Influence of pH and Competitive Adsorption on the Kinetics of Ligand-Promoted Dissolution of Aluminum Oxide

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The kinetics of \(\delta\)-Al\(_2\)O\(_3\) dissolution were examined in the presence of 8-hydroxyquinoline-5-sulfonate (HQS) and salicylate over the pH range 3–9. The greatest effects of both of these ligands on \(\delta\)-Al\(_2\)O\(_3\) dissolution were observed at pH values higher than those corresponding to maximal adsorbed ligand concentrations. Thus, calculated rate constants were pH dependent. For HQS, correlation between the fluorescence of the surface complex and the adsorbed HQS concentration indicates that the pH dependence of the rate constant cannot be explained by a change in the structure of the metal–organic surface complex. Rather, it is proposed that the rate-determining step in the dissolution reaction involves a mixed surface complex in which aluminum is coordinated by both the organic ligand and hydroxide. Similarly, dissolution rates in the presence of the competing adsorbates HQS and fluoride suggest a synergistic action of these two ligands. Dissolution rates predicted from measured adsorbed concentrations of both ligands assuming independent, parallel pathways for HQS– and fluoride-promoted dissolution underpredict observed dissolution rates at some adsorbed ligand concentrations. In contrast, dissolution rates in the presence of the competing adsorbates HQS and arsenate could be predicted simply by accounting for the displacement of HQS from the oxide surface by arsenate.

Introduction

Dissolution of aluminum-containing minerals and amorphous solid phases has been invoked as a dominant mechanism for acid neutralization in regions of carbonate-poor mineralogy (1, 2). Release of aluminum into solution has been observed in field acidification experiments (3–5) and in response to episodic acidification (6). Dissolved aluminum concentrations found in soil solutions can be sufficient to inhibit growth of sensitive tree species and this phenomenon has been implicated in forest decline (7). In soil formation processes, solubilization and translocation of aluminum and iron occur in response to elevated concentrations of CO\(_2\) and organic acids generated by microbial activity in the organic-rich uppermost soil horizons. A variety of low molecular weight organic acids have been identified in forest litter leachates and lysimeter percolates from a podzolized soil (8–10). These organic acids have been shown to enhance dissolution of oxide and silicate minerals (11–16) and the mobilization of metals from mineral horizons (8, 17, 18) in laboratory studies. Inorganic ligands, such as fluoride, can also promote the dissolution of aluminum oxides in the soil matrix (19), and fluoride has been shown to mobilize iron, aluminum, and organic matter in column studies (20). Elevated fluoride concentrations can occur in soils as a result of anthropogenic emissions (21, 22) or weathering of fluoride-bearing parent rocks (23).

A simple but useful model has been proposed by Stumm and co-workers where the influence of various surface species (including water, protons, hydroxides, and other inorganic and organic ligands) on dissolution rates is expressed as independent parallel reaction mechanisms (11):

\[ R_{\text{net}} = R_{\text{H}^+} + \sum R_i \]  

in which the reaction rate \(R\) (mol h\(^{-1}\) m\(^{-2}\)) corresponds to net \((R_{\text{net}})\), proton-promoted \((R_{\text{H}^+})\), and ligand-promoted \((R_i)\) dissolution. It has been demonstrated that the effect of various surface species on dissolution is a function of their surface concentration (11) so that

\[ R_i = k_i [M - L_i] \]  

where, for each ligand i, the rate of ligand-promoted dissolution is a function of the rate constant \(k_i\) (h\(^{-1}\)) and the surface concentration of metal organic surface complexes \([=M - L_i]\) (mol m\(^{-2}\)). The surface concentration of the ligand is pH dependent while the rate constant \(k_i\) is usually taken to be pH independent, at least over some pH range. In some cases, the observed pH dependence of the rate constant has been attributed to a change in the structure of the metal–organic surface complex with pH (23–25).

The relatively simple conceptual models that underlie eqs 1 and 2 have proven to be extremely useful for describing dissolution rates over a wide range of experimental conditions (far from equilibrium). In this work, however, the assumption of parallel, independent pathways for dissolution is shown to be insufficient to account for the observed synergistic effects of organic ligands and hydroxide or fluoride ions on the dissolution of \(\delta\)-Al\(_2\)O\(_3\). The interpretation of these observations may improve the understanding of oxide dissolution kinetics in natural environments.

