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LETTER

Zero-point-of-charge prediction from crystal chemistry and solvation theory

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Abstract—The pristine point of zero charge (pH_{PPZC}) is a property of each solid in water that is widely used in the interpretation of adsorption processes and dissolution rates. Considerable effort has gone into attempting to calculate the pH_{PPZC} values of oxides and silicates based on crystal chemistry and electrostatic models of the interaction between protons and OH surface groups. However, substantial discrepancies remain between calculated and measured values of the pH_{PPZC} even for simple oxides such as quartz. This implies that the widespread use of real and fictive components (e.g., $\text{Si}^{\text{IV}}\text{O}_2$ and $\text{Al}_2^{\text{IV}}\text{O}_3$) to interpret the surface characteristics of silicates is unwarranted.

In the present paper, I show that by adding electrostatic solvation theory to crystal chemical and electrostatic models, the differences between pH_{PPZC} values of crystalline solids can be accurately quantified. The new model sums free energy contributions associated with proton solvation, electrostatic repulsion of protons by cations underlying the surface, and electrostatic attraction of protons by oxygen anions near the surface. It results in a theoretical dependence of the pH_{PPZC} on the dielectric constant of the k th solid (ϵ_k) and the ratio of the Pauling electrostatic bond strength to the cation-hydroxyl bond length ($s/r_{\text{M-OH}}$), according to the equation

$$\text{pH}_{\text{PPZC}} = -0.5(\Delta\Omega_r/2.303RT)(1/\epsilon_k) - B(s/r_{\text{M-OH}}) + \log K_{\text{H}^+}^{\text{a}}$$

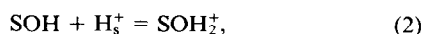
in which $\Delta\Omega_r$, B , and $K_{\text{H}^+}^{\text{a}}$ are constants. This relationship describes the pH_{PPZC} values of oxides and silicates to better than ± 0.5 and enables prediction of surface protonation reactions from the properties of the underlying crystal structure alone. These results suggest that the bonding of protons at the crystal-water interface is more analogous to the bonding in the bulk crystal structure than to the bonding in analogous aqueous complexes emphasized in other studies.

INTRODUCTION

THE CONCEPT OF SURFACE protonation of solids in contact with aqueous solutions has proved to be a considerable help in interpreting the adsorption of cations and anions on surfaces and the dissolution rates of solids (summaries by SCHINDLER and STUMM, 1987; WIELAND et al., 1988; DAVIS and KENT, 1990; DZOMBAK and MOREL, 1990; PARKS, 1990; HAYES et al., 1991). Single-site surface protonation reactions can be represented for a surface S by the reactions



and



where SO^- , SOH , and SOH_2^+ represent surface species, and H_s^+ represents a proton near the charged surface. The species H_s^+ is simply related to the proton in the bulk solution, $\text{H}_{(\text{aq})}^+$, by the work done in transferring the proton through the potential difference between the bulk solution and the charged interface (DZOMBAK and MOREL, 1990). The corresponding intrinsic equilibrium constants are given by

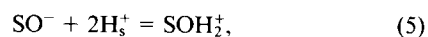
$$\log K_{\text{int},2} = \log [X_{\text{SOH}}/X_{\text{SO}^-}a_{\text{H}_s^+}] \quad (3)$$

and

$$\log K_{\text{int},1} = \log [X_{\text{SOH}_2^+}/X_{\text{SOH}}a_{\text{H}_s^+}] \quad (4)$$

where X_{SO^-} , X_{SOH} , $X_{\text{SOH}_2^+}$ represent mole fractions of the subscripted species and $a_{\text{H}_s^+}$ represents the activity of the proton near the surface. Other models of surface complexation involve more than one type of protonation site (e.g., HIEMSTRA et al., 1989a,b). Although such multisite models are not explicitly addressed here, it is expected that the theory developed below will also apply to them.

