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The relationship between surface charge and surface potential at the solid-liquid interface is often determined by a charge regulation process, the chemisorption of a potential determining ion such as H^+. A subtle ion-specific effect can be observed when other ions compete with the primary potential determining ion to bind to a surface site. Site competition may involve alternative ions competing for a first binding site, e.g., metals ions competing with H^+ to bind to a negatively charged oxide or carboxyl site. Second-binding sites with site competition may also be found, including amphoteric OH_2^+ sites, or anion binding to amine groups. In this work, a general theoretical model is developed to describe the competitive adsorption of ions at surface sites. Applied to the calculation of forces, the theory predicts a 20% increase in repulsion between titania surfaces in 1 mM NaCl, and a 25% reduction in repulsion between silica surfaces in 0.1M NaCl compared to calculations neglecting ion site competition. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4916519]

I. INTRODUCTION

Ion specific effects, or Hofmeister effects, are ubiquitous in all fields of physical chemistry.[1–6] They are observed in measurements of electrophoretic mobilities (zeta potentials),[7] surface charge titrations,[8,9] surface force measurements,[10] polymer and protein solubility,[11,12] pH,[13] and biological activity.[14–19]

Ion specific effects cannot be described by classical electrostatic models of salt solutions. Rather, they came to be understood as arising from chemisorption, or specific adsorption,[20] of ions to the surface, expressed as a shift in the effective charge of the surface (distinct from the charge of the diffuse layer of ions). More recently the role of nonelectrostatic physisorption of ions has come to be understood, arising to quantum mechanical van der Waals interactions of ions acting at a distance from the surface,[21–24] or due to size-dependent ion-water interactions at the cavity of an ion.[25–29] The two kinds of nonelectrostatic ion-surface interactions are connected, with the degree of chemisorption of ions at surface sites influenced by the degree of physisorption, including nonelectrostatic physisorption.[30]

Site binding of the hydrogen ion is the normal mechanism by which pH-sensitive materials acquire their surface charge, in which context it is often known as charge regulation.[31–35] In principle, the state of the regulated surface charge can be determined from atomic force microscopy (AFM).[36] The theory of the relationship between hydrogen ion binding and nonelectrostatic physisorption of the hydrogen ion was recently developed.[30] But that theory considered only site binding of a single ion. Proteins are zwitterionic biomacro-molecules, that is, carry both negative (i.e., carboxylate or phenolate) and positive (i.e., amine, imidazole, or guanidine) charged groups which act as adsorbing sites for other ions besides H^+. This phenomenon is particularly relevant in physiological conditions where $[H^+]$ is only 10^{-7} M whereas Na^+ and Cl^- are 10^6 times more concentrated. Both sodium and hydrogen ions compete for the same carboxylate site. In this paper, we therefore extend the theory of ion site binding (chemisorption) alongside ion nonelectrostatic physisorption, to account for ion competition at a surface site. The idea of ion site competition is illustrated in Fig. 1.

While a model of ion site competition is important for protein systems, it is also relevant elsewhere. For instance, measurement of high pH by glass electrodes is confounded by interfering substances (the "sodium error"), which introduces error into the pH measurement.[37,38] This can be understood as ion site competition between sodium and hydrogen ions for oxide sites on the surface of the glass electrode.[39]

The interaction of H^+ ions with oxide surface sites of metal oxides is often modelled as amphoteric, providing both positive and negative total surface charges depending on pH. Therefore in order to cover this case, we build ion competition for a general amphoteric site, that is, with double ion binding. The effect of ion competition on surface charge has been considered previously.[40–42] We extend the analysis to the effect of ion site competition on surface free energy and surface forces. To illustrate the model, we apply it to a system of oxide sites on a titania surface with competitive double binding (amphoteric competition) and on a silica surface (nonamphoteric). Application of the model to protein systems will be made elsewhere.
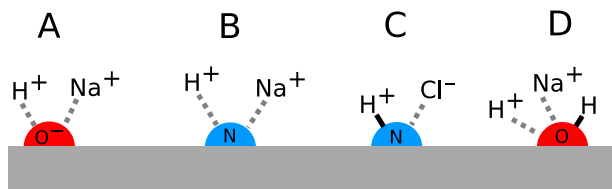
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FIG. 1. Illustrative cartoon of ion site competition. Metal ions compete with H^+ to bind to a charged oxide (or carboxylate) site (a) or a neutral amine site (b). An anion may bind to a protonated amine site (c). Competitive double binding may occur at a protonated amphoteric oxide site (d).

Our model does allow for the inclusion of nonelectrostatic physisorption (general nonelectrostatic ion-surface interactions acting at a distance from the surface) alongside chemisorption (specific site-binding). We argue that the separation of these two adsorption mechanisms enables a more complete description of ion adsorption. Nevertheless, nonelectrostatic physisorption is a secondary consideration in the theory presented here and is omitted from our illustrative calculations. We emphasis that the main innovation of this work is to describe the impact of competitive ion chemisorption at surface sites.

Calculated surface forces are frequently presented in terms of the disjoining pressure, which is the force between two parallel, flat surfaces with separation L between them, typically calculated (for symmetric surfaces) as

$$P = \sum_i c_i(L/2) - c_{i0}, \quad (1)$$

where c_{i0} is the bulk concentration of ion i and $c_i(L/2)$ is its concentration at the midplane between the two surfaces. Deniz and Parsons previously found[30] that this expression is incomplete for charge regulated systems where the single potential-determining ion experiences nonelectrostatic physisorption interactions. In this work, we extend that result to the case of competitive charge regulation. But more than that, we also reveal an additional pressure term which arises due to competitive double-binding at amphoteric sites, present even when nonelectrostatic physisorption is neglected. However, our analysis takes a thermodynamic approach using the total free energy of the system,[23,43] from which the disjoining pressure is a derived rather than fundamental quantity.

II. GENERAL ION COMPETITION AT SURFACE SITES

In general, a system may have a number of different types of chemisorbing surface sites, e.g., protein surfaces contain both acidic carboxylate and basic amine sites. The total surface charge is, indexing each type of site with s,

$$\sigma = \sum_s \sigma_s. \quad (2)$$

The surface density of each type of site is N_s. Neglecting any specific distribution of charge sites across the surface (which would introduce a lateral dependence of the potential on the x, y-coordinates parallel to the surface), the mean electrostatic potential $\psi(z)$ can be calculated by the Poisson-Boltzmann model from this total smeared surface charge σ.

Consequently the calculation (more precisely, the physics) of the total physisorption free energy F_{ps} remains, for a given total σ, unchanged by ion site competition.

