Sorption Phenomena at Environmental Solid Surfaces

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Abstract. Sorption phenomena from the aqueous and from the gaseous phase to solid surfaces play an important role for the fate of inorganic and organic compounds and of bacteria in the environment. Case studies illustrating the role of different sorption mechanisms for various classes of compounds and for bacteria are presented. They show that sorption at solid surfaces ranges from weak unspecific interactions to very specific and strong complexation. Strong surface complexation in particular affects the surface reactivity. Studies of model systems provide a conceptual framework to understand and predict the behavior of substances and of bacteria in complex environmental systems, such as aquifers and sediments.

Introduction

How does acid rain influence the weathering reactions within a watershed? Which part of the heavy-metals input into a lake is scavenged by settling particles and will be retained in the sediments? Do sorption processes sufficiently retard groundwater pollutants to secure our drinking water supplies? Will specialized bacteria introduced to clean up groundwater contamination spread out sufficiently to do their job? These are some of the questions for which sorption phenomena of dissolved and colloidal substances (*e.g.*, heavy metals, radionuclides, organic solvents, pesticides, bacteria, viruses) to solid surfaces are of primary importance. Sedimentation, transport with groundwater, bioavailability, (eco)toxicity, as well as the reactivity with regard to chemical and biological transformations are controlled by interactions of solid surfaces with pollutants [1–3]. Sorption phenomena play a significant role in numerous natural processes and systems, as in sedimentation processes and the regulation of the concentrations in solution of various compounds in rivers, lakes, and oceans, in the interactions

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between solid phase and solution in sediments, and in transport processes in soils and aquifers. Thus, knowledge of the mechanisms and factors that affect the distribution between the aqueous and solid phases is pivotal to assessing the fate of dissolved or colloidal matter in many natural environments. Research on processes at the solid-water interface was started at EAWAG some 25 years ago. Subjects of earlier interest have included: adsorption of cations and anions at oxide surfaces [4–6]; reactivity of adsorbed species with respect to mineral dissolution and redox reactions [7–10]; interactions of nonpolar organic substances with natural sorbents [11]. These earlier studies have provided a basis on which present projects build.

The examples that will be presented in this article are mostly related to the transport of various solutes and of bacteria in subsurface environments. An important characteristic of soils, sediments, and aquifers is the high concentration and the vast variety of natural surfaces that are in contact with dissolved solutes. Due to this high solids-to-water ratio, dissolved pollutants may be significantly retained in the subsurface, even by rather weak interactions with the solid matrix. Similarly, the movement of bacteria is limited by their tendency to adhere to subsurface particles [12]. Furthermore, processes at the air-water and air-particle interfaces may also be important. Direct adsorption from the gas phase on solid surfaces may be a significant exchange pathway for volatile compounds between atmosphere, soils, and vegetation. *In situ* volatilization is well-known in remediation techniques for certain pollutants of soils and aquifers.

The solid matrix typically present in sediments, aquifers, and soils comprises a large variety of constituents including mineral oxides (iron, aluminum, manganese, silicon oxides), calcium carbonate and other carbonates, clay minerals, sulfides, living and nonliving organic matter. Characteristics of the surfaces, and also of the bulk of these constituents, influence the type and the kinetics of sorption reactions. Important properties of the solids include specific surface area, type and number of reactive surface groups, acid-base properties of the surface groups, surface charge and its dependence on pH, structural features such as surface topology, porosity, or aggregation. The solid matrix encountered in natural environments typically is very heterogeneous with respect to its chemical composition and its structural features. Although the bulk of a certain subsurface matrix may contain only a few components, *e.g.*, quartz sand in a glacial outwash plain, the surface chemistry of this matrix can be intriguingly complex due to the presence of surface coatings. Such coatings consist of fine-grained particles, colloids, or thin precipitates and exhibit a high specific surface area, which may dominate the chemical properties of the system. Coatings often contain various iron- and manganese (hydr)oxides, sulfides, nonliving organic matter, or biofilms. Dissolution and precipitation, deposition and mobilization of organic and inorganic colloids, or bacterial growth add significantly to the complexity of natural subsurface systems.

In the following, we will discuss illustrative examples of interactions between dissolved species, gaseous molecules, bacteria, and solid surfaces at the molecular level from our own present research. Most of our mechanistic studies were conducted in well-defined model systems which were chosen to mimic the most important constituents and surface interactions occurring in natural systems. Sorption of pollutants to subsurface matrices typically involves a variety of different surfaces and often also several species of the solutes. We will nevertheless attempt to discuss how various types of interactions with solid surfaces affect the fate of various compounds and of bacteria in complex natural systems.

Sorption Mechanisms

Sorption is a general term that comprises *ad*sorption processes, which occur at the solid-solution interface, and *ab*sorption processes in which the solute penetrates

the bulk of the sorbing phase. We concentrate here on *ad*sorption processes at mineral/water and mineral/air interfaces.

The distribution of solutes between a fluid and a condensed phase is based on the forces that act between the sorbent, the sorbate, and the solvent. The forces range over many orders of magnitude and can be classified as *van der Waals*, coulombic, and *Lewis* acid-base interactions. *Van der Waals* interactions result from uneven charge distributions in (net) uncharged molecules and are relatively weak compared to other interactions, but they are ubiquitous, *i.e.*, they act between all kinds of molecules or particles (= nonspecific interactions). Coulombic interactions act between charged surfaces and cations and anions, and are also nonspecific. Specific interactions affecting uncharged molecules include *Lewis* acid-base interactions, such as the formation of H-bonds and specific electron donor-acceptor interactions between uncharged surface sites and molecules. Cations are bound specifically on mineral-oxide surfaces by complex formation with oxygen donor groups of the surface; anions are bound specifically by ligand exchange and complex formation with surface metal centers [1]. The case studies *i–vi* below will provide examples of various adsorption mechanisms.

