Kurze Mitteilungen

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The Role of Surface Coordination in the Dissolution of δ-Al_2O_3 in Dilute Acids*

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Abstract

Chemical processes at the hydrous-oxide solution interface – protonation of surface OH-groups and surface coordination with ligands (anions) – are important for understanding the dissolution of solid oxide phases. It is shown that the dissolution rate of δ-Al_2O_3 in dilute acids (pH 2.5–6) depends directly on the extent of surface protonation and on the concentration of surface complexes formed in the presence of oxalate, salicylate, citrate and benzoate.

Introduction

The processes occurring at the oxide/water interfaces, such as dissolution and precipitation (heterogeneous nucleation) of mineral phases are of importance in the weathering of rocks in the formation of soils and sediments and in the corrosion of metals and their inhibition; the rates of these processes are critically dependent on the coordinative interactions taking place on these surfaces [1].

The dissolution of oxides and other minerals in aqueous solutions is accompanied by a change in the coordinative partners of the solid constituent ions. For most slightly soluble minerals this rate of dissolution is controlled by reactions at the surface (and not by transport processes) [2–4] and thus depends on its coordination chemistry.

In a case study we have evaluated the effects of various complex forming organic anions and of H^+ (pH 2.5–6) on the dissolution kinetics of δAl_2O_3. The results can be generalized into a simple rate law that shows that the dissolution rate depends on the degree of surface protonation and on the relative concentration of anionic surface complexes.

The coordination chemistry of hydrous oxide surfaces. In aqueous solutions oxide surfaces adsorb H_2O in a dissociative way [5]. The resulting surface hydroxyl groups, $\geq$Me-OH, are amphoteric and can be looked at as a polymeric oxo-acid or base; its oxygen donor atom can coordinate with H^+ and metal ions [6–8]. The underlying central ion in the surface layer of the oxide – acting as a Lewis acid – can exchange its structural OH^- ions against other ligands (anions or weak acids) [7,8]. In most instances these surface complexes are of the inner sphere type [9].

Surface coordination equilibria can be described by the following schematic reactions:

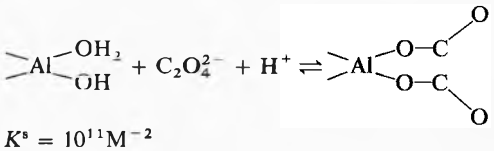
Acid-base: $> Me{-}OH \rightleftarrows Me{-}O^- + H^+$
$> Me\text{-}OH + H^+ \rightleftarrows > Me{-}OH_2^+$

Metal ions: $> MeOH + M^{2+} \rightleftarrows > MeOM^+ + H^+$
$(> MeOH)_2 + M^{2+} \rightleftarrows (> MeO)_2M + 2H^+$ (1)

Anions: $> MeOH + A^{2-} \rightleftarrows > MeA^- + OH^-$
$(> MeOH)_2 + A^{2-} \rightleftarrows (> Me)_2A + 2OH^-$

Acids: $> MeOH + H_2A \rightleftarrows > MeHA + H_2O$

Surface equilibrium constants, either experimentally determined or estimated from complex formation constants in solution can be used to predict the extent of surface binding (adsorption) as a function of pH and solution variables, e.g. the formation of oxalate surface complexes can be given by:



$K^s = 10^{11}M^{-2}$

where K^S is defined as

$K^S = \{\geq AlOx\} / \{\geq AlOHOH_2\}\,[Ox^{2-}]\,[H^+]$

Concentrations in { } are surface concentrations in moles kg^{-1} or moles m^{-2}, and concentrations in [ ] are in moles dm^{-3}.

Methods

In making dissolution experiments with hydrous oxides, special attention must be devoted to the properties of the surface. If heterogeneities of surface properties (different phases, different particle size, different surface energies) exist, parabolic dissolution rates are typically observed. Linear rate laws are usually obtained if the pretreatment renders the surface properties sufficiently homogeneous [1, 2, 10, 11].

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Pretreatment of δ-Al_2O_3: Dispersions of δ-Al_2O_3 (specific surface area = 100 m^2g^{-1}) (Degussa) were treated with dilute HF (1% by weight) and subsequently washed with H_2O. The dispersions were then "conditioned" by preexposing them for three days in a milieu similar to that used in the subsequent dissolution experiments.