To construct a general chemisorption model, we must choose whether to start from the dissociated or associated state. The traditional amphoteric model with two acid constants conceptually started from the doubly associated state.[30,32] But to evaluate the chemisorption free energy for the case of general ion competition, we must also establish a reference state. It is convenient to use the neutral uncharged surface as the reference state. But for different sites this means different things. For acidic sites, the neutral state is the associated site (with bound H^+). For basic sites, the neutral state is the dissociated site (no chemisorbed ion). For the sake of consistency with the commonly used acid constants pK_a, we write the equilibria as dissociation processes,

$$SX_i^{q_s+q_i} \rightleftharpoons S^{q_s} + X_i^{q_i} \quad (pK_i). \quad (3)$$
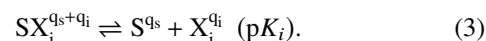
Note the differences from a standard simple amphoteric description. We allow the site to have its own dissociated charge q_s ($q_s = 0$ for basic sites, $q_s = -1$ for acidic sites). Likewise for generality, the ion may have an arbitrary charge q_i (the model applies to association of both cations and anions, univalent and multivalent). The equilibrium constants pK_i are dissociation constants, similar to acid constants. Extension of charge regulation to ion competition requires a multiplicity of equilibrium constants.[40]

Generalised amphotericity is then provided by dissociation from doubly bound states. In the general case any ion X_j may bind to a singly bound site SX_i, with

$$SX_iX_j^{q_s+q_i+q_j} \rightleftharpoons SX_i^{q_s+q_i} + X_j^{q_j} \quad (pK_{ij}) \quad (4)$$
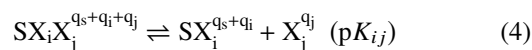
requiring a matrix of double-binding constants pK_{ij}, which will not in general be symmetric, $K_{ij} \neq K_{ji}$. Again, pK_{ij} are dissociation constants, akin to acid constants. Full dissociation, forbidding binding, is provided within this formalism (whether for single binding K_i or double-binding K_{ij}) by $K = \infty$, that is, by $pK = -\infty$.

A. Equilibrium surface charge per site

It is convenient to calculate the surface charge σ_s due to a given binding site s by using the total amount Γ_i of ion X_i bound to the site. The total charge due to site s is then

$$\sigma_s = q_s N_s + \sum_i q_i \Gamma_i. \quad (5)$$

Γ_i can be determined from the fraction of sites which have bound charge. Let α_i be the fraction of sites of type s which are occupied by ion X_i (by single association only), and let β_{ij} be the fraction of sites to which the two ions X_i and X_j are bound (double association). A standard acid site is a purely dissociative site where all $\beta_{ij} = 0$ and $q_s = -1$. A standard basic site likewise has $\beta_{ij} = 0$ together with $q_s = 0$. The fraction γ_s of bare, nonassociated sites is of course

$$\gamma_s = 1 - \sum_i \alpha_i - \sum_{ij} \beta_{ij}. \quad (6)$$

The equilibrium constants for Eqs. (3) and (4) may be written in terms of site binding fractions,

$$K_i = \frac{a_i \gamma_s}{\alpha_i} \quad (7)$$

and

$$K_{ij} = \frac{a_j \alpha_i}{\beta_{ij}}. \quad (8)$$

Here, a_i, a_j are the activities of ions X_i, X_j in solution. If the equilibrium constants are taken to be intrinsic equilibrium constants (relative to local ion concentrations), then a_i and a_j must represent the activities of the ions at the surface, that is, at the location of the surface sites. However, the same formalism equally applies to site binding of ions in Stern layers displaced some distance d_i away from the bulk interface. In this case a_i would refer to the activity of ion i at distance d_i. Alternatively, a_i and a_j may represent bulk activities, in which case the equilibrium constants must be taken as the effective constants relative to bulk.[44]

This allows the site binding fractions to be written in terms of equilibrium constants and ion activities in solution,

$$\alpha_i = \frac{a_i}{K_i A_s} \quad (9)$$

and

$$\beta_{ij} = \frac{a_i a_j}{K_i K_{ij} A_s}, \quad (10)$$

where A_s is a measure of the total degree of association,

$$A_s = 1 + \sum_m \frac{a_m}{K_m} \left(1 + \sum_n \frac{a_n}{K_{mn}} \right), \quad (11)$$

A_s is the inverse of the total degree of dissociation, that is, $\gamma_s = 1/A_s$.

For a given set of site occupation fractions α_i and β_{ij}, the total amount of X_i chemisorbed to the site, whether by single or double association, is

$$\Gamma_i = N_s \left(\alpha_i + \beta_{ii} + \sum_j \beta_{ij} \right). \quad (12)$$

Given the definitions of α_i and β_{ij} in Eqs. (9) and (10), we can write the amount Γ_i of bound X_i in terms of ion activities,

$$\Gamma_i = \frac{N_s a_i}{A_s K_i} \left(1 + \frac{a_i}{K_{ii}} + \sum_j \frac{a_j}{K_{ij}} \right). \quad (13)$$

Note that i is included in the sum over j, and that the factor A_s is a function of activities a_i.

B. Total chemisorption free energy per site

Calculation of the total surface free energy of a single isolated surface enables, for instance, the theoretically study of the impact of ionic adsorption on wettability. Calculation of the interaction free energy between two surfaces separated by distance L allows surface forces to be evaluated. In either case, the free energy contribution due to ion binding (chemisorption) must be included in the total free energy of the surfaces.

We evaluate the chemisorption free energy using the same philosophy applied previously to hydrogen ion chemisorption.[30] The total free energy $F_{total} = F_{ps} + F_{cs}$ is comprised of both physisorption (F_{ps}) and chemisorption (F_{cs}) components. The physisorption free energy contains an electrostatic contribution (attractive) due to the total surface charge and the distribution of ionic charges, an entropic contribution (repulsive) due to the density profile of ions, and a nonelectrostatic contribution due to ionic dispersion forces (often, though not always, attractive) or other nonelectrostatic physisorption interactions. The physisorption contribution does not depend on chemisorption except by way of the total surface charge. Therefore for the sake of brevity, we do not reproduce details here but refer to Ref. 23. The thermodynamic approach employed here draws on the analysis of surface forces presented by Overbeek in 1990.[43]

The chemisorption free energy integrates the change in free energy when an amount Γ_i of ion X_i is transferred between solution and surface site. The integration is taken between the amount Γ_i^0 of ion chemisorbed in the reference state and the final amount Γ chemisorbed at equilibrium. The reference state is always taken to be the neutral, uncharged surface, discussed in more detail below. If $\tilde{\Gamma}_i$ is the additional amount of ion X_i chemisorbed beyond that reference state, then the total chemisorption free energy for a given site s is

$$F_{cs}^s = \sum_i F_{cs}^i, \quad (14)$$

where

$$F_{cs}^i = \int_0^{\Gamma_i - \Gamma_i^0} d\tilde{\Gamma}_i \Delta F_{cs}^i(\tilde{\Gamma}_i). \quad (15)$$

