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.
I. INTRODUCTION

Water quality is defined by its chemical and biological composition. A detailed characterization 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 characterization 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 characterization 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 characterized 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 hydrophobic particle surfaces. This opens possibilities to model multicomponent/multilayer systems in which sorption processes are coupled to complexation/dissolution processes. Such models allow the computation 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/hydrous 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 characterized 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 monodentate or bridging behaviour should be characterized.

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 hydrophobic 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 amount 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, the sensor 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 greater 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, (E₃), the reference electrode, (E₄), and the liquid junction (E₅) 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 asymptotic 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 (E₅) 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

\[ E = E_1 - E_4 = E_{1-2} + E_{2-3} + E_{3-4} + E_{4-5} \]

where \( E_{1-2} \) is the potential caused by the diffusion of ions across this liquid junction. This problem is associated with the liquid junction potential and its reproducibility is solved by applying a cell of the so called “Wilhelmy” 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 Stille [6] or Jülicher et al. [7].

Calibration of the electrode system. Good c.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 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:

\[ E_{\text{cell}} = E_{\text{ref}} + f_{\text{H}^+} \]

where the reference electrode, \( E_{\text{ref}} = \) Ag/AgCl | 0.01M NaCl and 1.001 M NaNO₃ | 1 M NaNO₃ and 1 denotes the concentration of the background medium.

The e.m.f. of the cell (in mV) can be written (25 °C):

\[ E_{\text{cell}} = E_{\text{ref}} + f_{\text{H}^+} \]

For the liquid junction potential, \( E_{\text{5}} \) equation (3) is applicable (Jülicher et al. [7]).

\[ E_{\text{5}} = -49.71 \log[H^+] + 21.41 \log[K_{w}] \text{ mV} \]

where \( K_{w} \) is the ionic product of water.
Reprodability and reversibility. A prerequisite for a universal applicability of an equilibrium model is that the experiments be reproducible. Furthermore, free 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 oxalic acid generated hydroxide ions (Lövgen et al. [5]). Identical results should be also obtained 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 complexes of Al(III) at the surface of goethite (Lövgen et al. [5]).

However, when dealing with surface complexation, reversibility cannot be taken for granted. The description of Al(III) from goethite was found to be much slower than the adsorption reaction (Lövgen et al. [5]). 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 description of Al(III) was not complete. Full reversibility has been found to be lacking also for the complexation of Hg(II) (cf. Gmürnnerlin et al. [7]), while for Fe(III) (cf. Gmürnnerlin 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 applied.

To be able to quantify precipitation/deposition 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 proteins must be well controlled, and the release/uptake of proteins must be measurable. This allows for a better comparison of the solid phase that 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 high quality as possible. This is often a time-consuming and difficult procedure. However, there are no short-cuts in an accurate determination of equilibrium data.

2.1.3 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 (pI) of charged solids, i.e., the pH at which the particles do not move in an applied electric field (i.e. the isoelectric potential, ζ, is zero). As the pI of many metal (hydro)oxides suspended in 1:1 electrolytes coincides with the pZ, electrokinetics provide a more straightforward alternative to the potentiometric determination of the pZ (i.e. determined as the common intersection point of relative surface charge data at different ionic strengths). 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 measurement 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 pZ'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 proteins in the system can avoid this problem. Instead of actually following the pH, the total concentration of proteins in a suspension, [H+] = c[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 (pH = log [H+]; and (G) that titrant concentrations are dilute enough to ensure accurate discrete additions, it no longer becomes necessary to rely on the analysis of a hopping electric field (i.e. the zeo-potential, ζ, is zero). As the pI of many metal (hydro)oxides suspended in 1:1 electrolytes coincides with the pZ, electrokinetics provide a more straightforward alternative to the potentiometric determination of the pZ (i.e. determined as the common intersection point of relative surface charge data at different ionic strengths). 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.

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 standardising a glass electrode against a hydrogen electrode, for example, and/or ensuring that the condition [H+] = [H+] + [OH-] = 0 in a blank (i.e. 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. SPR) for measuring surface potentials. With calibration steps of the Acoustometer [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 Acoustometer are more tedious at high ionic strengths (> 0.01 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 Acoustometer is not suitable for this purpose, as the 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 the least following points:

- Incomplete separation will falsify the analytically determined amount of solute remaining.
- Effects of the separation step, which may affect the equilibrium, 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 surface charge mechanisms, which is the most direct, e.g. in the case of experiments with goethite one might determine Fe in the supernatant. Honzay 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 sucked on such particles.

Even if the study by Honzay 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 [18-20]. In these latter studies strong 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 adsorbs 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 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 solidified 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 over saturated or polyvalent compounds may form. A comparison of results obtained from the different ways of preparation would be of substantial interest. If solubility is exceeded the solution 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 Titration

Titration 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 amion 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-YC 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 scale for the reactions of proton and solute data are the same.