Experimental Procedures

Reagents. 8-Hydroxyquinoline-5-sulfonic acid (HQS) monohydrate (98%, Aldrich) was recrystallized from a large volume of hot water. NaClO\(_4\) (certified, Fisher), Na\(_2\)HAsO\(_4\)-7H\(_2\)O (ACS grade, Sigma), NaI (ACS, Aldrich), salicylic acid (ACS, Aldrich), HEPES [2-(4-(2-hydroxyethyl)-1-piperazino)ethanesulfonic acid](99.8%, Sigma Ultra), concentrated perchloric acid (trace metal grade, Fischer), and concentrated nitric acid (instrumental grade, EM Science) were used as received. Aluminum ICP standard solution (Alfa Aesar, specpure) was used for ICP-MS calibration. Al(ClO\(_4\)\(_2\)) stock solution was prepared by dissolving Al(ClO\(_4\)\(_2\))-9H\(_2\)O (99.9%, Alfa Aesar) in 3.5% HClO\(_4\) solution and was calibrated against ICP standard solution by ICP-MS. The stock solution was used for calibration of the UV spectrophotometer. All solutions were prepared with high-purity 18 M\(\Omega\) cm\(^{-1}\) water (Milli-Q UV Plus, Millipore).
The oxide used was \( \delta-Al_2O_3 \) (Degussa, Type C), which has a specific surface area of 100 m\(^2\) g\(^{-1}\) (26). For batch experiments, the oxide was washed with DI water and centrifuged. After discarding the supernatant, the oxide was resuspended in 0.01 M NaClO\(_4\). The solids concentration in the stock suspension was measured gravimetrically. For continuous-flow stirred-tank reactor (CFSTR) experiments, the oxide was used as obtained. Solid concentrations were measured gravimetrically after CFSTR experiments. Observed losses of the solids were always less than 5%, consistent with the expected loss due to observed oxide dissolution.

**Analytical Methods.** pH was measured with a pH meter (Orion, model 720A) and an Ag/AgCl combination electrode (Ross) calibrated at pH 4.0, 7.0, and 10.0. Total AI concentrations were measured by ICP-M/S (Perkin-Elmer, LS50B). Dissolved HQS species were measured using a diode array spectrophotometer (Hewlett-Packard, 8452A). Before the spectrophotometric measurements, the pH was adjusted to 7.5 by adding 1 N NaClO\(_4\) or NaOH. Dilution due to acid or base additions was accounted for. Free HQS and Al(HQS)\(_2\) were measured at 310 and 368 nm, respectively. Spectral interferences were observed and quantified by deconvoluting the spectra of the free and complexed ligand. The specific absorbances of the free ligand at 310 and 368 nm are \( \varepsilon \) (HQS, 310 nm) = 4.47 \( \times \) 10\(^4\) (L mol\(^{-1}\) cm\(^{-1}\)) and \( \varepsilon \) (HQS, 368 nm) = 0.39 \( \times \) 10\(^3\) (L mol\(^{-1}\) cm\(^{-1}\)). The specific absorbances of the Al ligand complex are \( \varepsilon \) (Al(HQS)), 310 nm) = 5.43 \( \times \) 10\(^3\) (L mol\(^{-1}\) cm\(^{-1}\)) and \( \varepsilon \) (Al(HQS)), 368 nm) = 11.66 \( \times \) 10\(^3\) (L mol\(^{-1}\) cm\(^{-1}\)). Despite the spectral interferences, mass balance calculations on the dissolved ligand concentration showed errors smaller than 2%. Also, dissolved metal concentrations measured spectrophotometrically were in very good agreement with ICP-MS measurements (close to 100% of the dissolved metal is complexed by HQS under experimental conditions). Total dissolved salicylate was measured at pH 7.5 (samples diluted 1:5) at 296 nm (\( \varepsilon \) (salicylate, 296 nm) = 37.22 \( \times \) 10\(^2\) (L mol\(^{-1}\) cm\(^{-1}\))). Addition of dissolved AI and complex formation had no influence on the absorbance spectra of salicylate.

Fluoride was measured with a fluoride ion selective combination electrode (Orion, model 9609). EDTA was added to the filtered solutions in order to complex dissolved aluminum.

