CI⁻ ADSORPTION ON AN Al₂O₃ SURFACE IN AN ELECTROLYTE

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CI- ADSORPTION ON AN Al2O3 SURFACE IN AN ELECTROLYTE

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ABSTRACT

We present a method for calculating the minimum energy configurations of atomic and molecular species adsorbing on defected solid surfaces in the presence of an electrolyte. The method couples a quantum region containing the adsorbing atom or molecule and neighboring lattice atoms to a continuum which may contain a real charge. A "molecular" surface surrounds the quantum zone, discretized into boundary elements facilitating the coupling of the Schrödinger and Poisson equations. The interfacial polarization created by the electrons in this zone, (from the Poisson equation using Green's functions) is incorporated into the Hamiltonian providing a reaction field for the next iteration quantum calculation. Lattice defects induce single and double layers of charge at the interface, treated as additional background charges in the Hamiltonian. We find that these polarization effects can reduce the binding energy of the Cl- and that a charged defect can displace the minimum and well depth of an adsorbing Cl-.
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I. INTRODUCTION

Adsorption of ions on mineral surfaces is important to a number of technologies, including soil-surface geochemical cycling, corrosion, waste isolation and environmental restoration (1). The initiation of pitting of aluminum in water vapor and chlorine environments has been associated with the adsorption of chloride ions on the surface of oxidized aluminum (2, 3). The chemistry of the adsorption process is related to the issue of the dissolution of glass in aqueous environments: It is found that doping with elements which can introduce charged defects in the near-surface region has a profound effect on the glass dissolution rate (4), presumably because the charges influence the chemistry of the interaction of the glass surface with water.

Although kinetic models have been successfully applied to these problems, the details of the energetics of such processes and the surface lattice location of the impinging ion remain unknown. In this paper, a coupled quantum-continuum method is presented which enables a major effect is quantified: the influence of the polarization due to the surrounding lattice and electrolyte on the electronic relaxations of the reacting species. Such molecular solvation investigations, predominantly in the computational biology community, have been extensively reviewed by Tomasi and Persico (5). Here we also include the effect on the electron distribution of the electric field of charges (vacancies and interstitials) in the continuum, thereby building upon our recently developed single- and double-layer coupled Schrödinger-Poisson Boltzmann method (6).

The Cl$^{-}$ ion interacts chemically with neighboring ions in the electrolyte and in the solid lattice; that is, there is a redistribution of electrons in the neighboring environment which can only be understood quantum mechanically. Beyond this region, polarization and atomic rearrangement effects may influence the behavior of Cl$^{-}$, effects which may be treated by atomic and continuum methods. Here, we surround the Cl$^{-}$ and its immediate neighbor Al and O atoms with a virtual molecular surface (see Fig. 1), a two-dimensional interface which encapsulates the quantum region, separating it from a polarizable dielectric continuum. From this point of view, Poisson's equation is satisfied in the quantum region and Laplace's equation applies in the surrounding continuum. The surface is discretized into boundary elements to facilitate the solution of these equations for the polarization of that interface. Elements of the continuum appropriately interface to the dielectric constant of the lattice or to the electrolyte as shown in Fig. 1.

Vacancies and charged interstitial ions in the surrounding lattice, that is, charges in the dielectric medium, create an additional electrostatic potential within the quantum region. From this "inverted" point of view, the continuum lattice region satisfies the Poisson equation and the inner quantum zone the Laplace equation. The electrostatic potential in the inner zone due to the lattice charges is reflected through the surface charges they induce at the molecular-continuum interface.
In this way, one contribution to the electrostatic potential in the quantum zone comes from the reaction field produced by the internal charge distribution itself. A second contribution comes from the surface charge at the interface induced by the charges in the dielectric continuum. Accurate calculations require coupling the solutions of the Schrödinger equation in the presence of induced surface charges obtained by solving Poisson's equation using the correct electronic charge distribution.

