Surface Charge and Ion Adsorption on Metal Oxides to 290°C

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The results of metal oxide surface protonation and specific ion adsorption studies are presented, which employed *in situ* pH monitoring in both conventional glass-electrode autotitrators to 50°C, and hydrogen-electrode concentration cells to 290°C. Our recent studies of rutile and magnetite surface protonation [1,2], and the sorption of Ca^{2+} on rutile surfaces [3] are reviewed, and modeling of these results are discussed, including the development of a method to estimate the pH of zero charge of oxide surfaces from 0 to 300°C. New results are discussed on the protonation of zirconium oxide surfaces to 50°C, and the sorption of Nd^{3+} on rutile surfaces from 25-250°C. We also discuss preliminary results on the sorption of oxalate and sulfate on rutile surfaces to 100°C. These studies demonstrate that both proton-induced surface charging and the specific adsorption of electrolyte ions on oxide surfaces increase as temperature increases into the hydrothermal regime.

1. Introduction

Terminal oxygen atoms at metal oxide surfaces react with water, forming hydroxylated sites that impart a pH-dependent surface charge. The association of solution counterions with this modified surface results in a complex structure, termed the Electrical Double Layer (EDL), idealized in Figure (1), which is taken from the extensive review of oxide surface chemistry recently published by Brown et al. [4]. Surface charge influences colloid transport and flocculation, adsorption of ions from solution, mineral dissolution/precipitation rates, growth morphologies, and other interfacial phenomena [4]. Hydrogen-electrode concentration cells (HECC's) have been used in our laboratories [1,2] to conduct potentiometric titrations of H^+ (or OH^-) adsorption and desorption on rutile (TiO_2) and magnetite (Fe_3O_4) powder surfaces in 0.01 to 1.0 molal NaCl, tetramethylammonium chloride (TMACl) and sodium trifluoromethanesulfonate (NaTr) media from 25 to 290°C at pH's of 3 to 10. These are the first such direct potentiometric studies of the protonation of mineral surfaces ever performed at temperatures greater than 95°C. We have also investigated the sorption of Ca^{2+} on rutile surfaces in NaCl media to 250°C [3]. Details of the operation of the HECC are described elsewhere in this proceedings volume [5] and the procedures for conducting mineral surface titrations are discussed in our recent publications [1-3].
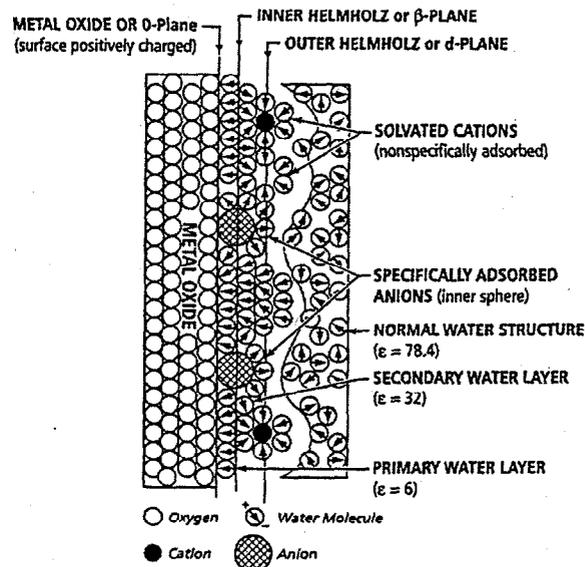

Figure 1. Schematic model of the Electrical Double Layer (EDL) at the interface of a positively charged metal oxide surface with an aqueous solution (from Brown et. al. [4]). Note that the terms *Helmholz* layer or plane, *Stern* layer or plane, and *Condensed* layer are used more or less interchangeably by various authors. Also, it is assumed that there is a *diffuse* layer of solution counterions extending out to the bulk solution composition.