1. Equilibrium with bulk

The incremental change in free energy $\Delta F_{cs}^i(\tilde{\Gamma}_i)$ is established by equilibrium with ions in bulk solution. Overall equilibrium is established when the change in free energy relative to bulk is zero, that is,

$$0 = \Delta F_i = \mu_{AX_i} - \mu_A - \mu_i^{bulk}. \quad (16)$$

This condition applies separately to both single and double equilibria. That is, in this context, A and AX_i represent either the bare site S^{q_s} and the singly associated site $SX_i^{q_s+q_i}$, or the single and doubly associated sites $SX_j^{q_s+q_i}$ and $SX_jX_i^{q_s+q_i+q_j}$ (where ion X_j is already bound). ΔF_{cs}^i is defined as

$$\Delta F_{cs}^i = \mu_{AX_i} - \mu_A - \bar{\mu}_i^{ps} \quad (17)$$

relative to the X_i ion in solution physisorbed at the surface (at the location of the site). Here, $\bar{\mu}_i^{ps}$ is the total physisorption free energy of the ion, that is, the chemical potential of the aqueous ion at the surface. But it is more convenient to write in terms of the excess chemical potential μ_i^{ps} relative to bulk, defining $\mu_i^{ps} = \bar{\mu}_i^{ps} - \mu_i^{bulk}$. Classically μ_i^{ps} refers to the electrostatic free energy of the ion in potential ψ, but in general, it also includes nonelectrostatic contributions such as ionic dispersion,[21,22,45] cavity free energy,[27,46] and volume exclusion entropy.[47] We might write $\mu_i^{ps} = q_i \psi + \mu_i^{NES}$. We then take $\Delta F_i = \Delta F_{cs}^i + \mu_i^{ps}$. The bulk equilibrium condition $\Delta F_i = 0$ then provides the

relation

$$\Delta F_{cs}^i = -\mu_i^{ps}. \tag{18}$$

We assume that this equilibrium condition holds at each charge transfer point $\tilde{\Gamma}_i$. That is, we assume the ionic diffuse layer is in equilibrium with bulk ions at each incremental surface charge state represented by $\tilde{\Gamma}_i$. This means μ_i^{ps} varies incrementally with $\tilde{\Gamma}_i$.

2. Chemisorption free energy via ion activities

We evaluate the chemisorption free energy Eq. (15) by applying the bulk equilibrium condition Eq. (18), obtaining an integral in $\int \mu_i^{ps} d\tilde{\Gamma}_i$. We do not in general know μ_i^{ps} as a function of $\tilde{\Gamma}_i$. But we do know the reverse, by way of the surface activity $a_i' = a_i^{\text{bulk}} \exp(-\mu_i^{ps}/kT)$ of the ion.

The chemisorption free energy in Eq. (15) (with Eq. (18)) may be transformed into an integral in $\int \tilde{\Gamma}_i d\mu_i^{ps'}$ (a Legendre transformation, $\int_0^{X_1} Y(X')dX' = X_1 Y(X_1) - \int_{Y(0)}^{Y(X_1)} X(Y')dY'$). But since $\mu_i^{ps'} = -kT \ln(a_i'/a_i^{\text{bulk}})$, we have $d\mu_i^{ps'} = -kT da_i'/a_i'$. The chemisorption free energy may be evaluated in the form

$$F_{cs}^i = -\mu_i^{ps}(\Gamma_i - \Gamma_i^0) - kT \int_{a_{i0}}^{a_i} \frac{\Gamma_i' - \Gamma_i^0}{a_i'} da_i'. \tag{19}$$

Γ_i' is the intermediate amount of X_i chemisorbed. That is Γ_i' is given by Eq. (13), replacing all a_i and a_j with intermediate values a_i' and a_j' (within the coefficient A_s also). The integration is made from the reference state where $a_j' = a_{j0}$ to the final state where $a_j' = a_j$. We represent the intermediate state by variable t from 0 to 1, such that each $a_j' = a_{j0} + t(a_j - a_{j0})$. Evaluation of the chemisorption free energy is therefore given finally by

$$F_{cs}^i = -\mu_i^{ps}(\Gamma_i - \Gamma_i^0) - kT\Gamma_i^0 \ln \frac{a_i}{a_{i0}} - kT(a_i - a_{i0})$$
$$\times \int_0^1 dt \frac{\Gamma_i'(t)}{a_{i0} + t(a_i - a_{i0})}. \tag{20}$$

Before proceeding with the integration from the reference to final state, it is convenient to consider the relationship between the physisorption contribution μ_i^{ps} and the total charge. As discussed above, we may split the physisorption free energy into electrostatic and nonelectrostatic components, $\mu_i^{ps} = q_i\psi_0 + \mu_i^{\text{NES}}$, where ψ_0 is the electrostatic surface potential at the site. But given the surface charge from Eq. (5), summing the leftmost physisorption term $F_{cs}^{[ps]} = -\sum_i \mu_i^{ps}(\Gamma_i - \Gamma_i^0)$ from Eq. (20) over all ions gives

$$F_{cs}^{[ps]} = -\psi_0(\sigma_s - \sigma_0) - \sum_i \mu_i^{\text{NES}}(\Gamma_i - \Gamma_i^0). \tag{21}$$

The electrostatic contribution (first term on the right) simplifies further by taking the neutral, uncharged surface, $\sigma_0 = 0$, as the reference state.

3. Reference state: Neutral uncharged surface

The reference state represented by Γ_i^0 and ion activity a_{i0} is the neutral uncharged surface, where $\sigma_s = 0$. When the surface site has zero charge $q_s = 0$, e.g., a basic site, then the reference state is the fully dissociated surface with $\Gamma_i^0 = 0$ and $a_{i0} = 0$ for all ions.

If, however, the bare surface site is charged ($q_s \neq 0$), then the reference state must be established by chemisorption of some ions, for which $\Gamma_i^0 \neq 0$. It is simplest to identify a specific "native" ion X_v, typically the hydrogen ion. More generally it could be possible to set the reference state with a mixture of chemisorbed (multiple ions for which $\Gamma_i^0 \neq 0$ but $\sigma_s^0 = 0$), but this would be a specialised situation requiring specific analysis.

