A predictive model of surface charge on oxides in aqueous electrolyte solutions: The extended triple layer model (ETLM)

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Although experimental studies of the surface protonation of oxides in electrolyte solutions have been carried out for many years (Davis and Kent, 1990), few attempts have been made to place the experimental measurements into a coherent framework that permits prediction for systems that have yet to be studied experimentally. The enormous range of different natural and synthetic oxides of interest, and the correspondingly large range of electrolyte types and ionic strengths of relevence to industrial and natural processes, accentuate the need for such a predictive model. The purpose of the present study is to review progress made towards a comprehensive model for the prediction of surface charge on oxides in electrolyte solutions.

Experimental data clearly show that surface charge depends on pH, ionic strength, and on the specific electrolyte in solution. Consequently, the triple layer model is used to analyse existing experimental data. It is extended with crystal chemical and Born solvation theory to make predictions of surface charge for an oxide in any specific 1:1 electrolyte over a wide range of ionic strengths. In order to do this, the key parameters of the triple layer model (Westall and Hohl, 1980) must be estimated in a consistent way. These include a site density for each mineral; the surface protonation equilibrium constants K_1 and K_2; the electrolyte adsorption constants K_{M+} and K_{L-}; and the inner layer integral capacitance C_1.

Prediction of surface site densities

Although idealized, the bulk crystal structure is our best clue as to the nature of the solid surface in water. By choosing specific cleavage or growth planes, it is possible to evaluate the total number of protonatable sites with minimal assumptions about the reactivities of the sites. However, the choice of cleavage or growth planes referring only to orientation, without a precise specification of where in the structure these planes occur, will yield inconsistent, meaningless results for estimates of site densities. The precise location of growth or cleavage planes in many oxide and silicate structures can be specified by requiring that the total Brown bond strengths are minimized on neutral or nearly neutral exposed surfaces (Koretsky *et al.*, 1998). Based on these criteria, different methods of counting the number of surface sites can be compared with the results of tritium exchange experiments. The method that best matches the tritium exchange results involves counting all dangling bonds on the surface. For example, for goethite with this method a range of values from 14.4. to 20.0 sites.nm^{-2} was obtained. Numerous site types and site densities for oxides and silicates in water have been established (Koretsky *et al.*, 1998).

Prediction of surface protonation equilibrium constants

Surface protonation of oxides in aqueous solutions has typically been represented by >SOH, >SOH$_2^+$, and >SO$^-$. These species permit representation of proton adsorption and desorption by equilibria such as

$$>SOH + H^+_{(aq)} = >SOH_2^+ \quad (1)$$
$$>SO^- + H^+_{(aq)} = >SOH \quad (2)$$

Corresponding to these equilibria are expressions of the law of mass action in systems subject to an electric field, which can be written

$$K_1 = (a{>}SOH_2^+/a_{>SOH}a_{H^+_{(aq)}})10(F\psi_0{}^{/2.303RT}) \quad (3)$$

and $K_2 = (a_{>SOH}/a{>}SO^- aH^+_{(aq)})10(F\psi_0{}^{/2.303RT})$ (4)

In Eqns. (3) and (4), K_1 and K_2 represent intrinsic equilibrium constants and ψ represents the mean potential at the oxide surface in an electrolyte solution.

The variation of experimental surface protonation constants for a variety of different oxides can be accurately described by explicitly taking account of crystal chemical and solvation theory for the adsorbing protons (Sverjensky and Sahai, 1996). The standard Gibbs free energy of the vth reaction is broken up into three contributions: an electrostatic proton interaction term ($\Delta G^0_{pi,v}$), a Born solvation

term ($\Delta G^0_{s,v}$), and a term intrinsic to the aqueous proton itself ($\Delta G^0_{ii,v}$) where

$$\Delta G^0_{r,v} = \Delta G^0_{pi,v} + \Delta G^0_{s,v} + \Delta G^0_{ii,v} \quad (5)$$

It follows that the logarithms of the equilibrium constants can be calculated from the following equations (where v is equal to 1 or 2):

$$\log K_1 = -(\Delta\Omega_{r,1}/2.303RT)(1/\varepsilon_k) - B_1(s/r_{M\text{-}OH}) + \log K_{ii,1}'' \quad (6)$$

$$\log K_2 = -(\Omega_{r,2}/2.303RT)(1/\varepsilon_k) - B_2(s/r_{M\text{-}OH}) + \log K_{ii,2}'' \quad (7)$$

