

Abstract

Electrostatic interactions between charged surfaces across an electrolyte solution are commonly described by boundary conditions of constant charge or constant surface potential. These two extremes are in general not appropriate for an equilibrium description of materials with ionizable surface groups, but do provide an upper and lower bound for the interaction energy. We propose a quantitative criterion which permits to evaluate the degree of charge regulation for surfaces with arbitrary electrostatic potential, as considered in the Poisson-Boltzmann theory. Our approach represents a generalization of the linearized regulation model proposed earlier for the framework of Debye-Hückel theory only. Like in the case of low surface potentials, the regulation behavior is generally determined by the competition between the capacities of the diffuse and the compact part of the electric double layer. Our results suggest a new way of using the limiting conditions of constant charge and constant potential to approximate the interaction free energy of charge regulating surfaces.

Introduction

The electric double layer interaction of two charged flat surfaces in an electrolyte solution is commonly calculated under the assumption that either the electrostatic surface potential or the surface charge density is independent of the surface separation [1]. A more elaborate model describes the charge density as due to ionizable surface groups maintaining chemical equilibrium at all surface separations [2]. The nonlinear charge density–surface potential relation resulting from the ionization isotherm for these so-called “charge regulating” surfaces, however, complicates the calculation.

Chan and Mitchell [3] have given a graphical interpretation of the corresponding interaction free energy, which for equal surfaces identifies the interaction at constant charge as an upper bound and the interaction at constant surface potential as a lower bound for the double layer repulsion. By linearizing the ionization isotherm around the equilibrium of the isolated surface, Carnie and Chan [4] have derived analytic expressions for the force and interaction energy, valid in the situation of low electrostatic potentials described by the Debye-Hückel equation. Their results imply a criterion of how similar the interaction under charge regulation will be to both limiting cases of constant charge and constant potential. They show that the regulation behavior is determined by the competition between the two capacities associated with the diffuse part and the compact inner part of the electric double layer; a large diffuse layer capacity leading to constant-charge-like behavior, and

a predominant capacity of the compact layer producing a constant-potential-like interaction.

In the following we will present a simple generalization of the above approach to arbitrary potentials. Geometric arguments indicate that a similar regulation criterion holds much more generally than the original derivation in the framework of Debye-Hückel theory would suggest. As a practical consequence, we propose a simple approximation for the interaction energy of charge regulating surfaces, when only the limiting results for constant charge and the constant potential are available from calculations.

The Electrostatic Surface Potential

The general concept of an electric double layer involves a diffuse part formed by mobile ions in the solution and a compact inner part containing immobile surface charges. The electrostatic potential at the interface of these two regions, subsequently called "surface potential" ψ , is determined by the structure of both the diffuse layer and the compact inner layer.

For charge regulating surfaces, the ionization reaction of the surface groups in the inner layer imposes a functional dependence of the surface potential on the surface charge density [3], which we will denote by $\psi^I(\sigma)$. Depending on the chosen surface complexation model, this function may reflect further structural features, such as for example, the presence of a Stern layer, but we will assume that the function does

not depend on the surface separation.

At the same time, the surface potential must obey a charge-potential relation dictated by the diffuse layer, which will be described by a function $\psi^D(\sigma, L)$. If the diffuse layer is described on the basis of the Poisson-Boltzmann equation, then for an isolated surface in a solution of monovalent electrolyte this relation is the familiar Grahame equation

$$\lim_{L \rightarrow \infty} \psi^D(\sigma, L) = \frac{2}{\beta e} \sinh^{-1} \left(\frac{\beta e \sigma}{2 \epsilon \epsilon_0 \kappa} \right), \quad (1)$$

$\beta^{-1} = kT$ being the thermal energy, κ^{-1} the Debye length, and $\epsilon \epsilon_0$ the total permittivity of the solution. For a finite surface separation L , this relation cannot be expressed analytically [2].

A schematic representation of the function ψ^I and the function ψ^D (for a finite and infinite separation) is given in figure 1. Their intersection point defines the charge and potential actually assumed by the surface in equilibrium.