Accepting a single reference ion X_v, the reference state may be treated as a single ion system where $\Gamma_i^0 = 0$ and $a_{i0} = 0$ for all other competing ions $i \neq v$. The general total surface charge in terms of all Γ_i is given by Eq. (5). The reference state with $\sigma_s = 0$ and Γ_v^0 from Eq. (13) provides a quadratic equation establishing the value of the reference activity a_{v0},

$$\frac{a_{v0}^2}{K_v K_{vv}}\left(2 + \frac{q_s}{q_v}\right) + \frac{a_{v0}}{K_v}\left(1 + \frac{q_s}{q_v}\right) + \frac{q_s}{q_v} = 0. \tag{22}$$

It is not constructive to write out the full solution for a_{v0} for general values of q_s. That general solution may however be interesting for particular surfaces. For instance, titania[48–50] iron oxide[50] and alumina[51,52] have been modelled with fractional site charges. The reference activity and ion chemisorption will have to be evaluated separately for specific surface models like these.

For the more common case where $q_s = -q_v$ (e.g., H^+ ions chemisorbing to oxide sites with charge -1), the reference activity is

$$a_{v0} = \sqrt{K_v K_{vv}} \quad \text{[for } q_s = -q_v]. \tag{23}$$

This establishes a finite reference activity for an amphoteric site which includes double association. It reduces to the case of an acidic site (single association only) where $K_{vv} = \infty$, yielding the acidic reference activity $a_{v0} = \infty$ (where $q_s = -q_v$).

The case of asymmetric charge ($q_s \neq -q_v$) may be evaluated for the case of an acid-like site with single association ($K_{vv} = \infty$),

$$a_{v0} = \frac{-K_v q_s/q_v}{1 + q_s/q_v} \quad \text{[for } K_{vv} = \infty]. \tag{24}$$

The corresponding amount of chemisorbed reference ion, calculated using Eq. (13), is given by the single expression

$$\Gamma_v^0 = -N_s \frac{q_s}{q_v}. \tag{25}$$

This expression for Γ_v^0 is valid for all cases except double association with asymmetric charge (i.e., $q_s \neq -q_v$ with $K_{vv} \neq 0$), for which we have not explicitly evaluated a_{v0}.

4. Total chemisorption free energy

With the amount of chemisorbed ion Γ_i and the reference activities a_{i0} determined, we can define the total chemisorption free energy. The free energy per site is

$$F_{cs} = F_{cs}^{el} + F_{cs}^{\text{NES}} + F_{cs}^{en} + F_{cs}^{\text{comp}}. \tag{26}$$

The initial term is the contribution due to electrostatic physisorption (first term in Eq. (21)),

$$F_{cs}^{el} = -\psi_0 \sigma_s,\qquad(27)$$

σ_s is the contribution from this site to the total surface charge and ψ_0 is the electrostatic surface potential.

F_{cs}^{NES} also refers to a physisorption contribution to the chemisorption free energy, the second term in Eq. (21). It arises from the nonelectrostatic physisorption component μ_i^{NES} in the excess chemical potential relative to bulk, of the ion in solution located at the surface,

$$F_{cs}^{NES} = -\sum_i \mu_i^{NES}\left(\Gamma_i - \Gamma_i^0\right)\qquad(28)$$

summing i over all competing ions. Under classical constant potential conditions (more precisely, constant chemical potential), F_{cs}^{NES} is the only contributing term[30] (alongside the electrostatic term of Eq. (27)). Under single-ion equilibrium conditions, $\Gamma_i - \Gamma_i^0 = \sigma/q_i$, and the nonelectrostatic physisorption component may be written as $F_{cs}^{NES} = -\mu_i^{NES}\sigma/q_i$. But this simplification cannot be made in the general case of competing ions.

F_{cs}^{en} is a site entropy contribution which arises due to the finite number of sites, N_s. More precisely, it is a contribution due to the entropy of fully dissociated sites,

$$F_{cs}^{en} = kTN_s \ln\frac{\gamma_s}{\gamma_0} + kT\sum_i \Gamma_i^0 \ln\frac{a_i}{a_{i0}},\qquad(29)$$

γ_s is the fraction of fully dissociated sites (Eq. (6)). γ_0 is the fraction of fully dissociated sites in the reference state. Recall that $\Gamma_i^0 = 0$ for all competing ions except the "native" ion which binds at the neutral reference state, for which in most cases $\Gamma_v^0 = -N_s q_s/q_v$ (see Eq. (25)). Hence the second term, due to the reference state (neutral, uncharged surface), is zero in the case where the site itself is uncharged ($q_s = 0$).

F_{cs}^{comp} arises due to competitive double-binding. That is, it is present only when multiple ions compete to bind doubly to site s (i.e., when K_{ij} is finite for more than one ion). F_{cs}^{comp} is small if competitive double binding is weak. This term is sufficiently complex that we give details separately in Sec. II B 5.

These expressions are valid for the general case of amphoteric ion site competition, including the complex case of amphoteric equilibrium of the reference ion with asymmetric charge, $q_s \neq q_v$, $K_{vv} \neq 0$, for which we have not explicitly evaluated a_{v0} and Γ_v^0.

5. General competitive amphoteric binding

If the surface site is nonamphoteric (all $K_{ij} = \infty$) or if only a single ion binds to the site (no ion site competition at all), then the competitive amphoteric (double binding) free energy term $F_{cs}^{comp} = 0$. F_{cs}^{comp} is also zero in the case of single ion amphotericity with competitive single binding, that is, where the reference ion may doubly bind with a finite K_{vv}, but where all other $K_{ij} = \infty$ (while multiple K_i are finite).

But for the general case of competitive double binding with multiple finite K_{ij}, F_{cs}^{comp} becomes nontrivial. It is convenient to split F_{cs}^{comp} into two parts,

$$F_{cs}^{comp} = F_{cs}^{comp-en} + F_{cs}^{two-bind},\qquad(30)$$

$F_{cs}^{comp-en}$ provides a correction to the site entropy term F_{cs}^{en}. $F_{cs}^{two-bind}$ is an entirely new term. $F_{cs}^{comp-en}$ and $F_{cs}^{two-bind}$ are typically both large in magnitude (as much as ten times the magnitude of F_{cs}^{en}) but with opposite signs. When competitive ion binding is weak (relative, say, to H^+ binding), then these two terms cancel such that F_{cs}^{comp} itself is small relative to the other chemisorption contributions.