Measurements on dissolution and surface complex formation. During the dissolution, pH (calibrated as -log H^+ concentration at a given ionic strength (0.1 M $NaNO_3$)) was kept constant with the help of an automatic titrator that added the H^+ (as HNO_3) used up in the dissolution reaction. Progress in dissolution (during 30 to 50 hours) was measured by following the concentration of dissolved Al(III), as determined by flameless atomic absorption. Dissolution rate was computed from the linear [Al(III)] vs time plots. The extent of ligand adsorption was measured in case of oxalate and citrate by using C-14 labelled compounds and in case of salicylate and benzoate by UV spectrophotometry (measurement of residual conc. in solution), respectively. The treatment of surface complex formation equilibria corresponds to that given earlier [7, 8].

Results and Discussions

The data obtained at different pH values and in presence and absence of organic acids can be generalized into a kinetic law according to which the rate of δ-Al_2O_3 dissolution, R, can be considered to be composed of a surface protonation $\{\geq AlOH_2^+\}$ dependent rate, R_H, and a rate, R_L, which depends on the concentration of ligand surface complexes ($\{\geq Al\text{-}L_i\}$, $\{\geq AlL_iH_j\}$) (Fig. 1).

$$R = R_H + R_L$$

R is time-independent and a function of surface area concentration.

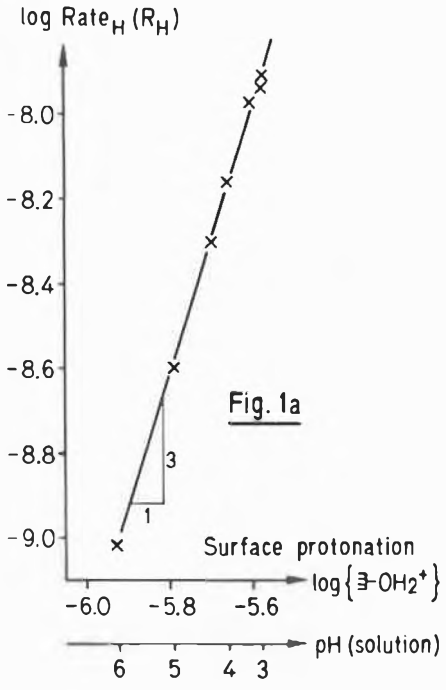
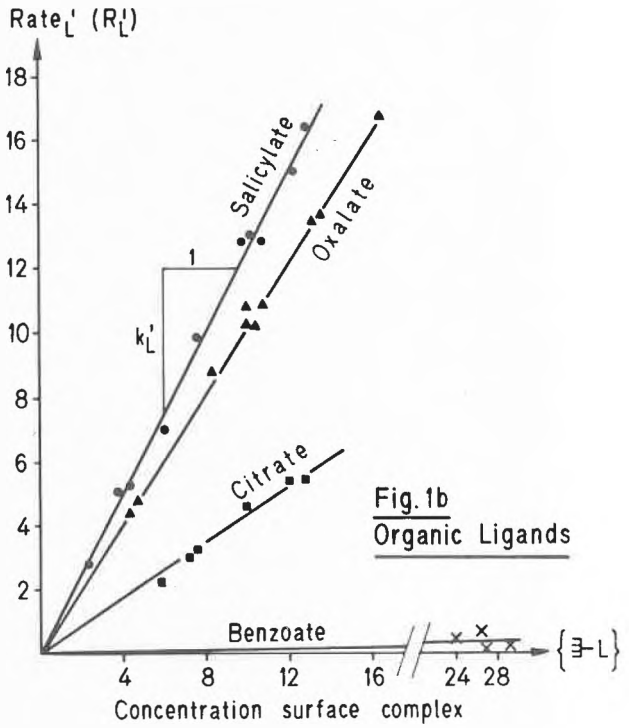


Fig. 1: The dependence of the rate of dissolution of δAl_2O_3 on pH (pH 2.5–6) and on surface complex forming anions.
a) The pH-dependence of R_H (moles m^{-2} h^{-1}) can be accounted for by considering the concentration of protonated OH-groups at the surface (moles m^{-2})



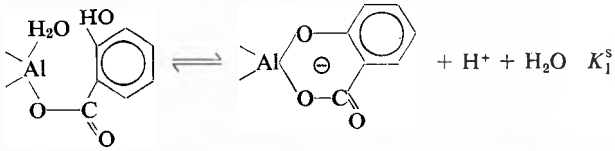
b) The dissolution rate on the presence of organic anions (pH 2.5–6) can be interpreted as a linear dependence on the surface concentrations of deprotonated ligands. R_L' (nmoles m^{-2} h^{-1}) is that portion of the rate which is dependent on surface complexes only. In case of citrate and salicylate at *p*H 4.5 corrections accounting for the protonation of the surface complexes were made. (See Fig. 2)