**Fluorescence.** The fluorescence of the HQS surface complex was determined as a function of pH, using a luminescence spectrometer (Perkin-Elmer, LS50B). Suspensions and solutions were measured, using a 12.5 mm square quartz cell and front surface illumination to avoid inner-filter effects by suspended particles. Excitation and emission wavelengths of 363 and 491 nm were used to measure fluorescence of the solids and of the dissolved Al–HQS complex (slit width 10 nm). \( \delta-Al_2O_3 \) stock suspension was diluted in 0.01 M NaClO\(_4\) and 5 mM HEPES buffer in several low-density polyethylene (LDPE) sample containers. The pH was adjusted in each sample to cover the desired pH range. After 24 h, the pH was readjusted. Ligand stock solutions were added to final concentrations of 200 \( \mu \)M (HQS) or 1000 \( \mu \)M (salicylate) with solid concentrations of 1.0 g/L. The pH was maintained by adding small volumes of 1.0 N HClO\(_4\) or NaOH. Samples were agitated in a wrist action shaker for 5 min (HQS) or 30 min (salicylate). The short reaction times were chosen in order to minimize oxide dissolution since elevated dissolved aluminum concentrations may lead to adsorption of aluminum complexes. Preliminary experiments indicated that HQS adsorption and concomitant surface fluorescence development was complete within 5 min. The reaction time was set to 30 min for salicylate based on preliminary experiments. In HQS adsorption experiments, samples were filtered through 0.025 \( \mu \)m filters (Millipore, mixed cellulose ester). The first 3 mL of the filtered volume was discarded. Ten milliliters was collected for spectrophotometric measurement of dissolved ligand concentrations. Samples involving salicylate were not filtered to avoid adsorption on filter material. These suspensions were centrifuged, and the supernatant was used for spectrophotometric analysis.

**Competitive Adsorption of HQS and Fluoride or Arsenate.** Competitive adsorption experiments of HQS and arsenate on \( \delta-Al_2O_3 \) were conducted at pH 7.5 and of HQS and fluoride at pH 5.5. The total HQS concentration was 200 \( \mu \)M for all experiments. Total As(V) concentrations varied from 0 to 0.01 M and fluoride concentrations from 0 to 0.001 M.

\( \delta-Al_2O_3 \) was suspended in 0.01 M NaClO\(_4\) and 5 mM HEPES buffer. After 24 h, the pH was readjusted. The suspension was split in several 30 mL low-density polyethylene (LDPE) sample containers. Ligand stock solutions were added to final ligand concentrations with a solid concentration of 1.0 g/L. The competing ligands [HQS/As(V) or HQS/fluoride] were added to the suspension at the same time. The pH was maintained within \( \pm 0.05 \) pH units by addition of small volumes of 1.0 N HClO\(_4\) or NaOH. After 5 min equilibration with stirring at ambient temperature, samples were removed and filtered through 0.025 \( \mu \)m filters (Millipore, mixed cellulose ester). The first 3 mL of the filtered volume was discarded. Ten milliliters was collected for measurement of dissolved species. Total dissolved Al was measured by ICP-MS and \([\text{HQS}]_{\text{free}}\) and \([\text{Al(HQS)}]_3\) were measured by UV spectrophotometry. Fluoride was measured with a fluoride-specific electrode after addition of EDTA stock solution to \([\text{EDTA}]_{\text{free}}\) of 10 mM to free fluoride from dissolved aluminum fluoride complexes. The dilution of samples was taken into account.

**Continuous-Flow Stirred-Tank Reactor Experiments.** The continuous-flow stirred-tank reactor (CFSTR) has been described previously (27, 28). The pH of all influent solutions was adjusted using HClO\(_4\) or NaOH (without HEPES buffer) at an ionic strength of 0.01 M (NaClO\(_4\)). Total dissolved metal concentrations in the effluent were measured by ICP-MS. CFSTR experiments were used to determine dissolution rates as a function of pH in the presence of HQS and salicylate at total, dissolved concentrations ([HQS]\(_{\text{dis}}\) or [salicylate]\(_{\text{dis}}\)) of 200 and 1000 \( \mu \)M, respectively, and in the absence of organic ligands. The influence of competing ligands on dissolution kinetics was measured in the presence of [HQS]\(_{\text{dis}}\) = 200 \( \mu \)M and ([As]\(_{\text{dis}}\) between 0 and 1 mM or [As]\(_{\text{dis}}\) between 0 and 1000 \( \mu \)M. In the presence of organic ligands or fluoride, CFSTR flow rates were set between 0.1 and 0.4 mL/min. Flow rates between 0.3 and 0.8 mL/min were used for measurements of pH-dependent dissolution in the absence of organic ligands. Steady-state dissolution rates were calculated from the average aluminum concentrations in the reactor effluent after steady-state conditions were reached (see ref 27, eq 8). Observed net reaction rates are considered true dissolution
rates; under the experimental conditions, solutions are far from equilibrium with aluminum oxides or (oxo)hydroxides, and precipitation should not occur.