A simple model presented in Section II provides an estimate of the magnitude of the effects and a means of validating the boundary element calculations. An iterative method to couple Poisson and quantum calculations is presented in Section III. Section IV contains the results and discussion.

II. MODEL CALCULATIONS: ESTIMATES AND VALIDATION

At a very rudimentary level of approximation, the Cl⁻ ion can be viewed as a point charge in a spherical cavity (the quantum zone) surrounded by a dielectric medium. The electrostatic potential at a point (e.g., a vacancy or interstitial site) outside such a cavity can be obtained analytically. At the same primitive level, the Cl⁻ ion inside the cavity experiences a potential due to a point charge (e.g., a vacancy) outside, an electrostatic problem solvable by the same analytic methods. The simple model provides a means for estimation of the effects and for validation of the more complex Poisson calculations to follow.

In Fig. 2, a spherical cavity is sketched surrounded by a dielectric continuum. The cavity either contains a unit point charge or is empty with an external point charge placed at z₁ along the z axis. The potential inside and outside the sphere is expanded in Legendre polynomials and the coefficients in the expansion determined by matching the value of the potential and normal component of the electric field at the sphere surface. Using this method, the electrostatic potential, ϕₙ, at a point p at distance r from the origin inside a spherical dielectric medium of radius R₀ containing a unit point charge Qₙ at distance z₁ from the origin (z₁ < R₀) is found to be (7, 8),

\[ \phiₙ = \frac{Qₙ}{\epsilon₁r} \sum_{n=0}^{∞} \left( \frac{z₁}{r} \right)^n Pₙ(\cos \vartheta) + \frac{Qₙ}{\epsilon₁R₀} \sum_{n=0}^{∞} \frac{(n+1)(1-\epsilon)}{(n+1)\epsilon + n} \left( \frac{z₁r}{R₀} \right)^n Pₙ(\cos \vartheta) \]  \[1\]

where \( \epsilon₁ \) is the dielectric constant within the sphere and \( \epsilon₂ \) the dielectric constant of the region surrounding it; \( \epsilon = \epsilon₂ / \epsilon₁ \). In Eq.1, \( \vartheta \) is the angle between the z axis and the vector r to the point p (r = |r|) and the \( Pₙ \)'s are the Legendre polynomials.
Similarly, the electrostatic potential at a point p outside this same sphere is given by,

\[ \phi_{\text{out}} = \frac{Q_{\text{in}}}{\varepsilon_1 r} \sum_{n=0}^{\infty} \frac{2n+1}{(n+1)\varepsilon + n} \left( \frac{z_1}{r} \right)^n P_n(\cos \theta) \]  

[2]

In Fig. 3, we have plotted the reaction electrostatic potential at the position of the internal charge using Eq.1 with \( r = z_1 \). The radius, \( R_0 \), of the sphere was chosen to be that for a Cl\(^-\) ion in a solid (15), i.e., \( R_0 = 3.0387 \) Bohrs (1.608 Å). The reaction potential is seen to be a large effect, due entirely to the polarization of the boundary by the internal charge. The effect is clearly greater for large discontinuities in dielectric constant (i.e., \( \varepsilon_2 = 10 \)). The difference in potential for a point charge at the origin and at 1.5 Bohrs from the origin (see Fig. 3) is \( \sim 0.04 \) a.u. (\( \sim 25 \) kcal/mole) and \( \sim 0.09 \) a.u. (\( \sim 56 \) kcal/mole) for \( \varepsilon_2 = 2 \) and \( \varepsilon_2 = 10 \), respectively, for this choice of \( R_0 \). Alumina has a dielectric constant of \( \sim 9.34 \) (9). The effect, due to polarization of the boundary by the internal charge, occurs independently of the existence of an external charge. Fig. 3 also provides a comparison with the numerical methods to be described later.

