends upon the bulk electrolyte concentration and surface charge density, which determine the concentration in the layer. The mechanism is clear in Figure 8, where it can be seen that there is a dense layer of counterions next to the wall and that there are almost no co-ions in this region. Slightly beyond one diameter ($d = 4.25 \text{ \AA}$) from the wall an inversion occurs, and the co-ion density exceeds the counterion density. It is emphasized that this is a local charge oscillation induced by the high surface charge on the wall. The bulk electrolyte is in the monotonic regime (with decay length $\kappa^{-1} = 5.4 \text{ \AA}$), and the density profiles and potential will decay monotonically beyond this surface region. In particular, although the surface is positively charged, the electrostatic potential turns negative

at about 3 \AA from the wall and remains negative. Measuring techniques that sample the double layer some distance from the surface will ascribe to the particle a charge with the wrong sign. For example, electrophoresis, in which the motion of a particle in an applied electric field depends upon the electrostatic potential at the zeta plane away from the surface, may show a highly charged particle stop and reverse direction as the concentration is increased, even though its actual surface charge remains unchanged. The point of zero charge and the subsequent reversed effective charge are not due to physical binding of counterions to the surface, or to chemical association or dissociation, but rather to the electrostatic attraction and layering of the counterions and exclusion of the co-ions due to packing in the diffuse part of the double layer adjacent to the surface.

The modified Poisson–Boltzmann theory was perhaps the first to predict charge reversal, where it was seen in a primitive model electrolyte (monovalent co-ions, divalent counterions) at 0.15 M.²¹ (The authors were careful to distinguish this surface-induced inversion of the ion profiles in the bulk monotonic regime from asymptotic oscillations present at higher concentrations.) The charge reversal, as evidenced by the inversion and the change in sign of the potential, were confirmed by simulations.²² Similar behavior was also seen in a 0.5 M 2:2 electrolyte, which is very near, in fact possibly beyond, the bulk monotonic–oscillatory transition. This was obtained with Monte Carlo simulations by Torrie and Valleau,²² with the singlet mean spherical approximation by Feller and McQuarrie²³ and with density functional approaches by Mier-y-Teran et al.²⁴ and by Patra and Gosh.²⁵ Ennis et al.¹⁵ have studied the effective surface charge and its reversal for interacting walls at large separations with the inhomogeneous hypernetted chain approximation. That approximation has also shown charge reversal in a 2:1 primitive model electrolyte.²⁶ It appears that charge reversal occurs more readily in mixed valence (divalent counterions) than in symmetric electrolytes. Finally, charge reversal has also been seen in singlet hypernetted chain calculations for a molecular aqueous double layer,^{27,28} where a solvent-induced fast screening regime was observed. In general, the values of the effective surface charge given above for the primitive model will be altered by a molecular solvent because they are a surface-sensitive property, although the asymptotic functional form will remain the same. Even within the primitive model their values will be affected by the size of the ions and any disparity in size or charge.

The above numerical results were obtained with a rather sophisticated theory for the double layer (the hypernetted chain approximation with the first bridge diagram), and they can be used to test more approximate theories. In particular, Attard et al.¹⁴ give a convenient analytic expression that is based upon the extended Poisson–Boltzmann approximation. This is essentially the solution of the mean spherical closure to the inhomogeneous Ornstein–Zernike equation for ions of zero size; it thus includes the effects of ion correlations but not those of excluded volume. The extended Poisson–Boltzmann formula for converting surface charge fitted on the basis of the nonlinear Poisson–Boltzmann approximation to actual surface charge can be expressed in terms of a fit to the linear Poisson–Boltzmann approximation using eq 6. Assuming that to a good enough approximation $\kappa \approx \kappa_D$ and $\nu \approx 1$, the result is

$$\bar{\sigma} = \sigma \frac{A}{2s} \left[1 + \frac{\beta q^2 \kappa_D}{4\epsilon} \{2I + \ln 2\} \right]^{1/2} \quad (8a)$$