Results

Effect of pH on Adsorption and Ligand-Promoted Dissolution. For the two organic ligands examined, salicylate and HQS, both ligand adsorption and \( \delta-Al_2O_3 \) dissolution rates in the presence of the ligands were observed to be pH dependent (Figure 1). The latter effect, however, also incorporates the pH dependence of \( \delta-Al_2O_3 \) dissolution rates in the absence of organic ligands. In the organic-free system, a minimum in the dissolution rate was observed near neutral pH; dissolution rates increased with decreasing pH below pH 6 and (even more strongly) with increasing pH above pH 7.5 (Figure 1b).

For salicylate (at a total concentration of 1000 \( \mu M \)), maximum adsorption was observed between pH 4.5 and 5.5 with significantly decreasing adsorption at both lower and higher pH (Figure 1a). In contrast, the maximum effect of salicylate on the rate of \( \delta-Al_2O_3 \) dissolution was observed at pH 6.3 (Figure 1b). Above this pH, the dissolution rate in the presence of salicylate declined sharply approaching the rates observed in the organic-free system. Salicylate had no effect on the rate of \( \delta-Al_2O_3 \) dissolution either above pH 7.5 or at pH 3.

Similar trends were observed with HQS (at a total concentration of 200 \( \mu M \)), but the disparate effects of pH on adsorption and dissolution rates were more pronounced. The adsorption of HQS occurs over a wider pH range than adsorption of salicylate with a maximum adsorption between pH 4.5 and 6.5 and a gradual decrease in adsorption above and below this range (Figure 2a). However, significant adsorption of HQS was observed even up to pH 8. The pH dependence of the fluorescence of the HQS surface complex is very similar to that of HQS adsorption, indicating that surface fluorescence is correlated to the adsorbed HQS concentration over the entire pH range. As with salicylate, the maximum effect of HQS on the rate of \( \delta-Al_2O_3 \) dissolution was observed not at the pH of maximum adsorption but at higher pH (Figure 2b). The presence of HQS had no effect on the \( \delta-Al_2O_3 \) dissolution rate at pH 3 and increased dissolution only slightly between pH 4 and 5.5. Between pH 6 and 8 dissolution rates were increased substantially by HQS with a sharp decrease above pH 8.5.

For both salicylate and HQS, ligand-promoted dissolution rate constants, \( k_L \), were calculated from the ligand-promoted dissolution rates, \( R_{net} \), and adsorbed ligand concentrations, \([=Mürnberg]\), based on eq 2. Ligand-promoted dissolution rates were calculated from the difference between net dissolution rates in the presence and absence of the organic ligand (\( R_{net} - R_{sol} \)) at a given pH. As can be seen in Figure 3, the values of \( k_L \) for both HQS and salicylate increase with the activity of OH\(^-\) at low [OH\(^-\)] (i.e., up to pH 6.7); for HQS, \( k_L \) reaches a maximum value at higher pH.

Influence of Competitive Adsorption of HQS and Arsenate on Dissolution Kinetics. The effects of arsenate, As(V), on HQS adsorption and HQS-promoted dissolution were examined at pH 7.5, where \( \delta-Al_2O_3 \) dissolution in the absence of HQS is negligible. At this pH, the maximum adsorbed concentration of As(V), \( 6 \times 10^{-7} \) mol m\(^{-2} \), is close to that of HQS, \( 5.8 \times 10^{-7} \) mol m\(^{-2} \). In batch adsorption
From the experiments, it can be seen that HQS is increasingly displaced as a function of the dissolved OH− concentration. As shown in Figure 4a, adsorbed As(V) concentrations were determined in batch experiments (see panel a). The open tilted square (○) indicates the proton promoted dissolution rate measured with the CFSTR in the absence of HQS or As(V). The solid line indicates the calculated dissolution rate according to eq 5. pH 7.5, 1 = 0.01 M NaClO4, solids concentration = 1.0 g/L. Adsorbed HQS concentrations were not determined. (b) Steady-state CFSTR dissolution rates of δ-Al2O3 as a function of the adsorbed HQS concentration (●) in the presence of 0–0.01 M [As(V)]diss at constant [HQS]diss = 200 μM. The adsorbed HQS concentrations in the presence of As were determined in batch experiments (see panel a). The open tilted square (○) indicates the proton promoted dissolution rate measured with the CFSTR in the absence of HQS or As(V). The solid line indicates the calculated dissolution rate according to eq 5. pH 7.5, 1 = 0.01 M NaClO4, solids concentration = 1.0 g/L.