The potential experienced by an internal unit test charge due to an external charge can also be solved for analytically by the same methods. The electrostatic potential, \( \overline{\phi}_{\text{in}} \), at a point p inside a spherical dielectric medium of radius \( R_0 \) produced by a unit point charge \( Q \) at distance \( z_1 \) from the origin (\( z_1 > R_0 \)) is given by

\[ \overline{\phi}_{\text{in}} = \frac{Q_{\text{out}}}{\varepsilon_1 z_1} \sum_{n=0}^{\infty} \frac{2n+1}{(n+1)\varepsilon + n} \left( \frac{r}{z_1} \right)^n P_n(\cos \theta) \]  

[3]

where the definitions of variables given for Eqs 1 and 2 above apply. Note that the potential outside due a charge inside (Eq 2) can be obtained from the expression for the potential inside due to a charge outside (Eq. 3) by interchanging \( r \) and \( z_1 \).

In Fig. 4 we have plotted the electrostatic potential (Eq. 2) at \( r = Z \) inside the spherical cavity created by a unit external charge at \( z_1 = 10 \) Bohrs alone (no reaction potential). Here the larger dielectric discontinuity (\( \varepsilon_2 = 10 \) compared to \( \varepsilon_2 = 2 \)) results in greater screening of the potential due to the external charge. The difference in potential at the unit test charge at \( z_1 = -1.5 \) Bohrs and \( z_1 = +1.5 \) Bohrs (with a unit point charge at 10 Bohrs outside the sphere) is \( \sim 0.025 \) a.u. (\( \sim 16 \) kcal/mole) for \( \varepsilon_2 = 2 \) and \( \sim 0.004 \) a.u. (\( \sim 2.5 \) kcal/mole) for \( \varepsilon_2 = 10 \), respectively. It is to be noted that the values plotted in Figs 3 and 4 pertain to unit point charges and will scale directly with the actual charge (i.e., Al is trivalent in Al\(_2\)O\(_3\)). The numerical method is found to be in quite reasonable agreement with the
analytic solutions, the disagreement increasing, not unexpectedly, as the boundary is
approached. We made similar comparison calculations moving the test charge at various
angles with the z axis, again finding reasonable agreement.

Fig. 4 provides us a means of anticipating the effect of the dielectric constant on the
potential experienced by a Cl⁻ ion in such a cavity due to an external charge (lattice
defect). For \( \varepsilon_2 = 2 \), there is a strong repulsion as the Cl⁻ ion approaches the charge (at
\( Z = 10 \)); for \( \varepsilon_2 = 10 \), the potential is significantly screened out.

The electrostatic potential at a point \( p \) outside this same empty sphere is given by,

\[
\bar{\phi}_{out} = \frac{Q_{out}}{\varepsilon_1 \varepsilon_2} \sum_{n=0}^{\infty} \left( \frac{r}{z_1} \right)^n P_n(\cos \theta) + \frac{Q_{out}}{\varepsilon_1 \varepsilon_2} \left( \varepsilon_2 - \varepsilon_1 \right) \sum_{n=0}^{\infty} \left[ \frac{n}{(n+1)\varepsilon + n} \right] \frac{R_0^{2n+1}}{Z_1^{n+1}} \frac{P_n(\cos \theta)}{r^{n+1}} \]  

[4]

Here, our interest is in the effect of a fixed external charge on the potential inside a
boundary. Although the discretization of the boundary changes in accordance with the
position of the Cl⁻ ion, the potential at \( r = z_1 \) (Eq. 4) is otherwise a constant.

These model calculations show that quite large energy differences ranging from a few
to tens of kcals/mole can be associated with the configuration of an ion both from reaction
fields and due to the presence of an external charge, the screening of the dielectric interface
having a critical quantitative effect. More complex calculations are required to better
quantify the effect.