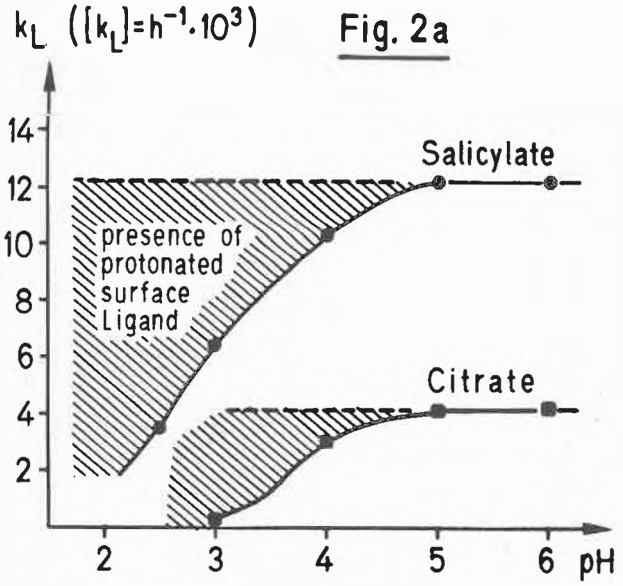
Protonation of surface-OH groups polarizes the Al-O binding; as shown by Fig. 1a, R_H depends on $\{\geq AlOH_2^+\}^3$. The replacement of an OH group by a nucleophilic ligand, L, also polarizes particular Al-O bonds and aids in the detachement of Al-L into solution. As Fig. 1 b indicates, R_L' depends linearily on the surface concentration of the (deprotonated) ligand surface complexes $\{\geq AlL\}$. Thus, generally the rate is given by

$$R = k_H\{\geq AlOH_2^+\}^3 + k_L(\{\geq Al\text{-}L\} + \{\geq Al\text{-}LH\} + ...) \quad (2)$$

Beeing far away from solubility equilibrium, the back reaction is negligible.

Fig. 2 shows that in case of salicylate and citrate, (but not in case of oxalate and benzoate), k_L decreases below pH = 4.5. Most likely this decrease is caused by the presence of protonated surface ligands at lower pH values. Because, as shown earlier [7, 8] the surface enhances in (comparison to the solution) the acidity of surface bound acidic ligands. Thus we infer that the H^+ dissociation equilibria of the surface complexes, e. g.,





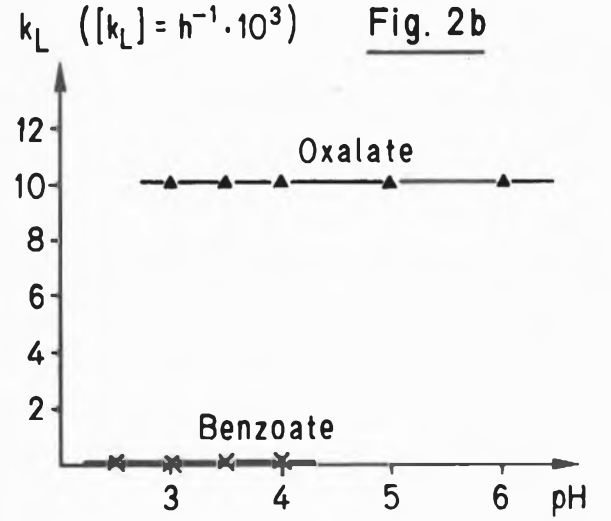


Fig. 2: The dependence of the ligand related dissolution rate constant on pH. The protonation of ligand surface complexes leads to protonated species which are significantly less effective on the dissolution (Fig. a)