where $A = 16(-1 + \sqrt{1 + s^2/4})/s$, the dimensionless surface

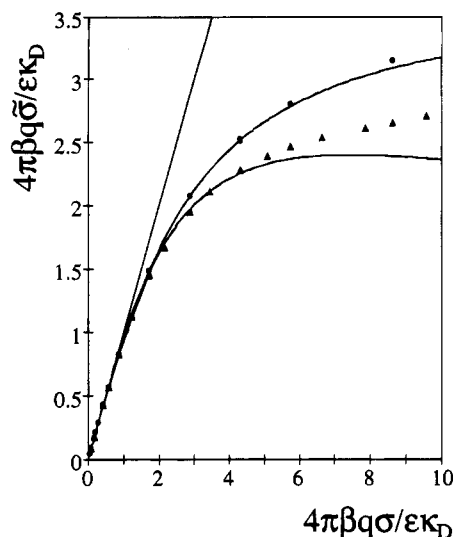


Figure 9. Extended Poisson–Boltzmann approximation (curves) for the effective surface charge density in 1 mM electrolyte compared to hypernetted chain data (symbols). The upper data are for monovalent electrolyte, and the lower data are for divalent electrolyte.

charge again is $s \equiv 4\pi\beta q\sigma/\epsilon\kappa_D$, and I is given by²⁹

$$I = \frac{1}{2} \left(1 + \frac{2z^2 - 3}{(2z^2 - 1)^3} \right) \ln 2 + \frac{2 - 2z^3 + z}{2z(2z^2 - 1)^2} - \frac{\sqrt{z^2 - 1}}{z} \left(1 + \frac{2z^2 + 1}{(2z^2 - 1)^3} \right) \tan^{-1} \sqrt{\frac{z - 1}{z + 1}} - \frac{1}{2} \left(1 - \frac{2z^2 - 3}{(2z^2 - 1)^3} \right) \ln(z + z^2) \quad (8b)$$

where $z \equiv \sqrt{1 + s^2/4}$. This extended Poisson–Boltzmann theory is tested for 1 mM monovalent and divalent electrolytes in Figure 9. One sees that it is relatively accurate over most of the regime shown. It can be seen that the extended Poisson–Boltzmann approximation is more accurate for monovalents than for divalents. The extended Poisson–Boltzmann approximation gives the primary correction to the mean field Poisson–Boltzmann theory due to ion correlations. As such, it can only be expected to be valid at low electrolyte couplings, which expectation has been confirmed with the singlet approach,³ and which is consistent with the inhomogeneous approach of Ennis¹⁵ for divalent electrolyte at two concentrations. It does tend to overestimate the decrease in the effective surface charge in the case of divalent electrolyte in Figure 9, which it also does at higher electrolyte concentrations.³ This is due to the Debye–Hückel closure approximation exaggerating the effects of ion correlations. That the extended Poisson–Boltzmann approximation quantitatively agrees with the hypernetted chain calculations indicates that it is electrostatic correlations rather than ion size that are primarily responsible for the difference between the actual and the effective surface charges, at least in the regime shown. This follows because the extended Poisson–Boltzmann theory includes the former but not the latter. The extended Poisson–Boltzmann theory gives a convenient representation of the effective surface charge in the low concentration regime, and that analytic formula should prove useful for interpolating to cases not explicitly covered by the present numerical data.

The fact that the effective surface charge is generally less than the actual surface charge has been apparent in all the data above, and it has been emphasized that this is due to the ion correlations that are neglected in the mean field Poisson–Boltzmann approximation. Paradoxically, the extended Poisson–Boltzmann theory actually says that at very low surface

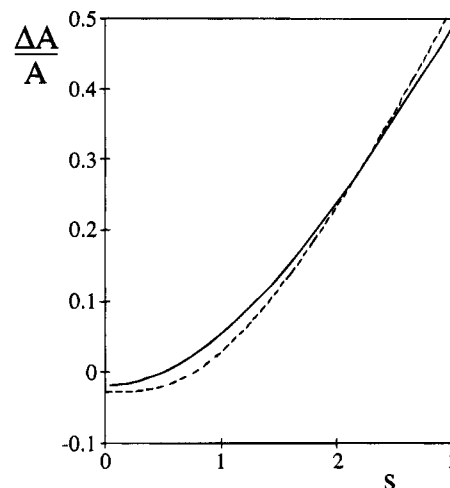


Figure 10. Relative change in the area per unit surface charge, $\sigma/\sigma - 1$, at low surface charge densities in the 0.1 M monovalent electrolyte. The solid curve is the hypernetted chain approximation, and the dashed curve is the extended Poisson–Boltzmann approximation.