Concentration were higher than in the absence of HQS; this effect decreased with increasing adsorbed fluoride concentrations (Figure 5b).

**Discussion**

The assumption of independent, parallel pathways for proton- and ligand-promoted dissolution (implicit in eq 1) does not exclude indirect effects of pH on ligand-promoted dissolution or of competing ligands in multiligand systems. For example, the adsorbed concentration of a ligand L does not exclude indirect effects of pH on ligand-promoted dissolution and the anionic ligands. These effects can be accounted for the observed results. Finally, a modified concept of synergistic effects of pH and competing ligands on ligand promoted dissolution is proposed.

**Effects of pH on Adsorbed Ligand Concentrations and on the Rate Constants for Ligand-Promoted Dissolution.** The effects of pH on adsorbed ligand concentrations are observed for both salicylate and HQS (Figures 1a and 2a). The observed decrease in adsorbed ligand concentrations at both low and high pH are consistent with expected speciation of the ligands and the oxide surface. Low pH favors protonation of the ligand in solution over adsorption. At high pH, the exchange reaction between surface hydroxyl groups and the adsorbing (deprotonated) ligand is less favorable with increasing hydroxide ion concentration and deprotonation of surface hydroxyl groups results in electrostatic repulsion between the negatively charged surface and the anionic ligands. These effects can be accounted for

**FIGURE 3.** (a) Ligand promoted dissolution rate constants kL in the presence of [HQS]diss = 200 μM (●) and [salicylate]diss = 1000 μM (○) as a function of the OH− activity in solution in the acidic pH range ([OH−] = 10−11–(5 × 10−4) = pH 3–6.7). 1 = 0.01 M NaClO4, solids concentration = 1.0 g/L. The OH− activities were calculated from pH measurements. Rate constants kL were calculated from observed dissolution rates and ligand surface concentrations according to eq 2. (b) Ligand promoted dissolution rate constants kL as a function of the dissolved OH− activity in the full observed pH range ([OH−] = 10−11–(2 × 10−4) = pH 3–8.3).

**FIGURE 4.** (a) Adsorption of HQS on δ-Al2O3 as a function of the total As(V) concentration. Adsorbed HQS concentrations were measured in batch experiments with an equilibration time of 5 min and [HQS]diss = 200 μM. Adsorbed As(V) concentrations were not determined. (b) Steady-state CFSTR dissolution rates of δ-Al2O3 as a function of the adsorbed HQS concentration (●) in the presence of 0–0.01 M [As(V)]diss at constant [HQS]diss = 200 μM. The adsorbed HQS concentrations in the presence of As were determined in batch experiments (see panel a). The open tilted square (○) indicates the proton promoted dissolution rate measured with the CFSTR in the absence of HQS or As(V). The solid line indicates the calculated dissolution rate according to eq 5. pH 7.5, 1 = 0.01 M NaClO4, solids concentration = 1.0 g/L.

**Influence of Competitive Adsorption of HQS and Fluoride on Dissolution Kinetics.** Like As(V) and HQS, fluoride also adsorbs strongly to the δ-Al2O3 surface and, because of its smaller size, can reach even higher adsorption densities. The maximum observed surface concentration of fluoride on δ-Al2O3 (1.9 × 10−6 mol m−2) approaches the surface site concentration determined by alkalimetric titration (2.1 × 10−6 mol m−2) (28, 29). In batch adsorption experiments (at pH 5.5), HQS is competitively displaced by fluoride; adsorbed HQS concentrations decrease as adsorbed fluoride concentrations increase (Figure 5a).

Although both fluoride and As(V) compete with HQS for adsorption sites at the δ-Al2O3 surface, the effects of these two competing ligands on δ-Al2O3 dissolution are strikingly different. In contrast to As(V), fluoride alone promotes the dissolution of δ-Al2O3 at pH 5.5; net dissolution rates were observed to be proportional to the adsorbed fluoride concentration (Figure 5b). In the presence of both HQS and fluoride, dissolution rates at a given adsorbed fluoride
by normalizing the ligand-promoted dissolution rate \( \left( R_{\text{Li}} \right) \) by the adsorbed ligand concentration \( \left[ \text{L} \right] \); if only the aforementioned effects are important, the resulting rate constant for ligand-promoted dissolution \( \left( k_{\text{Li}} \right) \) should be independent of pH. For both salicylate and HQS, however, the calculated values of \( k_{\text{Li}} \) vary with pH. Previous, similar observations have been attributed to pH-dependent changes in the structure of the metal–organic surface complex (11).