2. TiO₂, Fe₃O₄ and ZrO₂ Surface Protonation

Because H^+ (and/or OH^-) binding with terminal oxygen atoms is considered the surface-charge-determining reaction for oxide particles in aqueous solutions, potentiometric titrations of powdered minerals under conditions of known solution and solid masses and surface areas, known titrant compositions and masses, and continuously-monitored pH_m (defined as $-\log[H^+]$) allow determination of the proton-induced surface charge. The difference between the measured pH_m and that calculated solely from a mixture of the starting and titrant solutions, is computed in terms of micromoles of excess H^+ in solution per square meter of mineral surface exposed to the solution. This is then converted to surface charge density via the relationship

$$\sigma_0 \equiv \sigma_H = -F(\mu\text{moles excess } H^+)/m^2 \qquad (1)$$

where F is the Faraday constant (0.0965 Coulombs/μequivalent). The negative sign indicates that a positive value of excess H^+ in solution corresponds to net proton release from the surface, whereas a deficit of H^+ in solution results from proton uptake by the solid, resulting in positive surface charge. Because this proton-induced surface charge is confined to a fixed plane (Fig. 1), positive or negative surface charge buildup is inhibited by electrostatic repulsion between adjacent, like-charged sites on the surface. Counterions of opposite charge in the aqueous phase partially shield this surface charge build-up, resulting in the EDL (Fig. 1). This effect gives rise to the typical relationship of oxide surface titrations at constant temperature, but varying concentration of an electrolyte, such as NaCl, KNO₃, etc., as shown for rutile at 100°C in NaCl and tetramethylammonium (TMA) chloride solutions in Figure (2). The pH plotted in this and subsequent figures is converted to the activity scale using the activity coefficient model discussed in [1,2]. The "proton sorption isotherms" increase in slope with increasing ionic strength, but exhibit a common intersection point. This "pH_{cip}", in the case of truly "indifferent" electrolytes with symmetrical binding of the cation and anion on negatively or positively-charged surfaces, respectively, is coincident with the point of zero charge, "pH_{pzc}" of the surface. The fact that the sorption isotherms for rutile in TMACl media are significantly shallower than in NaCl media, indicates that the much larger TMA^+ cation is less effective at shielding negative surface charge buildup than Na^+.

In Figure (3), the proton sorption isotherms for magnetite in 0.03 and 0.3 molal NaTr solutions at

100°C are shown, expressed in terms of excess H^+ in solution, rather than surface charge. Several features of the magnetite isotherms are distinct from
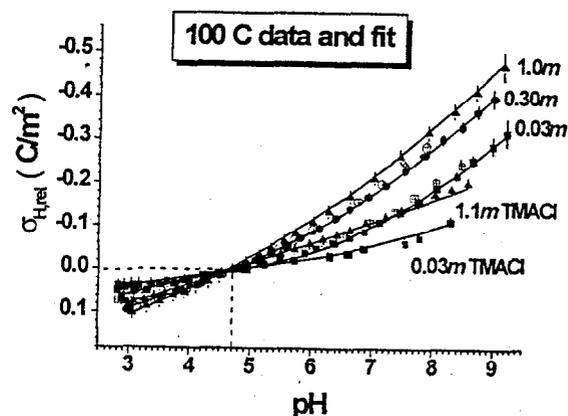

Figure 2. Rutile surface protonation isotherms in NaCl and TMACl media [1] at 100°C, expressed as surface charge calculated from eq. (1).

those of rutile. First, there is a sharp downturn in the isotherms at low pH, which is due to proton consumption by dissolution of this much more soluble phase, releasing Fe^{2+} into solution, despite the use of triflate, a "noncomplexing" anion [2]. Second, the pH_{cip} values do not correspond to the condition of nearly zero excess H^+ in solution. This was also true of our earlier studies of rutile surface protonation, using a solid phase that had not been pretreated hydrothermally in pure water at 220°C for a week or more [1]. This hydrothermal pretreatment
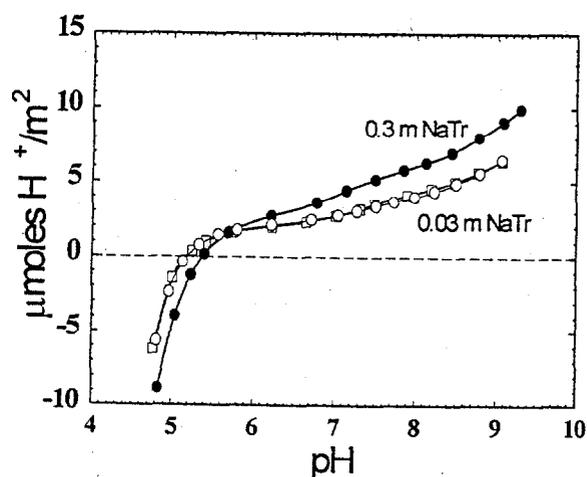