The site entropy correction $F_{cs}^{comp-en}$ is given by

$$F_{cs}^{comp-en} = -kTN_s C \ln\frac{\gamma_s}{\gamma_0},\qquad(31)$$

with a site entropy correction coefficient,

$$C = 1 - \sum_i \frac{\Delta a_i\left[a_{i0}(A_2 B_1 - A_1 B_2) + \Delta a_i(A_0 B_2 - A_2 B_0)\right]}{2A_2 S_i}.\qquad(32)$$

Here, $\Delta a_i = a_i - a_{i0}$,

$$A_0 = 1 + \sum_m \frac{a_{m0}}{K_m}\left(1 + \sum_n \frac{a_{n0}}{K_{mn}}\right),\qquad(33)$$

$$A_1 = \sum_m\left[\frac{\Delta a_m}{K_m} + \frac{a_{m0}}{K_m}\sum_n \frac{\Delta a_n}{K_{mn}} + \frac{\Delta a_m}{K_m}\sum_n \frac{a_{n0}}{K_{mn}}\right],\qquad(34)$$

$$A_2 = \sum_m \frac{\Delta a_m}{K_m}\sum_n \frac{\Delta a_n}{K_{mn}};\qquad(35)$$

and

$$B_0 = a_{i0}\left(1 + \frac{a_{i0}}{K_{ii}} + \sum_m \frac{a_{m0}}{K_{im}}\right),\qquad(36)$$

$$B_1 = a_{i0}\left(\frac{\Delta a_i}{K_{ii}} + \sum_m \frac{\Delta a_m}{K_{im}}\right) + \Delta a_i\left(1 + \frac{a_{i0}}{K_{ii}} + \sum_m \frac{a_{m0}}{K_{im}}\right),\qquad(37)$$

$$B_2 = \Delta a_i\left(\frac{\Delta a_i}{K_{ii}} + \sum_m \frac{\Delta a_m}{K_{im}}\right),\qquad(38)$$

$$S_i = K_i\left(A_2 a_{i0}^2 + A_0 \Delta a_i^2 - A_1 a_{i0}\Delta a_i\right),\qquad(39)$$

A_0 is Eq. (11) taken with activities a_{m0} from the reference state, and therefore $\gamma_0 = 1/A_0$. Note that the total degree of association (Eq. (11)) is given by $A_s = A_0 + A_1 + A_2$.

The second competitive double-binding term is

$$F_{cs}^{two-bind} = kTN_s \frac{D}{R}\left[\arctan\left(\frac{A_1 + 2A_2}{R}\right) - \arctan\left(\frac{A_1}{R}\right)\right],\qquad(40)$$

where

$$D = \sum_i \frac{\Delta a_i}{A_2 S_i}\left\{A_0 A_1 B_2 \Delta a_i - A_1^2 B_2 a_{i0} - 2A_2^2 B_0 a_{i0}\right.$$
$$\left. + A_2\left[a_{i0}(A_1 B_1 + 2A_0 B_2) + \Delta a_i(A_1 B_0 - 2A_0 B_1)\right]\right\},\qquad(41)$$

with

$$R = \sqrt{4A_0 A_2 - A_1^2}.\qquad(42)$$

Due to the square root defining R, the terms in Eq. (40) are only real if $A_1^2 < 4A_0A_2$. This may be true in some cases, e.g., when K_v and K_{vv} are relatively close. But it is not true in general. When $A_1^2 > 4A_0A_2$, imaginary constants cancel in R and in the $\tan^{-1}$ terms (via the relation $\tan^{-1}(iX) = (i/2)\ln[(1+X)/(1-X)]$), to give the alternative real expression,

$$F_{cs}^{\text{two-bind}} = kTN_s\frac{D}{2\tilde{R}}\ln\left(\frac{2A_0 + A_1 + \tilde{R}}{2A_0 + A_1 - \tilde{R}}\right), \qquad (43)$$

where

$$\tilde{R} = \sqrt{A_1^2 - 4A_0A_2}. \qquad (44)$$

C. Special cases

1. Single ion, symmetric amphoteric site

In the case of a single ion X_v binding to an amphoteric site with symmetric charge $q_s = -q_v$, the site entropy correction coefficient C and the competitive double-binding coefficient D are both zero, so both $F_{cs}^{\text{comp-en}} = 0$ and $F_{cs}^{\text{two-bind}} = 0$. For this case $a_{v0} = \sqrt{K_vK_{vv}}$ (Eq. (23)) and $\Gamma_v^0 = N_s$, and the site surface charge is $\sigma_s = q_v(\Gamma_v - N_s)$. The total amphoteric chemisorption free energy then reduces to

$$F_{cs} = -\mu_v^{ps}\frac{\sigma}{q_v} - kTN_s\ln\left(1 + \frac{K_v}{a_v} + \frac{a_v}{K_{vv}}\right)$$
$$+ kTN_s\ln\left(1 + 2\sqrt{\frac{K_v}{K_{vv}}}\right). \qquad (45)$$

With appropriate algebraic manipulation, this equation equals the equivalent formula in Table 1 of Ref. 30 (after replacing the term $\ln(2K_-/H_s + 1)$ with $\ln(2H_s/K_+ + 1)$).[53] It also matches that obtained by Chan[54] after identifying Chan's $e\psi_0$ as μ_v^{ps} (such that $\psi_0/ekT = -\ln(a_v/a_b)$, with a_b being the bulk activity of the hydrogen ion, $a_b = 10^{-pH}$).

2. Nonamphoteric ion competition: No double binding

If the site is not amphoteric, with no double binding at all, then all $K_{ij} = \infty$. In this case the competitive double binding contribution to the chemisorption free energy in Eq. (26) is not present, that is, $F_{cs}^{\text{comp}} = 0$. The fraction of fully dissociated sites is $\gamma_s = 1/(1 + \sum_m a_m/K_m)$.

For a base-like site where $q_s = 0$, $\gamma_0 = 1$, and $\Gamma_i^0 = 0$; and the site-entropic free energy is

$$F_{cs}^{\text{en}} = -kTN_s\ln\left(1 + \sum_m\frac{a_m}{K_m}\right) \qquad [q_s = 0, \text{all } K_{ij} = \infty]. \qquad (46)$$

For an acid-like site with nonzero q_s, $\gamma_0 = 1/(1 + a_{v0}/K_v)$ (v representing the native ion which neutralises the surface in the reference state). The reference activity a_{v0} and reference binding Γ_v^0 are given by Eqs. (24) and (25). For the common acid case of symmetric charge $q_s = -q_v$ (where $a_{v0} = \infty$), the terms in a_{v0} cancel and the site-entropic free energy is

$$F_{cs}^{\text{en}} = kTN_s\ln\frac{a_v/K_v}{1 + \sum_m a_m/K_m}$$
$$[q_s = -q_v, \text{all } K_{ij} = \infty]. \qquad (47)$$

The final general nonamphoteric case takes $q_s \neq -q_v$, with $a_{v0} = -K_v(q_s/q_v)/(1 + q_s/q_v)$. The site-entropic free energy with all $K_{ij} = \infty$ can then be written as

$$F_{cs}^{\text{en}} = kTN_s\ln\frac{(a_v/K_v)^{-q_s/q_v}}{1 + \sum_m a_m/K_m}$$
$$- kTN_s\ln\frac{(a_{v0}/K_v)^{-q_s/q_v}}{1 + a_{v0}/K_v}. \qquad (48)$$