Adsorption of uncharged organic molecules from a gaseous phase to surfaces is only controlled by *van der Waals* and *Lewis* acid-base interactions (see below case study *i*). An example of specific electron donor-acceptor interactions between uncharged organic compounds and mineral surfaces is shown in the case study *ii*. The partitioning of nonpolar organic solutes between the aqueous phase and particulate or colloidal natural organic matter is comparable to extraction of solutes from water by an organic solvent and is primarily driven by expulsion of the nonpolar compounds from the aqueous phase [11][13]; this process will not be further discussed here. Sorption of colloids and of bacteria onto surfaces have to take the *van der Waals* forces, the *Lewis* acid-base and the electrostatic interactions into account (case study *vi*).

Specific interactions of ionic compounds with oxide surfaces are described in terms of surface complexation [1][4][5][14][15]; examples of these interactions are presented in the case studies *iii, iv, v*. Mineral-oxide surfaces in contact with water are hydroxylated, and different kinds of surface hydroxy groups are present (>*S*–OH, reactive surface sites, where *S* stands for a cation of the mineral oxide, *e.g.* Fe^{III}, Al^{III}, Si^{IV}, *Fig. 1*) [1][14][15].

Several types of hydroxy groups that differ in their structure and in their reactivity may exist on the surface of a given mineral, *e.g.* of an iron hydroxide [16].

The hydrolyzed mineral surfaces show distinct acid-base properties that result in a net surface charge, according to:

$$>S–OH + H^+ \rightleftarrows >SOH_2^+ \quad \text{and} \quad (1a)$$
$$>S–OH \rightleftarrows >SO^- + H^+ \quad (1b)$$
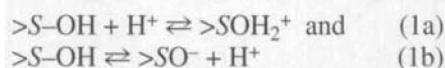
The adsorption of heavy metals onto mineral surfaces is explained in terms of surface complexation, in which the surface hydroxy groups act as ligands to bind cations (*Fig. 1*):

$$>S–OH + M^{z+} \rightleftarrows >S–OM^{(z-1)+} + H^+ \quad (2)$$
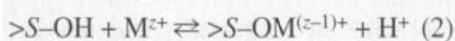
The denticity of the surface ligand is not unique, mono-, bi-, tri-, and tetradentate complexes have been found.

Dissolved anions and ligands are bound to oxide surfaces by ligand exchange, in which the surface hydroxy group may be replaced by another *Lewis* base (L$^-$). Preferentially, protonated hydroxy groups can easily be replaced by another ligand:

$$>S–OH_2^+ + L^- \rightleftarrows >S–L + H_2O \quad (3)$$
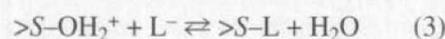
Complexes with a direct binding between the adsorbed metal and the oxygen of a surface hydroxy group, or the atom of an adsorbed ligand and a metal center at the surface, are defined as inner-sphere complexes (*Fig. 1*, upper part, see also case studies *iv* and *v*). More complex surface structures involving a metal ion and a ligand are known as ternary surface complexes [15][17][18]. Two types can be distinguished: >*S*–O–M–L and >*S*–L–M (see case study *iii*).

Eqns. 1–3 can be modeled with surface equilibrium constants [14][15][19][20]. These reactions obviously involve changes in the surface charge. The electrostatic interactions with the charged surface must therefore also be taken into account in modeling; various models have been proposed for this purpose [1][20].

Adsorption involving only the coulombic attraction between a charged surface site and a dissolved ion results in outer-sphere complexation (*Fig. 1*, lower part).

Ion exchange in clay minerals may be finally mentioned. In phyllosilicate minerals, such as clays, isomorphic substitution of structural cations (*e.g.*, Si^{IV} by Al^{III}) leads to permanent negative charges (>X–O$^-$) in the silicate layers which are balanced by exchangeable counterions at phyllosilicate surfaces (*Fig. 1*). Inner- and outer-sphere complexes may form at
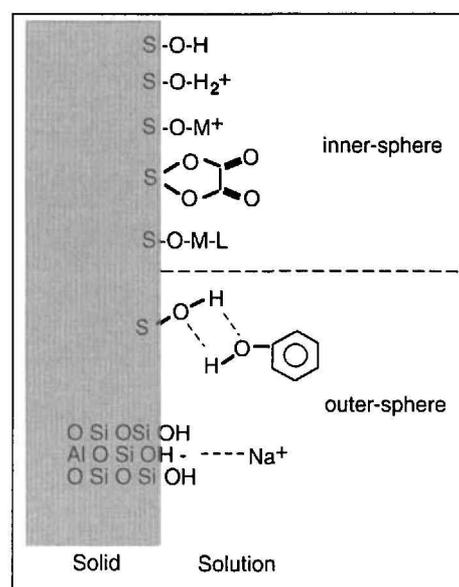
Fig. 1. *Schematic view of various sorption mechanisms on mineral-oxide and clay-mineral surfaces.* >*S*–OH *represents a reactive surface site, where* S *is a cation of the solid phase. The upper part of the figure shows inner-sphere complexes, with a protonated* >*S*–OH$_2^+$ *group, an adsorbed metal ion, an adsorbed ligand (oxalate), and a ternary complex. The lower part shows outer-sphere complexes, one complex involving H-bonds, and one between a negatively charged surface and a cation.*

>X–O$^-$ sites [21][22]. The cations C^{x+} at these rather unspecific sites (outer-sphere) may easily be exchanged by other metal ions (M^{z+}):

$$(z/x) (>X–O)_xC + M^{z+} = (>X–O)_zM^0 + (z/x)C^{x+} \quad (4)$$
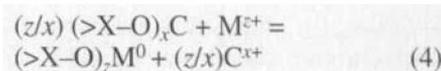
where the exchangable amount of charge is known as the cation exchange capacity of a clay mineral.