**Effect of pH on the Structure of Metal–Organic Surface Complexes.** It has been previously suggested that a shift in the structure of a metal–organic surface complex from a bidentate, mononuclear complex to either a monodentate or a binuclear complex would result in decreased rates of ligand-promoted dissolution (i.e., for identical adsorbed ligand concentrations) (11). In the case of HQS, the observed surface fluorescence provides direct evidence on the structure of the surface complex. HQS is a bidentate ligand that forms pseudooctahedral inner-sphere complexes with aluminum in solution (30). The dissolved aluminum HQS chelate exhibits strong fluorescence while the free ligand is virtually nonfluorescent (31). The fluorescence is localized on the ligand (32) and is due to a perturbation of its molecular orbital energy levels caused by the formation of the chelate between the phenol oxygen, the nitrogen in the fused aromatic ring, and the complexed metal (33, 34); the sulfonate group is not involved in metal binding. Therefore, the observed fluorescence of adsorbed HQS at the \( \delta-Al_2O_3 \) surface indicates the formation of bidentate inner-sphere surface complexes (35) analogous to the complex in solution. This observation has recently been verified by internal reflection Fourier transform infrared spectroscopy (36).

**FIGURE 5.** (a) Adsorption of HQS as a function of the adsorbed fluoride concentration with \([\text{HQS}]_{\text{tot}} = 200 \mu M\). Adsorbed concentrations were measured in batch experiments with an equilibration time of 5 min and pH 5.5, I = 0.01 M NaClO_4, 5 mM HEPES, solids concentration = 1.0 g/L. (b) Steady-state CFSTR dissolution rates of \( \delta-Al_2O_3 \) as a function of the adsorbed fluoride concentration with \([\text{HQS}]_{\text{tot}} = 200 \mu M\) and without HQS \( \phi \). pH 5.5, I = 0.01 M NaClO_4, solids concentration = 1.0 g/L. The lines indicate the calculated dissolution rates in the presence (---) and in the absence (- - -) of HQS according to eqs 7 and 6 using measured adsorbed ligand concentrations from batch experiments (see panel a).

Figure 2a shows that the surface fluorescence is correlated to the adsorbed HQS concentration over the entire pH range. A change in the structure of the metal–organic surface complex from bidentate to monodentate coordination (due to protonation of the phenol) would lead to a loss of fluorescence relative to the adsorbed concentration. A shift from mononuclear to binuclear surface complexes should at least result in shifts in the fluorescence spectrum (i.e., wavelengths of maximum excitation and/or emission) which were not observed. These observations suggest that pH-dependent changes in the structure of the HQS surface complex do not occur and cannot, therefore, explain the pH dependence of the rate constant for HQS-promoted dissolution of \( \delta-Al_2O_3 \).

In contrast, for salicylate, spectroscopic studies with ATR-FTIR (37) and polarized fluorescence (38) do suggest some change in the structure of the adsorbed salicylate complex between pH 5 and 7. While neither of these studies provides quantitative information on the concentrations of various surface species, they suggest a shift from bidentate to monodentate surface complexes. Such a change in the structure of the metal–organic surface complex may be the cause of the sharp decline in the rate of salicylate-promoted dissolution of \( \delta-Al_2O_3 \) observed between pH 6.5 and 7.

**Synergistic Effect of Hydroxide on Ligand-Promoted Dissolution.** To explain the observed pH dependence of the values of \( k_{\text{Li}} \) for both salicylate and HQS, it is necessary to consider not just the structure of the metal–organic surface complex but the entire coordinative environment of the surface metal center undergoing dissolution (i.e., detachment from the oxide lattice). Within the bulk oxide phase, a metal center is fully coordinated by oxygens of the oxide lattice. The dissolution process can be rationalized as a stepwise ligand exchange reaction in which the coordination of a metal center by the oxide lattice is exchanged for coordination by ligands from the solution phase according to a sequence such as:

\[
M(6,0) \rightarrow M(5,1) \rightarrow M(4,2) \rightarrow M(3,3) \rightarrow M(2,4) \rightarrow M(1,5) \rightarrow M(0,6) \tag{3}
\]

for an octahedrally coordinated metal center (27, 28). The indices indicate the coordination by lattice oxygens and adsorbed ligands, respectively. Although this dissolution sequence begins, for completeness, with a metal center in the bulk oxide, it is important to note that parallel dissolution reactions are thought to occur at surface sites with varying reactivity (e.g., steps, kinks, etc.) and that the regeneration of sites allows for steady-state dissolution (11).