3. Competitive binding at an acidic site

A common application of the site competition model will be to model a cation (labelled M) competing with a hydrogen ion for a negatively charged site such as a carboxylate group or an oxide site. In this case, with $q_s = -q_H$, we add the site-entropy contribution from Eq. (47) to the contributions arising from electrostatic and nonelectrostatic physisorptions, Eqs. (27) and (28), to obtain the total chemisorption free energy for the acidic site,

$$F_{cs} = -\psi_0\sigma_s - \mu_M^{NES}\Gamma_M - \mu_H^{NES}\Gamma_H + \mu_H^{NES}N_s$$
$$+ kTN_s\ln\frac{a_H/K_H}{1 + a_M/K_M + a_H/K_H}, \qquad (49)$$

where, from Eq. (13),

$$\Gamma_M = \frac{N_s a_M/K_M}{1 + a_M/K_M + a_H/K_H} \qquad (50)$$

and

$$\Gamma_H = \frac{N_s a_H/K_H}{1 + a_M/K_M + a_H/K_H}. \qquad (51)$$

D. Disjoining pressure

The total interaction free energy addressed above is sufficient for calculating surface forces. In general, the interaction free energy could be calculated for an arbitrarily complex surface geometry, for instance with a 3D solution to the Poisson-Boltzmann equation. The corresponding force is then computed by differentiation with respect to separation L between surfaces, $f = -dF/dL$.

In practice it is common to calculate the interaction energy between flat surfaces and then convert to an experimentally relevant force between curved surfaces by applying the Derjaguin approximation. For instance, AFM measures the force between a sphere and plane. The surface forces apparatus (SFA) measures the force between two crossed cylinders. The Derjaguin approximation provides a theoretical estimate of the force in both these curved geometries, using the interaction free energy between two flat surfaces.

Nevertheless, it is common in theoretical analyses to directly calculate the disjoining pressure $P = -dF/dL$ (Eq. (1)) rather than the interaction free energy F. When F is the interaction energy between two flat surfaces, then the disjoining pressure is the force between those flat surfaces, distinct from the force between curved surfaces measured by AFM or SFA. The disjoining pressure can only be converted (by way of the Derjaguin approximation) into a force between curved bodies by first integrating into an interaction free

energy. Both methods of calculation can be useful, for instance to validate the numerical correctness of the calculated force.

In the case of single ion charge regulation,[30] the site entropic contribution (from F_{cs}^{en}) to the total chemisorption disjoining pressure was found to partially cancel against the physisorption component (due to F_{cs}^{el} and F_{cs}^{NES}), such that the chemisorption disjoining pressure reduced to $P_{cs} = \psi\, d\sigma/dL + (\mu^{NES}/q)d\sigma/dL$, where q was the charge of the (single) ion. The classic disjoining pressure of Eq. (1) is obtained by cancellation of $\psi\, d\sigma/dL$ when nonelectrostatic physisorption is neglected (i.e., when $\mu^{NES} = 0$).

Under nonamphoteric ion competition (i.e., with no competitive double binding), this cancellation of terms still applies, except that the nonelectrostatic component cannot be reduced down to a single term in the site charge σ_s. That is, the disjoining pressure per site due to competitive chemisorption (with $K_{ij} = \infty$ when $i \neq j$) is

$$P_{cs} = \psi\frac{d\sigma_s}{dL} + \sum_i \mu_i^{NES}\frac{d\Gamma_i}{dL} \qquad (52)$$

replacing $\mu^{NES}d\sigma/dL$ with a sum over $\mu_i^{NES}d\Gamma_i/dL$. This expression is valid for all cases with no competitive double binding, where crossed double binding does not take place. That is, it is valid for multiple amphoteric binding (multiple finite K_{ii}, but $K_{ij} = \infty$ for $i \neq j$) and of course with competitive single binding (multiple K_i).

In the more general case of competitive double binding, some K_{ij} may be finite (e.g., an anion binding to a protonated site) and F_{cs}^{comp} is nontrivial. The explicit evaluation of the disjoining pressure in this case is formidable due to the complexity of the algebra. But the invalidity of Eq. (52) for the general case may be evaluated numerically. Calculation of the free energy directly from Eq. (26), compared against numerical integration of the pressure from Eq. (52), confirms that in the general case additional terms due to F_{cs}^{comp} (and F_{cs}^{en}) do need to be added to the disjoining pressure. If the classic disjoining pressure of Eq. (1), $P = \sum_i c_i(L/2) - c_{i0}$, is used under conditions of competitive double binding, then the calculated disjoining pressure will simply be wrong.

The requirement to use numerical derivatives to calculate the full disjoining pressure provides a significant argument in favour of calculating interaction free energies (and therefore surface forces) directly rather than indirectly via the disjoining pressure. In the most general case, the disjoining pressure corresponding to F_{cs}^{comp} is simply not available, except by numerical differentiation of the interaction free energy. But this is the very quantity that the disjoining pressure is used to calculate! Furthermore, even where an expression for the terms in the disjoining pressure is in principle available, for instance Eq. (52), it may require derivatives such as $d\Gamma_i/dL$ which are only available numerically. In general it is more precise, and more convenient, to calculate the interaction free energies directly rather than to calculate such numerical derivatives for the disjoining pressure.

III. ILLUSTRATIVE CALCULATIONS

A. Titania surface

An ion competition model was formulated by Sprycha to analyse the surface charge of a titania (anatase) sur-
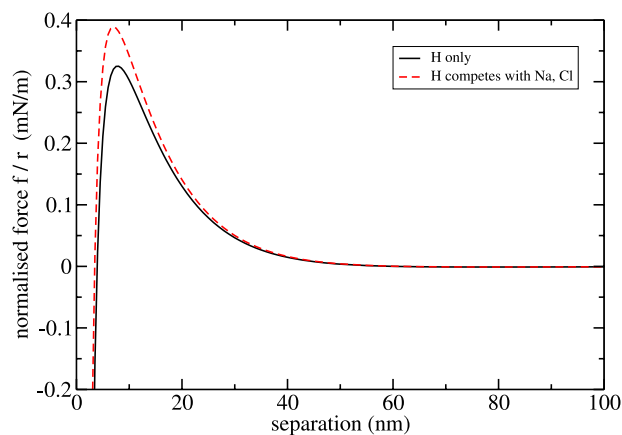

FIG. 2. Calculated force curves between titania surfaces at pH 7 in 1 mM NaCl. The solid black curve shows charge regulation with H^+ only (no ion competition); the dashed red curve includes ion site competition with Na^+ and Cl^- ions.

face.[40] Sprycha's model added Na^+ single binding ($pK_{Na} = -3.1$) and Cl^- double-binding (binding to a protonated site, $pK_{HCl} = -3.1$) onto a standard amphoteric site ($pK_H = 3.1$, $pK_{HH} = 3.1$). The site density was $N_s = 0.1198$ sites per $Å^2$. In order to focus on the impact of competitive site-binding, we here neglect general nonelectrostatic physisorption, taking $\mu_i^{NES} = 0$. The Hamaker constant for the van der Waals component of the total force was taken as $A = 14.69$ kT, calculated by nonretarded Lifschitz theory[55] using Bergström's average dielectric function of titania[55] and Dagastine's dielectric function for water[56] at 298 K.