The different adsorption mechanisms may be distinguished by studying the dependence of adsorption on various variables, such as pH, concentration of solutes, ionic strength, and the type and topology of the surfaces, and by interpreting the parameters of measured adsorption isotherms. The molecular structures at the surfaces can only be hypothesized on the basis of such studies. Spectroscopic studies (IR, NMR, EXAFS, *etc.*) are needed to provide detailed structural informations on adsorbed species (see case studies *ii* and *iv*). Detailed information on the structure of surface species is useful for predicting their reactivity (case study *v*).

Case Studies of Sorption

The following case studies illustrate various sorption mechanisms and their role for the fate of different substance

classes in the environment. The sequence runs from less specific to more specific types of interactions, and from uncharged organic molecules (case studies *i*, *ii*) to ionic compounds and their structure and reactivity at surfaces (*iii–v*). Finally, the adhesion of bacteria to surfaces is dis·cussed (*vi*).

i) *Adsorption of Organic Compounds from the Gas Phase to Liquid or Solid Surfaces*

Adsorption from the gas phase to surfaces may affect the transport of organic compounds in/between different environmental compartments: in the atmosphere (gas/particle partitioning), between the atmosphere and soil surfaces and in unsaturated soils.

The adsorption/desorption of organic compounds from the gas phase to natural surfaces usually is fast and reversible. At low concentrations (= typical environmental background concentrations) the adsorption isotherm is linear but it becomes nonlinear when the saturation concentration in the gas phase is approached. The adsorption equilibrium is determined by *van der Waals* and *Lewis* acid-base interactions between the adsorbing molecule and the surface (physisorption) [23][24]. These interactions can be described/predicted if adsorbate and adsorbents are characterized by three parameters each: one *van der Waals* parameter and one electron donor and acceptor parameter each for the calculation of *Lewis* acid-base interactions. In the literature, adsorption from the gas phase is often related to the vapor pressure of the

adsorbing compounds, as shown in *Fig. 2*. However, this is only correct for molecules that interact solely by *van der Waals* forces. A deviation from this rule must be expected and can be found experimentally for compounds which exhibit considerable *Lewis* acid-base interactions with the surface (*Fig. 2*) [25].

Besides the characteristics of adsorbent and adsorbate, temperature and in many cases relative humidity (RH) have a strong influence on the adsorption equilibrium. Relative humidity becomes important if the surface is hydrophilic (*e.g.*, most minerals). In this case, water molecules compete for the same adsorption sites on the surface and force the organic molecules to adsorb on the adsorbed water film rather than to the mineral surface. In the case of mineral surfaces, this leads to a strong decrease in the adsorption of organic compounds with increasing relative humidity, since the *van der Waals* interactions of organic molecules with water are much weaker than with a pure mineral surface. If RH is close to 100%, the adsorbed water film becomes so thick that any influence of the mineral surface on adsorption is inhibited. In this case, the adsorption coefficients (normalized to the adsorbent surface area) of a given compound are the same on different minerals (*Fig. 3*) [26].

ii) *Adsorption of Nitroaromatic Compounds from the Aqueous Phase to Clay Minerals*

Several classes of priority pollutants including substituted quinones, benzoni-

triles, and nitrated aromatic compounds (NACs) are reasonably good electon acceptors due to the electron deficiency of their aromatic π-systems. Such π-acceptors are known to form stable complexes with suited electron donors in solution. Thus, one potential sorption mechanism of these compounds is complex formation with electron-donor sites of environmental particles. Here, sorption of NACs to mineral surfaces serves to exemplify such electron donor-acceptor (EDA) interactions and the processes that affect this sorption mechanism in aqueous environments.

