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Current application of and future requirements for surface complexation models

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ABSTRACT

Surface complexation models have been used for thirty

years to explain surface charge and adsorption properties of minerals.

Macroscopic data and methods to obtain them are discussed along with their respective advantages and disadvantages. This includes titrations, electrokinetic experiments and adsorption measurements as well as combined approaches. Such data may be treated with computer codes to obtain thermodynamic data in the framework of a specified surface complexation model.

Currently used surface complexation models are covered as well as some non-standard models along with their respective advantages and disadvantages. The possible options for the different components of surface complexation models (protonation/deprotonation mechanism, structure of the electrostatic double layer and treatment of heterogeneity) are introduced. The required parameters for the different model components are discussed. Methods for independent determination of the parameters and data fitting procedures are evaluated. Selected model variations, which can be synthesized from the available options for the different components are discussed in detail.

Future requirements of the surface complexation models are discussed in the context of specific modelling purposes. Approaches, which allow in principle to cover a maximum of independent experimental data sources, are introduced. Various sources of experimental data, which have the potential to decrease the number of successful models, are described.

1. INTRODUCTION

Water quality is defined by its chemical and biological composition. A detailed characterisation of this composition is difficult but there is a necessity to be able to state whether the water is clean and safe or not. From a chemical point of view, a characterisation of the chemical speciation of inorganic and organic compounds is necessary to be able to define water quality. Today, it has become obvious that the toxicity of metals is to a great extent related to the different chemical forms (speciation) in which the metal ions are found. The transport and possible deposition of pollutants is also directly dependent on the speciation and its change along the transport route.

A characterisation of the chemical speciation is a great challenge. The complexity of natural waters in terms of its composition and variability in space and time is enormous. Furthermore, chemical speciation is intimately coupled to processes like precipitation, dissolution and above all adsorption/desorption processes. The solid-water interface plays a commanding role in regulating the concentrations of dissolved inorganic and organic compounds. Particles in natural systems are characterised by a great diversity (e.g. minerals, biota, humus) and a detailed understanding of processes taking place at the different solid-water interfaces is necessary to be able to do water quality assessments. In this context the famous Swiss environmental chemist W. Stumm [1] can be cited: "Almost all the problems associated with understanding the processes that control the composition of our environment concern interfaces of water with naturally occurring solids (minerals, soils, sediments, biota and humus)."

Recent applications of concepts of solution chemistry to interactions of solutes at the particle - water interface look promising. The development of different surface complexation models has implied a better and more detailed understanding of sorption processes at work at hydrous particle surfaces. This opens possibilities to model multicomponent/multiphase systems in which sorption processes are coupled to complexation reactions of the aqueous phase as well as precipitation/dissolution processes. Such models contain information of great value for the interpretation of the chemistry of natural waters but also for the understanding and optimization of many industrial processes.

Surface complexation studies have been performed by means of potentiometric titrations on a variety of metal(hydr)oxides particles. However, the number of reliable data sets is strongly limited. In many cases data are presented within very narrow concentration ranges and with often too short reaction times to reach "equilibrium".

Furthermore, tests for reproducibility and reversibility are

often lacking. This, in combination with poorly characterised particles/surfaces and the lack of reliable methods to experimentally give a qualitative and quantitative description of the total number of ionizable sites, has resulted in the presentation of a great number of models that all seem to explain experimental data quite well. However, for obvious reasons the scientific value of these models is low.

It should be borne in mind that macroscopic measurements like sorption studies in combination with potentiometric titrations yield just stoichiometries of the reacting components to form a surface complex and no information on a molecular level. Direct molecular level spectroscopic techniques (e.g. FT-IR, EXAFS) are therefore necessary to show whether the metal ion or the ligand is coordinated as an inner sphere complex or as an outer sphere complex or whether surface precipitates are formed. Furthermore, the coordinating mode of the metal ion/ligand in terms of mono- or bidentate or bridging behaviour should be characterised.

It is suggested that reliable surface complexation models can only be obtained by combining macroscopic studies with molecular level information.

The field of surface complexation is very important and still very much unexplored and certainly offers a future challenge to the scientific community within natural sciences.

The present paper attempts to cover experimental procedures and theoretical models. Focus is clearly on the most recent point of view of the authors. In this line the modelling is exemplified on some data from our laboratory. It is attempted to provide a critical point of view of the experimental procedures, models and their applications, which are covered herein.

2. EXPERIMENTAL APPROACHES

2.1 Acid base properties

2.1.1 Potentiometric titrations

A widely used technique to characterize the acid/base and complexing properties of hydrous particle surfaces is based on potentiometric titrations.

The predominant use of potentiometry in the context of surface complexation studies clearly concerns the acid/base properties of the sorbent (i.e. two-component systems: proton and surface). However, this technique can also be applied to multi-component systems (e.g. three-component systems: proton, surface plus a sorbate), but it would be restricted to sufficiently concentrated sorbate concentrations (e.g. > 1 mM). Properly applied it provides accurate data

over wide ranges of concentration and with the help of automatic measuring and data collecting systems, it has become possible to obtain large amounts of data within a reasonably short time period. Of critical importance in this work is to minimize errors in the determination of the "free" (e. g. H^+) ion activity, which puts constraints on the temperature control, on the measuring cell arrangement as well as on the electrode calibration procedure.

2.1.1.1 Experimental set-up

Temperature control. Since equilibrium constants in general are temperature dependent, any variation in temperature during the measurements will have a deleterious effect on the quality of recorded data. Of much higher significance is the fact that the electrode response itself is temperature dependent. This dependence is usually of the order of 1 mV deg^{-1} , [2]. Thus, it is essential that the experiments are performed under thermostated conditions of the order of ± 0.05 °C.

The cell arrangement. Two significantly different types of galvanic cells can be used to study equilibria in solution:

- i) chemical cells without liquid junction, in which two different electrodes are immersed in the same electrolytic solution, and
 - ii) cells with liquid junction potential, in which the electrodes are in contact with two different solutions which are connected through a salt bridge.
- In ii) the cell arrangement can be divided into three key parts: the measuring electrode, (E_+), the reference electrode, (E_-), and the liquid junction (E_j) between the measuring compartment and the reference compartment.

The measuring electrode. As the glass electrode is the most frequently used electrode for the measurement of activity, $\{H^+\}$, or concentration, $[H^+]$ of hydrogen ions, some comments upon its proper use will be made. Today, results obtained with the glass-electrode are entirely compatible with those obtained by use of the somewhat less convenient hydrogen electrode. However, it is important to stress that the response of the glass electrode has to be examined frequently. The best way to do this, is to perform a potentiometric titration in which one or several glass electrodes are matched against the hydrogen electrode. By preparing a solution consisting of different buffers, quite a broad $-\log[H^+]$ range can be covered. Typical faults to look for are, among others, a quite large deviation from the theoretical slope, especially at high pH and rapid variations in the asymmetry potential. This latter manifests itself as a failure to give a steady reading.

The reference electrode. Next to the hydrogen electrode, the silver-silver chloride ($Ag/AgCl$) electrode is probably the most reproducible and certainly the most reliable and

convenient electrode. It can easily be prepared [3], has short response times and gives constant potentials within ± 0.1 mV.

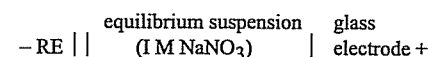
Liquid junction. A liquid junction potential (E_j) is formed if two adjoining solutions differ in concentration, mobility or charge of one or more ions. The e.m.f. of a cell that consists of two half-cells connected through a liquid junction is given by

$$E = E_+ - E_- + E_j \quad (1)$$

where E_j is the potential caused by the diffusion of ions across this liquid junction. The problems associated with the liquid junction potential and its reproducibility is solved by applying a cell of the so called "Wilhelm" type [4].

The junction potential of this cell has been found to be in fair agreement with values predicted by the simple Henderson equation, as discussed in detail by Hefter [5]. Accurate expressions for its medium dependence, with respect to H^+ and OH^- ions have been experimentally determined by Biedermann and Sillén [6] or Sjöberg et al. [7].

Calibration of the electrode system. Good e.m.f. data are dependent upon good electrode calibration procedures. The application of the constant ionic medium method, to minimize variations in the activity coefficients of the existing species, is to be recommended. This implies that a concentration scale with respect to H^+ (and other species as well) can be used. The free H^+ -concentration can be determined by measuring the e.m.f. of the cell:



where the reference electrode, RE = $Ag, AgCl \mid 0.01\text{ M NaCl}$ and $I-0.01\text{ M NaNO}_3 \mid 1\text{ M NaNO}_3$

and I denotes the concentration of the background medium. The e.m.f. of the cell (in mV) can be written (25 °C):

$$E(\text{mV}) = E_0 + 59.157 \log[H^+] + E_j \quad (2)$$

For the liquid junction potential, E_j , equation (3) is applicable (Sjöberg et al. [7]).

$$E_j = -49.7 I^{-1}[H^+] + 21.4 I^{-1} K_w [H^+]^{-1} \text{ mV} \quad (3)$$

where K_w is the ionic product of water.

E_0 is a constant that is to be determined in a solution of known $[H^+]$. An internal calibration to give E_0 should be the aim whenever possible. When titrating a suspension, this is however not always possible due to extensive dissolution within the calibration range $2.5 < -\log[H^+] < 4$.

Whenever possible, *in situ* calibrations should be performed. This implies a calibration of the electrode system in the presence of the solid phase, and requires that the proton consumption related to sorption/dissolution processes can be neglected or corrected for. Otherwise, E_0 has to be determined immediately before (and after) each titration in separate H^+ -solutions of known composition.

2.1.1.2 The titrations

Materials. Irrespective of whether natural or synthetically prepared minerals/particles are studied they should be characterized with respect to crystallinity (powder XRD), particle size and surface area. Predominating crystallographic cleavage planes should be identified, if possible. Ionic surface contaminants should be eliminated by washing, dialysis, or taken into account, as these may have an effect on the pH of suspended particles. In fact, it is essential to have a full understanding of the factors controlling the pH of suspension. Ideally it should correspond to the point of zero charge (pzc) (i.e. the pH at which the net surface charge is zero) but is often offset by residual ionic contaminants, and this is a common source of error in the determination of pzc's (see Section 2.1.2). A titration is usually performed by adding strong acid or base to the suspension to achieve a variation in pH. As an alternative to titrating with strong acid or strong base, coulometry offers a way of generating H^+ or OH^- ions with high accuracy in small amounts and in a very "clean" form. However, the inertness of the particles with respect to redox reactions has also to be investigated prior coulometric titrations. This can be done by performing parallel volumetric/gravimetric and coulometric experiments to ensure that identical results are obtained.

Equilibration criteria. In heterogeneous systems, fully stable potentials are seldom obtained within a reasonable time frame (e.g. 1 hour). Unless batch experiments are done, the magnitude of the derivative of the $E = f(t)$ curve should be given. A value of the order 0.6 mV h^{-1} , (or less) which corresponds to 0.01 pH h^{-1} , is recommended. If possible, extrapolation of the $E = f(t)$ curve to obtain some limiting E -value is an even better alternative.

Reproducibility and reversibility. A prerequisite for a universal applicability of an equilibrium model is that the experiments are reproducible. Furthermore, true equilibria require reversible reactions. The acid/base reactions

occurring at the goethite surface have proven to be both reproducible and reversible: titration curves from different titrations on one preparation of goethite coincide, as do curves from titrations with both acid and coulometrically generated hydroxide ions (Lövgren et al. [8]). Identical results should also be obtained in experiments with different batches of the same mineral, provided the surface area of the particles is the same. This has been demonstrated by results from a study of complexation of Al(III) at the surface of goethite (Lövgren et al., [8]).

However, when dealing with surface complexation, reversibility cannot be taken for granted. The desorption of Al(III) from goethite was found to be much slower than the adsorption reaction (Lövgren et al., [8]). Even when equilibrium appeared to be attained, i.e. when the drift in measured pH had ceased, 2.5 months after the final addition of acid, the desorption of Al(III) was not complete. Full reversibility has been found to be lacking also for the complexation of Hg(II) (cf. Gunneriusson et al. [9]), while for Pb(II) (cf. Gunneriusson et al. [10]) the complexation is reversible. A possible explanation for differences in reversibility between metal ions might be differences in ionic radii (and charge). With time, adsorbed metal ions with suitable size might diffuse into the surface layer of the solid and in this way become more strongly bound.

Variation in total concentrations. When metal complexation in homogeneous solution is being studied, it is considered important to vary both the metal to ligand ratio and to investigate different levels in total concentrations. The purpose of these variations is to gain information about complexes with different stoichiometry. The same principles is valid also when studying surface complexation, although, there are practical upper limits for useful concentrations of the solid phase that can be used.

To be able to quantify protonation/deprotonation processes from measured pH-changes, it is necessary to work with rather high levels in total concentrations of both the surface sites and metal ions/ligands. The mass balance of protons must be well controlled, and the release/uptake of protons measurable. This requires quite high total concentrations. There are, however, also good arguments to work at trace levels, i. e. closer to conditions valid in natural waters. In this case the potentiometric method must be complemented with some additional method. As an example, Müller and Sigg [11] and Palmqvist et al. [12], [13] have demonstrated that voltammetric methods can be used for *in situ* determination of trace metals.

As good data often will outlive the researchers that produce them, great efforts have to be made to collect data of as high a quality as possible. This is often a time-consuming and difficult job. However, there are no short-cuts in an accurate determination of equilibrium data.

2.1.2 Electrokinetic methods

Electrokinetic methods can be used to obtain experimental values of surface electric potentials at solid/solution interfaces. These are particularly useful in determining the isoelectric point (iep) of charged solids, i.e. the pH at which the particles do not move in an applied electric field (i.e. the zeta-potential, ζ , is zero). As the iep of many metal (hydr)oxides suspended in 1:1 electrolytes coincides with the pzc, electrokinetics provide a more straightforward alternative to the potentiometric determination of the pzc (i.e. determined as the common intersection point of relative surface charge data at different ionic strengths^a). Values of ζ obtained by electrokinetics may also be useful in corroborating the signs, trends and even the values of electric potentials predicted in surface complexation models, also in the presence of strongly sorbing cations and anions. There are however complications of experimental relevance that can impede to a correct interpretation of electrokinetic data.

Many ζ -potential data reported in the literature are collected by electrophoresis using laser Doppler velocimetry [14]. This technique requires extremely dilute solid suspensions to permit light scattered by particles under electrophoretic motion to be detected by a photodetecting apparatus. As the buffering capacity of such suspensions is essentially controlled by water one may expect significant uncertainties in pH measurements, especially at circumneutral values where the buffering capacity of water is at its weakest. Uncertainties at high pH are also likely to be important as typical glass electrodes reach their limits. The repercussions of such uncertainties on the determination of iep's is thus of major concern.

In general pH electrodes do not allow a reliable means of determining precise pH values of unbuffered solid suspensions in circumneutral to high pH's. Alternatively proper bookkeeping of the total concentration of protons in the system can avoid this problem. Instead of actually measuring the free concentration, the total concentration of protons in a suspension, $[H]_{\text{tot}}$, might be calculated from

^a The determination of the common intersection point should be carried out with titration data at many different ionic strengths. Charging curves at low ionic strength are particularly important as the pzc should be a buffering minimum, i.e. the point of zero slope. The alkaline part of the curve should also be of good quality, a difficult task if the pzc is above pH 9, where typical glass electrodes reach their limits. If these conditions are not satisfied the charging curves can be "convincingly" intersected at the pH of suspension, or any pH values in the vicinity. This is a common mistake in the literature and this is where electrokinetic measurements can be important, provided pH measurements are accurate.