III. METHOD OF CALCULATION

As discussed above, the Cl⁻ ion, together with its nearest neighbor Al⁺³ and O⁻² ions
are enclosed within a discretized molecular surface, forming a large "molecule". (We chose
a neutral configuration of Al₂nO₃n to complex with the Cl⁻.) Many methods exist for the
construction of this type of surface (10,11); the method used here is from ref (12).
Briefly, the surface is formed by slicing the molecule into (imaginary) planes along one
axis. An imaginary "solvent" ball is then rolled over (i.e., completely around) each plane
forming surface "dots" or nodes. Triangles are then formed by interconnecting the dots
and areas and normals are then associated with the dots. The number of planes, the
solvent ball radius, and the number of pieces the ball is divided into may then be varied to
obtain more or fewer dots and hence, presumably, greater resolution. Here, we allow the
surface to "follow" the motion of the Cl atom; a new surface is generated at each Cl
position. (Hence, a slightly different number of surface nodes is employed for each
position of the Cl; ~800 nodes is typical). The method differs in this regard from the approximation of Section II wherein a charge is moved in a fixed sphere.

Surface charges induced (and electrostatic potentials) on the boundary elements due to the electronic charge distribution of the (ClAl_{2n}O_{3n})^{1} cluster are obtained by the method of ref.(6). The potential, \( \phi_i(x) \), at a general point inside boundary \( i \) can be represented as

\[
\phi_i(x) = \int \frac{G\rho_i}{\varepsilon_i} dV_i + \frac{1}{4\pi \varepsilon_i} \sum_{k=1}^{N_b} \left[ \frac{G\phi_k}{\partial n_i} - \phi_i^s \frac{\partial G}{\partial n_i} \right] dS_k
\]

and in the solvent region by,

\[
\phi_i(x) = \frac{1}{4\pi} \sum_{k=1}^{N_b} \left[ -P \frac{\partial \phi_k}{\partial n_k} + \phi_i^s \frac{\partial P}{\partial n_k} \right] dS_k
\]

In the above, \( G \) is the Green's function for the Poisson Equation, \( P = G \exp(-\kappa r) \), \( \kappa \) is the inverse debye length (taken to be zero here); \( N_b \) is the number of boundaries (here=1); \( \varepsilon_i \) is the dielectric constant of region \( i \); \( \phi_i^s \) is the surface potential (\( \phi_i^s = \phi_k^s \) for \( k=i \)); \( \rho_i \) is the real charge distribution within \( i \). This distribution is often represented as fixed point charges; here we use the quantum-mechanically-derived electronic charge distribution (GAMESS, 13) as the inner source of real charge. This is a significant fundamental difference in that electronic relaxations due to the boundary charges are included. An advantage of the Green's function approach is that the electrostatic potential and electric field at any point inside a boundary is determined by the surface charges on that boundary. After some manipulation, a system of coupled linear equations is found for the surface potential and surface charge density on each element of a boundary. Solution of this system by the usual methods of linear algebra allows us to then use Eqs. (5) and (6) to obtain the potential everywhere. External charges may superimpose surface charge, all the coupling being made at the interface.

It is to be noted, however, that when electrostatic potential inside the boundary (the quantum zone) due to external charge(s) is to be derived from induced surface charges alone, both the single and double layers of charge (6) must be included. That is, the background charges in the Hamiltonian consist of hundreds of elemental charges in single and double layer configurations.

The calculation proceeds iteratively by first solving the Schrödinger equation for the electronic charge distribution and energy of the (ClAl_{2n}O_{3n})^{1} cluster along with the quantum-mechanically-derived electric field at the nodes of the boundary elements due this distribution (step 1). Poisson's equation is then solved for the region inside the
quantum zone and Laplace's equation outside to obtain induced surface charges on the boundary elements (step 2). The potential at any point outside (in the continuum region) is then easily obtained (Eq. 6). Next, the continuum region is viewed as a Poisson zone containing external charge(s) with the quantum zone satisfying Laplace's equation. The induced polarization charges on the boundary elements due to these external charges is then superimposed upon those already obtained in step 2. The total background charges (of order ~800 in number) are then added to the Hamiltonian, completing the first iteration (step 3).