Double Layer Interaction under Charge Regulation

Chan and Mitchell [3] have shown that for identical surfaces, the free energy per unit area at a given separation L can be expressed as

$$\mathcal{F}(L) = \int_0^{\sigma(L)} \psi^D(\sigma, L) d\sigma - \int_0^{\sigma(L)} \psi^I(\sigma) d\sigma. \quad (2)$$

We can interpret the first term on the right hand side of (2) as the free energy stored in the diffuse layer, and the second term as contribution of the compact inner part

of the double layer including the chemically stored energy. As pointed out in [3], the interaction free energy (per unit area)

$$F(L) = \mathcal{F}(L) - \mathcal{F}(\infty) \quad (3)$$

corresponds to the area enclosed by the curves $\psi^I(\sigma)$, $\psi^D(\sigma, L)$ and $\psi^D(\sigma, \infty)$; this is the vertically hatched area of figure 1. In the same way, the area obtained when $\psi^I(\sigma)$ is replaced by the curves $\psi = \psi^\infty = \text{const.}$ or $\sigma = \sigma^\infty = \text{const.}$ represents the free energy of interaction at constant potential (cp) or constant charge (cc), and clearly,

$$F^{(\text{cp})}(L) \leq F(L) \leq F^{(\text{cc})}(L).$$

Our aim is to see what fraction of $F^{(\text{cc})} - F^{(\text{cp})}$ actually contributes to the interaction energy in the regulating case; thus, we ask for the value of the "regulation parameter"

$$p(L) = \frac{F(L) - F^{(\text{cp})}(L)}{F^{(\text{cc})}(L) - F^{(\text{cp})}(L)}, \quad (4)$$

which can obviously take values between 0 for constant potential and 1 for constant charge conditions.

Carnie and Chan [4, 5] have linearized the function $\psi^I(\sigma)$ around the equilibrium value for the isolated surface and considered the Debye-Hückel limit of the function $\psi^D(\sigma, L)$ (dotted straight lines in figure 1). The interaction free energy thus found is represented by the diagonally hatched area.

In typical applications, $\psi^I(\sigma)$ can be a rather straight, featureless curve between the point describing the isolated surface (point C in figure 1) and some equilibrium

point (E) at a finite separation of interest [6]. We therefore suggest to linearize $\psi^I(\sigma)$ around the equilibrium charge density σ^∞ for infinite separation as proposed in reference [4] for a treatment on the level of Debye-Hückel theory. Since the regulation parameter p ($= \text{area(ACE)}/\text{area(ACDE)}$) in figure 1) is mainly determined by the local behavior of both curves, it seems consistent to also linearize $\psi^D(\sigma, L)$ locally (and not globally as it is done in the Debye-Hückel approach).

First we note that replacing the segment ACDE of figure 1 with the triangle ACD, will not affect the ratio p very strongly — not even if $\psi^D(\sigma, L)$ is locally curved. Next, we approximate the slope of the secant AD by its large separation limit, the inverse of the diffuse layer capacity

$$\frac{1}{C^D} = \frac{\partial \psi^D}{\partial \sigma}, \quad (5)$$

which is evaluated at the equilibrium charge density σ^∞ of the isolated surface. If the Poisson-Boltzmann equation is used to describe the diffuse layer, then the capacity is given by [1]

$$C^D = \epsilon \epsilon_0 \kappa \cosh(\beta e \psi^\infty / 2). \quad (6)$$

In the same way, we introduce the capacity of the compact inner layer (called “regulation capacity” [4, 5])

$$\frac{1}{C^I} = -\frac{d\psi^I}{d\sigma}, \quad (7)$$

evaluated again at σ^∞ . When the segments ACE and ACDE (figure 1) are approximated as triangles, the regulation parameter is given by the ratio of their areas and can be expressed as a ratio of lengths $BE/CD = AB/(AB + BC)$. With the

capacities C^D and C^I given by AB/BE and BC/BE respectively, we find for the regulation parameter of equation (4) in this approximation

$$p = \lim_{L \rightarrow \infty} p(L) = \frac{C^D}{C^D + C^I}. \quad (8)$$

The same parameter describes the effect of charge regulation on the equilibrium value of the surface charge and potential [7].

$$\frac{\psi - \psi^{(\text{cp})}}{\psi^{(\text{cc})} - \psi^{(\text{cp})}} = \frac{\sigma - \sigma^{(\text{cp})}}{\sigma^{(\text{cc})} - \sigma^{(\text{cp})}} = p, \quad (9)$$

We conclude that the regulation behavior of flat surfaces is governed quite generally by the competition of two capacities that reflect how easily charge can be stored in either the compact or the diffuse part of the double layer.

Whenever the diffuse layer capacity prevails surface will interact at constant charge; if, on the other hand, the capacity of the compact inner layer dominates, surface will interact at constant surface potential. Every form of intermediate behavior will be characterized by a value of the regulation parameter p between 0 and 1.