The values of the individual intrinsic protonation constants $\log K_{\text{int},1}$ and $\log K_{\text{int},2}$ are dependent on the particular electrostatic model adopted (e.g., constant capacitance, diffuse double layer, triple layer; see the summary by HAYES et al., 1991), the sum of Eqns. 1 and 2 is simply related to the pristine point of zero charge (pH_{PPZC} , DAVIS and KENT, 1990), which is experimentally measured, independent of electrostatic models of the solid-water interface. For any given model of the solid-water interface, the pH_{PPZC} is traditionally represented by the protonation reaction



which is the sum of Eqns. 1 and 2. When the concentrations of the charged surface species are equal, i.e., a zero-charge

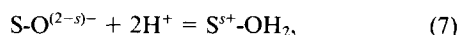
surface, the pH_{PPZC} is related to the intrinsic equilibrium constant for Eqn. 5 according to

$$\text{pH}_{\text{PPZC}} = 0.5 \log K_{\text{int.,H}^+,k} = 0.5 \log K_{\text{H}_{\text{g}}^+,k}, \quad (6)$$

where $K_{\text{int.,H}^+,k}$ refers to the adsorption of H_{g}^+ onto the k th solid which is equal to $K_{\text{H}_{\text{g}}^+,k}$ for the adsorption of $\text{H}_{\text{(aq)}}^+$ onto the k th solid at a surface potential of zero.

In a landmark paper, PARKS (1965) showed that a simple electrostatic description of the interaction between protons and M-OH surface groups made it possible to express a major part of the differences between the pH_{PPZC} values of simple oxides in terms of charge and radius of the cation(s) in the solid (see also STUMM et al., 1970). Major exceptions to this model included quartz and amorphous silica, both containing IV-coordinate silicon ($\text{Si}^{\text{IV}}\text{O}_2$). The model was extended to silicates (PARKS, 1967) by taking the pH_{PPZC} values of silicates to be the weighted sum of pH_{PPZC} values of the individual oxides. Experimental rather than calculated pH_{PPZC} values for real species such as $\text{Si}^{\text{IV}}\text{O}_2$ were used, but calculated values for fictive species such as $\text{Al}^{\text{IV}}\text{O}_3$ had to be used, even though the theory could not predict $\text{Si}^{\text{IV}}\text{O}_2$. Despite this problem, which was discussed and emphasized by PARKS (1967), and despite the experimental studies of SPRYCHA (1982) and TCHAPEK et al. (1974) for Zn_2SiO_4 and kaolinite, which were very critical of the idea of combining oxide components to generate silicate properties, the idea has had widespread application in recent studies of surface protonation and in interpretations of the mechanisms of dissolution rates of silicates (CARROLL-WEBB and WALTHER, 1988; BRADY and WALTHER, 1989; BLUM and LASAGA, 1991; WOGELIUS and WALTHER, 1991; and below).

In order to try to improve upon the basic electrostatic model developed by PARKS (1965, 1967), YOON et al. (1979) developed a combined crystal chemical and electrostatic theory of protonation. Instead of Eqn. 5, which relies on analogy with aqueous complexation reactions, YOON et al. (1979) suggested that protonation should be represented from a crystallographic standpoint by addition of the protons to a dangling oxygen with residual charge s , according to



where s represents the Pauling bond strength. For a crystal with a single cation type and site with valence Z and coordination number ν ,

$$s = Z/\nu. \quad (8)$$

For more complex structures with i cations and sites in equal abundances,

$$s = \sum(Z_i/\nu_i)/i. \quad (9)$$

Accordingly, the effective charges on the positive and negative sites of the surface are not $+1$ and -1 , respectively, as implied by Eqn. 5, but instead are represented by $+s$ and $2-s$ respectively, as shown in Eqn. 7. From Eqn. 7, a Law of Mass Action expression can be derived for the zero point of charge condition (YOON et al., 1979):

$$\log K_{\text{int.,H}^+,k} = \log \{[(2-s)/s]/(a_{\text{H}^+})^2\}. \quad (10)$$