Figure 3. Magnetite surface protonation isotherms in NaTr media at 100°C [2].

was avoided in the case of magnetite, in order to minimize oxidation of the surface. The effect of dissolution of the solid phase complicated the

interpretation of the pH_{cip} values for magnetite, such that a derivative analysis was performed to determine the pH of minimum slope in the 0.03 m NaTr isotherms at each temperature, which were then assumed to reflect the pH_{pzc} of the solid [2].

The pH_{pzc} of rutile and magnetite as a function of temperature are compared in Figure (4), along with the results of [6,7] over a much narrower temperature range. The temperature dependencies of the pH_{pzc} values for these solids are strikingly similar, and also nearly identical to the temperature dependence of the neutral pH in pure water ($1/2pK_w$). The dashed curves are estimates calculated from a temperature extrapolation [8] of the revised MUSIC model [9], which involves
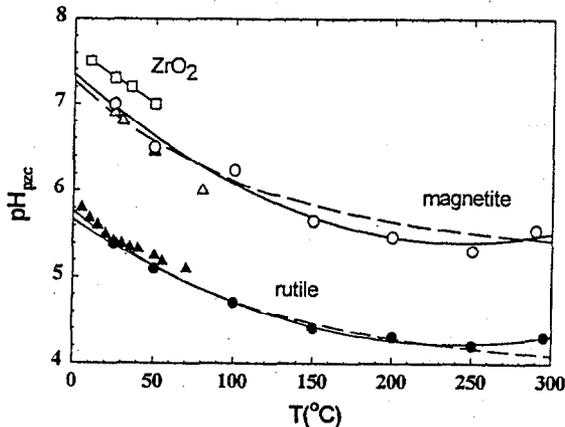

Figure 4. pH_{pzc} values for rutile (solid circles) and magnetite (open circles) obtained in our laboratories, compared with the results of [6] (solid triangles) and [7] (open triangles). Solid lines are regressions through our results and dashed lines are MUSIC model estimates. Preliminary pH_{pzc} data for TOSOH ZrO_2 are shown as open squares.

estimation of the undersaturation of bond valence of surface oxygen atoms bonded to one, two or three metal ions in the underlying oxide crystal lattice. The densities and partial charges of these surface sites are determined from detailed structural analysis of the oxide phase. For rutile, we have used the structural interpretation of the particle surface suggested by [10], assuming that the 110, 100 and 101 crystal faces are represented in the ratio 0.6:0.2:0.2. For magnetite, the crystal structure interpretation of [11] was used, with ratios of the 110, 100 and 111 crystal faces of 0.57:0.23:0.20 determined from SEM images of the much larger magnetite particles. Surface protonation constants (K_{Hy}) are estimated in the MUSIC model [9] using the relationship,

$$\log K_{Hy} = -A^{25}(V + \Sigma s_{Me-O} + m(s_H) + n(1-s_H)) \quad (2)$$

where A^{25} is the slope obtained from regression of a large number of logK values for homogeneous protonation reactions of oxygen-bearing aqueous species at 25°C, versus the undersaturation of charge on the oxygen ligand. V is the valence of oxygen (-2.0), Σs_{Me-O} is the sum (one, two or three for single, double or triple coordination, respectively) of the bond valence values for the metal-oxygen bonds (Me-O) of interest, m is the number of donating H-bridges with adsorbed water (requires the presence of an H atom in the deprotonated, negatively charged species), s_H is the bond valence of an adsorbed proton (+0.8), and n is the number of accepting H-bridges with adsorbed water. For singly coordinated surface oxygens (m+n)=2, for doubly coordinated surface oxygens (m+n)=1 or 2, and for triply coordinated surface oxygens (m+n)=1. The s_{Me-O} values were computed using the Brown bond valence approach [8,12].