We evaluated the ion concentration profiles of the ionic diffuse layer (due to physisorption) using a numerical solution to the 1-D nonlinear Poisson-Boltzmann equation between two flat surfaces, applying a charge-regulated boundary condition (Eq. (2) with Eq. (5)). We computed the total interaction free energy between two flat surfaces and converted to a force between curved surfaces using the Derjaguin approximation.

Calculated force curves at pH 7 in low salt (1 mM NaCl) are shown in Fig. 2, comparing the calculation with full ion competition (Na^+ and Cl^-) against the more conventional calculation with only H^+ charge regulation (same pK_H and pK_{HH} for both calculations). Ion site competition introduces a 20% increase in the height of the repulsive peak. The precise cause of the difference in forces cannot be ascribed to any single component. Decompositions of both forces, with and without ion competition, are shown in Fig. 3. With ion competition included, both the direct (ionic) electrostatic and chemisorption electrostatic (Eq. (27)) components become broadly more repulsive (or less attractive), while the ionic entropic component becomes less repulsive. The chemisorption site-entropic changes dramatically, losing its attractive quality, but only at very short separations less than 5 nm. We broadly interpret the change in force curve seen in Fig. 2 as simply a consequence of the shift in surface charge due to ion site competition.

The force curves calculated in high salt (0.1M NaCl) are shown in Fig. 4, compared against the van der Waals (Hamaker) force. On the face of it, the high salt behaviour, interpreted through conventional DLVO-style thinking, does
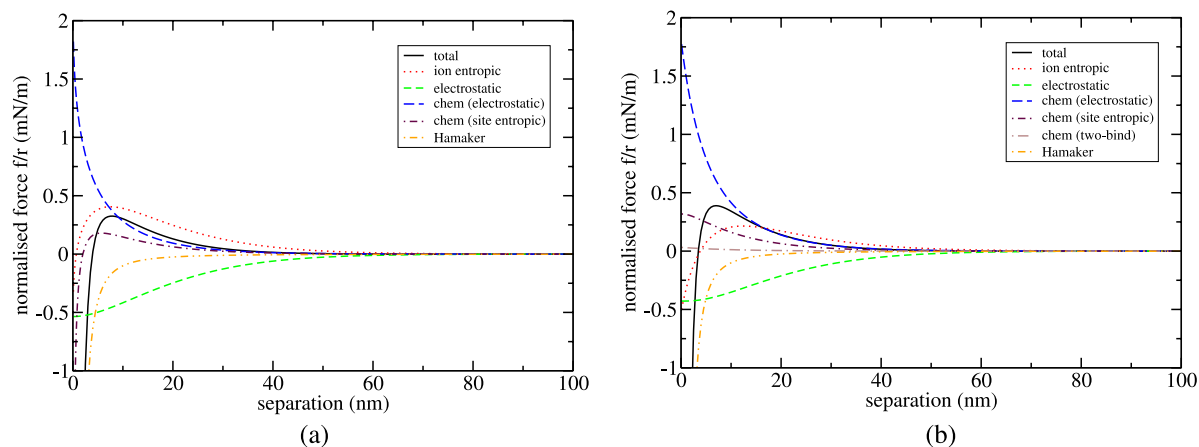
FIG. 3. Components of calculated force curves between titania surfaces at pH 7 in 1 mM NaCl. (a) Charge regulation with H$^+$ only (no ion competition). (b) Charge regulation with ion competition from Na$^+$ and Cl$^-$ ions. "Chem (electrostatic)" refers to F_{cs}^{el}, Eq. (27), "chem (site entropy)" is F_{cs}^{en}, Eq. (29), "chem (two-bind)" is $F_{cs}^{two-bind}$, Eq. (43).

not seem interesting. High electrostatic screening means electrostatic (ionic) contributions to the total force are attenuated, leaving only the van der Waals attractive force. Consequently no effect due to ion competition would be expected and is not seen in Fig. 4. The breakdown of the force into components, Fig. 5, tells a more subtle story. In the absence of ion competition, repulsion due to hydrogen charge regulation arises dominantly from chemisorption site entropy. But its magnitude is not sufficient to oppose van der Waals attraction. Under ion competition, however, the chemisorption site entropic contribution F_{cs}^{en}, Eq. (29), becomes attractive. Repulsion is dominated by the competitive double-binding term $F_{cs}^{two-bind}$ from Eq. (43). The magnitude of both terms is comparable to the van der Waals force. But because of the difference in sign, the chemisorption terms F_{cs}^{en} and $F_{cs}^{two-bind}$ largely cancel, allowing van der Waals attraction to remain dominant.

Comparison of Fig. 2 against Fig. 4 suggests that in some cases the impact of ion site competition is more likely to be felt at low salt concentrations rather than high salt. But ion site competition is determined by ion-specific binding
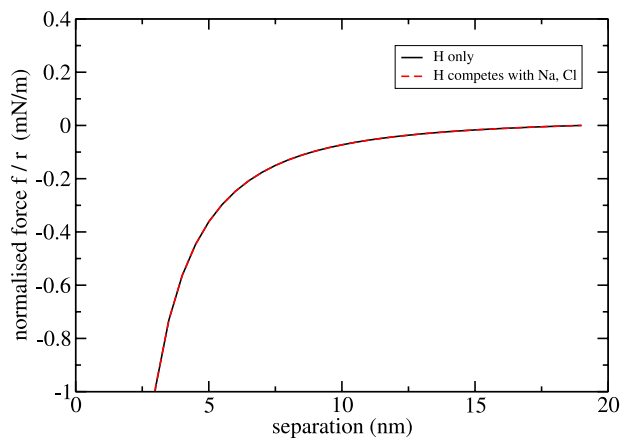
constants. It follows that ion site competition may help explain the relatively rare observations of Hofmeister series at low concentrations.[57–59] Hofmeister effects are more commonly observed in high salt conditions above 0.1M.