Specifically, YOON et al. (1979) combined crystal chemical theory and electrostatic theory to express $K_{\text{int.,H}^+,k}$ in terms of Pauling bond strength (s) and metal-OH bond length ($r_{\text{M-OH}}$, see Table 1) by

$$\log K_{\text{int.,H}^+,k} = 2A - 2B(s/r_{\text{M-OH}}), \quad (11)$$

where A represents the sum of a Coulombic attraction term (between the adsorbing protons and the surface oxygen) and a chemical bonding term, and B represents a Coulombic repulsion term (between the adsorbing protons and the surface oxygen). In practice, both A and B have been treated simply as constants established by regression (YOON et al., 1979), as originally developed by PARKS (1965, 1967). Equations 10 and 11 were then combined to express the pH_{PPZC} in terms of $s/r_{\text{M-OH}}$ and s :

$$\text{pH}_{\text{PPZC}} = A - B(s/r_{\text{M-OH}}) - 0.5 \log [(2-s)/s]. \quad (12)$$

This approach to calculating the zero point of charge of oxides still leaves major discrepancies between calculated and measured values of pH_{PPZC} (e.g., 3.7 units for SiO_2 , and 2.0 for BeO ; YOON et al., 1979). These discrepancies are substantial enough to indicate that perhaps there is an additional effect that is not accounted for in the above crystal chemical/electrostatic model of surface protonation. Although covalent effects have been emphasized in other more recent theoretical studies (RUSSO and NOGUERA, 1992a,b), there is an additional effect that has been almost completely neglected, that can be treated electrostatically, and that will account for the above discrepancies. It will be shown below that this effect is associated with the solvation of aqueous protons. STUMM et al. (1970) and BLESÁ et al. (1990) have discussed possible solvation effects during protonation, and solvation effects have been demonstrated to be of importance for predicting cation adsorption (SVERJENSKY, 1993).

Finally, because the pH_{PPZC} values of silicate minerals have been approximated as the sum of simple oxides (as discussed above), the discrepancies described above that are associated with the calculation of the pH_{PPZC} values for the simple oxides must lead to much greater uncertainties in calculating and predicting the surface protonation of silicates. As noted above, the oxide summation concept has been widely applied to aid mechanistic interpretation of surface titration and dissolution rate data for silicates (e.g., CARROLL-WEBB and WALTHER, 1988; BRADY and WALTHER, 1989; BLUM and LASAGA, 1991; WOGELIUS and WALTHER, 1991). It will be shown below that a more appropriate concept for silicates is to express surface protonation in terms of fundamental parameters characteristic of each bulk, individual silicate crystal structure.

INCLUSION OF SOLVATION THEORY INTO A THEORETICAL MODEL FOR SURFACE PROTONATION

The similarity of the adsorption of near-surface protons (Eqn. 1) with the representation of the adsorption of near-surface cations according to



suggests that the recent application of Born solvation theory to cation adsorption (SVERJENSKY, 1993) may also be useful in treating protonation reactions. Following JAMES and HEALY's (1972) treatment of Born solvation, the free energy associated with solvation during adsorption can be represented in terms of the dielectric constants of the solid (ϵ_k), the interfacial water ($\epsilon_{\text{int.}}$), and bulk water (ϵ_w). It follows (SVERJENSKY, 1993) that the intrinsic equilibrium constants for adsorption of the $\text{M}^{\text{+}}$ cation on the k th solid (log

Table 1. Crystal structure properties and zero point of charge values at 25 C and 1 bar.