In the case of HQS-promoted dissolution, steric considerations suggest that, at certain stages of the stepwise dissolution sequence, other ligands from solution (such as water or hydroxide) must also coordinate the surface metal center. A possible sequence of coordinative configurations for HQS-promoted dissolution would be:

\[
\text{Al} \quad (4,2) \quad \text{HQS} \quad (3,3) \quad \text{Al} \quad (2,4)
\]

where mixed surface complexes are formed in which aluminum is coordinated by HQS and hydroxide. Alternatively, coordination of the surface metal center exclusively by HQS and the lattice oxygens could be postulated; then, the \( M(3,3) \) metal center would be coordinated by two HQS molecules, one as a bidentate and the other as a monodentate ligand, and the \( M(2,4) \) metal center by two bidentate HQS ligands. Given the size of HQS (or of salicylate), it is unlikely that a single surface metal center could be coordinated by more than one organic ligand.
If a mixed surface complex is involved in the stepwise dissolution sequence, then the increase in $k_i$ with increasing pH can be rationalized. Substitution of hydroxide for water in the inner coordination sphere of the aluminum aquo complex is known to increase the rate of water loss from the metal (39). Similarly, it may be that the substitution of hydroxide (or possibly even an oxo anion) for water in the mixed surface complex would substantially increase the lability of the remaining bonds between the surface metal center and the lattice oxygens, thus increasing the rate of detachment of the metal from the surface. This suggests that the value of $k_i$, as [OH$^-$] approaches zero (Figure 3a) may correspond to reaction of a mixed complex incorporating water. For HQS, a maximum value of $k_i$ is reached at high [OH$^-$], which may correspond to reaction of a mixed complex incorporating hydroxide (or oxo anion). Eventually at high pH, however, the rate of HQS-promoted dissolution is limited by displacement of the ligand from the surface and increasing uncertainty in the value of $k_i$, to be expected as the adsorbed HQS concentration becomes small.

**Influence of Competitive Adsorption of HQS and Arsenate on Dissolution of $\delta$-Al$_2$O$_3$.** Since As(V) absorbs strongly at aluminum oxide surfaces (40-42) but does not itself promote oxide dissolution, the competitive adsorption of As(V) and HQS causes a retardation of HQS-promoted dissolution. The rate of $\delta$-Al$_2$O$_3$ dissolution in the presence of competitively adsorbing HQS and As(V) can be predicted successfully simply by accounting for the decrease in adsorbed HQS concentration in the presence of As(V). The rate of $\delta$-Al$_2$O$_3$ dissolution at pH 7.5 in the presence of both HQS and As(V) can be predicted (based on eq 1) from the expression

$$R_{\text{net}} = R_{\text{H}, \text{pH}7.5} + k_{\text{HQS}, \text{pH}7.5} [\text{HQS]}_{\text{ads}}$$

Note that eq 5 does not include any contribution from $k_{\text{As(V)}[\text{As(V)}]_{\text{ads}}}$ [i.e., $k_{\text{As(V)}} \approx 0$] and the adsorbed HQS concentrations in the presence of As(V) correspond to those shown in Figure 4a. This simple expression provides a good fit to the data using the values $R_{\text{H}, \text{pH}7.5} = 2 \times 10^{-9}$ mol h$^{-1}$ m$^{-2}$ (compare Figure 2b, filled squares) and $k_{\text{HQS, pH}7.5} = 0.036$ h$^{-1}$ as indicated by the solid line in Figure 4b.