$[H]_{\text{tot}} - [H^+] + [OH^-] = 0$. This condition should hold as long as the proton uptake by the solid is insignificant in the total proton balance of the system. In fact, provided (i) that one works on a concentration scale ($\text{pH} = -\log [H^+]$), and (ii) that titrant concentrations are dilute enough to ensure accurate discrete additions, it no longer becomes necessary to rely on the readings of the glass electrode to determine pH. Instead, one can calculate pH from $[H]_{\text{tot}}$ a very attractive option especially when the iep is in the alkaline region. Note also that the accuracy of this method is at its best if suspensions are titrated as described in the preceding section, with the only difference that some of the contents of the suspension are pumped, through an air-tight set-up, to the electrophoresis cell for the measurements and then recycled back in the titration vessel for subsequent titrant additions. This option is best checked against alternative methods (i.e. calculations based on a surface complexation model calibrated under more favourable conditions) because of the assumptions involved.

An alternative is to determine ζ -potentials electroacoustically [15], a method that requires concentrated suspensions (> 0.5 vol.-%) of understandably large buffering capacity. Uncertainties of measurements at high pH are however not eliminated, but can be minimised by standardizing a glass electrode against a hydrogen electrode, for example, and/or ensuring that the condition $[H]_{\text{tot}} - [H^+] + [OH^-] = 0$ in a blank (i.e. in the absence of the solid suspension) is fulfilled throughout the pH range of interest.

Of more general concern one may find advantages and disadvantages in using electrophoresis (with laser Doppler velocimetry) vs. electroacoustics. For instance, while the calibration steps of the Acoustosizer [15] tend to be simple and reliable, successful electrophoresis results rely heavily on the alignment of the cell. Regular capillary scans are therefore important to ensure that measurements are carried out at the stationary phase. The Fast Field Reversal technique (Malvern Instruments Ltd.) however allows measurements to be done in principle anywhere in an electrophoretic cell, although measurements at the centre are more reliable. This technique is also useful for measuring larger particles that sediment more rapidly than true colloids. Measurements and data treatment with the Acoustosizer are more tedious at high ionic strengths ($>> 0.01 \text{ M}$) as background electrolytes contribute to the overall electroacoustic signal [16]. Background measurements are therefore required for each ionic strength studied and pH values that increase the conductivity of a pH-neutral electrolyte. Moreover, at electrolyte concentrations above 0.1 M the Acoustosizer must be recalibrated with CsCl solutions of identical conductivity to the ionic strength of interest and the results are recovered from a far more involved treatment of the data [16].

2.2 Adsorption experiments

2.2.1 Batch experiments

Most adsorption experiments are carried out in the batch mode. Known amounts of solid, solute and electrolyte are placed in a test tube and rotated for a defined period under a controlled atmosphere at constant temperature and pressure. In the end of the experiment the pH of the suspension is measured (before or after solid-liquid separation) and the amount of solute remaining in solution is analytically obtained. From a mass balance for the solute the amount adsorbed is determined. The results have the largest errors when the amount added is similar to the amount remaining in solution (i.e. little adsorption). Potential problems can also be seen in the solid-liquid separation step. These encompass at least the following points:

- Incomplete separation will falsify the analytically determined amount of solute remaining.
- Effects of the separation step, which may affect the equilibria, may lead to compression of double layers (e.g. ultra-centrifugation) or losses of solute during filtration (adsorption of solute to filter material)

The so-called solid-concentration effect has often been related to such artefacts (e.g. incomplete solid-liquid separation). Whether such an artefact occurs can in principle be verified in several ways. One way is by determination of the amount of sorbent in the supernatant, e.g. in the case of experiments with goethite one might determine Fe in the supernatant. Honeyman and Santschi [17] labelled their hematite radioactively to actually test for possible problems in solid liquid separation. They found hematite in the supernatant samples. Unfortunately, such particles passing through filters are usually the smallest ones with the largest specific surface areas and therefore relatively large amounts of solute can be sorbed on such particles.

Even if the study by Honeyman and Santschi [17] clearly showed that solid-concentration effects may be associated with solid-liquid separation, the solid-concentration effect still circulates in the recent literature without verifying such issues [18]. In these latter studies another feature may be responsible for the observed effects: the authors studied metal ion sorption onto goethite in the presence of a phosphate buffer to control pH; however, phosphate strongly sorbs onto goethite itself, so that observed particle concentration effects should not be interpreted without considering the action of phosphate. It is probable that the metal ions were sorbed on a phosphated goethite.

Another issue related to solid – liquid separations may be discussed if the solubility of sorbing material is exceeded in the bulk solution (or at the sorbent surface). It is crucial in experiments whenever solubilities may be exceeded. For full

control of the sorption process, use of acidified metal ion solutions and gradual increase of the pH-values (by mildly concentrated base solution) is required. Otherwise, the solution phase may be at least locally oversaturated or polynuclear compounds may form. A comparison of results obtained from the different ways of preparation would be of substantial interest. If solubilities are exceeded the solute is precipitated and might be (completely, partially or not at all) found in the supernatant phase depending on the conditions chosen for the separation step (i.e. filter width, centrifugation speed). Distinction between adsorption and (surface) precipitation is usually not possible based on macroscopic data alone so that the interpretation of the macroscopic data is difficult.

2.2.2 Titrations

Titrations have been discussed in some detail in section 2.1.1.2 also with respect to metal adsorption. These very useful experiments are often not carried out despite the fact that most of the experimental studies involve the titration of the sorbent (which is required for modelling). Consequently in many cases set-ups for titrations are available. The proton data in the presence of the metal ion and surface have to be measured under conditions, where the resolution is sufficiently good to discriminate the acid-base behaviour of the solid in the presence of the metal from that of the solid alone. This usually requires high metal concentrations or large volumes. Similar data can be obtained with anion sorption. It is strongly suggested at this point that these kind of macroscopic data should be obtained. Not only spectroscopic data are most helpful in deciding on mechanisms. The macroscopic data are usually still required for estimations of thermodynamic quantities and the more data sets and data sources are available, the more can be said about uncertainty.

2.2.3 Combined experiments

An elegant way around the problems related to solid-liquid separation is the application of ion-selective electrodes (ISEs). Ludwig and Schindler [19] have applied such electrodes to the Cu-TiO₂ system. Good agreement between the results obtained with the ISE and in conventional batch experiments was reported. Experiments in the Cu-goethite system have been carried out by Robertson and Leckie [20]. Similar attempts with other metals have failed [21]. One major advantage of using ISEs is that titration (i.e. proton data) and uptake data (i.e. solute adsorption data) are obtained simultaneously without disturbance of the system. Such an approach furthermore assures that the time scales for the reactions of proton and solute data are the same.

Finally the imposed equilibrium criteria for both electrodes can be used to constrain subsequent titrant additions. The above mentioned consistency is not always obtained when data from short-term titrations and those from adsorption experiments of usually longer duration are merged in one model [22].

3. SURFACE COMPLEXATION MODELLING

3.1 Components of a surface complexation model

Surface complexation models (we distinguish a number of models, which have certain aspects in common^b) can be seen as being composed of various parts, which all correspond to acknowledged phenomena. The components treated here concern the protonation mechanism of surface functional groups, the impact of surface heterogeneity (site heterogeneity: i.e. surface functional groups may be discretely distributed, different surface functional groups with each having its own non-distributed reactivity, or they may alternatively be distributed continuously, with each site having a reactivity distribution) and the importance of electrostatics (i.e. the structure of the electric double layer; the treatment in this chapter is restricted to a mean-field approach and deviations from this approach are only shortly discussed). The above components are inherent to all surface complexation models. Consequently non-electrostatic adsorption models are not considered to be surface complexation models in the context of this paper. To some extent the three items should be discussed in all surface complexation modelling studies. However, in most cases there is no discussion as to why one of the options available for each of the three components is chosen. Such a choice should be closely related to the purpose of the modelling. E.g. inclusion of truly mechanistic issues (surface complex structure) requires a detailed model; i.e. it makes little sense to apply structural information in a model say for heavy metal adsorption, if the nature of the surface sites involved cannot be accounted for. In the other extreme for a model that does not attempt to resolve structure, the simplest model should be chosen. Different degrees of simplification are possible. If one is not interested in surface charge, the simplest model would not involve an acid-base model and a simple non-electrostatic model approach, starting directly with an adsorption reaction is sufficient. Whenever reliable data are available for the acid-base model, the simplest model accounting for these data is proposed as well as for generally accepted tendencies which may arise due to the variation of the experimental parameters (such as ionic strength or background electrolyte composition). Typically,

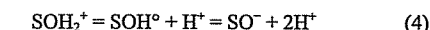
^b Some authors refer to the surface complexation model, which we would call surface complexation theory.

sufficiently simple models can be found for most systems and the only requirements of such models that can be presently fulfilled is their internal consistency. Inclusion of many sources of data will help to limit modelling options. For some data sources, however, there is some debate, on whether and how to involve them (e.g. electrokinetic data; these may be quite helpful, but quantitative use may also be assessed).

3.1.1 Protonation mechanism

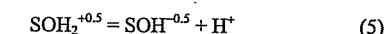
The protonation mechanism is discussed for "generic" surface sites (SOHⁿ, n being the charge of the site), contrary to "mechanistic" surface sites (discussed in the next section). Such generic surface sites are the most widely used representations of surface functional groups. For these sites two major approaches exist to describe their acid base behaviour:

- (i) the 2-pK approach, which involves two consecutive protonation steps on one generic surface group:



SOH⁰ is the "generic" surface site (for a one-site model), which can yield or take up a proton. This mechanism, which has been originally proposed by Parks [23], is the conventional protonation mechanism, which is usually mentioned in the major text-books.

- (ii) the 1-pK approach, which is characterised by the SOH₂^{+0.5} "generic" surface site, to which one deprotonation step is applied:



This protonation mechanism has been introduced by van Riemsdijk and co-workers [24]. The 1-pK formalism can be interpreted as a (sometimes even mechanistically realistic) simplification of a very complex reality, which is equally successful in the description of experimental data compared to the equivalent 2-pK model, but with a significant reduction in adjustable parameters. In particular cases, the 1-pK model can also be interpreted as a special case of a more comprehensive (truly mechanistic) model.

The protonation mechanism may be related to the comparable reactions in solution. If the second deprotonation for the SOH₂^{+0.5} species (i.e. the formation of the SO^{-1.5} species) behaves as a comparable aquo-group in aqueous solution, it should not be of importance, because in

solutions consecutive de-protonation of one functional aquo-unit is typically separated by more than 10 pH units.

From this point of view the 1-pK mechanism would be a more reasonable analogue to aqueous solutions than the 2-pK mechanism, since in models based on the latter consecutive protonation typically occurs within a rather narrow range of pH. In attempts to justify or interpret the surface group used with the 2-pK mechanism, alternative interpretations of the SOH^o group in terms of a combination of a SOH^{-0.5} and SOH^{+0.5} groups have been proposed. Unfortunately, such justification of the use of equation (4) results in some conceptual problems with surface complexes involving bidentate binding. Whereas the notion still makes sense for the individual fractional charge groups, the "combined" group when adsorbing some solute is always a bidentate.

A further advantage of the 1-pK model is that the logarithm of the stability constant corresponding to the surface chemical reaction is directly related to experimental data, because it is identical to the pristine point of zero charge (PPZC). For the 2-pK model two stability constants must be determined (i.e. fitted). These two pK-values are often chosen to be symmetrical around the PPZC, so that a reduction to one as yet unknown parameter for the 2-pK formalism is possible if the PPZC is known. However, this actually can always be seen as an unnecessary complication in terms of the number of adjustable parameters, which will propagate when e.g. temperature dependencies are to be incorporated. The PPZC can be measured as a function of temperature or predicted by theory^c [25].

A final point in favour of the 1-pK approach is that the "generic" surface sites may be corresponding to the "mechanistic" surface sites. For goethite they would be equivalent to singly coordinated surface sites, which are actually to a large extent responsible for the variable goethite surface charge, when the multisite complexation (i.e. MUSIC) model is taken as the reference. Nevertheless a reasonable approximation of the full MUSIC model is not possible based on site density and affinity constants of the singly coordinated group alone, because with one site and a pK corresponding to the PPZC the site density of the singly coordinated sites is not sufficient to explain the experimentally observed proton uptake.

3.1.2 Structure of the electrical double layer

A second distinction among surface complexation models is due to the postulated structure of the electrical double layer.

^c It should be kept in mind here that the precautions discussed previously with respect to the determination of PPZCs are in all models crucial to obtain reliable model parameters.

Figure 1 shows the models, which are implemented in the standard speciation codes allowing for surface complexation (e.g. FITEQL [26], MINTEQA2 [27], ECOSAT [28] or SOLGASWATER [29]). The structure of the electrical double layer defines model inherent charge/potential relationships, which allow calculation of the respective potentials from a balance over the surface species, which contribute to the charge in the respective planes. Thus the electrostatic effects on the surface chemical equilibria are accounted for in some model dependent fashion. Figure 1 indicates the conditions, under which the different electrostatic models are expected to apply. One important constraint is given by ionic strength. Conditions of high ionic strength typically decrease the influence of the diffuse layer and the compact part of the double layer dominates. As a consequence the constant capacitance model (CCM) (Figure 1a) is a good approximation at high ionic strength.

In the other extreme at sufficiently low ionic strength the diffuse layer model (Figure 1b) is expected to be a good approximation. These two simple models do not explicitly account for the formation of ion-pairs between charged surface groups and the ions of the electrolyte, which is instead possible with the electrostatic models involving more layers (Figure 1c and Figure 1d). Such ion-pairs will additionally contribute (neutralising) charge to the particles that must be accounted for in the electroneutrality condition. For the CCM such an electroneutrality condition for the particles is not part of the model. The constant capacitance model should be taken to be electrolyte specific, but it is also ionic strength specific and thus extremely limited. In the purely diffuse layer model the experimentally observed electrolyte specific behaviour of a sorbent can not be described with one parameter set.

The more elaborated the structure of the interface becomes in a model, the more realistic the model is expected to be accepting the respective assumptions (e.g. mean-field approximation). A multi-layer model would be judged to be more realistic because it may consider various phenomenologically expected aspects:

- anion and cation of the electrolyte have different sizes and therefore their charges should not be placed in the same plane; consequently, in a model that attempts to account for this aspect one additional layer (i.e. one plane of adsorption) is required compared to the traditional application of the triple layer model
- adsorbed multivalent ions other than background electrolyte ions or protons might have substantial size with the charges sitting in different positions in the surface complex; consequently, the respective charges should be adequately distributed over various planes of adsorption; charge distribution is much more flexible with more planes of adsorption available.