Among the major groups of naturally occurring solids, phyllosilicates (silicate minerals with a layer structure) exhibit by far the highest affinity for NACs [28][29]. A combination of structure adsorptivity and *in situ* spectroscopic (^{13}C-NMR, ATR-FTIR, UV/VIS, XRD) investigations revealed the adsorption mechanism(s) of NACs at phyllosilicates [30][31]. Stable complexes between oxygens of siloxane surface(s) (e$^-$ donors) and NACs (e$^-$ acceptors) account for the strong sorption of NACs in *aqueous* systems (see *Fig. 4*) and are referred to as n-π EDA interactions according to the orbitals involved. Other adsorption mechanisms such as H-bonding or direct coordination of NO_2 groups to surface sites were not important in aqueous environments, but contributed to the adsorption of NACs from apolar solvents. Adsorbed NACs were oriented coplanar to the siloxane layers and exhibited a high degree of mobility, consistent with fast and reversible sorption. This type of ad-
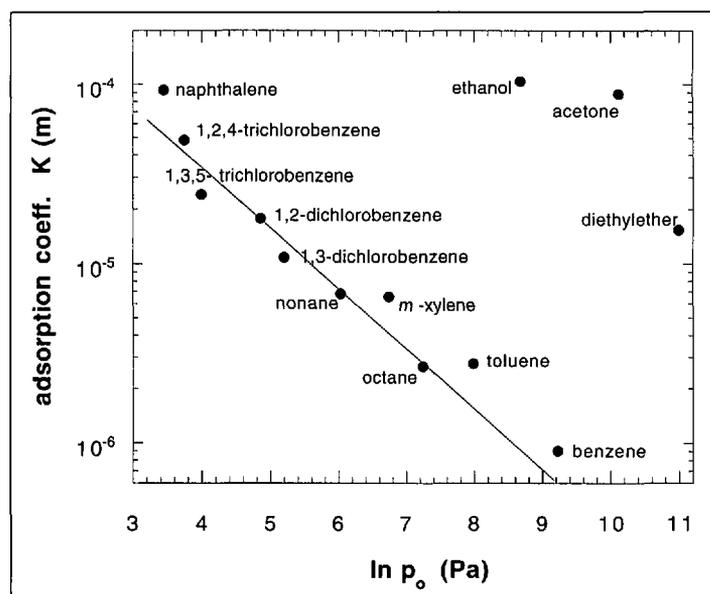
Fig. 2. *Adsorption coefficients (K* in mg m^{-2} /mg m^{-3}) *of different compounds on a quartz surface at 70% relative humidity and 20° as a function of saturated vapor pressure* p$_o$ (extrapolated from data measured at higher temperatures [26][27]). The line through the alkanes represents the adsorption that is expected due to *van der Waals* forces only.
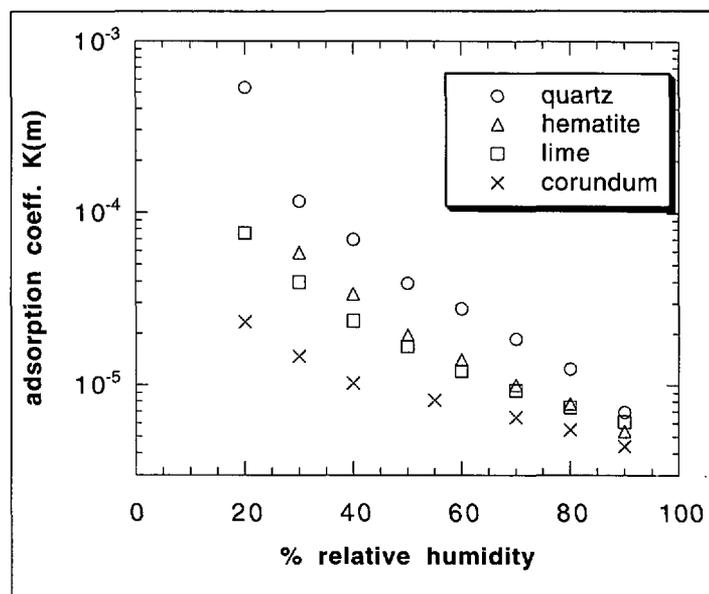
Fig. 3. *Adsorption coefficients (K* in mg m^{-2}/mg m^{-3}) *of 1,2-dichlorobenzene on different mineral surfaces as a function of relative humidity at 20°* (based on temperature-extrapolated data from [26][27])

sorption does not involve an exchange with OH sites, and is thus different from the ligand exchange mechanism described below for oxalate and succinate.

The extent of EDA complex formation was determined by steric factors and by the π-acceptor and n-donor properties of NACs and siloxane oxygens, respectively. Depending on the minerals and the NACs involved, adsorption constants exceed those caused by nonspecific interactions by several orders of magnitude. Generally, planar NACs with several electron-withdrawing substituents exhibit highest sorption. Relative to each other, sorption of different NACs was independent of mineralogical properties, indicating that similar sites are involved in EDA complex formation at all types of phyllosilicate minerals. Thus, K_d values measured on any type of model phyllosilicate may be used to estimate the *relative* extent of adsorption of π-acceptors to natural subsurface matrices, irrespective of the types and abundance of phyllosilicates present.

The accessibility of siloxane sites for π-acceptors is restricted by the presence of hydrated exchangeable cations (*Fig. 4*; see also *Eqn. 4*). Significant EDA complex formation takes place only in the presence of weakly hydrated exchangeable cations (*e.g.*, K^+, NH_4^+). The hydration sphere of strongly hydrated exchangeable cations (*e.g.*, Na^+, Ca^{2+}) decreases the accessibility of siloxane sites for EDA complex formation. Thus, cation exchange is a crucial geochemical process that controls the accessibility of siloxane sites for π-acceptors due to the different sizes of the hydrated cations.

The mechanisms described here open new perspectives with regard to the remediation of certain contaminated groundwaters. Injection of electrolytes may be a promising but so far neglected way to control the adsorption and thus the bioavailability and the transport of contaminants such as nitroaromatic explosives (*e.g.*, trinitrotoluene = TNT) and other pollutants with significant tendency to form EDA complexes.

iii) *Adsorption of Metal-EDTA Complexes to Iron Oxides*

EDTA (ethylenediaminetetraacetate), a synthetic ligand that strongly complexes many metals of environmental concern, has been observed in natural waters, even in some groundwaters, in the concentration range 10^{-9}–10^{-7} M, due to inputs from wastewater [32]. In order to evaluate the influence of EDTA on the mobility of heavy metals (such as lead, copper, cobalt) during infiltration processes into groundwater, the interactions between the surfaces of iron oxides (goethite, α-FeOOH, and amorphous iron oxides), various metal ions, and EDTA have been studied [18][33][34].