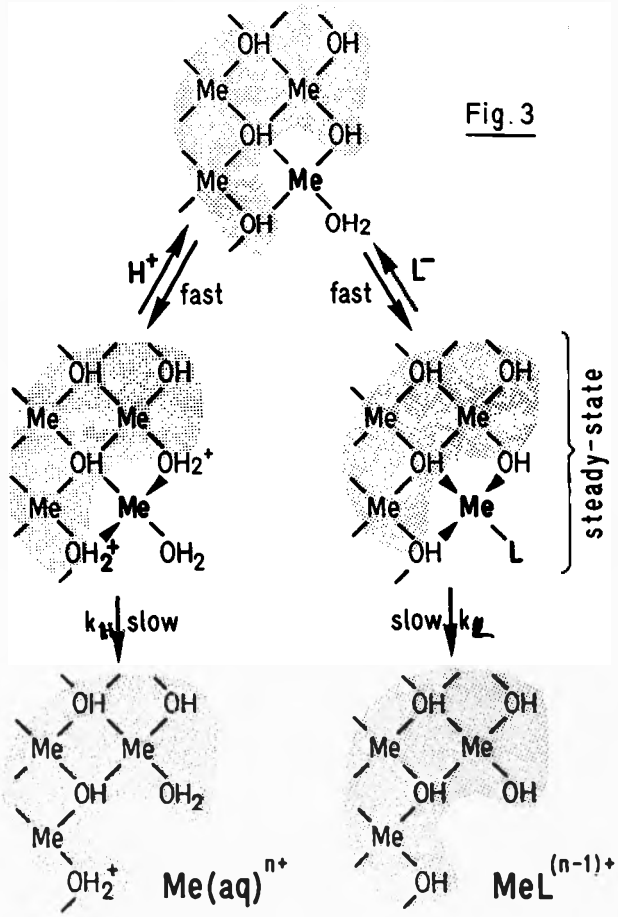


Fig. 3: Schematic representation of surface reaction controlled dissolution of hydrous oxides. The polarization of the Al–O bonds by the protonation of surface OH-groups and the formation of surface complexes with suitable ligands enhance the subsequent detachment of Al.aq of AlL_x groups. The detachment, probably occurring primarily at kink or step sites, is rate determining.

are shifted to the left at pH values < 5. In case of oxalate, over the pH range investigated the deprotonated surface complex prevails. Benzoate that can only form monodentate complexes, $\geq$Al–OOC–C_6H_5, obviously is much less efficient than the deprotonated bidentate (mononuclear) surface complexes. Equation (2) can be rewritten as

$$R = k_H \{\geq AlOH_2^+\}^3 + k_L' \{\geq Al\text{–}L\} + k_L'' \{\geq Al\text{–}LH\} + \ldots \quad (3)$$

with $k_L' = k_L \alpha_L$ where $\alpha_L = (1 + K_1^s/[H^+])^{-1}$, i.e. the fraction of surface species present in the deprotonated form. The back reaction is neglected. For the calculation of $R_L' = k_L' \{\geq Al\text{–}L\}$, pk_1^s-values of 3.0 and 3.7 were used for the salicylate and citrate surface species, respectively. In case of oxalate and benzoate pK_1^s is less than

2.5. Fig. 3 depicts in a simplified way how H^+ and ligands modify the surface and weaken the Al–O bonds. These reaction steps are relatively fast. The subsequent detachement of a Al.aq or AlL_x group, probably occurring preferentially at a kink or step site of the surface, is rate determining.

The interpretation given to the results obtained in this case study is of a more general nature and can be extended to the systems involving other ligands, other oxides, aluminium silicates and other minerals. A reinterpretation of the results of other researchers on the dissolution of various oxides by *Grauer* and *Stumm* [11] have shown that the dissolution kinetics in most cases can be accounted for by surface controlled reaction orders. The fractional reaction orders on H^+ and ligand (anion) that have typically been reported are compatible with direct dependence on the concentration of surface species. The weathering of minerals is known to be enhanced by surface complex forming ligands such as oxalate and fulvates, usually present in soil-water systems. Our interpretations

provide surface-coordination and chemical explanations for and lend support to recent treatments on the kinetics of geochemical reactions [3, 4].

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References

1 *W. Stumm, G. Furrer* und *B. Kunz:* Croat. Chem. Acta, *58*, 585 (1983).
2 *R. A. Berner:* Early Diagenesis, Princeton University Press, (1978).
3 *A. C. Lasaga* and *R. J. Kirkpatrick:* eds., Kinetics of Geochemical Processes (1978).
4 *P. Aarland* and *H. C. Helgeson:* Am. Journal of Science, 282 (1982) 237.
5 *P. Schindler:* Adsorption at the Solid Liquid Interface, M. A. Anderson and A. Rubin, eds., Ann Arbor Press, Michigan (1982).
6 *W. Stumm* and *J. J. Morgan:* Aquatic Chemistry, J. Wiley & Sons, 2nd ed. (1981).
7 *L. Sigg* and *W. Stumm:* Colloids and Surfaces 2 (1981) 101.
8 *R. Kummert* and *W. Stumm:* J. Colloid Interf. Sci. 75 (1980) 373.
9 *H. Motschi:* Natw. (1983) in print.
10 *R. Petrovic:* Geochim. Cosmoch. Acta 40 (1976) 1509; *R. Petrovic, R. Berner* and *M. B. Goldhaber,* ibid 40 (1976) 537.
11 *R. Grauer* and *W. Stumm:* Colloid and Polymer Sci. 260 (1982) 959.