| PHASE | ϵ_k^a | s/r_{M-OH}^b | Exptl. pH _{PPZC} ^c | Calc. pH _{PPZC} |
|--|----------------|----------------|--|--------------------------|
| α -SiO ₂ | 4.578 | 0.3818 | 2.9 | 2.91 |
| Al ₂ Si ₂ O ₈ (OH) ₄ | 11.8 | 0.2754 | 4.5 | 4.66 |
| α -TiO ₂ | 120.91 | 0.2248 | 5.8 | 5.21 |
| Fe ₃ O ₄ | 20000 | 0.1768 | 6.6 | 7.10 |
| α -Fe ₂ O ₃ | 25.0 | 0.1645 | 8.5 | 8.47 |
| α -Al ₂ O ₃ | 10.43 | 0.1711 | 9.1 | 9.37 |
| α -Al(OH) ₃ | 8.4 | 0.1716 | 10.0 | 9.84 |
| MgO | 9.83 | 0.1070 | 12.4 | 12.24 |
| <hr/> | | | | |
| PHASE | ϵ_k^a | s/r_{M-OH}^b | Exptl. pH _{PPZC} ^c | Calc. pH _{PPZC} |
| BeO | 7.16 | 0.1890 | 10.2 | 9.5 |
| CaO | 11.95 | 0.0976 | | 12.3 |
| NiO | 11.9 | 0.1077 | 9.85-11.3 | 11.8 |
| CuO | 18.1 | 0.1686 | | 8.6 |
| ZnO | 8.49 | 0.1676 | 8.7-9.3 | 10.0 |
| FeO(OH) | 11.7 | 0.165 | 9.0-9.7 | 9.4 |
| amorphous SiO ₂ | 3.807 | 0.3818 | 3.5 | 3.9 |
| β -MnO ₂ | 10000 | 0.2301 | 4.6-7.3 | 4.8 |
| SnO ₂ | 9.0 | 0.2177 | 7.3 | 7.7 |
| ZrO ₂ | 22.0 | 0.1803 | | 7.9 |
| ThO ₂ | 18.9 | 0.1456 | 9.0-9.3 | 9.6 |
| UO ₂ | 24.0 | 0.1480 | | 9.2 |
| CaTiO ₃ | 165.0 | 0.1409 | | 8.8 |
| MgAl ₂ O ₄ | 8.3 | 0.1703 | | 9.9 |
| FeAl ₂ O ₄ | 40.0 | 0.1693 | | 7.9 |
| ZrSiO ₄ | 11.5 | 0.1559 | | 9.8 |
| Zn ₂ SiO ₄ | 12.99 | 0.2389 | 7.4 | 6.1 |
| ANDALUSITE | 6.9 | 0.2531 | 5.2-7.8 | 6.9 |
| KYANITE | 7.8 | 0.2402 | 5.2-7.9 | 7.1 |
| SILLIMANITE | 11.0 | 0.2736 | 5.6-6.8 | 4.9 |
| FORSTERITE | 7.26 | 0.1972 | 10.5 | 9.1 |
| GROSSULAR | 8.53 | 0.2113 | | 8.1 |
| ALMANDINE | 4.3 | 0.2135 | | 10.4 |
| OH-TOPAZ | 5.0 | 0.2413 | | 8.6 |
| JADEITE | 10.0 | 0.1930 | | 8.5 |
| WOLLASTONITE | 8.6 | 0.2370 | | 7.0 |
| DIOPSIDE | 8.02 | 0.2338 | | 7.3 |
| HEDENBERGITE | 17.4 | 0.2333 | | 5.9 |
| ANTHOPHYLLITE | 8.0 | 0.2497 | | 6.6 |
| TREMOLITE | 8.0 | 0.2402 | | 7.0 |
| TALC | 5.8 | 0.2634 | | 7.0 |
| MUSCOVITE | 7.6 | 0.2539 | | 6.6 |
| PHLOGOPITE | 7.6 | 0.2194 | | 8.0 |
| LOW ALBITE | 6.95 | 0.2920 | 6.8 | 5.2 |
| H-ALBITE | 6.95 | 0.3533 | 2.0 | 2.6 |
| MICROCLINE | 5.48 | 0.2889 | | 6.1 |
| H-MICROCLINE | 5.48 | 0.3549 | 2.4 | 3.3 |
| ANORTHITE | 7.14 | 0.2809 | | 5.6 |

The first eight phases in the table and their properties were regressed with Eqn. 18 to generate $-0.5(\Delta\Omega_r/2.303RT) = 21.1158$, $B = 42.9148$, and $\log K_{H^+}'' = 14.6866$. All other calculated values of pH_{PPZC} were predicted using these coefficients in Eqn. 18.