The A^{25} parameter was estimated [9] from the protonation constants of a wide range of aqueous species, such as $Fe(OH)_3{}^\circ{}_{aq} + H^+ \Leftrightarrow Fe(OH)_2{}^+ + H_2O$ and $H_3SiO_4{}^- + H^+ \Leftrightarrow H_4SiO_4{}^\circ{}_{aq}$, taking into account the electrical work involved in neutralization of the negative charge for the latter type of reaction. We have used a similar approach in the calculation of A^T parameters at temperatures other than 25°C by assuming that all terms in parentheses in eq. (2) are temperature-independent. However, for aqueous species, we allowed the average coordination number (CN), used to calculate $s_{Me-O} = z/CN$, where z is the central metal ion charge, to decrease with increasing temperature, using an empirical relationship derived from spectroscopic studies (cf. [13]). From analysis of the available and reliable data on high temperature aqueous reactions, the A parameter in eq. (1) is closely approximated by

$$A^T = -3.877 + 6189.15/T + 0.016191(T) \quad (3)$$

where T is the absolute temperature. Using this equation and the partial charges on the various surface sites, the average pH_{pzc} values for the bulk oxide particles were estimated for rutile and magnetite, as shown by the dashed lines in Fig. (4), and found to be well within the experimental uncertainty in the pH_{pzc} values. In order to experimentally calibrate the extrapolation to high temperature, the individual site densities were allowed to vary slightly, in order to match the observed pH_{pzc} values at 25°C.

Figure (5) shows a representative set of sorption isotherms for ZrO_2 obtained from Nippon Silica Glass USA, Inc (Tosoh Ceramics Division, TZ-0), which was repeatedly treated in boiling deionized water prior to titration. Additional studies with ZrO_2 obtained from Alfa Chemicals, Inc., which was hydrothermally treated prior to use, exhibited distinctly different sorption isotherm behavior at temperatures up to about 200°C, lacking distinct pH_{cip} values. At higher temperatures, the Alfa ZrO_2 did exhibit clear pH_{cip} values and an ionic strength dependence of the isotherms similar to that of rutile. There is evidence that at low temperatures, the Alfa ZrO_2 extensively hydrates, which may affect the titration results. The TOSOH ZrO_2 does not appear to hydrate significantly, and because of its high pH_{pzc}, may be an excellent candidate for anion adsorption studies. Preliminary pH_{pzc} values for this solid from 10 to 50°C are shown in Fig. (4).
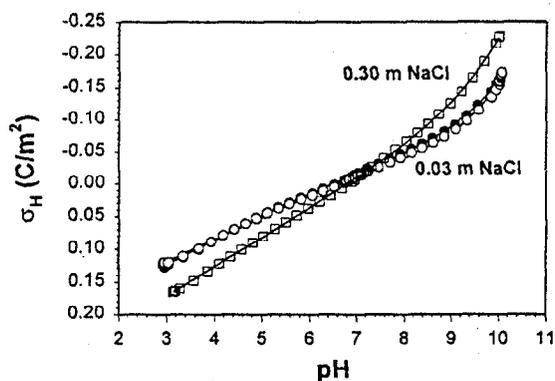

Figure 5. TOSOH ZrO_2 surface protonation isotherms at 50°C in 0.03 and 0.3 molal NaCl.

2. Specific Ion Adsorption Studies

Multivalent cations and anions are known at room temperature to interact strongly with charged mineral surfaces, but heretofore, there has been little information available for elevated temperatures. In our recent studies of Ca^{2+} sorption on rutile surfaces in NaCl media [3], we showed that millimolal levels of Ca^{2+} in 0.03 and 0.30 molal NaCl greatly elevated the negative surface charge density, as illustrated for one condition in Figure (6.).

As can be seen, Ca^{2+} begins to strongly influence the proton-induced surface charge at a pH significantly below the pH_{pzc} determined in NaCl media alone. At higher temperatures, this effect is even more pronounced, with significant negative surface charge enhancement beginning nearly a full pH unit below the "pristine" pH_{pzc} at 250°C [3]. In addition to pH titrations, experiments were also conducted in which samples were periodically
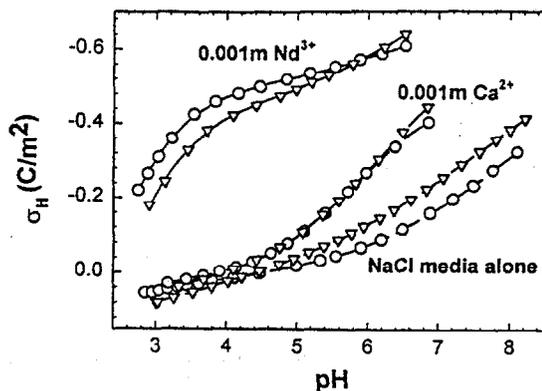