The first term on the right hand side of each equation involves the inverse of the dielectric constant of the mineral ($1/\varepsilon_k$) which arises from the solvation term in Eqn. (5). The second term involves the Pauling bond strength per angstrom. For an oxide containing only one kind of cation polyhedron, the Pauling electrostatic bond strength (s) is calculated from the cation charge (Z) and the coordination number of the cation (n_c) using

$$s = Z/n_c \quad (8)$$

It is assumed that the distance from the centre of the metal M to the adsorbed proton is given by $r_{M\text{-}OH}$ according to

$$r_{>M\text{-}OH} = r_{M\text{-}O} + 1.01 \quad (9)$$

In Eqn. (9), $r_{M\text{-}O}$ represents the mean value of the metal-oxygen bond length around the cation in the bulk solid and the O-H bond length was taken to be 1.01 Å. The standard Gibbs free energy of adsorption of the proton is then assumed to be proportional to the Pauling bond strength per angstrom ($s/r_{>M\text{-}OH}$). The numerical coefficients, e.g. $\Delta\Omega_{r,1}$, B_1, and $\log K_{ii,1}''$, are known from calibration of the equations with experimental results. Based on Eqns. (6) and (7), and known values of the dielectric constant and Pauling bond strength per angstrom, numerous predictions of K_1 and K_2 for oxides and silicates can be made.

Prediction of electrolyte adsorption equilibrium constants

Equilibria for the adsorption of a 1:1 electrolyte (ML) can be written

$$>SO^- + M^+_{(aq)} = >SO^-M^+ \quad (10)$$

$$>SOH^+_2 + L^-_{(aq)} = >SOH^+_2L^- \quad (11)$$

Corresponding to these equilibria are expressions of the law of mass action which can be written

$$K_{M^+} = (a{>}SO^{-M^+}/a{>}SO^- a_{M^+_{(aq)}})10^{(F\psi\beta/2.303RT)} \quad (12)$$

and

$$K_{L^-} = (a{>}SOH^+_{2L^-}/a_{>SOH^+_2} a_{L^-_{(aq)}})10^{(-F\psi\beta/2.303RT)} \quad (13)$$

where ψ_β refers to the mean potential on a plane at a distance β from the surface (Davis and Kent, 1990). The surface equilibrium constants K_{M^+} and K_{L^-} refer to adsorption of the electrolyte cation M^+ and anion L^- on the β-plane in the triple layer model. Based on Born solvation theory, it would be expected that sets of values of $\log K_M$ and $\log K_L$ on a range of different solids would correlate with $1/\varepsilon$ of the solids consistent with equations of the form

$$\log K_{M^+} = -(\Delta\Omega_{r,M^+}/2.303RT)(1/\varepsilon_k) + \log K_{ii,M^+}'' \quad (14)$$

$$\log K_{L^-} = -(\Delta\Omega_{r,L^-}/2.303RT)(1/\varepsilon_k) + \log K_{ii,L^-}'' \quad (15)$$

where the coefficients $\Delta\Omega_{r,M^+}$, $\Delta\Omega_{r,L^-}$, K_{ii,M^+}'' and K_{ii,L^-}'' were calibrated with experimental data (Sahai and Sverjensky, 1996*a*). Furthermore, from Born solvation theory, it is expected that $\Delta\Omega_r$ is a function of the inverse of the effective electrostatic radii of the cations or anions, which results in predictive equations for $\Delta\Omega_{r,M^+}$ and $\Delta\Omega_{r,L^-}$ (Sahai and Sverjensky, 1996*b*). Similarly, the intrinsic equilibrium constants $\log K_{ii,M^+}''$ and $\log K_{ii,L^-}''$ correlate with the inverse of the effective electrostatic radii of the corresponding aqueous cations. Eqns. (14) and (15) thus permit prediction of the electrolyte adsorption constants for the triple layer model for a wide variety of cations, anions and solids.

Prediction of the inner layer electrolyte capacitance C_I

The integral capacitance (C_I) in the triple layer model has long been a parameter obtained solely by regression of experimentally determined surface charge data as a function of pH and ionic strength (Westall and Hohl, 1980; Davis and Kent, 1990). Because of the great variety of assumptions used in such regressions, such capacitances are often only fit parameters. Recent progress towards developing a predictive method for estimating C_I values can be descibed using the analogy between a parallel plate capacitor and the triple layer model of a mineral surface in water. This analogy results in the expression of C_I in terms of the dielectric constant in the double-layer region between the 0- and the β-planes (ε_d) and the separation of these two planes (β) according to,

$$C_I = \varepsilon_d\varepsilon_0/\beta \quad (16)$$

where ε_0 is the permittivity of free space.