charge densities the fitted surface charge becomes greater than the actual surface charge.¹⁴ The hypernetted chain calculations presented here now confirm that rather unexpected prediction, as can be seen in Figure 10. Attard et al.¹⁴ rationalized this behavior by arguing that ions are effectively repelled from an inert wall due to attractive correlations with ions in the bulk electrolyte (the Onsager–Samaras effect). At low surface charge densities this depletion of the electrolyte near the surface becomes important and results in less screening of the surface charge by the double layer than is predicted by Poisson–Boltzmann theory. That is, there is a repulsion of counterions from the wall, which gives rise to an effective surface charge that is greater than the actual surface charge. This effect, which was seen in all of the electrolytes analyzed above, may be difficult to measure in practice because it is relatively small and it occurs at extremely low surface charge densities. Nevertheless, Ennis¹⁵ has confirmed the prediction for divalent electrolyte, showing a larger effect in 0.3 M than in 0.125 M; he also shows that the extended Poisson–Boltzmann approximation appears quantitatively accurate for the latter system in the low surface charge regime.

Conclusion

Given the very widespread use of the Poisson–Boltzmann approximation to interpret measurements of the properties of the eclectic double layer, it is desirable to relate the effective surface charge that appears in that theory to the actual surface charge of the system. The effective surface charge is the quantity that makes the mean field approximation fit the measured data, and it corrects for the neglect of correlations due to electrostatics and to ion size. The reason that the Poisson–Boltzmann approximation is capable of describing the double layer with an effective surface charge is because the properties of the double layer decay exponentially at a rate approximately equal to the Debye length, at least in the asymptotic regime. This observation provides the basis for calculating the relationship between the effective and the actual surface charge, since one simply equates the coefficient of the Poisson–Boltzmann asymptote to that given by more sophisticated theories. This procedure gives a precise and unambiguous characterization of the amount of correlation-induced ion condensation in the double layer.

In this paper data were given for several electrolytes that will enable the actual surface charge to be obtained from measure-

ments of the surface charge fitted with the Poisson–Boltzmann approximation. The singlet hypernetted chain theory with the first resummed bridge diagram was used for the calculations, and this is known to provide an accurate and reliable description of the properties of the isolated double layer. The data obtained here are consistent with those obtained by Ennis¹⁵ by the inhomogeneous hypernetted chain approximation. Thus, these data allow measurements to be fitted with the simplest mean field theory and the value of the surface charge to be quantified at a level equivalent to using a modern integral equation theory for the double layer.

The effective surface charge calculated here relied upon the asymptotic properties of the double layer. This showed that there was a unique quantity that characterized the electrostatic potential, and double-layer density profiles, and the interaction between particles. Hence, the data for the effective surface charge are applicable to a variety of measurement techniques. Although the formal analysis applied in the asymptotic regime, it was also demonstrated that the nonlinear Poisson–Boltzmann theory could be applied at small separations with its own effective surface charge. The relation between the latter and the effective surface charge that corrects the linear Poisson–Boltzmann theory was given, eq 6, and this should be useful for experiments that sample the double layer close to the surface.

The extended Poisson–Boltzmann theory for the effective surface charge¹⁴ was tested and found to be accurate at low electrolyte concentrations. This analytic formula complements the numerical data and extends the coverage to those cases not explicitly treated here. That particular approach includes dielectric images,¹⁴ which can have important effects at low surface charge densities. These were ignored in the data presented here, as were the effects of ion asymmetry; results were given only for the restricted primitive model. Perhaps the most serious simplification is the continuum one, in which the water molecules enter only through the dielectric constant. Because the effective surface charge relies upon the behavior of the ions in the double layer near the surface, the structure of the water in this region can be expected to affect their condensation and adsorption.

Of course, the Poisson–Boltzmann theory also utilizes this simplified model and in addition neglects the effects of correlations due to ion size and charge. The latter are included here at quite a sophisticated level of treatment, and so the data for the surface charge may be relied upon within this model. One does not expect the results obtained here to be qualitatively changed by a more complicated model. In particular, the surface charge fitted by the Poisson–Boltzmann approximation should in general be less than the actual surface charge. This is due to ion condensation because of electrostatic correlations; it should not be taken literally as physical or chemical ion binding

but simply as an effective quantity that corrects the neglect of correlations in the Poisson–Boltzmann theory. Similarly, the saturation (maximum) of the apparent surface charge in a given electrolyte is due to the mean field theory underestimating the electrostatic potential seen locally by the counterions. Finally, the charge reversal at higher electrolyte concentrations and surface charge densities is again due to ion correlations but relies upon their size to establish a close-packed layer of counterions next to the surface. This overneutralization of the surface charge gives rise to a change in the sign of the electrostatic potential a few angstroms from the surface and has consequences for the interpretation of mobility and streaming potential measurements.