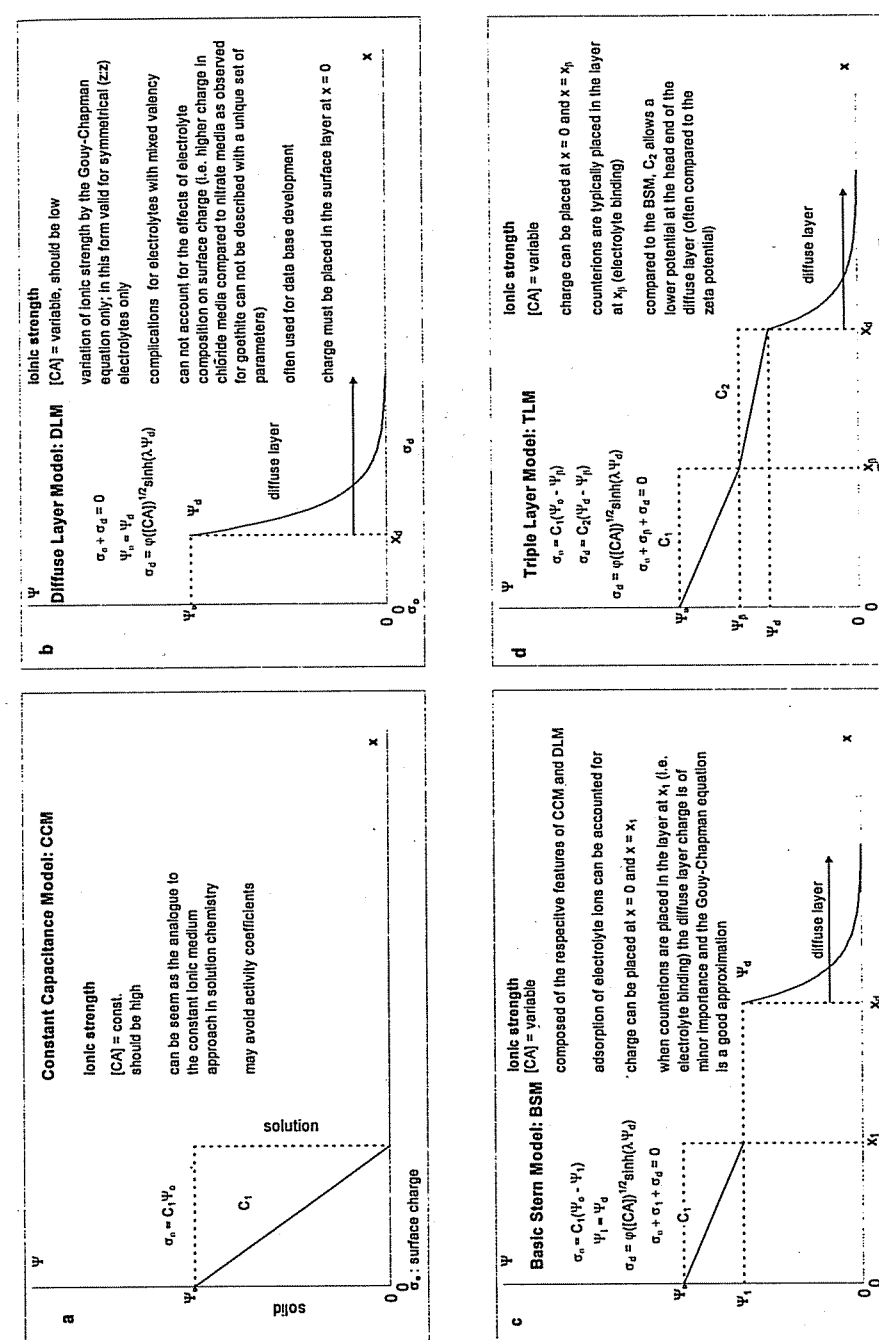


Figure 1
Standard electrostatic models. Schematic presentation of the structure of the electrical double layer.

An understanding of the structure of the electrical double layer is also essential to account for ζ -potentials measurements^d. Values of Ψ_o , the surface electric potential, are not usually measurable quantities at the oxide-water interface in suspensions. These are rather calculated within the framework of a SCM coupled with an EDL. It is nonetheless possible to compare at least the polarity of such values to ζ -potentials, which are experimentally determined values of Ψ at the *shear plane* [14] of a surface. Behind this plane lie the compact layer encompassing several layers of water molecules that have adsorbed to complete the coordination environment of bare surface metal atoms, or as a result of favourable hydrogen bonding, electrostatic conditions, and/or incipient surface roughness. These few layers of water molecules separate charged surface sites from electrolyte counterions and can be treated as a charge-free layer in a parallel-plate molecular capacitor of constant capacitance, C . The potential at the solution-side of the surface water molecules, Ψ_p , is theoretically decreased to:

$$\Psi_p = \Psi_o - \frac{\sigma_o}{C} \quad (6)$$

where σ_o is the surface charge density and Ψ_o is the potential at the surface. Values of Ψ damp out to zero in the diffuse layer (dl). As the shear plane is at or outside the compact layer ζ is therefore usually a fraction of Ψ_o .

The success of a surface complexation model can be tested by its ability to mimic the trends and values of ζ . While the exact position of the shear plane can be debatable, strong evidence supports the concept that the shear plane lies close to the head of the diffuse layer such that $\Psi_p = \Psi_{dl} = \zeta$ [14,30]. This assumption would however no longer hold if an adsorbate, whose width would exceed that of the compact layer, were to push the shear plane towards the diffuse layer. In this case an equation describing Ψ_{dl} as a function of the distance from the head of the diffuse layer can be required. Alternatively, when solid surfaces are sufficiently charged the resulting strong electric field strengths ($E = d\Psi/dx$) can increase the viscosity of interfacial water [31,32,33] and displace the shear plane. The shear plane is likely to migrate to an equilibrium point corresponding to a constant, maximum, value of ζ . This can be misleading evidence to some kind of site saturation with respect to potential-determining ions, evidence that can be verified by other experimental approaches (e.g. potentiometric titrations and adsorption experiments). If a solid surface truly exhibits a pH-variable charge but a constant value of ζ , a modified version of the Smoluchowsky equation can be used [32]:

$$\mu = \epsilon \epsilon_o \int_0^{\zeta} \frac{d\Psi}{\eta(E)} \quad (7)$$

^d Note that to obtain zeta-potentials from the raw electrokinetic experiments some assumptions are required.

where $\eta(E)$ is a field-strength-dependent function of viscosity [33], ϵ is the dielectric constant of water at the interface, ϵ_o is the permittivity of vacuum, and μ the electrophoretic mobility. Analytical integrations of Eq. 7, proposed by Lyklema [32], allow surface complexation models that predict pH-variable electric surface potentials to predict constant values of ζ . Lastly, electric field-strength dependent values of ϵ have also been measured [34,35] and predicted [36,37], but it has also been shown that these are not sufficiently strong at the shear plane to significantly modify $\epsilon = 78.5$, i.e. the value of water [38].

Other concerns that can impede to a straightforward interpretation of ζ -potential data arise from the aspect ratio, the distribution of surface charge on solid particles, and surface conductance. The Smoluchowsky equation ideally holds for spherical particles, which is rarely the case for metal (hydr)oxides. There are fortunately several correction functions that can be applied to electrophoretic and electroacoustic measurements on prolate and oblate particles [14,15]. Generally, the deviations are not too significant provided the distribution of charge on the solid surface is relatively homogeneous. In contrast, non-spherical particles of acute heterogeneous distributions of charge, such as clay minerals, can potentially exhibit non-zero mobility at the pzc, i.e. the iep does not coincide with the pzc [39]. Surface conductance [40,41], where significant ionic mobility behind the shear plane modifies particle mobility, can also be a problem for some solids, such as kaolinite [16]. Possibilities of these types cannot be ignored and, if deemed significant, their importance should be tested before validating electric surface potentials determined by surface complexation model.

3.1.3 Heterogeneity

The above equations for simple acid-base reactions with a surface functional group invoke one type of "generic" surface group. In reality, it is expected that several distinct surface groups exist. Also, it must be assumed that functional units of nominally identical surface groups have variable affinities to some solute (e.g. to a proton). This may e.g. be caused by defects in the structure of a sorbent close to the surface.

From these statements at least two aspects of heterogeneity should be phenomenologically considered:

- "discrete" differences in properties (i.e. different surface sites)
 - "distributed" (i.e. continuous) properties of otherwise identical surface sites (affinity distributions).
- These are discussed in the following.

3.1.3.1 Discrete site heterogeneity

This aspect is best discussed with an "ideal" crystal plane of

some solid (i.e. the solid is assumed to be free of those defects which might influence the reactivity of the different sites).

In Figure 2 discrete site heterogeneity is exemplified by a goethite crystal plane. Assuming that the goethite bulk structure is a valid assumption for the goethite surface in an aqueous electrolyte solution, a range of surface functional groups may be distinguished, where the surface oxygen is bound to one, two or three iron atoms. Figure 3 supplements Figure 2 with the nomenclature for the different functional groups.

The simplest (de)protonation formalism is assumed to apply for each of the distinct functional groups. This means that in a truly mechanistic model, strictly speaking, knowledge of the overall PZC of a sorbent is not enough, but the individual proton affinity constants for the different sites must be known for each crystal plane of importance. At present two theoretical approaches exist, which yield these affinity constants:

- Hiemstra and van Riemsdijk [42] consider the structure of the sorbent. They estimate the proton affinities of the various sites from the bond valence.
- Rustad and co-workers [43] apply molecular modelling

to obtain proton affinities.

Figure 4 shows the surface charge density of the goethite crystal plane in Figure 2 calculated with both options. The overall fits to the surface charge curve are equally good. However the surface speciation (i.e. the contribution of the different groups to the overall surface charge) is very different:

- With the model parameters from Hiemstra and van Riemsdijk [42] only one surface group shows variable pH behaviour (Figure 4a). All other groups only adjust the overall charge so that the calculated and measured PZC coincide. Thus for this crystal plane most surface groups do not display variable charge at all over the pH range of interest, but rather influence the zero level (i.e. the overall PZC of the crystal plane). In fact only one surface group (the singly co-ordinated one) shows variable charge behaviour in the pH range of interest. It is also apparent that the MUSIC approach requires that two kinds of triply co-ordinated hydroxyls are present. The complex features can be substantially simplified by using a single ("semi-generic") site 1-pK approximation, where only one surface hydroxyl (can be identified with the singly coordinated group and would have the same site density) is used with a proton affinity which

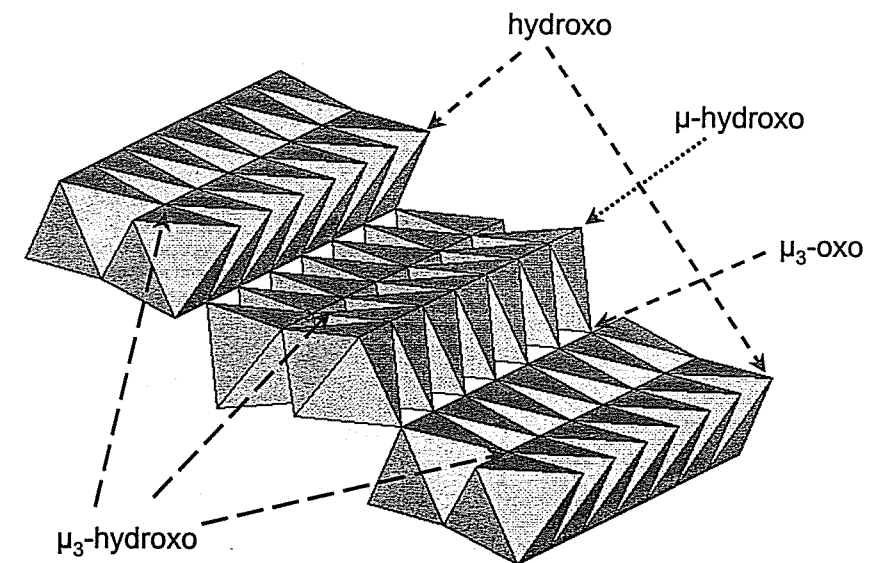
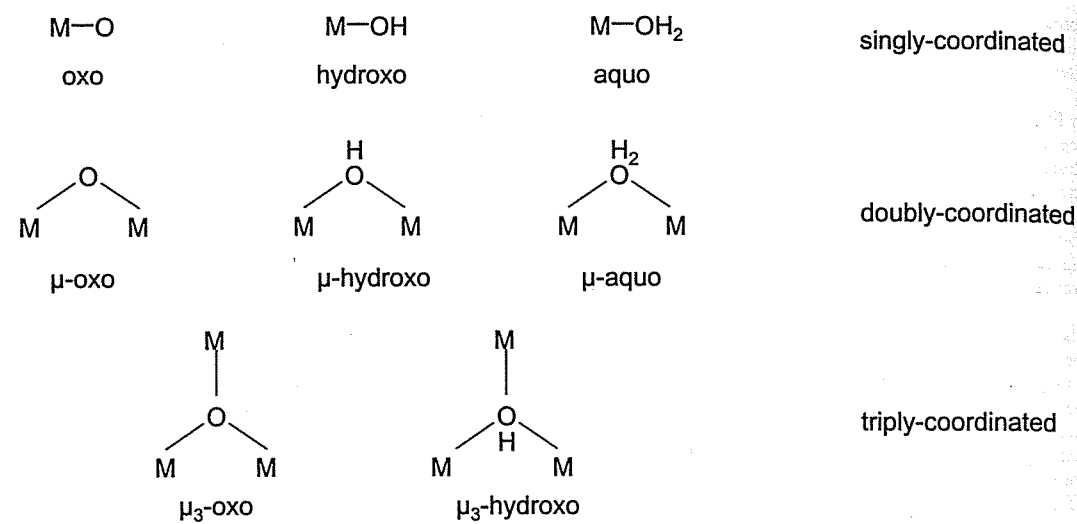


Figure 2

Structure of the {110} crystal plane of goethite (α -FeOOH), see also Figure 3 for explanation of terms.



M: metal center of the oxide, hydroxide or oxyhydroxide

Figure 3
Nomenclature of surface functional groups according to IUPAC terminology.

corresponds to the overall point of zero charge of this crystal plane. To what extent this approximation can actually be used in further going adsorption studies is another issue, e.g. when surface spectroscopy shows that several kinds of surface functional groups are involved in the formation of an important surface complex then the full model would ideally be required in a mechanistic interpretation of such data with a surface complexation model.

The model parameters from Rustad and co-workers [43] yield a completely different speciation, where all surface groups show pH-dependent behaviour, and where one of the surface hydroxyls is even predicted to violate the 1-pK protonation scheme (i.e. subsequent protonation steps of one oxo-group within a narrow pH range, Figure 4b).

At present the predictions of the individual proton affinity constants for goethite based on the bond-valence principle by van Riemsdijk and co-workers are not in agreement with independent calculations by Rustad and co-workers [43]. For silica Rustad and co-workers found unrealistic values [44],

which were more recently discussed by Tossel and Sahai [45]. These latter authors claim, that erroneous assumptions by Rustad and co-workers resulted in the unrealistically high protonation constants for silica. Tossel and Sahai furthermore state that this error also occurred in the study of other minerals by Rustad and co-workers, but that the errors cancelled out in those systems.

In most of these attempts the first step is to describe the surface based on the sorbent structure. The MUSIC model treats the interface to be a consequence of the crystallographic structure. Molecular modelling techniques make use of different approaches depending on the nature of the computations [46]. Those making use of small clusters, embedded or not, will always result in a discrete heterogeneity, while those using supercell-like clusters or periodic boundary conditions may not necessarily result in such problems. Concerns also arise from whether protons present in a structure persist at the interface [47], and if they do whether these form intramolecular hydrogen bonds and if these are strong or not [30]. Distances between atoms affected by surface relaxation (causing different distances

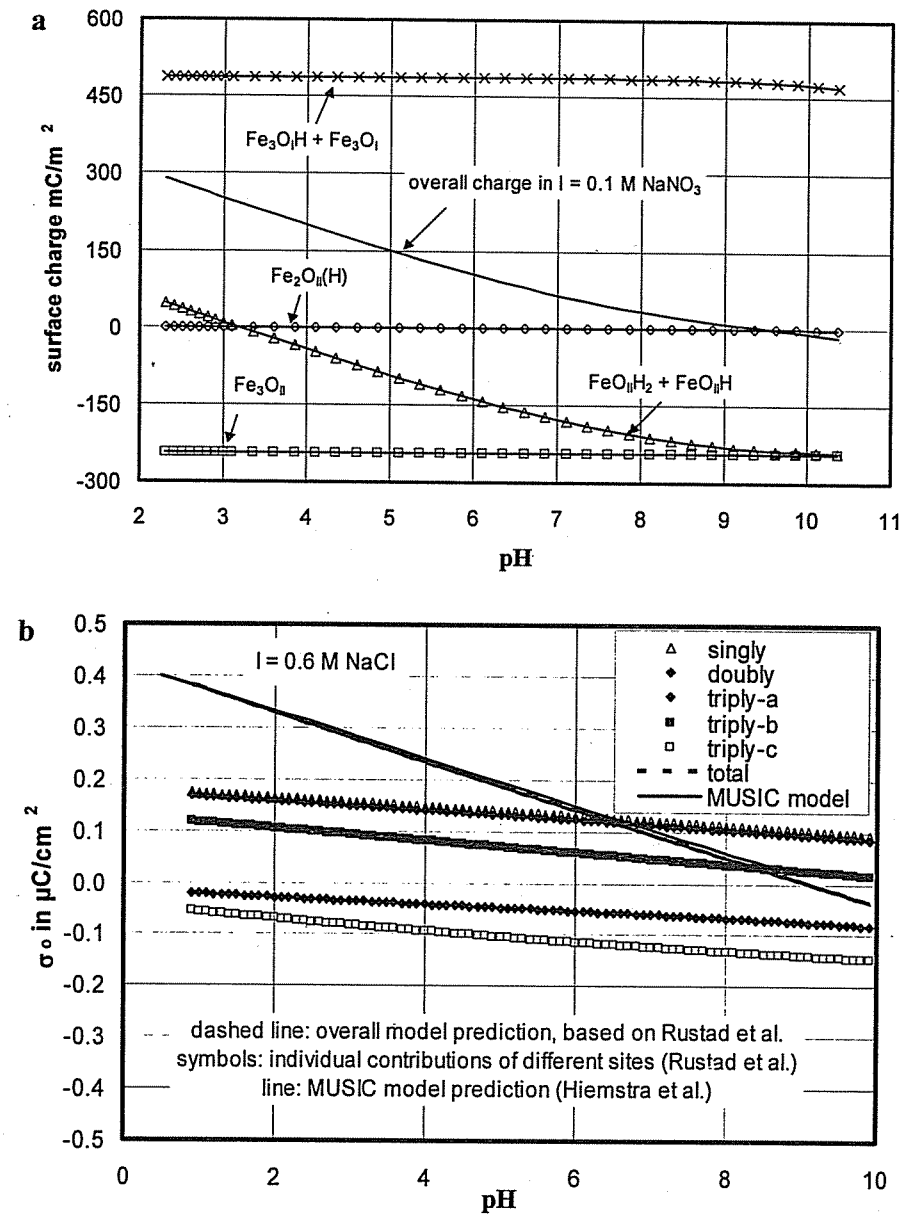


Figure 4
Surface speciation of the {110} goethite surface plane according a) to the MUSIC model and b) results of first principles calculations. The differences in ionic media do not affect the relative distributions of surface species.