**Influence of Competitive Adsorption of HQS and Fluoride on Dissolution of $\delta$-Al$_2$O$_3$.** In contrast to As(V), fluoride alone promotes the dissolution of $\delta$-Al$_2$O$_3$ at pH 5.5. The dissolution rate is proportional to the adsorbed fluoride concentration. As shown by the solid line in Figure 5b, a good fit to the data is obtained using the expression

$$R_{\text{net}} = R_{\text{H}, \text{pH}5.5} + k_{f, \text{pH}5.5} [F^-]_{\text{ads}}$$

with $R_{\text{H}, \text{pH}5.5} = 3 \times 10^{-9}$ mol h$^{-1}$ m$^{-2}$ and $k_{f, \text{pH}5.5} = 0.0139$ h$^{-1}$. In the presence of both fluoride and HQS, dissolution rates can be predicted assuming independent, parallel reaction pathways using the adsorbed HQS and fluoride concentrations measured in batch experiments (Figure 5a) and the rate constants for fluoride-promoted dissolution in the absence of HQS and for HQS-promoted dissolution in the absence of fluoride. The rates as a function of the adsorbed fluoride concentration have been calculated using the expression

$$R_{\text{net}} = R_{\text{H}, \text{pH}5.5} + k_{f, \text{pH}5.5} [F^-]_{\text{ads}} + k_{\text{HQS, pH}5.5} [\text{HQS}]_{\text{ads}}$$

with $k_{\text{HQS, pH}5.5} = 0.0126$ h$^{-1}$ and [HQS]$_{\text{ads}}$ from batch experiments (Figure 5a). As can be seen in Figure 5b (dashed line), this model provides a good fit to the data at low [$F^-]_{\text{ads}}$ and at low [HQS]$_{\text{ads}}$ (i.e., at high [H-]$_{\text{ads}}$) but underpredicts the observed dissolution rates at intermediate [F$^-]_{\text{ads}}$ and [HQS]$_{\text{ads}}$.

This suggests that the effects of adsorbed HQS and fluoride on $\delta$-Al$_2$O$_3$ dissolution are not strictly independent and that fluoride, like hydroxide, can have a synergistic effect on HQS-promoted dissolution. Fluoride is a small, monodentate ligand with a high affinity for complexation of aluminum in solution (43) and at the aluminum oxide surface (44, 45). Thus, formation of a mixed surface complex with HQS and fluoride could be hypothesized to have a similar labilizing effect on the surface metal center as proposed for the mixed surface complex with HQS and hydroxide.

Mixed complexes of aluminum with organic ligands and fluoride have been reported in solution; one example is the complex Al(EDTA)F$_2$ (46). Fluoride has a labilizing effect on water in the inner coordination sphere of the aquo aluminum complex; coordination by a single fluoride ion results in an approximately 50-fold increase in the water-exchange rate (47). Thus, analogy with complexation in solution (and its kinetic effects) supports the hypothesis of the labilizing effect of a mixed surface complex.

**Concluding Remarks**

The weathering of oxide minerals in natural systems occurs in the presence of a complex mixture of dissolution-promoting ligands (including both inorganic and organic species), which can profoundly affect processes such as soil formation. In this study, examination of the effects of pH and competing adsorbates on the rates of $\delta$-Al$_2$O$_3$ dissolution demonstrates that previous models for pH- and ligand-promoted dissolution, in which independent, parallel dissolution pathways are assumed, can account only in part for the experimental observations. The assumption does seem to hold in the case of $\delta$-Al$_2$O$_3$ dissolution in the presence of arsenate and the organic ligand HQS, where HQS promotes oxide dissolution and arsenate adsorbs to the $\delta$-Al$_2$O$_3$ surface but does not promote dissolution. In this case, the decrease in HQS-promoted dissolution rates with increasing arsenate concentrations is consistent with displacement of HQS from the $\delta$-Al$_2$O$_3$ surface by the competing adsorbate, arsenate.

In contrast, neither the observed effects of pH on HQS-promoted dissolution of $\delta$-Al$_2$O$_3$ nor the observed rates of $\delta$-Al$_2$O$_3$ dissolution in the presence of HQS and fluoride is consistent with the model of independent, parallel dissolution pathways. Rather, the experimental observations suggest that HQS-promoted dissolution is further enhanced by hydroxide or fluoride. It is hypothesized that the dissolution reaction involves a mixed surface complex in which the aluminum is coordinated by HQS and either hydroxide or fluoride. An analogy with the labilizing effect of substitution of hydroxide or fluoride for water in the aquo aluminum complex then suggests that formation of such a mixed surface complex would increase the rate of detachment of the surface aluminum from the lattice. Such synergistic effects could result in mineral weathering in natural systems being more rapid than would be predicted based on the ability of individual components of soil solutions to promote dissolution.

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