In the next iteration, step 1 is repeated to again obtain the quantum electronic distribution, resulting in a new energy and updated set of electric fields at the boundary elements. Poisson's equation (step 2) is then solved to provide an updated set of induced surface charges due to the inner zone and then solved once again (step 3) with the outer zone the Poisson region. Again, the induced surface charges are added to the Hamiltonian. The calculation is iterated until the RHF energy of the quantum zone at iteration N is within ~0.0005 a. u. of that found at iteration N-1. We found, in practice, that only a few such iterations (3-5) are required to achieve convergence. Of course, the quantum self-consistent-field calculation has its own iterative solution, which we allow to converge at each of our coupled quantum-Poisson iterations.

In this way, we include the effect of the reaction potential (see Fig. 3) of the boundary on the quantum region using its own (quantum chemical) source of real charge. The total charge enclosed within the boundary is reflective of the accuracy of the wave functions employed. Here, we generally employ 6-31G functions; minimal basis set STO3G functions were also employed for comparison purposes. We normalize the charge enclosed (calculated to be ~0.88e) to the known (-1e) result. The polarization of the surface by an external charge(s) is included in the quantum calculation by also adding its induced single and double layers of surface charge in the Hamiltonian.

IV. RESULTS AND DISCUSSION

In Fig. 5, we plot the energy of a (ClAI4O6)⁻¹ cluster using a minimum basis set as a function of the distance of the Cl along the z-axis (see Fig.1) normal to the plane described by three Al atoms forming the z=0 plane. In these calculations, the dielectric constant at boundary elements outside the quantum cluster at or above the z=0 plane was taken to be ε₁=78.5 (water) whereas below the z=0 plane the dielectric constant, ε₂, was chosen to be 2 or 10, as indicated in the figure. The zero of energy for the Cl⁻ at an infinite distance from the surface (for other than the vacuum case) was taken to be the solvated (Born) energy. The bare (ClAI4O6)⁻¹ molecule has a minimum at z~3 Bohrs from the surface and a binding energy of ~ -0.12 a. u. for this initial set of wavefunctions. When a polarizable interface is introduced (no external charge: Q=0), this binding is decreased by ~0.01 a. u.
(−6 kca/mol) while the minimum is only slightly effected; the Cl− energetically prefers to be surrounded with the higher dielectric constant medium, water, than with that of the lattice. The reduction is greater for the lower dielectric medium (es2=2) than for es2=10, consistent with the increased disparity in induced polarization.

When a external lattice charge \((Q = -3e)\) is introduced (at \((x,y,z) = (0,0,-10)\) Bohrs), the binding energy is further reduced (to \(\sim -0.04\) a. u. for es2=2) and the position of the minimum displaced away from the charge. Here a dramatic dependence on the dielectric constant, es2, of the lattice (continuum) is seen (Fig. 5). A large dielectric constant serves to screen the charge from the inner cluster and hence reduce its effect. This is consistent with the suggestion of the primitive spherical model (Fig. 4).

In Fig. 6, the energy of a \((\text{ClAl}_4\text{O}_6)^{-1}\) cluster using 6-31G wavefunctions is plotted. The essential features of the minimum basis set results (Fig.5) remain, but there are, not unexpectedly, numerical differences. The bare molecule (vacuum) binding energy is found to be \(\sim -0.07\) a. u. with the Cl minimum at \(z \sim -4.2\) Bohrs. The reaction field alone (\(Q = 0\)) reduces the binding energy in much the same way as for the minimum basis set calculations and has little effect on the position of the minimum. The introduction of the external charge (\(Q = -3e\)) again exhibits a strong dielectric constant dependence, reducing the binding energy for es2=2 to \(\sim -0.02\) a. u. and displacing the minimum to \(\sim -5.5\) Bohrs.

In the development of this method, we have focused on the possible effect of an external charge on the minimum energy configuration of a Cl− ion impinging on the surface of Al2O3. We find that a large continuum dielectric constant (es=10) can result in screening of the electric field in the quantum region. For a dielectric constant of es=2 we find an external charge, although partially screened, can displace the Cl from its zero-charge equilibrium configuration. These results suggest that charged defects in SiO2 (es=4.) may be more important in influencing chemical reactions than in Al2O3 (es=9.34(9)).