between atoms at the surface as compared to the respective atoms in the structure) may also result in heterogeneities. All of the above problems can have a profound effect on the discrete proton affinities of surficial oxygens. In the case of the MUSIC model, the characteristics of the bulk are assumed to extend to the surface, while molecular modelling can take these interfacial effects into account. There are however many untested uncertainties related to molecular modelling. A quantum chemical approach to this problem, for example, will highly depend on the chosen methods, the basis set(s), the size and geometry/symmetry of the cluster, and the embedding technique [46], while molecular dynamics making use of a periodic boundary will depend on the choice of interaction potentials. *Ab initio* molecular dynamics [48] on large solid supercells might help solve these problems and perhaps introduce explicit solvent effects on the intrinsic proton affinity of surface oxygens.

The role of water structure at interfaces in the context of electrolyte adsorption has been discussed by Dumont and co-workers [49]. Based on previous work, these authors propose to consider structure breaking or structure making properties of the solids and electrolyte ions. This model can phenomenologically explain experimentally observed lyotropic adsorption sequences.

Structure making electrolyte ions would be small ions with high charge. Structure making interfaces would have water molecules strongly attached. Structure making electrolyte ions would be well adsorbed on structure making surfaces, since water molecules which otherwise would be strongly ordered can be released, resulting in a net gain in entropy. These phenomenological approaches allow a qualitative explanation of many features and thus stress the importance in considering the properties of the solvent in the discussion of interfaces. Surface complexation models can indirectly account for these effects to some extent by the choice of capacitance values, which correspond to distances in the interfacial layers, and by the location in which electrolyte ion charges are placed. These can in principle be chosen according to the size of hydrated electrolyte ions.

Most of the above cited applications realised the importance of the presence of different functional groups, so that agreement at least on this aspect is achieved. In the corresponding modelling applications these different functional groups are typically considered as distinct entities. Thus for every functional group, for which a distinct proton affinity⁶ is obtained, only this proton affinity is taken into account.

⁶ The applications with respect to predicting affinities presently do not go beyond proton affinities.

⁷ Proton affinities of nominally identical groups are not necessarily identical and may differ for different crystal planes.

This first heterogeneity approach considers "discrete" sites which make up a heterogeneity of the interface through the variety of sites. This can be described by equation (8):

$$\theta_{t, \text{solute}} = \sum_j (f_j \theta_{j, \text{solute}} \{K_{j, \text{solute}}, [\text{solute}]\}) \quad (8)$$

In equation (8), [solute] is the molar solute concentration in solution, θ is the surface coverage (adsorbed amount of solute divided by total amount of surface sites), f_j is the fraction of surface sites of class j , $K_{j, \text{solute}}$ is the affinity constant for the local sorption isotherm describing the interaction between the solute and the surface site j ; the index t stands for the overall (total) adsorption.

3.1.3.2 Continuous heterogeneity

A second often applied approach might start from a classical one-site surface complexation model but involves a continuous distribution of site properties. This approach takes into account that the model surface sites are not energetically homogeneous, i.e. they may display more or less different affinities.

In the context of surface complexation, a sorbent with only one reactive surface group might be a typical example where the actual application of such a model would be reasonable. Otherwise, this approach has been typically applied to "generic" surface sites for different models. The model would be characterised by equation (9)

$$\theta_{t, \text{solute}} = \int_{\text{range}} (\theta_{\text{solute}} \{K_{\text{solute}}, [\text{solute}]\} \Xi \{ \log K_{\text{solute}} \}) d \log K_{\text{solute}} \quad (9)$$

and would correspond to a continuous distribution (Ξ) of affinity constants for one surface site (no distinction with respect to the class of surface sites is considered). Integration occurs over the range of affinity constants. This approach requires a distribution function $\Xi \{ \log K_{\text{solute}} \}$ for the affinity constant.

In most cases a single site model does not correspond to what is actually expected. Therefore, a combination of equations (8) and (9) is in principle required to account for the different distinct sites and their potential individual continuous heterogeneity. This results in

$$\theta_{t, \text{solute}} = \sum_j (f_j \int_{\text{range}} (\theta_{j, \text{solute}} \{K_{j, \text{solute}}, [\text{solute}]\} \Xi_{j, \text{solute}} \{ \log K_{j, \text{solute}} \}) d \log K_{j, \text{solute}}) \quad (10)$$

Major problems in treating equation (10) are:

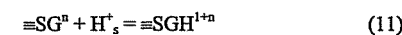
- The knowledge of the presence of different surface groups is often restricted to well defined solids, such as well crystallised goethite; even for such solids, there may be a debate about the actual crystal planes [30]; for powders the determination of crystal planes is at present a formidable task; for environmentally relevant samples, such as coatings of reactive minerals on sand, the characterisation will also be so problematic that it is a formidable task to obtain the necessary information to apply sophisticated models.
- Different affinity distributions can be assumed, but currently the experimental determination of distributions involves such questionable assumptions as the absence of electrostatics.

In the context of surface heterogeneity, it should also be acknowledged, that defects probably exist on most surfaces to some extent. These will result in very reactive sites, which might be of particular importance for the interaction with trace components as long as other significantly competing adsorbing solutes are absent. Consequently, it is very probable that such very reactive sites exist in as far unknown amounts, even if presentations like Figure 2 tend to suggest the perfect crystal plane.

3.2 Formalism of surface complexation theory

Combining a (de)protonation mechanism with a theoretical model for the electric double layer results in a formalism to calculate the free energy of adsorption or the respective intrinsic stability constant for a surface species.

As the simplest example the adsorption of a proton to an arbitrary surface functional group, $\equiv\text{SG}^n$, with charge n is considered. The interaction of this group with a proton "close to the surface", denoted by H^+_s , may be written as a surface chemical reaction:



Adsorption of one proton is accompanied by the transfer of one charge unit from the bulk solution (which is characterised by the measurable proton concentration $[\text{H}^+]$) to the interface. In some simple splitting of the process, a first step involves the transfer of the proton from the bulk of the solution to some plane "close to the surface". Then the surface functional group may react with the proton close to the surface to form a protonated surface group. For both particle and bulk solution an electroneutrality condition holds. Therefore, co-adsorption of one negative charge unit is required typically by an anion from the background

electrolyte, which in the constant capacitance model is not considered at all, in the purely diffuse layer model occurs in the diffuse layer only, and in the Stern model or the triple layer model besides the diffuse layer additionally occurs through the formation of ion pairs. According to the transfer of the proton, the absolute charge in the plane of proton adsorption is increased by 1. In particular for the 1-pK model, it appears that the precharged generic group causes problems of conceptual understanding to many groups, which hampers its wider application.

A simple distinction between chemical contributions (arising from bond formation) and electrostatic effects (originating from the charge build-up) is assumed. The electrostatic effects, which in reaction (11) would tend to hinder adsorption of another proton both to that surface group (which is unrealistic within 10 pH units of the first protonation step), but also to neighbouring surface groups (which experience the charge transferred by the first proton; discrete ion effects), and to all other surface groups (which are considered in a mean-field approach, where discrete ion effects are neglected). This means that charges, which are present far away from a certain functional group, have the same effect as those in the direct vicinity of that group. The overall free energy of adsorption for this reaction would be

$$\Delta G_{\text{ads}} = \Delta G_{\text{bond}} + \Delta G_{\text{elec}} \quad (12)$$

The quantitative distinction depends on the different electrostatic models, which were shown above. For reaction (11) a mass law equation can be written as

$$K_+^{\text{int}} = [\equiv\text{SGH}^{1+n}] \cdot [\equiv\text{SG}^n]^{-1} \cdot [\text{H}^+_s]^{-1} \quad (13)$$

K_+^{int} is the intrinsic stability constant for proton adsorption to $\equiv\text{SG}^n$, which is valid in the absence of charge when $[\text{H}^+_s] = [\text{H}^+]$ and accounts for the chemical contribution represented as ΔG_{bond} in equation (12). This involves the free energy change related to the interaction of a proton already close to the surface with the surface functional group. The overall (measurable) stability constant (valid also for charged interfaces) is given by

$$K_+ = [\equiv\text{SGH}^{1+n}] \cdot [\equiv\text{SG}^n]^{-1} \cdot [\text{H}^+]^{-1} \quad (14)$$

This defines the concentration of the proton "close to the surface" and in the bulk solution as well as the electrostatic contribution ΔG_{elec} to the overall reaction. The relation between equations (13) and (14) requires a functional relationship between the concentration of the proton in the bulk solution and at the interface, which typically is a Boltzmann-factor

$$[\text{H}^+_s] = [\text{H}^+] \cdot \exp \{ -F \cdot \Psi_o / (R \cdot T) \} \quad (15)$$

This factor represents the energy required for the transfer of one proton (here equivalent to one charge unit) from the bulk solution close to the surface. R, T and F are the gas constant, absolute temperature and Faraday's constant, respectively and Ψ_0 is the surface potential.

Usually the mass law equations are written in terms of concentrations. This would be appropriate for the aqueous species in a constant ionic medium. For the above reaction, both for the proton at the surface and the surface functional groups in principle activity corrections are required for extrapolation of the stability constant to zero ionic strength. By some authors, these corrections are considered to be lumped into the Boltzmann-factor. A sound treatment in a thermodynamic sense is hampered by the inability of experimental determination of activity coefficients both for solutes "close to the surface" and for the surface functional groups. There is no reason to assume that they would not change with pH and ionic strength. Due to the small distances between reacting entities at surfaces discrete ion effects are expected to contribute to deviations from ideality. The unverified assumption in the treatment of the surface chemical equilibria is either that the ratio of the activity coefficients is about unity. Alternatively the deviations from ideality are considered to be lumped together in the electrostatic correction term.

The models in Figure 1 may be called "standard electrostatic models". They are implemented in the most prominent codes available for surface complexation calculations. However, other models exist. Some variants are shown in Figure 5. From this figure and from the literature it is apparent that variations and even combinations of the electrostatic models are possible. Probably there are very few variations, which have not yet been applied, mentioned or suggested with respect to the four standard models, unfortunately even beyond known reasonable limits of the models. This might serve as an indication of how diverse surface complexation modelling is. Consequently, most approaches can be justified by authors in some way by reference to previous papers. Also the obtained fit to the experimental data often justifies use of a specific model.

In the following the different "standard" electrostatic models (Figure 1) are described in some more detail:

The CCM (constant capacitance model, model a) [50] is best used in analogy to the constant ionic medium approach in aqueous chemistry. As a consequence the parameters are restricted to one value of high ionic strength (in terms of composition and concentration of the electrolyte). It is assumed that the drop in potential in the inner part of the electric double layer at the high electrolyte concentrations is so extensive that the diffuse part can be completely neglected.

The experimentally observed variation of surface charge with ionic strength (again in terms of composition and concentration of the electrolyte) cannot be handled with one parameter set.

The diffuse layer model (DLM) [51, 52] includes no compact layer. The concept holds best at low values of ionic strength. It cannot distinguish between different electrolyte ions (i.e. nitrate and chloride ions behave equally in this model). The analogue in aqueous solutions is the Debye-Hückel limiting law. Non-specificity of the electrolyte is in fair agreement with the experimental observations at low ionic strength for solutions, but for mineral surfaces the surface charge density may be affected by the nature of the counter-ion (i.e. for goethite the surface charge density at constant pH will be higher in chloride than in nitrate media) [53]. As a consequence a unique sorbent inherent DLM parameter set will not be able to describe ion-specific effects at interfaces. The Gouy-Chapman equation, which is typically involved in the model implementations, is restricted to symmetrical electrolytes. However, in many situations aqueous solutions may contain mixtures of rather weakly adsorbing ions (Ca^{2+} , Na^+), so that the background electrolyte is not symmetrical.

Model c is the basic Stern model (BSM) [24] and combines an inner layer with a diffuse layer. It allows to cover a range of ionic strength and for electrolyte specificity by the ion-pair formation between the ions of the electrolyte and the oppositely charged surface functional groups. The BSM is the simplest model that is able (i) to cover a broad range of ionic strength and (ii) to describe electrolyte specific behaviour.

The TLM (model d, triple layer model) [54, 55] has an additional layer compared to the BSM and is as the latter electrolyte ion specific. By the additional layer the potential at the head end of the diffuse layer is lowered and was often considered necessary for a direct, successful comparison between the diffuse layer potential and measured ζ -potentials.