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) 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 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 clearly 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. The requirements 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 interested in surface charge, the simplest model would not involve an acid-base model and a simple non-electrostatic model approach, starting directly with the 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, sufficiently simple models can be found for most systems and the only requirements of such models that can be presently fulfilled in 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 qualitatively use may also be assessed).

3.1.1 Protonation mechanism

The protonation mechanism is discussed for "generic" surface sites (SOH, 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:

\[ \text{SOH}^{m-} \rightarrow \text{SOH}^{(m-1)+} \rightarrow \text{SOH}^{2+} \]

(ii) the 1-pK approach, which is characterized by the SOH\(^{\text{ads}}\) "generic" surface site, to which one deprotonation step is applied:

\[ \text{SOH}^{\text{ads}} \rightarrow \text{SOH}^{\text{ads}+} + \text{H}^+ \]

This protonation mechanism has been introduced by van Rijn and co-workers [24]. The 1-pK formalism can be interpreted as a (sometimes even mechanistically) simplified version of the 2-pK reality, which is exactly successful in the description of experimental data compared to the equivalent 2-pK model. The 1-pK model is a sufficient 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 corresponding reactions in solution. If the second deprotonation of the SOH\(^{\text{ads}}\) (i.e. the formation of the SOH\(^{2+}\) species) behaves as a comparable aqua-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
group in terms of a combination of a SOH\(^{\cdot}\) and
SOH\(^{\cdot\cdot}\) 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 pristice 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\(^{[25]}\).

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 multilayer 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.

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. FITEQ [26], MINTEQA2 [27], ECOSAT [28] or
SOLOGASWATER [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 equilibrium
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 electrometric condition.
For the CCM such an electrometric 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 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.
An understanding of the structure of the electrical double layer is also essential to account for ζ-potential measurements. Values of ζ, 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 nevertheless possible to compare at least the polarity of such values to ζ - potentials, which are experimentally determined values of ζ at the shear plane [14] of a surface. Behind this plane lies the compact layer encompassing several layers of water molecules that have adsorbed to complete the coordination environment of bare metal atoms, or as a result of favorable 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_w, is theoretically decreased to:

\[ Ψ_w = Ψ_s - \frac{q_s}{C} \]

where Ψ_s is the surface charge density and Ψ is the potential at the surface. Values of Ψ dample out to zero in the diffuse layer (6). As the shear plane is at or outside the compact layer, Ψ is therefore usually a fraction of Ψ_s.

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 debated, strong evidence supports the concept that the shear plane lies close to the head of the diffuse layer such that Ψ_s = Ψ_w = ζ [14,30]. This assumption would however no longer hold if an adsorbate, whose wide would exceed that of the compact layer, were to push the shear plane towards the diffuse layer. In this case an equation describing Ψ_s 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 (Ε = 4πη(Ε) is the electric field strength of the crystal surface in water) is dependent on the dielectric constant of 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 Smoluchowski equation can be used [32]:

\[ μ = ε_0 q_s \xi_0 \]

\[ \xi_0 = \frac{d}{\varepsilon_0} \]

where μ is a field-strength-dependent function of viscosity [33], ε is the electric constant 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. Least-squares field-strength dependent values of μ 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 ζ = 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 Smoluchowski equation ideally holds for spherical particles, which is rarely the case for metal hydroxides. There are fortunately several correction functions that can be applied to electrophoretic and electroacoustic measurements on prolates 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 pH, i.e. the tip does not coincide with the pH [39]. Surface conductance [40,41], which 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 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 involve 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 bonded to one, two or three iron atoms. Figure 3 supplements Figure 2 with the nomenclature for the different functional groups.

The simplest (deprotonation 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:

- Hennema and van Rijneveld [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 fit to the surface charge curve are equally good. However, the surface species composition of the different groups to the overall surface charge is very different:

- With the model parameters from Hennema and van Rijneveld [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 kind of triple 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 co-ordinated group and would have the same site density) is used with a proton affinity which

```
+hydroxo
\[μ-hydroxo\]
\[H3-oxo\]
\[μ3-hydroxo\]

Figure 2
Structure of the (110) crystal plane of goethite (α-FeOOH), see also Figure 3 for explanation of terms.
```

Note: In the corrected version of the code, the script was updated to reflect the changes in the text, including correcting the reference number in the equation and updating the reference citation. The text was reviewed to ensure clarity and coherence, and the diagram was updated to reflect the changes in the text.
M: metal center of the oxide, hydroxide or oxyhydroxide

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

The model parameters from Rastad 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 4).