Figure 6. Rutile protonation isotherms at 150°C at 0.03m (circles) and 0.30m (triangles) ionic strength in NaCl media with and without Ca^{2+} or Nd^{3+}.

removed from solution for total calcium analyses, while continuously monitoring pH throughout the titration. These "sorption edge" experiments indicate that at the "pristine" pH_{pzc}, almost none of the added Ca^{2+} is adsorbed at 25°C, while at 250°C, approximately 50% of the added Ca^{2+} is associated with the surface.

We used a simple "one-pK_H" surface protonation approach ($logK_H = pH_{pzc}$) to fit our rutile proton sorption isotherm data in NaCl media [1], in which the Na^+ and Cl^- were assigned to separate Stern planes, but the binding constants to oppositely-charged surface sites were assumed to be equal. A diffuse layer was also assumed, the potential distribution of which was computed from Gouy-Chapman theory. In modeling the Ca^{2+} sorption isotherms in NaCl media, we first fit our results in NaCl media alone, using the same approach, but allowing the Na^+ and Cl^- binding constants to vary independently. The binding constants and overall Stern layer capacitances from this model were then fixed, but an additional Stern layer, immediately adjacent to the mineral surface, was introduced for Ca^{2+}, and the Ca^{2+} binding constants and capacitances were permitted to vary. Furthermore, Ca^{2+} was also assumed to form a tetradentate complex with four adjacent, negatively-charged surface sites, as has recently been suggested for the binding of Sr^{2+} on rutile surfaces from synchrotron X-ray standing wave studies [14]. This produced an excellent fit to the sorption isotherm data at all conditions.

In our original model [1] and the new model, the binding constants and capacitance values for Na^+ are clearly highly covariant, and both exhibit weak increases with temperature. However, logK values of the Ca^{2+} binding constants derived from the new model vary nearly linearly with temperature,

increasing from approximately 0.5 to 3.2 from 25 to 250°C, and are nearly independent of solution ionic strength. This may reflect a more covalent bonding of Ca^{2+} to the surface, while Na^+ and Cl^- interact according to longer-range electrostatic forces. The capacitance values of the Ca^{2+} layer are very high, indicating a separation distance less than that of the hydrated ion radius. This is consistent with the X-ray standing wave results, indicating contact binding, that may penetrate into the surface plane.

The effect of Nd^{3+} on rutile surface charge is profound, as shown in Fig. (6). Even at 25°C, significant increase in the negative surface charge, relative to NaCl media alone, was exhibited up to 2 pH units below the pristine pH_{pzc}, with nearly 100% adsorption attained at the pH_{pzc} at all conditions studied (25-250°C). This is shown in Fig. (6) by the parallelism of the Nd-present and NaCl-alone isotherms above about pH 4.5. We have not begun modeling these results yet, but they bear important implications for the transport of tri-and tetravalent ions (including actinides, rare earth elements, etc.) in subsurface environments, as well as industrial systems, particularly at elevated temperatures.
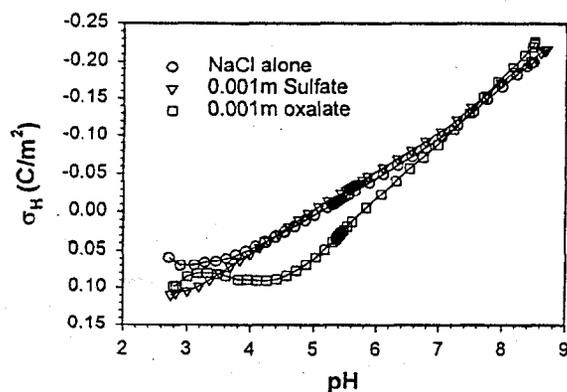

Figure 7. Rutile surface sorption isotherms at 50°C in NaCl solutions at 0.30 molal ionic strength in solutions with and without added sulfate or oxalate.