In this section specific models are introduced, which are not "standard" models. Their "degree" of applicability is discussed based on what can be achieved by the model and what can be gained by the model compared to a simpler model. Figure 5 shows two such examples:

The first (Figure 5a) introduces various additional features as compared to the standard models. The three plane model (TPM) features include:

- More planes of adsorption: The TPM (Figure 5a) allows charges to be placed in the surface plane, in the plane, where the head end of the diffuse layer is situated, and in an intermediate plane; in the typical application of the model the electrolyte ions are placed in the d plane; with

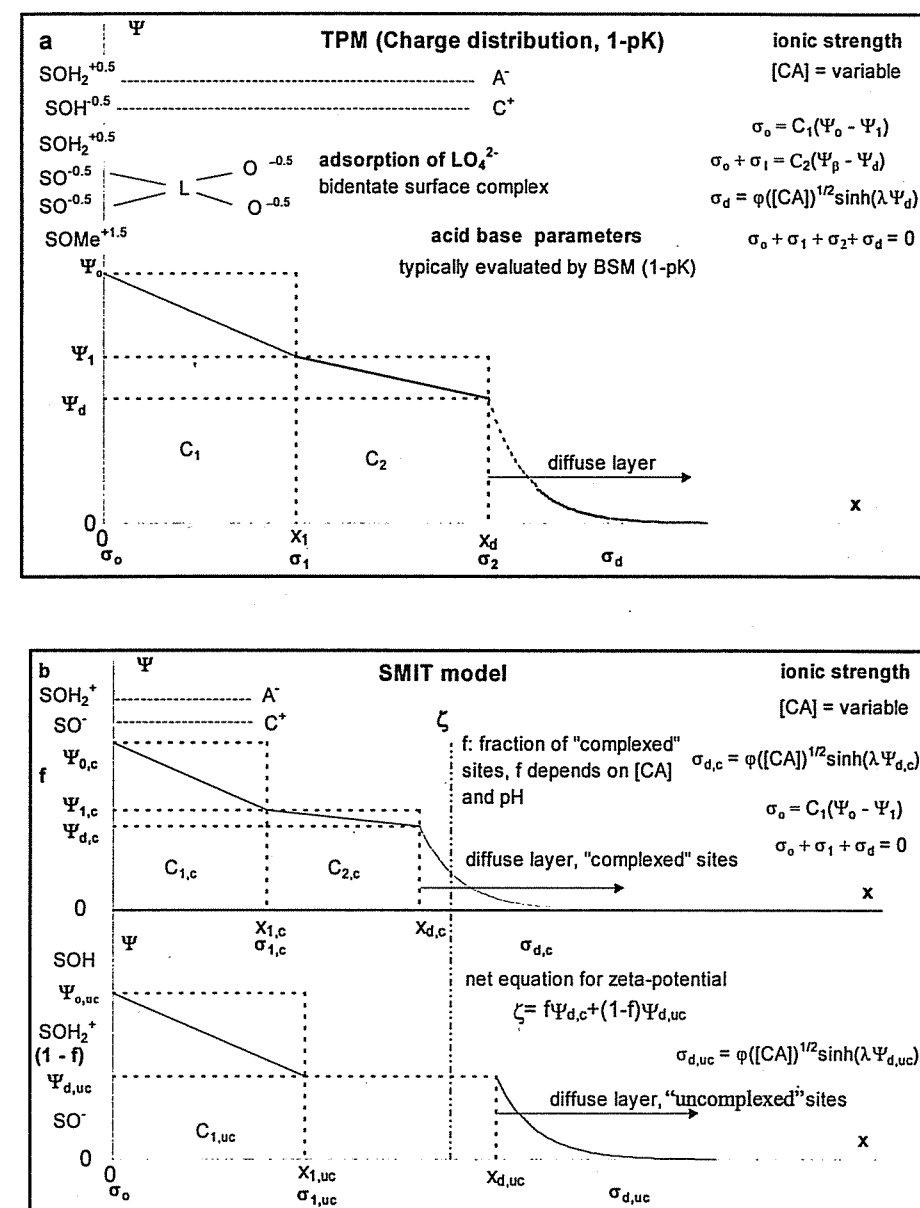


Figure 5

Two non-standard model options (detailed description, see text); a: TPM (three plane model), b: Smit model.

respect to the TLM, where no charges are placed in the respective d plane, the electrolyte ions bound as ion-pairs are "in contact" with the diffuse layer. Note that the TLM as implemented in codes such as FITEQL is based on the equations of the original papers, which equate the diffuse layer charge to the charge in the d-plane, whereas the TPM requires another formulation of the charge balances.

- Charge distribution (CD) concept (Figure 5a): Although already mentioned by Davis *et al.* [55] charge distribution has not been involved in surface complexation models until more recently [56]; instead adsorbing ions have been treated as point charges whether a model dealt with small cations or bulky ligands with several functional groups; charge distribution allows to allocate parts of the charge transferred to the particles in an adsorption process to different planes; technically, the same effect can be obtained by introducing e.g. combinations of inner- and outer-sphere surface complexes as point charges (for each surface complex one stability constant is required); for estimation of charge distribution coefficients the Pauling bond valence concept [82] can be used; electrolyte ions are typically considered as point charges both in the compact part (as ion-pairs) and in the diffuse part of the electrostatic double layer.

Acid-base parameters for a TPM can be evaluated by the equivalent BSM. The relation between the capacitance values allows constraints on the optimum couples of C_1 and C_2 . Problems will arise when charges of adsorbed solutes may reach further towards the solution than what is allowed by C_{tot}

$$1/C_{tot} = 1/C_1 + 1/C_2 \quad (16)$$

In Figure 5a, a bidentate surface complex is shown. Such multi-dentate complexes can also be used with other models of course but it is important to note that the formation constants of multi-dentate surface complexes may need to be corrected for the suspension concentration. Most computer programs do not allow automatic corrections of these features; therefore, care must be taken that they are correctly taken into account when calculating the respective stability constants.

With generic 1-site models one may avoid this e.g. by introducing $(SOH)_2$ entities for bidentates. As long as the total amount of bidentates is much lower than the total amount of the generic site this approach is a valid approximation. For mechanistic models with different types of sites the situation becomes more complicated and the by-pass is no longer possible.

For mechanistic descriptions of ion adsorption the three

plane model with charge distribution offers extensive flexibility; this can of course be used to fit all involved parameters like the composition of surface complexes, capacitance values, charge distribution coefficients and stability constants. However, these parameters can also be constrained using e.g. the Pauling bond valence [57, 58] or by equation (16).

The electrostatic part of the second model (Figure 5b) was originally proposed by Smit [59]. Smit invoked very low values for the outer-layer capacitance. The values of about 0.2 F/m^2 typically used in the TLM can be significantly lowered. According to work quoted by Smit this corresponds to experimental observations.

The original Smit model splits the surface plane in two sections, one characterised by the fraction $1-f$ of the overall surface (respectively the surface sites, where only uncomplexed surface groups are present) and another section characterised by the fraction f of the surface sites where ion-pairs are formed with the electrolyte. For the two sections separate electrostatic model concepts are introduced: a BSM (obviously without electrolyte binding) for the fraction $1-f$ and a TLM for the fraction f . This separation is of course artificial. A mean value of the ζ -potential is calculated from the equation given in Figure 5b.

In this model, the overall capacitance of the inner layers varies with pH and ionic strength as is expected for the field strength at the interface. One might be tempted to assume that the structure of the first water layers will not be constant.

The features in the original Smit model (i.e. combination of a BSM and TLM, 2-pK formalism) are not unique. The compartment principle itself allows a huge amount of options such as combination of different electrostatic models or adding supplementary compartments when e.g. a sorbing molecule would be introduced. This increases the number of options and in view of the number of the already available models this might be a problem. However, in some situations such an option might be useful: e.g. a case in which a bulky molecule adsorbs to a mineral surface in the presence of an electrolyte. Compared to a standard Smit model (two compartments) used for the acid-base properties of the mineral, the addition of the molecule may cause an extensive distance between adsorbed charge (introduced by the molecule) and the charge transferred to the interface by functional groups of the molecule, which are oriented towards the solution side. This distance might not fit in the acid-base model, simply because of the size of the molecule. Potentially available spectroscopic information about the interaction of the molecule with the surface (e.g. outer-sphere and inner-sphere, orientation) might further support certain hypotheses. In other words, charges of functional groups of the adsorbed molecule would go beyond the

distance given by $x_{d,uc}$ in Figure 5b. The mean plane obtained for the ζ -potential would shift further towards the solution side of the interface, which would actually lead to a significant effect on the ζ -potential at high loadings. Also the orientation of adsorbed molecules might be affected: outer-sphere complexes, which might be "flat" at the interface at low loadings, might be forced to change their orientation at higher loadings. For high loadings of benzenecarboxylates on goethite it turned out that experimental ζ -potentials could not be described by conventional models [60] (c.f. Section 4).

This section has given some idea about the number of models circulating in the literature and indicated that further model variations would be possible and plausible. With a closer look at the existing models, it is even possible (but sometimes difficult) to discriminate slight variations, which are then given independent names (e.g. extended TLM). The extensive terminology emerging from this appears exaggerated given that the modifications are really of minor nature. Associated with all the existing models are the respective adjustable parameters, which will be discussed in the following section.

3.3 Parameter estimation

Unfortunately, at present it is impossible to have estimates for model parameters for all the surface complexation models and all systems. Therefore, there is a continuous development with more and more parameters becoming available. Different models are in use, and the model parameters are model dependent, so that much of the experimental data available will need to be re-modelled. This modelling always involves determination of parameters. The best way to do this is to rely on adequate independent information. Nevertheless it is necessary to numerically fit some parameters to the experimental data at present. In the following the (adjustable) parameters are introduced and discussed. In a subsequent section the importance of experimental error estimates is discussed, without which the numerical fitting results are meaningless.

3.3.1 Adjustable parameters

Adjustable parameters cannot be independently determined. The decision which parameter is known and which must be adjusted can result in controversial debates concerning the experimental or theoretical assumptions invoked to define the parameters. The parameters and their respective functionalities will be first described: some parameters are model independent and linked to measurable particle or suspension properties and some are associated with the respective model.

3.3.1.1 Physical particle and suspension properties

- Specific surface area:
 - Required to estimate surface site concentrations (e.g. from specific surface site densities). If speciation calculations are carried out on the basis of surface specific units, the experimental data pertaining to the surface must be transformed from molar concentrations. The CCM allows the complete treatment on a mass specific basis and specific surface area only has to be involved, if surface specific site densities are to be used.
 - Specific surface area may be estimated from gas adsorption; for in situ methods other probe molecules are used (e.g. EGME method [83]). Also, microscopic methods can be used to evaluate the size of particles. Particle size distributions, which can e.g. be obtained with set-ups for micro-electrophoresis or with acoustosizers, allow to calculate mean specific surface area for either known or assumed particle geometries.
- Suspension density
 - The amount of particles (the mass of solid) present in suspension is required to estimate surface site concentrations. The latter is an important input to computer programs such as FITEQL.
 - For powders, this parameter is obtained by weighing the solid before contact with the liquid. It must be assured that all weighed powder actually is transferred into the reaction vessel. This might be operationally difficult, if the powder is added during a titration.
 - The solid content of a stock suspension is estimated from its dried mass. It must be assured that the samples are representative and do not change the solid stock suspension. Also the sample must not be dried at temperatures where phase transformations of the solid (e.g. loss of water from the structure) are possible. Finally, contributions from the background electrolyte and, if relevant, other chemicals have to be taken into account.
 - An alternative would consist of measuring the proton adsorption isotherm to yield the amount of solid from a master-curve. Such a procedure would assure that the sample corresponds to samples used in previous experiments. Problems with stock suspension may arise, when the properties of the particles change with time (actual ageing processes) or when contaminations are possible (e.g. silica from glass containers).

- Particle morphology:
 - From truly mechanistic modelling studies, it has become obvious that information about the dominating crystal planes is required. Such studies are restricted to well defined particles.
 - Powders or amorphous sorbents are difficult to describe in the required detail from the point of view of structure. However, analysis of the particle topography (e.g. surface roughness) may help to justify values for capacitance values and therefore such investigations should be part of the particle characterisation for any sorbent.

These particle properties can in principle be determined with some confidence and there is broad agreement. For the modelling parameters discussed in the subsequent section, similar agreement would be highly desirable. Unfortunately, the modelling parameters are obtained in very different ways, ranging from graphical procedures and numerical optimisation to approximate estimations.

3.3.1.2 Modelling (adjustable) parameters

- Capacitance values: All models except purely diffuse layer models involve capacitance values; these can be interpreted with respect to distances between respective surface planes (or for the thickness of a layer):

$$C_L = \epsilon_L \epsilon_0 / d_L \quad (17)$$

where C_L is the capacitance of layer L , ϵ_L is the mean dielectric constant of the medium in this layer, ϵ_0 is the permittivity of free space, and d_L is the thickness of the layer. Usually, ϵ_L is not known, but it may be assumed to vary between dielectric saturation (at surfaces with strong water structuring, ϵ_{sat} is about 6) and pure water (78.5⁸).

Work by Bourikas *et al.* [61] on various polymorphs of TiO_2 provides an example for the estimation of capacitance values with a Stern model. Since symmetrical electrolyte binding is not assumed, at sufficiently high values of ionic strength shifts of points of zero charge are expected. For the different samples two distinct capacitance values are obtained: 0.9 F/m^2 for particles with a "smooth" surface and 1.7 F/m^2 for other particles for which a certain surface roughness is assumed. Such a pragmatic approach allows to use electrolyte independent capacitances, which has major practical advantages for mixed electrolyte solutions. Furthermore, similar capacitance values have been

⁸ At 298.15 K; in many speciation codes, the variation of ϵ_L as a function of temperature is not handled, which is of importance for the Gouy-Chapman equation.

reported for goethite and gibbsite by the same group [47, 62] for samples with and without surface roughness. This would significantly simplify the application of models and model parameters to mixed solids and/or mixed electrolytes.

Site concentrations/densities:

Site concentrations/densities should ideally be considered particle properties. Nevertheless they are often adjusted numerically and are therefore discussed in this section. Site concentrations/densities are of fundamental importance especially from the point of view of solution chemists. A comparable parameter in solution chemistry would be ligand concentration in a metal-ligand system. A potentiometric study of ligand acid-base properties or complex formation between a ligand and a metal requires ligand concentration as the parameter of utmost importance.

In analogy to solution chemistry, experimental approaches are described in the literature to determine site densities: the most frequently encountered approach involves the saturation of the surface by protons or hydroxyls (e.g. Lövgren *et al.* [8], Marmier *et al.* [63], Hoins [64]; the data of Marmier *et al.* [63] is puzzling as the blank titrations appear to be erroneous). Some groups have assessed the measurements in the pH regions relevant to site saturation because of the expected errors in the evaluation of the experimental data since total and free proton concentration become similar and proton uptake is not an important percentage compared to the amount of protons added to the system. Site density is an important parameter and results obtained by Gunneriusson [21] indicate that the site density of goethite is higher in sodium chloride media than in sodium nitrate media of the same concentration. Furthermore, the measured site densities are much lower than the values expected from crystallographic estimations. Finally, there is little agreement on the treatment of this parameter. We therefore attempted to find answers to this question during a three year long experimental study. The results [65] indicate that an increase in ionic strength caused an increase of the saturation level and that with chloride the saturation was always higher than with nitrate for the same background electrolyte concentration. Thus site density determined by titration at most can be a "conditional" particle property. Surface charge data in 0.6 M sodium chloride medium obtained by coulometric backtitration of supernatant samples suggest no saturation but substantially higher proton uptake (by up to 60 %) compared to the continuous

titration. The obtained charging curve in 0.6 M NaCl could be predicted with the MUSIC model. These experimental results strongly favour site densities from crystallographic considerations for such well characterised sorbents as goethite. For powders with at present no possibility to obtain such estimations new experimental approaches are necessary. Also for the well defined sorbents such approaches would be highly desirable to verify assumptions about amount and reactivity of surface sites.

Another option is to numerically fit the density of one or more sites to a surface complexation model [66,67]. This approach usually results in a simultaneous fit of at least one site density and one stability constant. In one notable case [66] up to three site concentrations and associated affinity constants were co-optimized. Although not reported, the parameters are likely to be highly correlated [68]. A numerical co-optimization of site densities and stability constants should also be avoided because the fitted site densities are typically close to the maximum values of the surface charge experimentally obtained (and thus depends on the pH range studied).

Total site concentrations have also been determined by tritium exchange experiments. This approach cannot distinguish between surface sites of different coordinations. Assumptions based on crystallographic considerations are therefore preferable at present. High (crystallographic) site densities result in low correlations with stability constants.

Stability constants:

They can at present not be established experimentally. Because of the presence of several distinct sites and electrostatic effects in the measured overall surface charge curves no information about nature and reactivity of these sites can be directly obtained. Some groups (e.g. Schulthess and Sparks [69]), who unlike all other groups observed steps in the proton adsorption isotherm, interpreted these to be indicative of individual sites with individual reactivities. Schwartz and co-workers [70] attempted to obtain the pK_a values of oxides by spline analysis of the charging curve. They made the major assumption that electrostatics could be neglected, which is necessary in the spline analysis; a proton consumption function free of electrostatic effects must be available; derivatives of the spline fitting results were compared to predicted proton affinity constants.

The modern multi-site approach is relatively rarely

applied whereas "generic" surface sites in one-site models are the rule, mostly in combination with a 2-pK formalism. In this context a 1-pK model need not be discussed, since the stability constant corresponds to the measurable point of zero charge.

In the 1-pK approach observed changes in the point of zero charge with ionic medium must be accounted for. This can only be done by applying ionic strength dependent points of zero charge (CCM, DLM) or by applying non-symmetrical electrolyte binding (BSM, TLM). For 2-pK models similar adjustments are necessary. For a CCM type approach this is not really crucial, because these models apply, if used consequently, to only one value of ionic strength (in terms of composition and concentration). For the DLM type approaches it is apparent, that one comprehensive parameter set can not explain experimental data including shifts in the point of zero charge, which are only due to the electrolytes present. Whenever these shifts occur at high ionic strength, one might argue that the conventional DLM (Gouy-Chapman equation) would not be appropriate.