^a Dielectric constants from OLHOEFFT (1981) except for BeO, MgO, CaO, and ZnO (Shannon et al., 1992b), SiO₂, Al₂O₃, and grossular (Shannon and Rossman, 1992), ZrO₂ and ZrSiO₄ (Subramanian and Shannon, 1989), MgAl₂O₄ (Shannon and Rossman, 1991), diopside and anorthite (Shannon et al., 1992a), amorphous silica (Shannon, 1993). Values for H-albite and H-microcline were assumed to be the same as for albite and microcline. The value for willemite (Zn₂SiO₄) was estimated following the procedure in Shannon (1993).

^b Computed by averaging all cation sites (i) with molar abundance N_i using $s/r_{M-OH} = \frac{[\sum_i (s/r_{M-OH})_i N_i]}{[\sum_i N_i]}$, where s for the ith site was obtained using Eqn. 8, and r_{M-OH} for the ith site is calculated from $r_{M-OH} = r_{M-O} + 1.01$ Angs (Yoon et al., 1979). Values of s and mean values of r_{M-O} were obtained from Smyth and Bish (1988). Values for H-albite and H-microcline were calculated as for albite and microcline omitting consideration of the alkali sites.

^c From Davis and Kent (1990): except for Al₂Si₂O₈(OH)₄, Al(OH)₃, BeO, and MgO which are from Carroll-Webb and Walther (1988), Hiemstra et al. (1987), and Parks (1965); NiO (Parks, 1965; Tewari and Campbell, 1976); CaO, ZnO, and SnO₂ (Parks, 1965); MnO₂ (Balistreri and Murray, 1982); amorphous silica (Bolt, 1957); goethite (Evans et al., 1979; Zeltner and Anderson, 1988); willemite (Sprycha, 1982); andalusite, kyanite, and sillimanite (Parks, 1967); forsterite (Wogelius and Walther, 1991); albite (Blum and Lasaga, 1991); H-albite and H-microcline (Parks, 1967).

$K_{int..M_k^{++},k}$) can be broken up into a fundamental solvation contribution and a contribution characteristic of the sorbing cation ($\log K'_{ii,M^{++}}$), resulting in a dependence of $\log K_{int..M_k^{++},k}$ on the inverse of the dielectric constant for the kth solid ($1/\epsilon_k$) according to

$$\log K_{int..M_k^{++},k} = -(\Delta\Omega_r/2.303RT)(1/\epsilon_k) + \log K'_{ii,M^{++}}, \quad (14)$$

where the terms involving $1/\epsilon_{int.}$ and $1/\epsilon_w$ are included in the $\log K'_{ii,M^{++}}$ term. The success of this approach suggests that $1/\epsilon_{int.}$ is a constant in these systems (SVERJENSKY, 1993). In Eqn. 14, the Born solvation term $\Delta\Omega_r$ defined by

$$\Delta\Omega_r = \Omega_{SO_{M^+}} - \Omega_{SO^-} = \Omega_{SO_{M^+}}^{abs.} - \Omega_{SO^-}^{abs.} \quad (15)$$

replaces the term $\Omega_{M^{++}}$ in Eqn. 6 of SVERJENSKY (1993) in order to emphasize a dependence on the overall Eqn. 13 above. The absolute values of $\Omega_j^{abs.}$ for each jth species are defined in terms of $(\eta/4)Z_j^2/r_{e,j}$, where η is equal to 166.027 kcal · A · mole⁻¹, Z_j is the charge of the jth species, and $r_{e,j}$ is an effective electrostatic radius (SVERJENSKY, 1993 and references therein).