Interactions in this system include complexation of the metals by EDTA in solution, adsorption of metal ions and of EDTA to the Fe-oxide surfaces (>FeOH groups), and the formation of ternary complexes >Fe-EDTA-M, where >FeOH represents a surface OH group and M a metal ion. Ternary complexes of the type >Fe-EDTA-M are formed at low pH with the divalent metal ions (Pb^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Co^{II}), whereas these M^{II}-EDTA complexes hard-

ly adsorb at pH > 7–8 (*Fig. 5*). The pH dependence of the adsorption of the M^{II}-EDTA complexes follows the typical pattern of anion adsorption to an oxide surface, whereas the adsorption of free metal ions would increase with pH. In contrast to these divalent metals, the Co^{III}-EDTA complex is hardly adsorbed, and the Fe^{III}-EDTA complex is adsorbed over a wide pH range. These results indicate the occurrence of specific interactions, depending on the structure and stability of the different M-EDTA complexes in solution.

The formation of ternary complexes may thus only lead to binding of divalent metal ions to FeOOH surfaces at low pH (< 7), whereas at higher pH, the metals are mobile as EDTA complexes. Co^{III}-EDTA complexes would be mobile over the whole pH range. Depending on the metal ion involved, the adsorption step is followed by a slow dissolution step of the iron oxides at low pH, that leads to the exchange of a metal ion (*e.g.*, Pb^{II}) against Fe^{III} in solution. This type of exchange can only take place at pH lower than about 7.

iv) *IR Spectroscopy for the Study of the Structure of Adsorbed Molecules*