This regulation criterion, equation (8), is the generalization of a result previously reported by Carnie and Chan [4]. They showed that on the level of Debye-Hückel theory and linearized $\psi^I(\sigma)$, the interaction energy per unit area (the diagonally hatched area between the dotted lines in figure 1) is given by [8]

$$F(L) = \varepsilon \varepsilon_0 \kappa (\psi^\infty)^2 \frac{\exp(-\kappa L)}{1 + \Delta \exp(-\kappa L)} \quad (10)$$

with

$$\Delta = \frac{C^I - C^D}{C^I + C^D} = 1 - 2p, \quad (11)$$

and $C^D = \epsilon\epsilon_0\kappa$. For arbitrary potentials, no analytical expression is available for the interaction energy. Yet, the parameter p in its general form characterizes the location of the interaction energy between its limits for constant charge and constant potential even when none of these energies can be written down explicitly.

This parameter can easily be computed from the common double layer models.

In the common situation where the double layer interaction can be evaluated for the cases of constant charge and constant potential only, an obvious way of accounting for charge regulation is to approximate the interaction (free) energy per unit area by

$$F_{\text{approx}}(L) = F^{(\text{cp})}(L) + p \left[F^{(\text{cc})}(L) - F^{(\text{cp})}(L) \right], \quad (12)$$

where p is the constant given by equation (8). Clearly, this approximation will be best for large separations L . In the Debye-Hückel case with linearized regulation (10), the relative error at finite separation introduced by (12) is

$$\frac{F_{\text{approx}}(L) - F(L)}{F(L)} = \frac{4p(1-p)}{\exp(2\kappa L) - 1}.$$

In that case, the error is below 5% down to surface separations of $1.5 \kappa^{-1}$. A model study of different types of charge regulating surfaces [6] indicates, that for realistic values of the surface potential and the regulation parameter, the approximation (12) is applicable down to much smaller separations.

Conclusion

A local linearization of both charge density – surface potential relations characterizing the diffuse and the compact part of the electric double layer proves useful to describe the interaction of charge regulating surfaces at arbitrary potentials. Like in a description based on the Debye-Hückel equation, a characteristic regulation parameter taking values between 0 for interaction at constant potential and 1 for interaction at constant charge, is simply given by the ratio of the diffuse layer capacity to the sum of the diffuse layer capacity and the inner layer capacity. This regulation parameter is also convenient for an approximation of the interaction free energy under conditions of charge regulation in terms of the limiting results for constant charge and constant surface potential.

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References

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- [6] S. H. Behrens and M. Borkovec, submitted for publication.
- [7] The neglect of the local curvature of $\psi^D(\sigma, L)$ will introduce a larger error in equation 9 than in the approximation of $p(L)$ by p .
- [8] The expression on the right hand side of (10) differs by a factor of 2 from an expression given in reference [4], where the interaction free energy per unit area of just *one* plane is considered.

Figure 1. Schematic representation of the charge-potential relations $\psi^I(\sigma)$ and $\psi^D(\sigma, L)$ and of the Debye-Hückel limit for $\psi^D(\sigma, L)$. The intersection of $\psi^I(\sigma)$ and $\psi^D(\sigma, L)$ corresponds to the equilibrium value of the surface charge and potential, the hatched area between the curves is a measure of the interaction energy. The curve $\psi^I(\sigma)$ is replaced by the horizontal line at $\psi_d = \psi_d^\infty$ in the constant potential limit and by the vertical line through $\sigma = \sigma^\infty$ in the constant charge limit; for the regulated case, $\psi^I(\sigma)$ is approximated by its tangent in the equilibrium point for infinite separation. Inset: the contribution to the interaction energy for the different boundary conditions. The interaction parameter p is given by the ratio of the area of ACE to the area of ACDE, which we approximate as triangles.

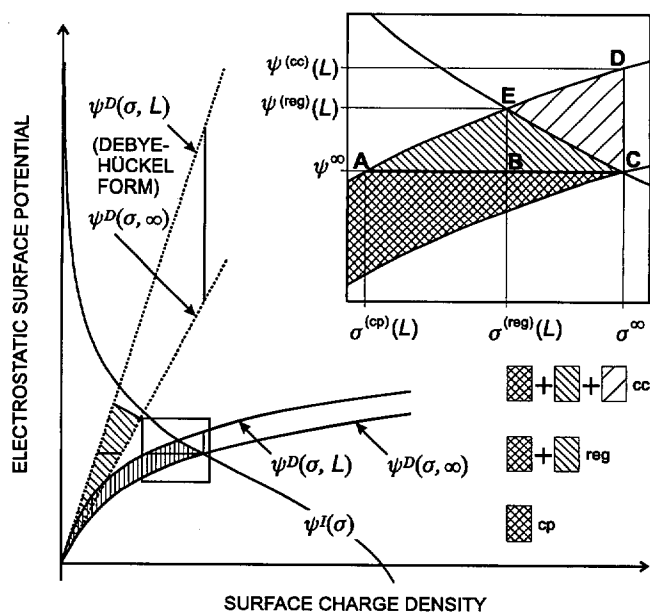


Figure 1.