The similarity of Eqns. 5 and 13 suggests that $\log K_{int..H^+,k}$ (or $\log K_{H(aq),k}'$) in Eqn. 6 should also depend on $1/\epsilon_k$ according to

$$\log K_{H(aq),k}' = -(\Delta\Omega_r/2.303RT)(1/\epsilon_k) + \log K'_{ii,H^+}, \quad (16)$$

where

$$\Delta\Omega_r = \Omega_{SOH_2^+} - \Omega_{SO^-} \quad (17)$$

and $\Omega_{SOH_2^+}$ and Ω_{SO^-} are individual Born coefficients. Consequently, pH_{PPZC} values for a series of solids should also depend on $1/\epsilon_k$. Again, it is assumed here that $1/\epsilon_{int.}$ and $1/\epsilon_w$ are constant and can thus be included in the term $\log K'_{ii,H^+}$. The calculations discussed below are consistent with this assumption.

Experimental pH_{PPZC} values of selected crystalline oxides and silicates are summarized in Table 1 and Fig. 1a. It can be seen in Fig. 1a that, although there is a dependence on $1/\epsilon_k$, solids containing tetravalent cations and/or tetrahedrally coordinated cations are displaced down to low values of pH_{PPZC}. This suggests that the fundamental dependence on crystal chemistry described in earlier studies (PARKS, 1965, 1967; YOON et al., 1979) could be linked to the solvation theory described above for a more complete description of surface protonation.

In the present study, I combine the electrostatically based crystal chemical approach (YOON et al., 1979) with electrostatically based solvation theory (SVERJENSKY, 1993). There are two ways to do this in the context of the present paper: by (1) adopting the traditional representation of surface charge (Eqns. 5 and 6) and then combining Eqns. 6, 11, and 16, or (2) by adopting the fractional charge representation of ref. 6 (Eqns. 7 and 10) and then combining Eqns. 12 and 16. Because the solvation theory already developed (SVERJENSKY, 1993) refers to the traditional representation of surface charge, it is more consistent to consider an equation of the form

$$\text{pH}_{PPZC} = -0.5(\Delta\Omega_r/2.303RT)(1/\epsilon_k) - B(s/r_{M-OH}) + \log K_{H^+}'' \quad (18)$$

The first term on the right hand side of this equation refers to the part of the solvation contribution which depends