Currently, only few spectroscopic methods are able to provide structural information on organic compounds and a number of important inorganic compounds adsorbed on aqueous mineral surfaces. All surface spectroscopic methods that require a high vacuum are obviously not applicable in the presence of water.

IR and Raman are sensitive and noninvasive *in situ* methods and provide structural information on organic and inorgan-
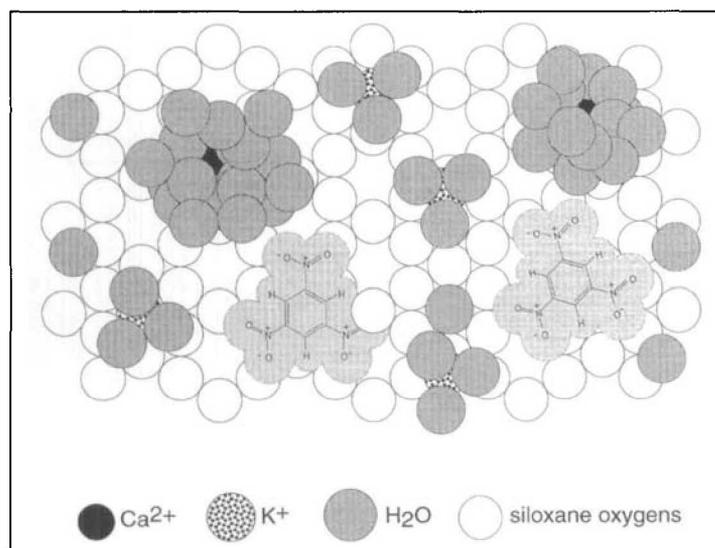
Fig. 4. S*chematic representation of a basal siloxane layer of phyllosilicate minerals in the presence of hydrated exchangeable cations and adsorbed nitroaromatic compounds.* Adsorbed NACs (*e.g.*, 1,3,5-trinitrobenzene) form a coplanar electron donor-acceptor (EDA) complex with weakly hydrated siloxane oxygens. All compounds are depicted using *van der Waals* dimensions. Adapted from [29].
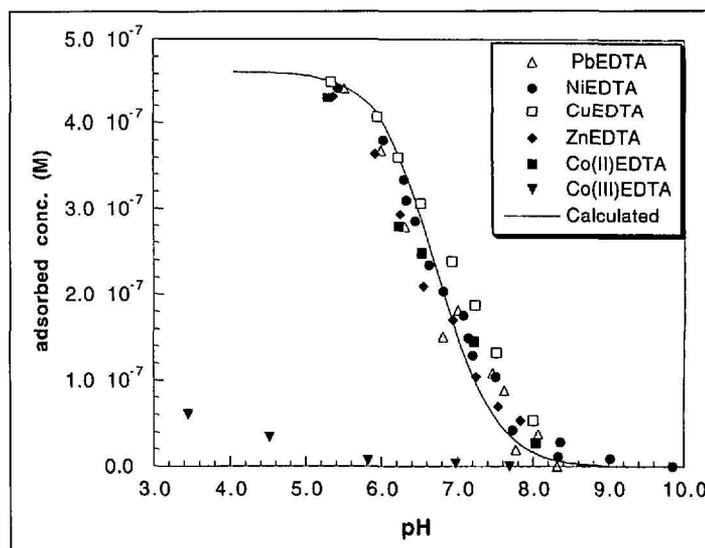
Fig. 5. *Adsorbed concentrations of Pb^{II}-, Ni^{II}-, Cu^{II}-, Zn^{II}-, Co^{II}- and Co^{III}-EDTA complexes on the α-FeOOH surface as a function of pH* (0.46 g/l α-FeOOH, total concentration of MEDTA $4.6 \cdot 10^{-7}$ M). The line is calculated using a surface complexation model with an average constant for the binding of a MEDTA complex [18].
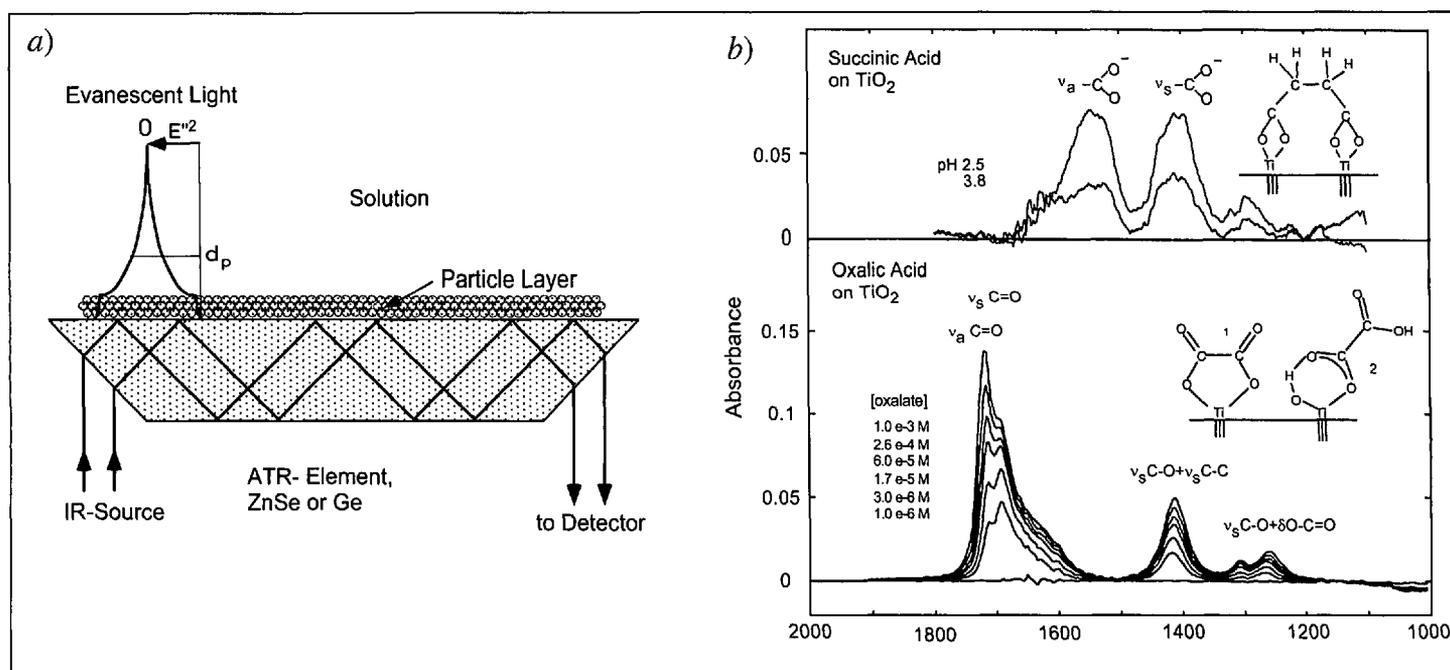
Fig. 6. a) *Scheme of an ATR cell.* Upon each reflection on passing through the ATR crystal, the evanescent light interacts with the particle layer and the liquid. The penetration depth (dp, at which the light intensity decays to 1/e) is 1.39 μm at 1100 cm^{-1}. The ATR crystal is mounted in a cell made of polypropylene that holds the solution. b) *Spectra of oxalate adsorbed on TiO$_2$ at pH 3 as a function of oxalate solution concentration.* Also shown is succinate on TiO$_2$ at different pH values. Characteristic vibrations and possible structures in agreement with the spectra are indicated in the figure (see text).