References and Notes

- (1) Carnie, S. L.; Torrie, G. M. *Adv. Chem. Phys.* **1984**, *56*, 141.
- (2) Blum, L. *Adv. Chem. Phys.* **1990**, *78*, 171.
- (3) Attard, P. *Adv. Chem. Phys.*, in press.
- (4) Theoretically, it is known that the actual decay length of the bulk electrolyte and consequently of the double layer begins to depart from the Debye length at higher concentrations,^{5–7} but the departure remains relatively small until the decay length is so short as to preclude measurement or until oscillations replace the monotonic decay. An effective Poisson–Boltzmann surface charge is only realistic in the monotonic regime.
- (5) Stillinger, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1960**, *33*, 1282.
- (6) Stell, G.; Lebowitz, J. L. *J. Chem. Phys.* **1968**, *48*, 3706.
- (7) Outhwaite, C. W. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1214, 1670.
- (8) Ballone, P.; Pastore, G.; Tosi, M. P. *J. Chem. Phys.* **1986**, *85*, 2943.
- (9) Attard, P. *Phys. Rev. E* **1993**, *48*, 3604.
- (10) Ennis, J.; Kjellander, R.; Mitchell, D. J. *J. Chem. Phys.* **1995**, *102*, 975.
- (11) Evans, R.; Leote de Carvalho, R. J. F.; Henderson, J. R.; Hoyle, D. C. *J. Chem. Phys.* **1994**, *100*, 591.
- (12) Kjellander, R.; Mitchell, D. J. *J. Chem. Phys. Lett.* **1992**, *200*, 76.
- (13) Kjellander, R.; Mitchell, D. J. *J. Chem. Phys.* **1994**, *101*, 603.
- (14) Attard, P.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Phys.* **1988**, *89*, 4358.
- (15) Ennis, J. Ph.D. Thesis, Australian National University, 1993. Ennis, J.; Kjellander, R.; Marčelja, S. Manuscript in preparation.
- (16) Attard, P.; Miklavic, S. J. *J. Chem. Phys.* **1993**, *99*, 6078.
- (17) Marčelja, S. *Biophys. J.* **1992**, *61*, 1117.
- (18) Kjellander, R.; Marčelja, S. *J. Phys. Chem.* **1986**, *90*, 1230.
- (19) Attard, P.; Wei, D.; Patey, G. N. *J. Chem. Phys.* **1992**, *96*, 3767.
- (20) Torrie, G. M. *J. Chem. Phys.* **1992**, *96*, 3772.
- (21) Bhuiyan, L. B.; Outhwaite, C. W.; Levine, S. *Mol. Phys.* **1981**, *42*, 1271.
- (22) Torrie, G. M.; Valleau, J. P. *J. Phys. Chem.* **1982**, *86*, 3251.
- (23) Feller, S. E.; McQuarrie, D. A. *J. Phys. Chem.* **1992**, *96*, 3454.
- (24) Mier-y-Teran, L.; Suh, S. H.; White, H. S.; Davis, H. T. *J. Chem. Phys.* **1990**, *92*, 5087.
- (25) Patra, C. N.; Gosh, S. K. *J. Chem. Phys.* **1994**, *100*, 5219.
- (26) Kékicheff, P.; Marčelja, S.; Senden, T. J.; Shubin, V. E. *J. Chem. Phys.* **1993**, *99*, 6098.
- (27) Torrie, G. M.; Kusalik, P. G.; Patey, G. N. *J. Chem. Phys.* **1989**, *90*, 4513.
- (28) Patey, G. N.; Torrie, G. M. *Chem. Scr.* **1989**, *29A*, 39.
- (29) *I* is given by eq 3.23 of ref 14, which results from integrating eq 3.20 for the case of no dielectric images. That integral appears divergent, presumably due to a typographical error; eq 3.23 itself appears to be reliable.

JP951158M