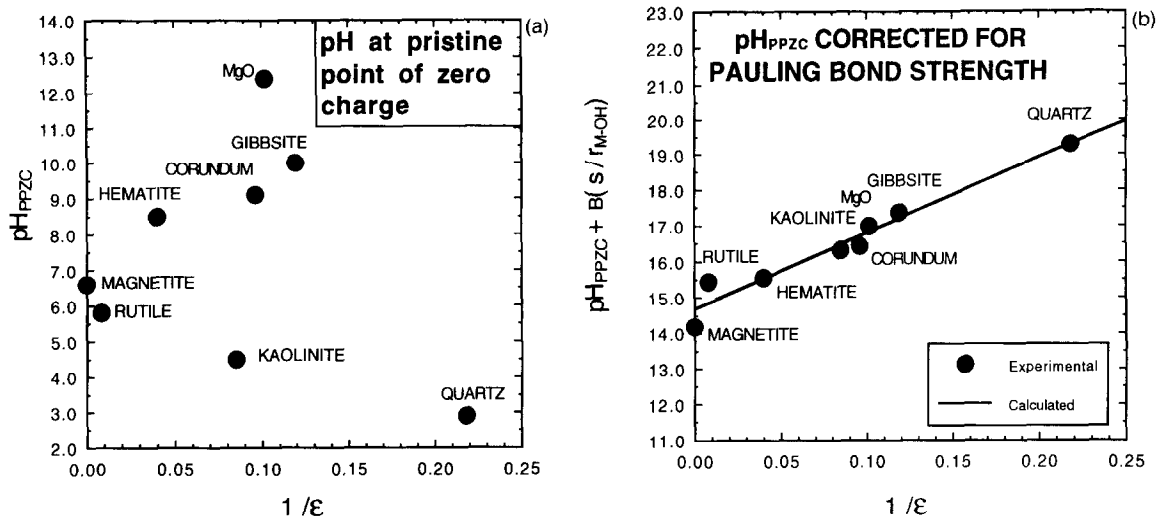


FIG. 1. Correlation and prediction of pH_{PPZC} values of selected crystalline oxides and silicates versus values of the inverse of the dielectric constant ($1/\epsilon$). (a) Experimental values of pH_{PPZC} vs. $1/\epsilon$. Note that solids with higher charged cations and/or lower coordination numbers are displaced to lower values of pH_{PPZC} . For example, progressively higher charged cations occur in the following VI-fold coordinated species: MgO (+2 cations), hematite, corundum and gibbsite (+3 cations), and rutile (+4 cations). Magnetite and kaolinite contain mixtures of IV-fold and VI-fold cations; and quartz contains the unusual combination of +4 cations (only) in IV-fold coordination. (b) Values of pH_{PPZC} corrected for the ratio of the Pauling bond strength (s) to the metal-OH radius ($r_{\text{M-OH}}$). The line represents a regression of the data with Eqn. 18 and coefficients given in Table 1.

strongly on the properties of the solid (i.e., $1/\epsilon_k$), the second term refers to the electrostatic repulsion of the surface proton by the cations immediately underlying the surface (see Eqn. 11). The final term is a combination of a general intrinsic binding constant for the proton on the surfaces of all oxides and silicates (this includes all nonelectrostatic effects), together with the remaining part of the solvation contribution that depends on $1/\epsilon_{\text{int}}$ and $1/\epsilon_w$ (see above) and the term for the electrostatic attraction of the surface proton to the oxygen anions at the surface (the "A" term in Eqn. 11). According to Eqn. 18, the surface protonation reaction associated with the zero point of charge should depend linearly on both the bulk dielectric constant of the solid (ϵ_k) and the ratio of Pauling bond strength to radius ($s/r_{\text{M-OH}}$). Equation 18 expresses the strength of binding of protons to the surface in terms of properties of the bulk crystal structure underlying the surface.

RESULTS

Although numerous values of the zero point of charge (pH_{ZPC}) of many different kinds of solids abound in the literature, few accurate values of the *pristine* point of zero charge (pH_{PPZC}) for well-characterized crystalline solids are available (e.g., DAVIS and KENT, 1990). The problems associated with poorly characterized and/or noncrystalline solids have been extensively discussed by PARKS (1965, 1967). In the present study, I have used the critical compilation of DAVIS and KENT (1990), supplemented with a few other data as summarized in the eight values of pH_{PPZC} given at the top of Table 1. These data were regressed using Eqn. 18 and values of (ϵ_k) and the ratio of Pauling bond strength to radius ($s/r_{\text{M-OH}}$) given in Table 1 resulting in the calculated line shown in Fig. 1b and the calculated values of pH_{PPZC} in Table 1 and Fig. 2a and b.

It can be seen in Figs. 1 and 2 and Table 1 that Eqn. 18 gives a remarkably close agreement between calculated and measured values of the pH_{PPZC} , typically less than 0.5 of a pH unit even for solids as diverse as MgO and kaolinite. It appears that the combination of crystal chemical theory with an electrostatic theory of proton-M-OH interaction and simple solvation theory can account completely for the differences between the adsorption of protons on different solids. It can also be noted from Figs. 1 and 2 that the values of (ϵ_k) and the ratio of Pauling bond strength to radius ($s/r_{\text{M-OH}}$) for *simple oxides and the more complex silicates* are sufficient to characterize the surface protonation of these solids. Consequently, it appears to be possible with Eqn. 18 to characterize crystalline solids of all types simultaneously, *based on the crystal structure of each individual solid*. There is no need to regard the surface properties of silicates as the sums of the simple oxides.