ic molecules through their vibrational spectra. However, neither Raman nor IR (or any of the above-mentioned methods) is inherently surface-sensitive. The signal from surface species has to be subtracted from the signal of the bulk solid and the suspension.

To be able to use structural information in the context of quantitative surface complexation models, we measure vibrational spectra of surfaces in direct contact with aqueous solutions, as a function of solution parameters such as concentration, pH, ionic strength, temperature, *etc.* Since H$_2$O is a strong IR absorber, normal transmission spectroscopy requires cell path lengths of 10–20 μm. A technique that conveniently provides the equivalent of such short path lengths is Attenuated Total Reflection (ATR)-FTIR. *Fig. 6, A* illustrates the principle of ATR and of our technique. The ATR crystal is coated with a 1–2 μm thick layer of a high-specific surface area mineral-oxide powder in direct contact with aqueous solution. After recording a background spectrum with layer and solvent, spectral changes are followed after addition of an adsorbent to the solution. Due to adsorption, the concentration in the particle layer soon exceeds the solution concentration and the major contribution to the spectra originates from adsorbed compound. Remaining contributions from dissolved species can be subtracted with independently measured solution spectra. Sets of IR spectra measured as a function of solution para-

meters allow a direct link between spectral information and quantitative complexation models.

We have measured FTIR spectra of oxalate on TiO$_2$ [35], a number of dicarboxylic acids on TiO$_2$ (anatase and rutile), hematite, goethite, and lepidocrocite, of sulfate on hematite [36], of nitroaromatic compounds on clay minerals [31], and of salicylic acid on aluminum and iron oxides [37]. As an example, *Fig. 6, B* (lower panel) shows the spectra of oxalate adsorbed on TiO$_2$ as a function of aqueous oxalate concentration at pH 3. These spectra differ from those of dissolved oxalate species (H$_2$Ox, HOx$^-$ and Ox^{2-}), but are similar to the spectra of bidentate metal-oxalate complexes with known structures. This is a clear indication for inner-sphere coordination on the surface. As expected, spectral amplitudes increase with aqueous concentration, and in addition, the spectral shape changes. Under the assumption that the vibrations are primarily determined by the internal structure of adsorbed oxalate and to a lesser degree by weaker interactions between neighboring molecules, we interpreted the observed spectral changes as evidence for the formation of different surface structures. To separate the spectra, we assumed that the formation of each complex can be described by independent *Langmuir* or *Frumkin* adsorption isotherms. The mathematical procedures and details are described in [35]. We suggest the formation of bidentate (chelating or bridging) struc-
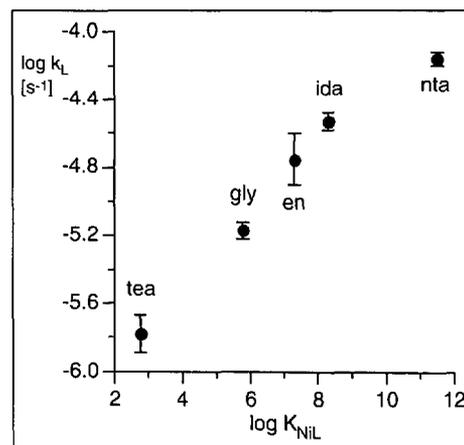
Fig. 7. *Rate coefficient (k$_L$) for ligand-induced dissolution of bunsenite NiO (s) at pH 8.5 as a function of the nickel-ligand stability constants for the dissolved complexes at equilibrium* (data from [44]). The ligand abbreviations are tea (triethanolamine), gly (glycine), en (ethylendiamine), ida (iminodiacetate), nta (nitrilotriacetate).

tures on the surface (*Fig. 6, B,* 1). At lower pH, an additional protonated structure is formed (*Fig. 6, B,* 2). An important feature in the oxalate-surface complexes are the strong bands at 1680 and 1710 cm^{-1} from predominantly C=O bonds. In contrast, an experiment with succinic acid did not show bands above 1600 cm^{-1}, and there was no evidence for the formation of additional protonated complexes at lower pH. The symmetric and asymmetric –COO$^-$ stretching vibrations were not shifted much from their positions in aqueous solutions, consistent with independent binding of the two carboxylate groups.
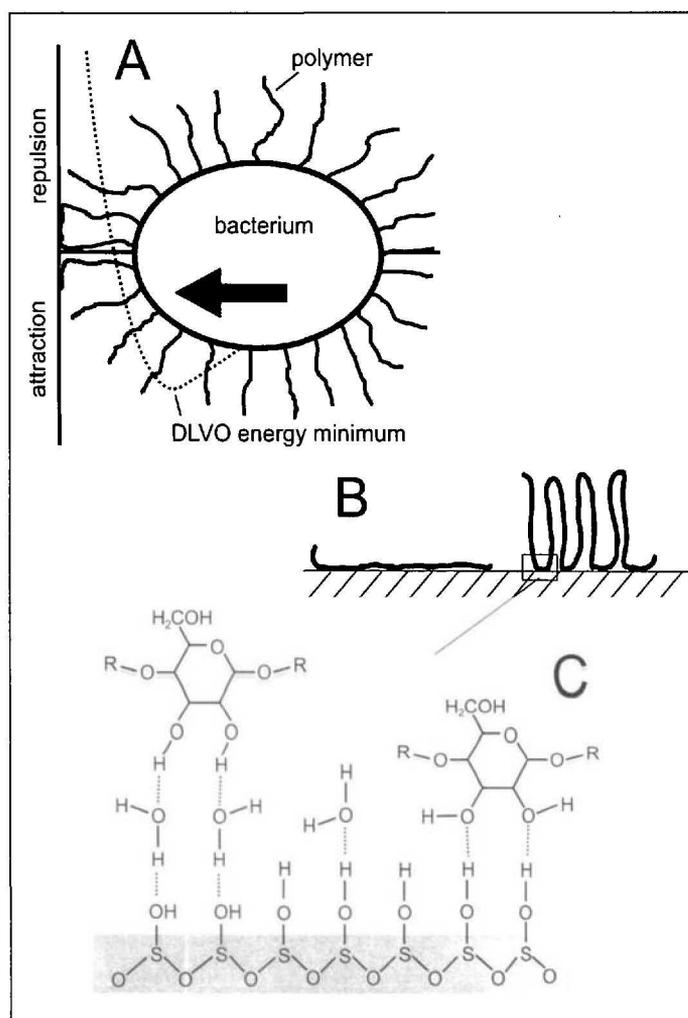
Fig. 8. *Schematic view of the mechanism of bacterial adhesion to mineral oxides.* Adsorption of surface polysaccharides pulls gram-negative bacteria beyond the DLVO energy minimum (dotted line) and results in irreversible adhesion (*A*). Macroscopic (*B*) and microscopic (*C*) view of polysaccharide adsorption to mineral oxides.

FTIR measurements also probe how the surface structure of the oxide affects adsorption mechanisms. Measurements with dicarboxylic acids on a range of surfaces show characteristic spectral differences. On most surfaces, there are several spectral components in a set of measurements, indicative of various sites and/or crystal faces.