Of course, multiple vacancies and interstitials exist in these lattices and may well superimpose larger fields than our single point charge. Surface relaxation effects are known to be large in Al2O3 (1) and should be included by utilizing the results of other methods (14). Surface defects such as steps kinks and jogs can be readily incorporated into the calculation by appropriate description of the molecular surface (12).
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Fig. 1: a) $\text{Cl}^-$ in an electrolyte adsorbing on an Al$_2$O$_3$ surface. The nearest-neighbor lattice atoms to the Cl$^-$, along with the Cl$^-$ ion, are enclosed within a virtual molecular surface (shown by dots) beyond which the lattice is treated as a polarizable dielectric continuum. b) Top view of cluster. c) Side view of cluster including an external charge below. Light-shaded (dark-shaded) dots indicate the interface is to the dielectric constant of the electrolyte (lattice).

Fig. 2: Model calculations of a point charge $Q$ inside and outside a "cavity" having dielectric constant $\varepsilon_1$ and radius $R_0$ surrounded by a dielectric medium of dielectric constant $\varepsilon_2$. See Eqs (1-4).
Fig. 3: Reaction electrostatic potential (Eq. 1) produced by a unit point charge inside a spherical cavity of radius $R_0 = 3.0387$ Bohrs (1.608 Å) appropriate for a crystalline Cl$^-$ ion (15). The potential is plotted as a function of the position of the charge along the z-axis (see Fig. 2). The reaction potential is seen to be a large effect, due entirely to the polarization of the boundary by the internal charge. The numerical method is found to be in quite reasonable agreement with the analytic solutions.

Fig. 4: Electrostatic potential (Eq. 2) at $r=Z$ inside the spherical cavity created by a unit external charge at $z_1 = 10$ Bohrs (see Fig. 2). This potential is the same as that at a test charge outside at $r=z_1$ due to a unit charge inside at $r=Z$ (Eq. 3). Note the larger dielectric discontinuity results in greater screening of the potential due to the external charge. It is to be noted that the values plotted in Figs 3 and 4 pertain to unit point charges and will scale directly with the actual charge. The numerical method is found to be in quite reasonable agreement with the analytic solutions.
Fig. 5: Energy of a (ClAlO$_4$)$_4$ cluster using a minimum basis set as a function of the distance of the Cl along the z-axis (see Fig. 1) normal to the plane described by three Al atoms forming the z=0 plane. The dielectric constant outside the quantum cluster at or above the z=0 plane was taken to be $\varepsilon_2 = 78.5$ (water) whereas below the z=0 plane the dielectric constant, $\varepsilon_{z_2}$, was chosen to be 2 or 10, as indicated. Note the reduction in binding energy caused by the reaction field of the interface to the continuum. The position and depth of the minimum is displaced when an external charge ($Q=-3e$ at (0,0,-10) Bohrs) is included, an effect which is strongly affected by the dielectric constant, $\varepsilon_{z_2}$.

Fig. 6: Energy of a (ClAlO$_4$)$_4$ cluster using a 6-31G basis set as a function of the distance of the Cl along the z-axis (see Fig. 1) normal to the plane described by three Al atoms forming the z=0 plane. The dielectric constant outside the quantum cluster at or above the z=0 plane was taken to be $\varepsilon_2 = 78.5$ (water) whereas below the z=0 plane the dielectric constant, $\varepsilon_{z_2}$, was chosen to be 2 or 10, as indicated. Note the reduction in binding energy caused by the reaction field of the interface to the continuum. The position and depth of the minimum is displaced when an external charge ($Q=-3e$ at (0,0,-10) Bohrs) is included, an effect which is strongly affected by the dielectric constant, $\varepsilon_{z_2}$. These results are consistent with those of Fig. 5.
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