In the 2-pK formalism determination of proton affinity constants from experimental data has been based on two different approaches: graphical procedures or numerically. Graphical procedures involve various kinds of approximations, such as knowledge of the site density parameter for the calculation of reaction quotients as a function of the charge of the oxide. Extrapolation of these to zero surface charge yields the intrinsic reaction quotient which is not supposed to be affected by electrostatics. Unfortunately, close to the point of zero charge the expected straight lines are often not obtained and a significant curvature occurs. Whenever points of zero surface charge and zero surface potential are not coinciding (i.e. when electrolyte binding can affect the point of zero charge), the extrapolated value corresponds to zero surface charge but surface potential is not zero and the exponential (i.e. electrostatic) term is different from unity. Consequently, graphical procedures must be corroborated by determination of the true point of zero charge or the point of zero potential of the sorbent sample. Several graphical methods exist, which additionally allow estimation of capacitance values from the slope of the plots. Simple extrapolation methods can be used for the CCM and were also used with the DLM. Use with a TLM resulted in ionic strength dependent stability constants. Consequently, double extrapolation techniques were developed with extrapolations to zero surface charge and to zero ionic strength (i.e.

zero surface potential). Double extrapolation requires smooth lines to be drawn. A detailed analysis of double extrapolation techniques showed that application to synthetic data did not result in the expected parameters [71]. Graphical methods are not really an option.

Improvement over the graphical methods is possible by numerically fitting a certain model to experimental data. Codes like FITEQL [26] allow input of several kinds of experimental data to which models can be fitted without these simplifying assumptions involved in graphical methods. Additionally, constraints arising from the experimental data can be incorporated by setting up the problem in an appropriate way. Numerical fitting becomes the more difficult the more adjustable parameters are involved, because of no convergence with numerous adjustable parameters or due to high correlations among optimised parameters. Missing information on the site density parameter may be crucial in this respect (see above).

Stability constants fitted to some value of site density of a generic site may involve more problems, which are linked to the arbitrarily assumed nature of the generic site:

- use of published parameters requires self-consistent values of site densities and stability constants and capacitance values; mixing of parameters from different literature-sources may produce surface charge density versus pH curves, which may have nothing to do with the actual sorbent studied (note that the same may happen for consistent parameters (i.e. from one literature-source) because of the sample dependent acid-base properties).
- multidentate surface complexes modelled with a generic site model (because of respective molecular scale information about the structure of the surface complex) may give an inconsistent thermodynamic and mechanistic description, whenever surface groups contributing to the modelled surface complexes do not contribute to the generic surface sites; thus one has to assure that the generic sites and the mechanistic sites contributing to the surface complex are consistent.

In realistic surface complexation models (where realistic means realistically accounting for expected features) site densities are only known for well-defined sorbent samples. For ill-defined natural sorbent samples and powders this is no more than an illusion at present. As a consequence, realistic acid-

base constants for such sorbent samples are difficult to obtain. Attempts have been discussed above for goethite and are largely based on the bulk structure of goethite. Realising that two different approaches yield two very different modes of speciation is somewhat discouraging, but without such approaches truly mechanistic models cannot be parametrised at all.

- Electrolyte binding constants:

Electrolyte binding constants are typically used in the multi-layer models. But they have also been used with the constant capacitance model. This is difficult to understand, since one might as well have chosen the Stern model and gained the possibility for accurately describing ionic strength dependencies. The multi-layer models may also be used without involving electrolyte binding. In this case the counter charge due to the background electrolyte is entirely placed in the diffuse layer.

Evaluation of electrolyte binding constants has been restricted to graphical approaches and numerically fitting experimental data with the same problems as discussed above. Furthermore, attempts have been made to measure electrolyte adsorption, which involves the measurements of very little amount adsorbed compared to relatively high solution concentrations. Such experimental results may therefore be associated with relatively large experimental errors. Even if reliable results were obtained, one may wonder what was actually measured. In the model framework it might be the amount of ions fixed in the respective plane of adsorption plus (part of) the diffuse layer contributions.

Results of X-ray standing waves measurements may resolve the distribution of ions in the diffuse layer. Since similar information can be inferred from surface complexation models such data would in future be another option to test these models. It might be helpful to further include electrokinetic data obtained at high ionic strength. Shifts of isoelectric points give a strong indication on electrolyte ion adsorption. Similar hints can be obtained from extensive stability measurements in different electrolytes, which yields the adsorption sequence of the electrolyte ions tested. Predictions using parameters by Bourikas *et al.* [61] for the diffuse layer potential of TiO₂ in sodium nitrate can be shown to nicely compare to measurements by Kosmulski *et al.* [72], which indicate that no IEP is observed in sodium nitrate concentrations equal and above 0.9 M within the studied range of pH-values. Such results may not be considered too surprising

realizing that critical coagulation concentrations can be found at many pH values by just increasing the salt concentration sufficiently.

- Surface species and surface complex stability constants: The stoichiometry of surface species can be seen as adjustable. In mechanistic studies, which allow to make interpretations on binding and protonation states of surface complexes, it is possible to fix the stoichiometry and the charge distribution. Whether surface species are plausible can be further checked by application of the bond-valence principle, which can be coupled with spectroscopic information [73]. The latter can also help to estimate reasonable values for the charge distribution factors in charge distribution models. All this certainly allows a restriction in the many options which would otherwise be available. On ill-defined substrates this is not straightforward, because one needs to make sure that generic sites correspond to actual sites. Significant simplifications are possible in case only one surface species is present [58], but this is most probably rather the exception than the rule. Surface species stoichiometry and the associated stability constants are to some extent interrelated. It might be interesting to optimise surface species stoichiometry numerically, but high correlations between the stoichiometric factors and the stability constants are probable. Alternatively, direct coupling of macroscopic data and spectral information might reduce the degree of freedom.

3.3.2 Experimental data and error estimates

A numerical estimation of surface complexation parameters requires good experimental data and reasonable estimations of the experimental errors. Modeling parameters estimated without experimental errors tend to be obsolete as their confidence intervals cannot be reasonably estimated. It is thus essential that a computer code allows input of individual experimental error estimates. In this context surface complexation modelling has no sound foundations because error estimations are hardly ever communicated, a problem that is even more serious when parameters are evaluated on only one set of data at one total reactant/sorbent ratio. In this context the range of data should be as wide as possible. Strictly speaking a model only holds for the conditions for which it was derived. Extrapolations beyond these are not necessarily safe. Therefore, a model (and of course the data set itself) has a higher quality if the applicability is wide.

Error estimates as used with the wide-spread code FITEQL (vers. 1-3) can be shown to be incapable of correctly

imitating actual error estimates (Figure 6); version 4 of FITEQL has included enhanced error handling, which was previously implemented in a modified version of FITEQL2 [74].

It appears necessary to include such fundamental issues in the study of surface complexation. Again the range of experimental conditions may be discussed. For example for many surface spectroscopic studies the conditions for which data may be obtained are currently restricted. Many methods are used with very high metal or ligand concentrations, which may result in different mechanisms compared to the macroscopic data. Other methods require very low concentrations, which results in other problems. In all these cases it becomes very important to have an estimate about the possible errors involved (i.e. how to weight the individual data and data sources). Errors such as shown in Figure 6 can give some idea, but it is necessary to realise that the respective setups may influence the errors as much as specific aspects of solution preparation etc. Good experimentation always involves an estimation of experimental errors, which should be clearly stated.

3.3.3 Goodness of fit criteria

In this section we shall make again reference to FITEQL [26] as it is a widely used code with a robust algorithm to solve complex sets of non-linear equations. The objective function to be minimised by FITEQL is

$$V_y = (W)SOS/DF \quad (18)$$

where (W)SOS stands for the (Weighted) Sum Of Squares and is defined as

$$WSOS = \sum_{n=1, np} (Y_n^2 / s_{Yn}^2) \quad (19)$$

where $Y_n = (C_{exp} - C_{mod})_n$ is the difference between experimental and modelled concentration at data point n of a total of n_p data points, and s_{Yn}^2 is the error estimate for the component for which C data are available. DF stands for degree of freedom and is defined as

$$DF = n_p n_{II} - n_u \quad (20)$$

The parameter n_{II} is the number of components for which a simultaneous material balance and free concentration constraint is available and n_u is the number of optimised components.

WSOS/DF = 1 would indicate that the differences between model and experiment statistically correspond to the experimental error estimates. No model would be expected better than that. Therefore, discussion of this goodness of fit criterion in modelling exercises with error estimates below

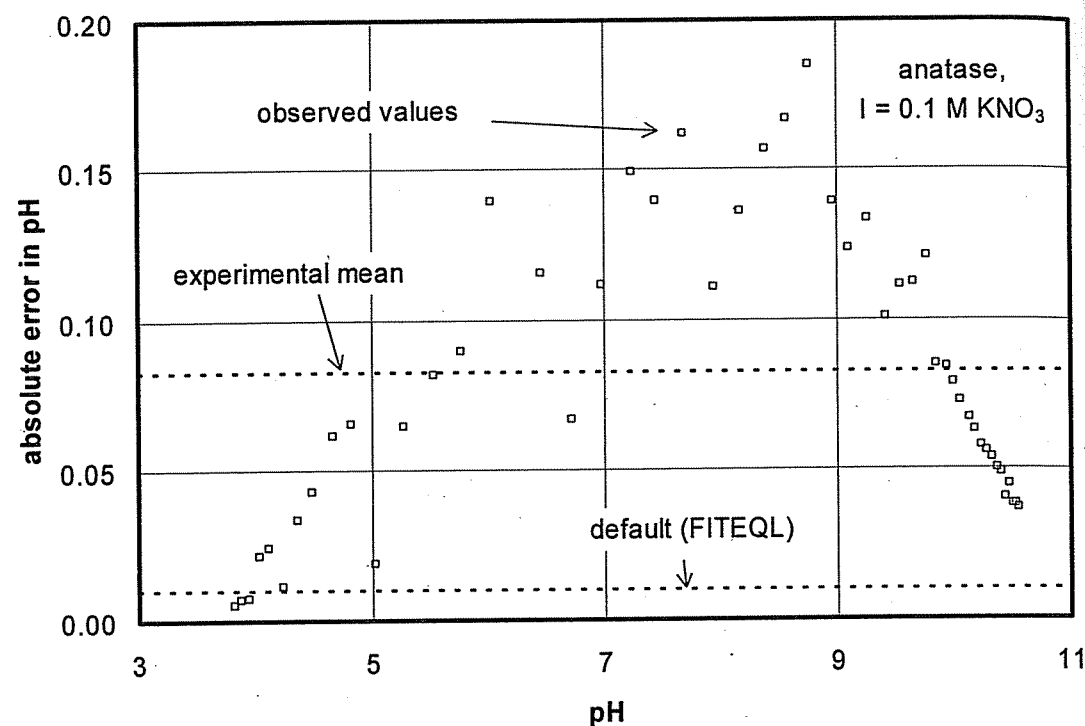


Figure 6

Comparison of actual and calculated FITEQL error estimates (modified from Lützenkirchen [74]) for anatase (TiO_2).

unity overinterpret the experimental data. The inverse of the squared experimental error estimates are also called weighting factors. They accomplish a weighting of the experimental data, i.e. if the error of data point n is estimated larger than that of data point $n+1$, minimisation of Y for n will result in a smaller contribution to the minimisation of WSOS than the same minimisation of Y for $n+1$. Thus the error estimates decide on which part of the experimental data the parameter estimation will be concentrated. With wrong error estimates the important data may be the wrong data. Thus weighting makes sense only with realistic error estimates.

Alternatively if no idea about the error estimates is available the weighting factors can be set to unity. This leads to strong weighting of those data points with large Y , which is typically the case for data with large C_{exp} (at least initially). So this is a special case of data weighting and should by no

means be considered objective.

Use of the goodness of fit parameter to estimate the overall success of a model is most efficient, when actual error estimates are correctly used. Values close to unity allow then the conclusion that a reliable model has been achieved. Note that in this context additional constraints, such as known surface complex stoichiometries (from spectroscopy) should have been included in a structural model. Violation of such constraints for structural models devalidates acceptable goodness of fit factors.

Use of goodness of fit parameters for comparative purposes is easier. As long as the error estimates are the same for the input files for different models (electrostatic models, surface complex stoichiometry), direct comparison of the goodness of fit allows to say whether one model is better than another. However, no absolute conclusion about the quality of the

model should be drawn with fictitious error estimates. This statements applies to the constraint $0.1 < V_Y < 20$ in the FITEQL manuals which is generally misleading.

3.4 Limits

Limits exist with respect to the capabilities of the modelling tools and to the models themselves. Surface complexation models can be very sophisticated tools that allow to close the gap between macroscopic and molecular observations. However, this is mostly limited to well-defined sorbents. In principle if the sorbent properties cannot be characterised, the modeller and the spectroscopist do not know with what kinds of surface sites they are dealing. The model then requires assumptions about the reactivity and the density of at least one (generic) surface site. Only if this (generic) surface site can be expected to be equivalent to an actual surface site there is actual mechanistic consistency between model and data. One should however not draw the conclusion that a model that describes both macroscopic data and observed features (in particular multidentate bonding) adequately describes the mechanism. There might still be a difference between generic sites and the actual sites involved in the multidentate surface complex.

The example goethite can further serve as a warning in that even for the most recent, very sophisticated estimations of reactivity, discrepancies exist with respect to the surface speciation as obtained from different methods. Such discrepancies must be explained in the future. Previously it was possible to argue that the molecular modelling approach led to wrong results for silica and thus should not be trusted. From more recent results it can be argued that the features that led to the silica results do not apply to iron (hydr)oxides [45]. Still the two protonation steps within a narrow range of the doubly coordinated sites obtained in the calculations might favour the MUSIC model. However, surface speciation of bare goethite surfaces by spectroscopic methods should reveal the true speciation mode before this issue can be settled.

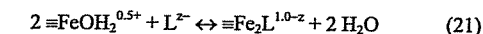
The modelling tools are restricted in the use of different data sources. Thus it is difficult to introduce different kinds of data in one input data file with the standard FITEQL programs. To improve this, modifications have been elaborated that allow the input of various types of data or even data on one system with different sorbent preparations. Direct coupling of speciation in terms of a macroscopic model and microscopic data by using adsorption data and spectroscopic data simultaneously might be a good option.

At this point (i.e. before passing to the application) some warnings about the successful use of sophisticated mechanistic models is appropriate. These latter suggest that

many of the model parameters have been predicted and few adjusted. On the other hand it was often shown how successful different surface complexation models may be and examples exist which show that sophisticated model concepts can lead to successful predictions based on erroneous assumptions. The MUSIC concept has been evaluated in this chapter as an ideal concept for the mechanistic description of adsorption phenomena on well-defined solids. It is a fact that the previous version of the model was based on the wrong goethite morphology and still predicted correct surface charge curves for this mineral. With the correct morphology and the predicted affinities for the different surface groups a point of zero charge of about 5 is obtained, which is outside the reasonable range. The next version of the MUSIC model required refinements, which made this model even more complex and the assumptions necessarily involved can not be independently verified. It is nevertheless very valuable to have some parameters at hand to minimise those that need to be determined numerically.

4. EXAMPLES FOR COMBINED EXPERIMENTAL/MODELLING STUDIES

The advent of surface-sensitive spectroscopic methods has provided a means of determining the coordination modes of surface complexes at solid/solution interfaces. At the same time it has revealed important discrepancies with proposed species that were previously justified by a good fit to macroscopic adsorption data. A particularly insightful modelling approach that has emerged in the past decade considers the contribution of all kinds of surface sites on dominant crystal planes of particles, namely the MUSIC model [56,75,76]. Provided the solid particles of interest are well crystallised and display only a few dominant crystal faces the MUSIC model is a framework that allows the prediction of surface complexes at the molecular-scale. In this approach the coordination modes of surface complexes are constrained to the limited possibilities offered by the specific disposition of surface sites. Consider the {110} plane of goethite, for example which exhibits singly-, doubly- and triply-coordinated oxygens (Figure 1, Figure 7b). If spectroscopic data provide evidence for a bidentate inner-sphere surface complex and one assumes that singly-coordinated oxygens are the most likely involved in this complex, then the stoichiometric coefficients of the mass action equation describing this reaction are constrained to only two of these sites and one adsorbate, L^{z-} .