Our studies to date with rutile indicate that Cl^-, the most significant monovalent anion in natural and industrial settings, interacts only weakly with rutile surfaces, even at high temperature. Triflate, a much larger synthetic monovalent anion was found to interact very similarly with positively charged rutile surfaces below the pH_{pzc}. Because of the high solubility and rapid dissolution of magnetite at low pH, this phase did not prove suitable for anion adsorption studies. While rutile is quite insoluble,

even at low pH, its pH_{pzc} is also low, limiting the practical working range in which to study anion adsorption effects. Despite this limitation, we have begun studies of the effect of oxalate ($^-OOCCOO^-$) and sulfate (SO_4^{2-}) on rutile surface charge in NaCl media, as illustrated at 50°C in Figure (7). At this condition, sulfate appears to interact no differently than Cl^-, presumably due to the rigid nature of this "hard" anion and its much larger radius than that of chloride. However, oxalate strongly enhances positive surface charge even above the pristine pH_{pzc} (5.1 at 50°C), most likely by forming bidentate complexes with positively-charged surface sites, just as it binds with cations in solution. The enhancement in surface charge due to oxalate exhibits a maximum at a pH of about 4.5, below which the effect reduces to near zero. This is undoubtedly due to protonation of free oxalate in solution with decreasing pH [15].

The sorption isotherms in Fig. (7) exhibit unusual curvature below pH 3. This may be due to experimental difficulties in calculating small differences between large measured and calculated proton concentrations in solution at this low pH. This is another reason why it is advantageous to study anion adsorption using solids with higher pH_{pzc}'s.

4. Discussion

These studies demonstrate that the surface charging characteristics of metal oxides can be readily and precisely studied at high temperature, using HECC cells to monitor the pH_m of the solution during potentiometric titrations with acid and base. Furthermore, the results obtained are completely compatible with results obtained using conventional glass electrode methods at low temperature. This has been confirmed in our laboratories by the coincidence of rutile surface protonation isotherms and oxalate effects using the same solid phase, but HECC cells vs. a Mettler DL70 autotirator and a Ross Semimicro combination glass electrode calibrated against NaCl-HCl solutions of the same ionic strength as the test solution. We have also demonstrated good agreement between our results and those of [6,7] for the pH_{pzc} of rutile and magnetite at temperatures up to 90°C.

As illustrated for rutile in Figure (8), the charging of metal oxide surfaces for a given pH increases with increasing ionic strength, and this effect is enhanced with increasing temperature, most likely due to the decrease in the dielectric constant of water, which weakens the bonding of hydration waters to both aqueous ions and charged surfaces, favoring closer approach of solution species to the

surface and greater counterion shielding. The specific binding of multivalent cations and anions is also shown to markedly increase with increasing temperature.

These observations demonstrate that charging of metal oxide surfaces and colloidal particles becomes a much more important feature of their reactions
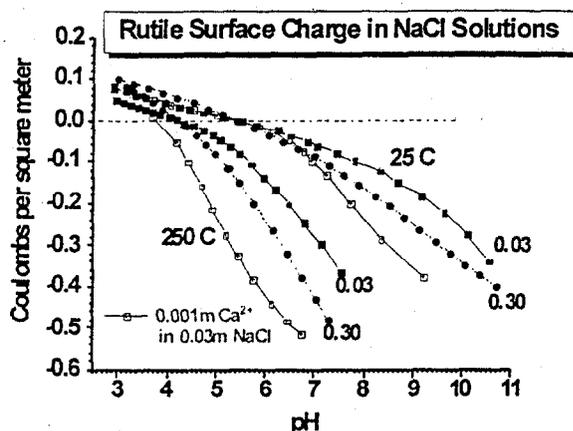

Figure 8. The effect of temperature (25 vs. 250°C) and ionic strength (0.03 vs 0.3m), as well as the presence of millimolal Ca^{2+}, on the proton-induced surface charge of rutile in NaCl media.

with aqueous solutions under hydrothermal conditions. This will no doubt strongly influence the transport of colloidal particles, the dissolution and precipitation kinetics of the solid phases, growth morphologies, and the mobility of toxic metals, radionuclides, organic acid anions and other highly charged ions in hydrothermal systems.

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