Predicted values of pH_{PPZC} for a number of solids of geochemical interest are also summarized in Table 1. Most of these are plotted in Fig. 3a which displays where many solids of geochemical interest lie in terms of the fundamental variables in the theoretical model developed in this paper. The parameter s/r is, of course, just the averaged Pauling electrostatic bond strength per angstrom (see Table 1). The parameter ϵ_k is the averaged low frequency permittivity of the solid, which can be related to, and in fact predicted from, atomic polarizabilities (SHANNON, 1993). Consequently, provided that the crystal structure is known, both s/r and ϵ_k can be obtained. It can be seen that most silicates are predicted to have pH_{PPZC} values in the range 5 to 9, whereas many oxides lie in the range 8 to 10. It should perhaps be emphasized that in the present study both s/r and ϵ_k refer to bulk values because the zero points of charge considered here also refer to bulk values. However, both s/r and ϵ_k are actually directional

ANDERSON, 1988) which agrees extremely well with the theoretical value of 9.4 calculated here. It should also be noted that few poorly crystalline or amorphous solids are considered here. Although excellent agreement between theory and measurement was obtained in the case of amorphous silica (Table 1 and Fig. 3b), it is difficult to define values of s/r_{M-OH} and/or ϵ_k for solids such as amorphous ferric hydroxide, birnessite, and γ -alumina.

CONCLUSIONS

Several more results of interest follow from the practical application of Eqn. 18 summarized above. First, the constant B is simply related to the effective dielectric constant near the mineral-water interface in the context of Eqn. 5 (YOON et al., 1979; D. A. Sverjensky et al., unpubl. data). Because the present study shows that B appears to be a constant for all oxide and silicate minerals ($B = 42.9148$, Table 1), it follows that *the effective dielectric constant near the mineral-water interface is the same for all oxides and silicates*. For the particular reaction of interest involving the adsorption of two protons (Eqn. 5), the effective dielectric constant is calculated to be about 5.7 in magnitude. This is remarkably close to the limiting value of 6 at 25 C and 1 bar proposed by JAMES and HEALY (1972) and ANDERSEN and BOCKRIS (1964).

Second, the constant $\log K_H^+$ in Eqn. 18 involves the combination of a number of terms derived from Eqns. 6, 11, and 16. These include an intrinsic constant for the binding of the protons onto the surface SO^- groups. This intrinsic constant takes account of all the effects, presumably mainly chemical, not included in the electrostatic theory discussed above. The present calculations suggest that this intrinsic binding constant is a characteristic of *all oxides and silicates*. Presumably this constant would differ for proton binding on solids dominated by other anions such as sulfides.

Perhaps the most surprising result of the success of Eqn. 18 is that surface reactions can be so well modeled based on properties of the bulk crystal structure. Recent studies have placed enormous emphasis on the analogy between surface complexes and aqueous complexes (SCHINDLER and STUMM, 1987; DAVIS and KENT, 1990; PARKS, 1990; WIELAND et al., 1988). For example, empirical correlations of the $\log K$ values of surface protonation reactions with aqueous acidity constants have often been cited as supporting evidence of this analogy (SCHINDLER and STUMM, 1987; WIELAND et al., 1988). However, the scatter on such correlations is substantial. Furthermore, some species (e.g., amorphous silica) lie so far from the line of best fit (SCHINDLER and STUMM, 1987) that the apparent correlation itself must be questioned. In contrast, the present study has shown that surface protonation on all kinds of solids (including both quartz and amorphous silica) can be accurately calculated from the dielectric constant of the solid and the Pauling bond strength divided by radius in the solid. This suggests that much more emphasis should be placed on analogies between the bonding of the surface protonated species and the bonding in the underlying crystal structure than has been considered to date.

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