A maximum adsorption density is then controlled by the site density of only the singly-coordinated site and the electrostatic contributions to the Gibbs free energy of

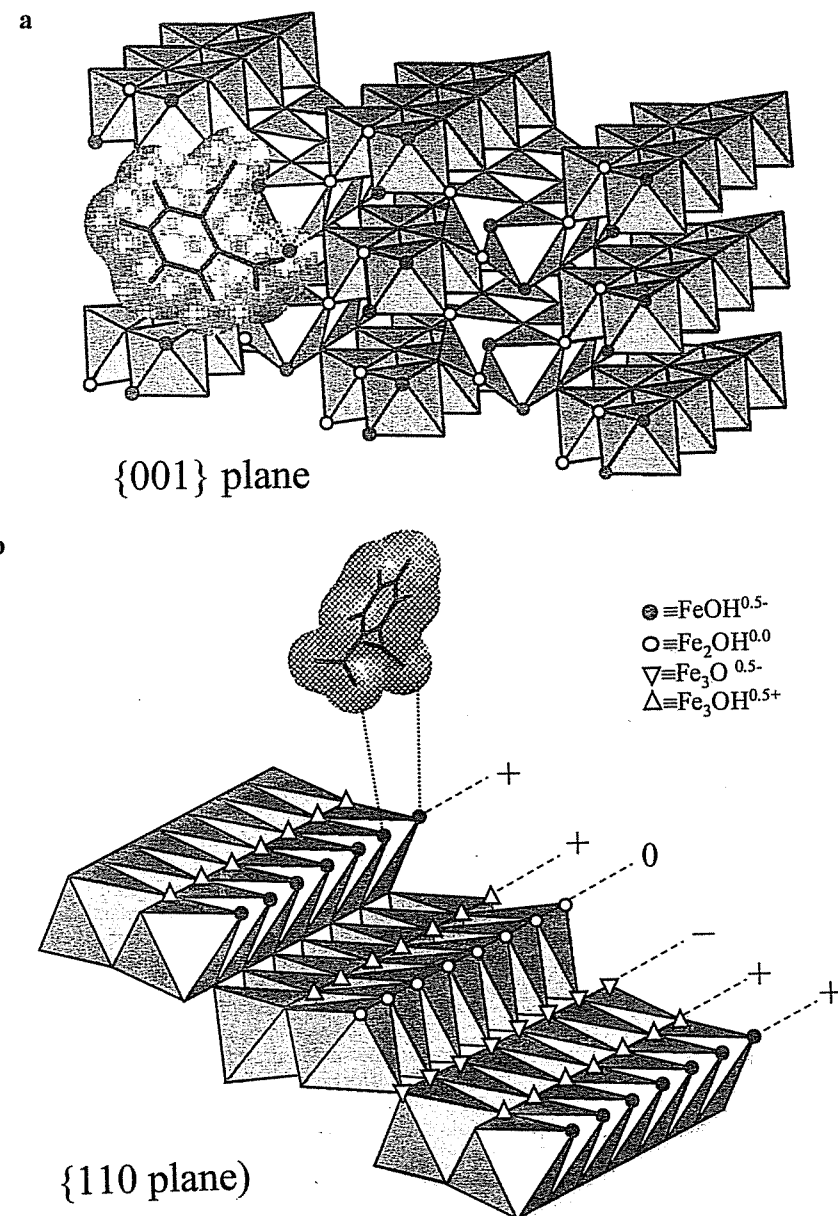
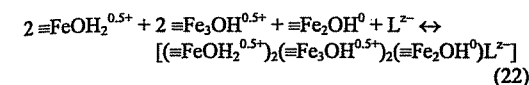


Figure 7

Structure of the {001} (a) and {110} (b) planes of goethite displaying singly-, doubly- and triply-coordinated surface oxygens. (a) shows an inner-sphere phthalate (1,2-benzenedicarboxylate) surface complex with two adjacent singly-coordinated sites from the same Fe(III) surface octahedron. (b) shows an outer-sphere phthalate complex with two adjacent singly-coordinated sites of different Fe(III) surface octahedra. As mentioned in the text this complex is rather generic. Phthalate molecules were generated with the computer program PC SpartanPro v. 1.0.1. with HF/3-21G^{*}. The shaded volume is defined by the 0.002 isodensity surface.

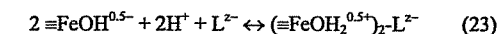
adsorption. Conversely, if an outer-sphere complex is said to be attracted to a patch of sites of favourable charge (and/or possibilities for hydrogen-bonding) then all types of sites may be invoked:



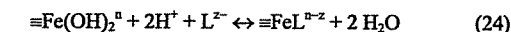
While the geometry of surface complexes is mostly postulated by virtue of the constraints of the MUSIC model, some spectroscopic methods (e.g. EXAFS) provide fairly rigorous constraints and an increasing number of molecular modelling studies give insight into plausible possibilities. In spite of remaining uncertainties with respect to concepts as fundamental as the relative and absolute proton affinity constants of surface sites and the question of electrolyte adsorption [42,43], the MUSIC model has been successful at providing a macroscopic and microscopic description of surface complexes on metal (hydr)oxides. This section provides some applications of the MUSIC model using the example of the surface complexes of three benzenecarboxylates.

A number of infrared spectroscopic studies have shown that many carboxylates display pH-dependent coordination modes on metal (hydr)oxides [77,78,79,80]. Carboxylates mostly adsorb at pH values below the pzc (Figure 8), where the alkaline region part is usually dominated by

outer-sphere complexes and the acidic region characteristic of coexisting outer- and inner-sphere complexes. The slopes of the adsorption edges of benzenecarboxylates of different charge are also smaller for ligands of larger charge [81]. Whilst the onset of the edges at high pH (and thus of the outer-sphere complexes) vary with the charge on the benzenecarboxylate, the onset of the inner-sphere complex at circumneutral pH is relatively constant, cf. Figure 9). Thus, while electrostatic conditions are likely to control the charge-dependent slopes of the adsorption edges, more intrinsic chemical reactions control the formation of inner-sphere complexes, as expected. The outer-sphere complex was modelled as a bidentate binuclear complex with only singly-coordinated sites of the {110} plane:



where the charges of L^{z-} were set in the 1-plane of the TPM. This species is certainly generic and there are more realistic schemes that better represent outer-sphere complexation in a mechanistic fashion. Consider, for example, the zones of positive and neutral sites shown in Figure 7b. The constant onset of the inner-sphere complex can be ascribed to the pH region where two adjacent sites on the edge of one Fe(III) surface octahedron are protonated, such that:



where L^{z-} is a ligand of charge $z-$. Ab Initio infra red frequency calculations furthermore support the concept that

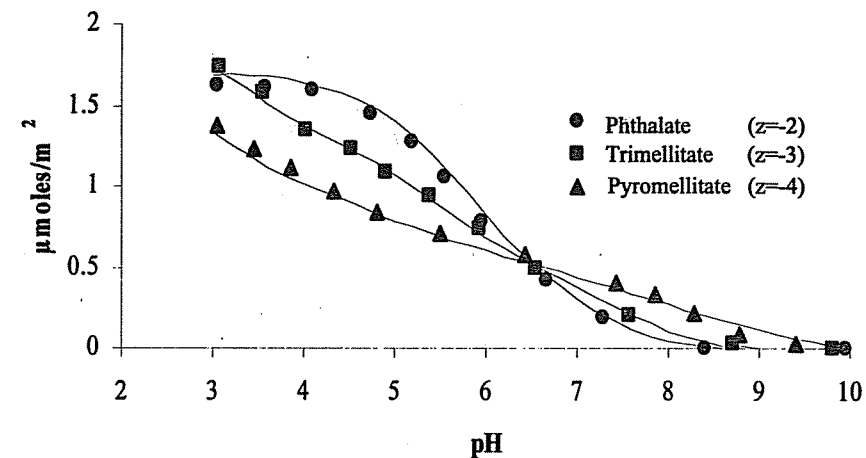


Figure 8

Surface concentration ($\mu\text{moles}/\text{m}^2$) of phthalate (1,2-benzenedicarboxylate), trimellitate (1,2,4-benzenetricarboxylate), and pyromellitate (1,2,4,5-benzenetetracarboxylate) on goethite in 0.1 M NaNO_3 at 298.2 K. Total ligand concentration = $2.22 \mu\text{moles}/\text{m}^2$.

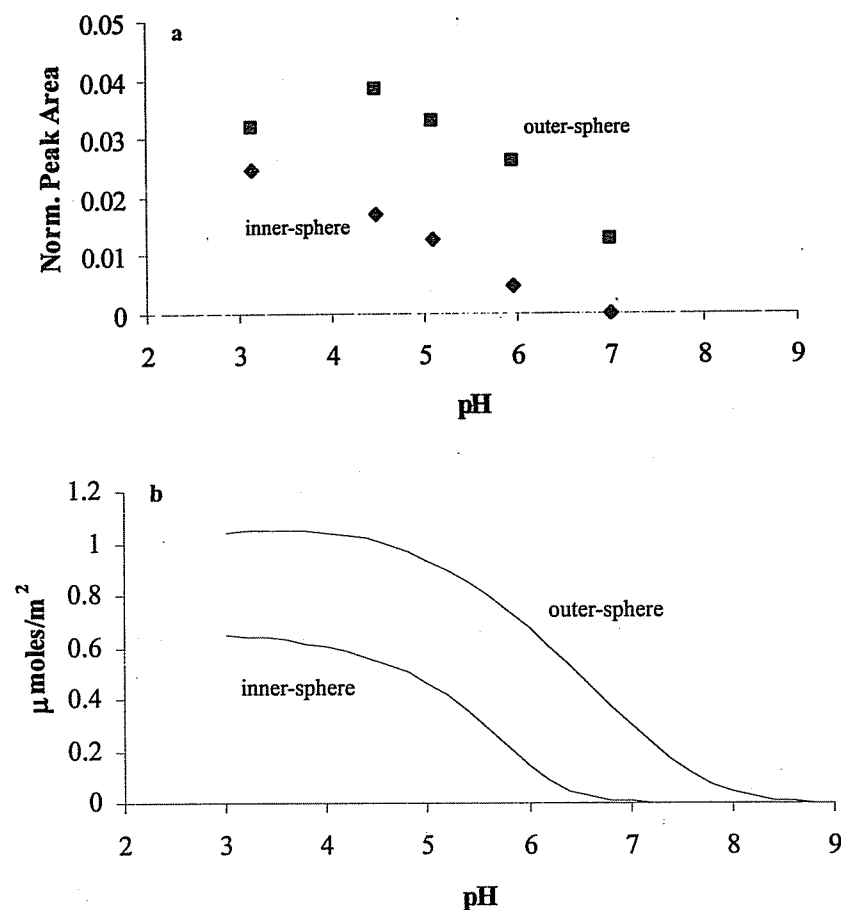


Figure 9

(a) Normalised infrared peak area of symmetric stretching vibration band corresponding to the inner- and outer-sphere surface complexes of phthalate. (b) Surface speciation calculated from models of [79]. Same experimental conditions as in Fig. 2.

the inner-sphere complexes are mononuclear chelates, and not binuclear bidentate complexes [77]. In the MUSIC framework, this species can only form at terminations of acicular goethite particles (e.g. the {021} or {001} planes); the mass action equations are then written with the appropriate surface components.

A semi-quantitative treatment of the infrared spectra was used to outline the pH-dependency of the inner- and outer-sphere complexes (Figure 9a). These trends were reproduced

with reactions 23 and 24 by co-optimising the formation constants and C_1 and C_2 , the capacitances of the inner and outer layers, respectively. The qualitative agreement between the infrared data and the surface speciation of phthalate surface complexes can be appreciated by comparing Figure 9a with Figure 9b. The success of this approach is mostly ascribed to the distinction made between Fe(III) octahedral edges that allow inner-sphere complexes and other sites allowing outer-sphere complexes. Previous models using one generic site (of similar density to the

singly-coordinated sites used in [79]) did not yield a satisfactory surface distribution of inner- and outer-sphere complexes, giving justifications to the models of [79].

Surface complexation models must also predict the total proton balance in order to describe the buffering capacity of solid suspensions in the presence of adsorbates. For example, Figure 10 shows the predicted proton budget of a phthalate-bearing goethite suspension in the presence and absence of phthalate surface complexes. The increased protonation state of the system in the presence of phthalate gives evidence that protons co-adsorb with phthalate, giving rise to the following scenarios:

- phthalate adsorption promotes the formation of even more $\equiv\text{FeOH}_2^{0.5+}$ sites, by virtue of Le Châtelier's principle and of favourable electrostatic conditions;
- phthalate surface complexes are protonated.

Scenarios (i) and (ii) could be distinguished with infrared spectroscopy. In [79,80] all benzenecarboxylate surface complexes were found to resist protonation at pH ranges where protonation of solution species is dominant. Phthalate, for instance, resists protonation altogether, supporting Scenario (i). Trimellitate and pyromellitate, on the other hand, can protonate but exhibit larger acidities than their

solution counterparts. The models also predict the protonation of the outer-sphere complex on the grounds that outer-sphere complexes should be more basic than inner-sphere complexes.

The success of these models rely heavily on the optimal values of C_1 and C_2 which are in turn related to the total (Stern) capacitance, C_{Tot} with Eq. 16, where values of C_2 (C_1) were larger (smaller) for ligands of larger charge. The effect of these capacitance values on the apparent formation constant, K_{app} can be understood with:

$$\ln K_{\text{app}} = \ln K_{\text{int}} - \frac{\Delta z_0 F \Psi_0}{RT} - \frac{\Delta z_1 F \Psi_1}{RT} \quad (25)$$

where K_{int} is the intrinsic formation constant for reaction 24. For an outer-sphere complex with $\Delta z_0 = 2$ and $\Delta z_1 = -2$, larger (smaller) values of C_2 (C_1) contribute in decreasing both right hand side terms of this equation, thereby decreasing the value of K_{app} . In other words the slope of the adsorption edge is smaller for larger (smaller) values of C_2 (C_1). Therefore, pyromellitate ($z = -4$) requires a larger (smaller) value of C_2 (C_1) than trimellitate ($z = -3$) and phthalate ($z = -2$), and trimellitate requires a larger (smaller) value of C_2 (C_1) than phthalate (Figure 10). Larger values of

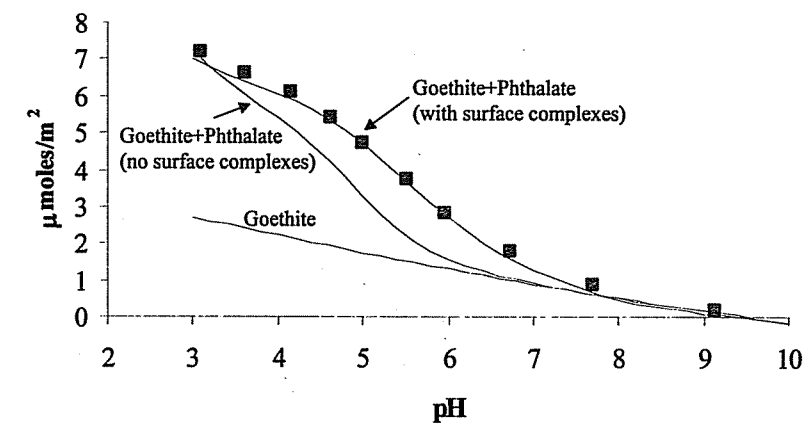


Figure 10

Bound proton concentration in a goethite suspension, expressed in terms of $\mu\text{moles/m}^2$ (i.e. encompassing adsorbed and solution concentrations of protons) calculated as $(H_{\text{Tot}} - [\text{H}^+] + [\text{OH}^-])/s$, where s is the total surface area (m^2/L). Model predictions [79] are for the following three case scenarios: (1) goethite in the absence of phthalate, (2) goethite in the presence of phthalate, neglecting phthalate surface complexes, and (3) goethite in the presence of phthalate, accounting for phthalate surface complexes. Phthalate concentration of $3.36 \mu\text{moles/m}^2$; otherwise same experimental conditions as in Figure 8.