B. Silica surface

Ion specificity in surface forces between silica surfaces in various chloride salt solutions has been measured by Chapel,[42] following earlier measurements of silica in NaCl solution by Grabbe and Horn.[41] Chapel interprets his measured force curve in terms of competitive adsorption between H$^+$ and metal ions at surface oxide sites (no double binding), with 50 Å^2 area per site. From Chapel's estimates of the surface potentials of isolated surfaces, the corresponding surface charge may be evaluated by a nonlinear Poisson-Boltzmann calculation (with constant potential). A least-squares fit comparing these surface charges at different NaCl concentrations with the regulated surface charge from Eq. (5) allows us to estimate the silica dissociation constants, pK_H = 5.378 and pK_{Na} = 0.491. Note that these estimates differ significantly from Chapel's own evaluation, pK_H = 6.35 and pK_{Na} = 3.25. Chapel's binding constants generate a charge regulated surface potential (of the isolated surfaces) of only −2 mV in 0.1M NaCl at pH 5.5, an order of magnitude different from his constant potential estimate of −45 mV. The reason for the discrepancy may be understood by considering Chapel's large coefficient for sodium binding, pK_{Na} = 3.25, which is six orders of magnitude greater than Sprycha's sodium binding constant to titania. Consequently at high NaCl concentrations (0.1M), Chapel's constant results in a discrepantly large amount of Na$^+$ binding to silica oxide sites, effectively neutralising the entire surface. We suspect that Chapel's fitting procedure may have caught the binding constants in a local minimum, missing the values which we have found. Our dissociation constants generate an isolated surface potential of −48.3 mV in 0.1M NaCl at pH 5.5, close to Chapel's constant potential value of −45 mV. As for titania, we here neglect general nonelectrostatic physisorption ($\mu_i^{NES} = 0$) in order to focus purely on the impact of competitive site-binding.
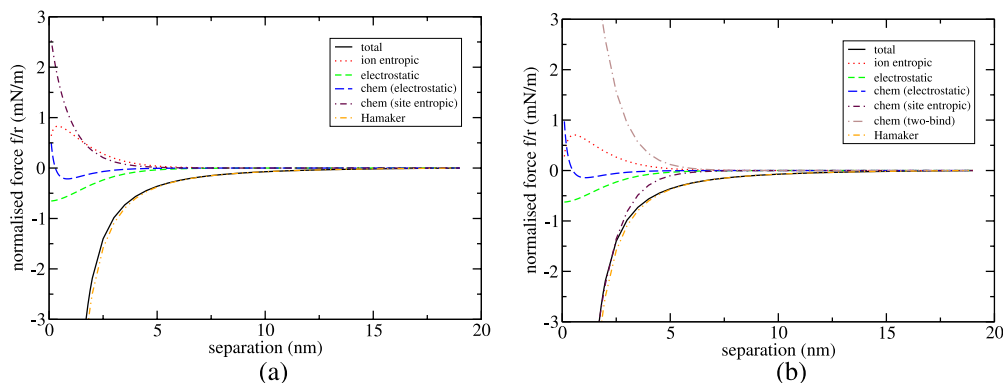

FIG. 4. Calculated force curves between titania surfaces at pH 7 in 0.1M NaCl. The solid black curve shows charge regulation with H$^+$ only (no ion competition); the dashed red curve includes ion site competition with Na$^+$ and Cl$^-$ ions.

FIG. 5. Components of calculated force curves between titania surfaces at pH 7 in 0.1M NaCl. (a) Charge regulation with H^+ only (no ion competition). (b) Charge regulation with ion competition from Na^+ and Cl^- ions. "Chem (electrostatic)" refers to F_{cs}^{el}, Eq. (27), "chem (site entropy)" is F_{cs}^{en}, Eq. (29), "chem (two-bind)" is $F_{cs}^{two-bind}$, Eq. (43).
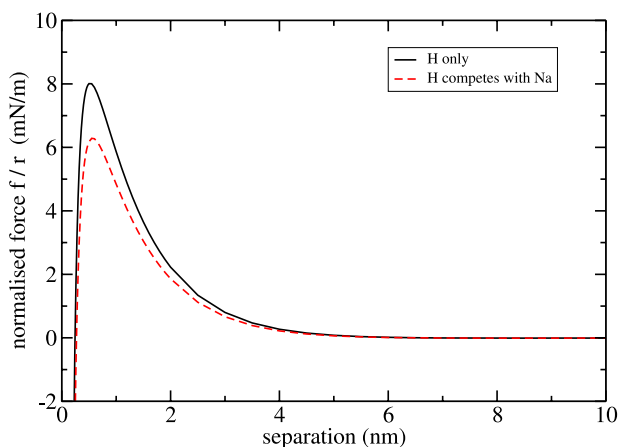

FIG. 6. Calculated force curves between silica surfaces at pH 5.5 in 0.1M NaCl. The solid black curve shows charge regulation with H^+ only (no ion competition); the dashed red curve includes ion site competition with Na^+ and Cl^- ions.

The effect of ion site competition on the force between silica surfaces is illustrated in Fig. 6, showing the force curve in 0.1M NaCl at pH 5.5 with and without Na^+ binding competing with the main H^+ binding. The Hamaker constant for the van der Waals component of the total force was taken as $A = 1.448\ kT$, calculated by nonretarded Lifschitz theory using Grabbe's dielectric function for silica[60] and Dagastine's dielectric function for water[56] at 298 K. The effect of ion site competition is strong on silica, with the repulsive peak suppressed by 2 mN/m, or about 25%. The additional binding of Na^+ on top of H^+ binding results in a reduction in the total surface charge, reducing the degree of entropic repulsion caused by formation of the ionic diffuse layer.

IV. CONCLUSION

We have derived the contribution to the total free energy (and hence to surface forces) arising due to competitive adsorption of ions to sites on a surface. The theory covers both competitive single ion binding (e.g., acidic or basic sites) and competitive double binding (e.g., amphoteric sites).

The theory provides a more general expression for the chemisorption free energy and surface force (disjoining pressure) developed previously[30] for single ion binding. It

also introduces a entirely new term arising from competitive double binding.

The significance of ion site competition depends on the strength of the competitive ion binding constants compared to the binding constants of the hydrogen ion. Compared to calculations neglecting ion site competition, a 20% increase is predicted in the repulsive peak of the surface force between two titania surfaces in 1 mM NaCl at pH 7. But the impact of ion site competition on titania surfaces is negligible in 0.1M NaCl at pH 7, suggesting that ion site competition may play a role in low concentration Hofmeister effects. By contrast, a 25% decrease in repulsion is found between silica surfaces in 0.1M NaCl at pH 5.5.

ACKNOWLEDGMENTS

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