A long-term goal is the development of surface structure-reactivity relationships, *e.g.*, in the context of pollutant degradation on mineral surfaces. In current projects, we collect FTIR spectra *in situ* during photochemical and thermal reactions and apply a combination of multicomponent fitting, surface complexation models, and kinetic modeling to separate spectral components and kinetic processes.

v) *Sorption and Reactivity for the Dissolution of Minerals*

Dissolution reactions of minerals are fundamental for the weathering processes. Estimating the rates and the scale of surface reactions is important to make predictions for the long-term behavior of environmental systems. The influence of ligand adsorption on the dissolution rates of oxides has been demonstrated in systems involving carboxylic ligands, *e.g.*, oxalate, phthalate, and malonate [9][38]. It has been shown that the dissolution reactions of oxides are surface-controlled and that surface complex formation facilitates the release of ions from the surface.

Recent studies carried out at the University of California, Davis, aim at evaluating the reactivity at surfaces by considering the better understood similar reactions in solution [39–44]. By hypothesis, mechanisms of the release of metals from a mineral surface are profoundly similar to ligand exchange reactions around dissolved metal complexes, because general features of the metal coordination at surfaces resemble the corresponding complexes in solution.

A correlation between the dissolution rates of different oxides or orthosilicates and the first-order rate constants of water exchange around the divalent transition-metal ions in solution has been demonstrated [39]. While the reactions commonly proceed much slower at surfaces than in solution, the reactivity trends and ranges are commonly similar.

The water-exchange rate around a dissolved cation changes (often enhances) if the metal center is complexed by a ligand [45]. In a similar fashion adsorbed ligands (*Fig. 1*) enhance the dissolution rates of minerals. The denticity of the ligands may be an important factor enhancing water-exchange rates of dissolved complexes [45], as well as the dissolution rates of oxide minerals [40]. Recent work [39–44] compared exchange mechanisms for dissolved complexes with the possible reactions that are controlling the dissolution of simple oxides and indicated relationships between water-exchange rates in solution and dissolution rates.

In cases where the activated surface complex of a dissolving surface species presents structural similarity with the dissolved complexes, a correlation between the stability constants of the metal-ligand complex and the dissolution rate coefficients may be expected. Such a linear free-energy relation (LFER), as shown in *Fig. 7*, may also be used for predicting the trends of reactivity.

The hypothesis that surface complexes react in a similar manner as dissolved complexes is a useful guide to predicting and rationalizing kinetic data from surface reactions, although such predictions may not be valid in all cases.

vi) *Adhesion of Bacteria to Surfaces*

Adhesion of many bacteria to surfaces is largely controlled by long-range (> 2 nm) electrostatic, *van der Waals*, and *Lewis* acid-base interactions [46][47]. All three forces are accounted for in the extended DLVO theory (*Derjaguin-Landau-Verwey-Overbeek*) of colloidal stability. In some cases, however, theory does not explain all adhesion phenomena. For instance, adhesion of negatively charged bacteria to negatively charged surfaces is achieved when the electrostatic repulsion is suppressed by high ion concentrations. However, once adhered to the surface, these bacteria remain sorbed, even when the medium is diluted to ionic strengths at which adhesion would not have occurred [48]. Such irreversible adhesion indicates the anchorage of bacteria to the surface *via* their surface polymers (*Fig. 8*).

To quantify the contribution of polymer attraction and to identify the type of bonding to glass and other mineral oxides, we compared the sorption of *1*) three gram-negative bacteria, *2*) lipopolysaccharide micelles of these bacteria, and *3*) isolated polysaccharides thereof [49][50]. While DLVO forces become less important when going from bacteria to polysaccharides, polymer contributions become dominant. IR spectroscopy showed that all polymers formed hydrogen bonds either with surface hydroxy groups of SiO_2, Al_2O_3, and

TiO_2, or with surface-bound water (*Fig. 8, C*). At low concentrations, polysaccharides spread on the surfaces because multiple hydrogen bonds where formed (*Fig. 8, B*). Due to competition at high surface coverage, adsorbed polysaccharides formed loops between the few adsorbed monomers. Calculations show that the extent of hydrogen bonding between bacterial surface polysaccharides and glass is sufficient to result in irreversible adhesion of bacteria to glass.

For the positively charged bacterium *Stenotrophomonas maltophilia* 70401, the DLVO theory predicts efficient adhesion to glass, which is in contrast to the experimentally observed low adhesion efficiency of this bacterium. The discrepancy may be explained by a second type of polymer interactions, in combination with a low affinity of the polysaccharides for SiO_2. Due to the high packing density of the surface polysaccharides, the polymer layer of these cells is rather rigid. The resistance of the cell envelope against compression hinders the bacteria to approach the glass surface close enough to be sufficiently attracted by DLVO forces.

Conclusions and Outlook

This work presented some of the topics and experimental approaches that are currently pursued at EAWAG in the field of environmental surface chemistry. We focus on a mechanistic understanding of (equilibrium) processes occurring at solid-water interfaces. The characterization of environmental solids by various methods is described in the article by *Hug et al.* [51]. Although using predominantly model systems, we have tried to identify crucial environmental factors that affect the interactions of various solutes and of bacteria with solid surfaces. This approach provides a conceptual framework that can be applied to gain also insights into more complex natural systems such as sediments and aquifers. However, the difficulties in extrapolating from well-defined model systems to complex environmental systems should not be underestimated. Under complex geochemical conditions, predicting the fate of pollutants, on the basis of reactions characterized in model systems and of parameters defining the natural system (such as number of reactive sites), often fails due to inadequate system characterization. Nevertheless, the transfer and up-scaling of basic theory and mechanistic information to complex systems or even to the field scale is a major objective of modern environmental (sur-

face) chemistry. Examples of how the sorption behavior or the reactivity of solutes can be used to probe for reactive sites under complex geochemical conditions are presented in [52], this issue.

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