Δz_1 also decrease K_{app} but not enough to account for the different slopes of the adsorption edges. It hence becomes appealing to ponder on the significance of the trends of C_1 and C_2 as a function of the charges of benzenecarboxylates. In electrochemical parlance, the capacitance of a charge-free layer is related to its thickness, d_L (with Eq. 17), i.e. as the capacitance increases, the thickness of the charge-free layer decreases. Let us consider only the outer-sphere complexes of phthalate, trimellitate and pyromellitate. According to that equation, the thickness of the 2-plane would decrease in the order $d_{L,phthalate} > d_{L,trimellitate} > d_{L,pyromellitate}$. Unfortunately, the framework of the calculations does not allow an unambiguous inference to be made on d_L because of the relationship between C_1 and C_2 , i.e. Eq. 16. By virtue of equation 17, if the thickness of the second layer varies then the thickness of the inner layer also has to vary, an unlikely scenario considering the interpretation of the infrared spectra. It was proposed that the broadening of the anti-symmetric C-O stretching vibrations of the benzenecarboxylates suggests that outer-sphere complexes are directly hydrogen-bonded to the surface sites $\equiv FeOH_2^{0.5+}$, with no intermediate chemisorbed water molecules [79]. The thickness of the inner layer would therefore be expected to be the same for any benzenecarboxylate. Moreover, the value of C_2 results from calculations where all charges of the outer-sphere complexes are located in the 1-plane while it is

likely that charges are distributed between different planes of adsorption. Therefore, C_2 is not a measure of the thickness of the phenyl ring but can only be of electrostatic relevance and simply remains an adjustable parameter. A different treatment of the electric double layer is required to attempt a reconciliation between the capacitance of the SCM with one of electrochemical/physico-chemical relevance, work that is actually under progress. Albeit this shortcoming, the interpretation of the infrared spectra, in combination with ζ potential data (Figure 11), give some support to the trends just mentioned. First, we note that all benzenecarboxylate-bearing goethite suspensions have net positive surface charges (i.e. the sum of charge of adsorbed protons and benzenecarboxylates is positive) and that all surface complexation models predict positive surface potentials (Figure 12a). However, while phthalate only yields positive ζ -potentials, similar surface loadings of trimellitate and of pyromellitate generate strongly negative values. It can then be deduced that trimellitate and pyromellitate exhibit unbound carboxyl groups on the solution-side of the goethite/water interface, supporting the idea that the phenyl rings are more or less perpendicular to the surface. Next, we recall that the infrared data suggests a close interaction between one set of ortho-positioned carboxyls and positively-charged surface sites in the outer-sphere complex, implying that phenyl rings are somewhat

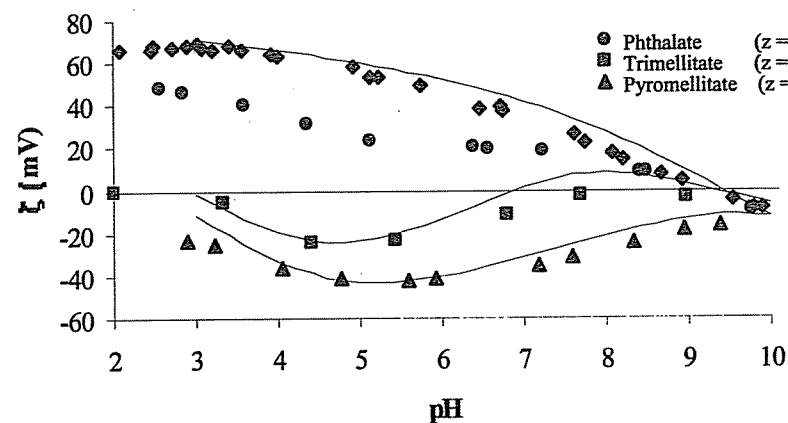


Figure 11

Electroacoustic ζ -potential data for goethite suspensions in the presence and absence of benzenecarboxylates (about $2 \mu\text{moles/m}^2$) in 0.1 M NaNO_3 at 298.2 K. Model predictions in the absence of benzenecarboxylates are made with assumption $\Psi_0 = \zeta$ with the BSM, and those for trimellitate and pyromellitate with $\Psi_3 = \zeta$ with the FPM (Figure 12b), whereby the charges of unbound carboxyl groups are set in the 3-plane. Phthalate could not be modeled accurately with this method as its charges are confined to the 0- and 1-planes.

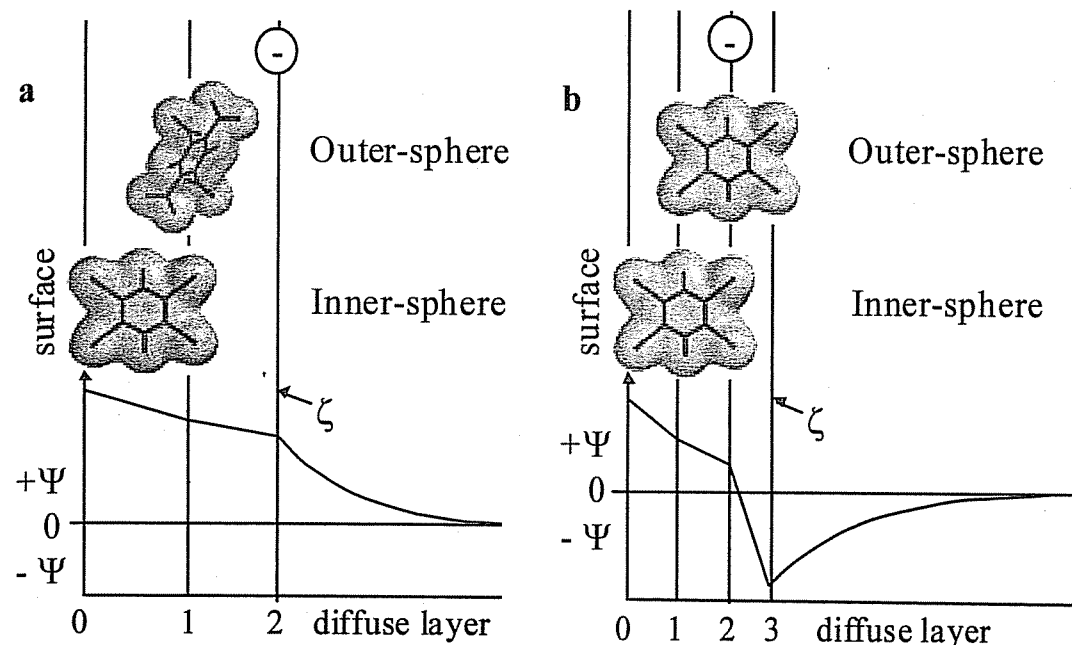


Figure 12

Surface electric potential profiles for benzenecarboxylate-bearing goethite suspensions according to (a) the TPM and (b) the FPM. Note that the 3-plane in the FPM is responsible for reversing the surface potential of the shear plane, while the net surface charge is positive. Pyromellitate molecules were generated with the computer program PC SpartanPro v. 1.0.1. with HF/3-21G^{*}. The shaded volume is defined by the 0.002 isodensity surface.

perpendicular to the surface. From here, the trends in d_L can be postulated in terms of the tilt of the phenyl ring resulting from the interaction of unbound carboxyl groups and neighbouring positive sites; the degree of tilting would understandably be stronger for pyromellitate than for trimellitate. Secondary interactions involving unbound carboxyls is also supported by the significantly larger K_{app} of the outer-sphere complex of pyromellitate.

The negative ζ -potentials of trimellitate and of pyromellitate thus revealed a flaw in the models proposed in [79, 81]. This discrepancy can be alleviated by modifying the structure of the electric double layer model. A simple modification is to add a compact layer to the TPM, yielding the Four Plane Model (FPM) shown in Figure 12b [60]. The same modelling parameters of [81] can be used with the only difference that the unbound carboxyl groups of trimellitate and of pyromellitate are set in the 3-plane and the

capacitance is optimised to yield a good fit to the ζ -potential data. This approach is successful at predicting ζ -potential data at a wide range of strong surface loadings. Improvements to this approach, in the lines of the ideas of Smit [59], are currently under investigation.

In conclusion, while there are obviously uncertainties that remain unresolved the MUSIC model combined with the TPM or the FPM provides an interesting framework that allows surface complexation models to be consistent with a wide range of experimental methods used in surface chemistry.

5. CONCLUSIONS

There is an urgent need for a more detailed understanding of the chemical processes taking place at the particle-water

interface. Sensitive surface spectroscopic techniques are currently being developed that allow characterization of chemical processes at hydrous particle surfaces on a molecular level. This information is of utmost importance and has to be considered in the interpretation of the kinetics and thermodynamics of surface complexation reactions. A combination of macroscopic data and molecular level characterization, under identical experimental conditions, should form the basic data sets in surface complexation modeling. It should be stressed that in applying the modern surface techniques the traditional macroscopic measurements must not be forgotten. In both respects, the importance of collecting high quality data and specifying the experimental conditions under which they have been collected must be kept in mind. It is suggested that the following appropriate information should be given:

- i) The purity of reagents, solvents and the procedures for purification.
- ii) The temperature, composition of ionic medium and ionic strength(s).
- iii) Solid, metal and ligand concentrations as well as their different ratios.
- iv) The origin of the solid and/or the way it has been synthesized.
- v) A characterization of the solid with respect to morphology and surface area. For crystalline particles a presentation of predominating crystallographic cleavage planes is most valuable.
- iv) Instrumentation and an explicit description of the method(s) of calibrations; when a pH-electrode is used it should be stated whether an activity or concentration scale with respect to H^+ is used.
- vi) Reaction time of the different datum points in the pH/pM titrations to reach stable potentials. If no stable potentials are obtained, the drift criteria should be stated.
- vii) Results from reproducibility and reversibility tests.
- viii) Unambiguous definition of the model parameters given.
- ix) An unbiased search for the speciation scheme combining macroscopic data (e.g. potentiometry, sorption studies, electrokinetic measurements) with molecular level information (e.g. FTIR/FTRaman, XAS, XPS).
- x) A visual presentation of the fit of the model to the experimental data.

Because of possible sorbent sample inherent deviations the combination of microscopic and macroscopic measurements should be done simultaneously in the course of the study of a certain system. Only in this fashion (unnecessary) uncertainties can be avoided:

If different laboratories study one system (i.e. one group makes a spectroscopic study and another group a macroscopic studies) it must be ascertained that the spectroscopic data are actually compatible with the macroscopic data. The most obvious source of problem might be the observed difference in behavior for nominally

identical sorbents. Further problems with respect to the required compatibility may arise from different experimental procedures (equilibration times etc.). In this respect the above mentioned information must be included to allow judgement of the compatibility. Unfortunately, journals tend to limit space for the authors and the space goes at the expense of the experimental details despite the fact that the quality of the experimental data critically depends on those details.

In the modeling it is important to state its purpose. For mechanistic models comprehensive approaches are required, which are able to take into account the properties of the sorbent surface. For non-mechanistic models, the simplest model in terms of adjustable parameters is to be preferred, which allows to account for the observed features. In this respect the ultimate requirement of all models must be to be mechanistically close to reality. One of many challenges from the point of view of the surface complexation models is therefore the characterisation of powders in terms of their dominating crystal planes. A potential danger is the already published melange of simplistic thermodynamic models with atomistic constraints. From our point of view this melange only makes sense if a mechanistic model of the surface is available. With generic sites it might be possible to describe a bidentate surface complex of course, but to what kind of sites the generic sites correspond is not really clear. At best they might correspond to actually proton active sites, which are responsible for pH-dependent charge, but a bidentate surface complex might as well involve sites, which are inert for proton interactions over the pH-range of interest. The MUSIC model approach for goethite clearly indicates such possibilities. In such case, the incorporation of mechanistic information may thus result in an erroneous/inconsistent link between microscopic and macroscopic levels.

The ever evolving computational power will allow to add further approaches to the study of solid/liquid interfaces by allowing molecular modelling calculations to complement the spectroscopic and macroscopic data or identifying the most probable crystal planes of powders. Spectra of surface species and experimentally obtained bond distances may be verified. First attempts to calculate gas-phase affinity constant for the formation of surface species are also available at this point. Thus an ever reducing degree of freedom may result and surface complexation models will be constrained from many points of view. This and the increasing resolution of the spectroscopic methods will in the coming decades lead to important findings.

Acknowledgements

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Adsorption of metal ions on activated carbons in aqueous solutions

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ABSTRACT

Adsorption studies of Na(I), Cs(I), Ag(I), Tl(I), Co(II), Sr(II), Zn(II), Cd(II), Cu(II), Pb(II), Cr(III), and Cr(VI) from aqueous solutions on activated carbons are reported. Most of the activated carbons used have been obtained from agricultural by-products (almond shells, olive stones, and peach stones). These activated carbons have been characterized using different techniques in order to know their textural characteristics (surface area and pore size distribution) and chemical nature. Some selected activated carbons have been treated to introduce oxygen and nitrogen surface complexes. The influence of different parameters such as: textural characteristics of activated carbons, chemical nature of the activated carbon surface, solution pH, and the presence of electrolytes in solution, on the metallic ions adsorption has been analyzed.

1. INTRODUCTION

The use of activated carbons to remove inorganic and organic pollutants from waters is widely extended, due to the fact that these materials are unique and versatile adsorbents because of their high surface area, porous structure, high adsorption capacity, and surface chemical nature, which can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process

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[1-4]

It is argued that a large surface area and a suitable pore size distribution are necessary but not sufficient attributes of an optimised adsorbent for both inorganic and organic solutes. While the importance of carbon surface chemistry has been recognised for a long time, the exact nature of this importance and the desirable chemical surface characteristics have been quite controversial and often misunderstood [4].

The adsorption of inorganic solutes, as metallic species, is a topic of great practical interest because of water treatment and metal recovery applications. Its fundamental aspects are also important for the preparation of carbon-supported catalysts [5,6], where the catalyst precursor is typically dissolved in water prior to its loading onto the porous support.

In the case of the adsorption of inorganic compounds on activated carbons from aqueous solutions, the chemical nature of the adsorbent determined by the amount and nature of the surface complexes [7] has, in general, more influence than the surface area and porosity of the adsorbent. Furthermore, the adsorption process can depend on the presence of other dissolved substances like inorganic electrolytes or organic matter (e.g., humic substances) that are present in surface waters or deep ground water [8] as a result of the decay of vegetation. These substances can change the surface charge density of the adsorbent, block some adsorption sites, and form complexes with the trace metals [9,10]. All of these phenomena would affect the

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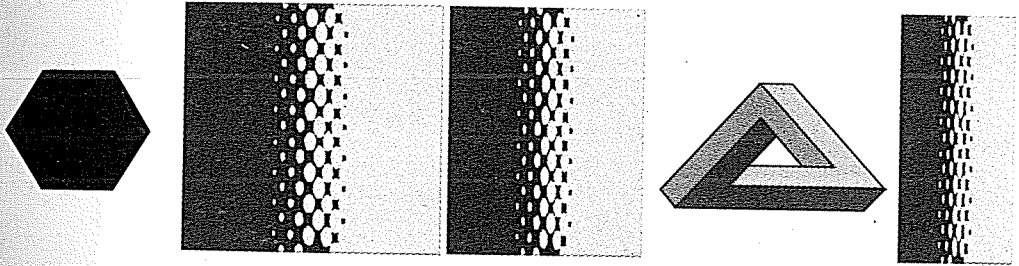
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