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 Rastad and co-workers [43]. For silica Rastad 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 Rastad 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 Rastad 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 [39]. Distances between atoms affected by surface relaxation (causing different distances

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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 surface 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 [44], while molecular dynamics making use of a periodic boundary will depend on the choice of interaction potentials. Ab initio molecular dynamics [48] on large surface supercells might help solve these problems and perhaps introduce explicit solvent effects on the intrinsic proton affinity of surface oxygens.

The role of the 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 hydrotropic adsorption sequences.

Structure making electrolyte ions would be small ions with high charge. Structure making surfaces 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 interior of the water molecules in which the electrolyte ions are placed. These can in principle be chosen according to the size of hydrated electrolyte ions.

Most of the above cited applications realized 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 affinity is obtained, only this proton affinity is taken into account.1

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

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 various sites. This can be described by equation (8):

\[ \theta_{\text{total}} = N_{\text{solute}}/(K_{\text{solute}} + K_{\text{water}}) \]  

(8)

In equation (8), [solute] is the molar solute concentration in solution, \( K_{\text{water}} \) is the surface coverage (absorbed amount of solute divided by total amount of surface sites), \( \theta_0 \) is the fraction of surface sites of class \( j \), \( K_{\text{solute}} \) is the affinity constant for the local sorption isotherm describing the interaction between the solute and the surface site \( j \); the index \( j \) 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 solvent 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):

\[ \theta_{\text{total}} = \text{log}(1 - (K_{\text{solute}}/K_{\text{water}})) \times \text{log}(K_{\text{solute}}) \]  

(9)

and would correspond to a continuous distribution (3) 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 \( \xi(\log(K_{\text{water}})) \) 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:

\[ \theta_{\text{total}} = N_{\text{solute}}/(K_{\text{solute}} + K_{\text{water}}) \]  

(10)

Current applications of and future requirements for surface complexation models

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 crystallized geothite; 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 reactants as long as other significantly competing adsorbing solutes are absent (complementarity), it is very probable that such very reactive sites exist in as far unknown amount, even if presentations like Figure 2 tend to suggest the perfect crystal planes.

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, \( \text{sOG} \), with charge \( n \) is considered. The interaction of this group with a proton "close to the surface", denoted by \( \text{H}_n^+ \), can be written as a surface chemical reaction:

\[ \text{sOG} + \text{H}_n^+ = \text{sOG}^n+ \]  

(11)

Adsortion of one proton is accomplished by the transfer of one charge unit from the bulk solution (which is characterized 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 a 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 the proton and bulk solution an electrochemical 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 tri-layer model the diffuse layer 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 stress-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

\[ \Delta_G = \Delta_G^\text{chem} + \Delta_G^\text{elec} \]  

(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

\[ K_{\text{ads}} = [\text{sOG}^n+] [\text{H}_n^+]^{-1} \]  

(13)

\( K_{\text{ads}} \) is the intrinsic stability constant for proton adsorption to \( \text{sOG} \), which is valid in the absence of charge when \( [\text{H}_n^+] = [\text{H}^+] \) and accounts for the chemical contribution represented as \( \Delta_G^\text{chem} \) 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

\[ E_n = [\text{sOG}^n+] [\text{H}_n^+] \exp(-\Delta_G/RT) \]  

(14)

This defines the concentration of the proton "close to the surface" and in the bulk solution as well as the electrostatic contribution \( \Delta_G^\text{elec} \) to the total free energy. In 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

\[ [\text{H}_n^+] = [\text{H}^+] \exp(-\Delta_G/RT) \]  

(15)
This factor represents the energy required for the transfer of one proton (three 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 \( \psi_s \) is the surface potential.

Usually the molar 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 solutions “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 equilibrium 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 ion 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 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) [5], [52] includes a 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 treatment of the DLM parameter set will not be able to describe ion-specific effects at interfaces. The Oosu-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, 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 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 \( \zeta \) 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 of the electric double layer at high electrolyte concentrations is so extensive that the diffuse part can be completely neglected.

<table>
<thead>
<tr>
<th>a</th>
<th>TPM (Charge distribution, 1-pK)</th>
<th>ionic strength</th>
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<tbody>
<tr>
<td>SOH*</td>
<td>A'</td>
<td>[C(A)] = variable</td>
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<td>SOH*+</td>
<td>C'</td>
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<td>SOH*+</td>
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<td>SMOK*+16</td>
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<td>acid base parameters</td>
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<td>SMOK*+16</td>
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<td>typically evaluated by BSM (1-pK)</td>
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b | SMIT model | ionic strength |
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<td>SOH*+</td>
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<td>diffuse layer, &quot;complexed&quot; sites</td>
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<td>SOH*+</td>
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<td>( \sigma_{4a} = \alpha(CA) \sinh(L) )</td>
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<tr>
<td>SOH*+</td>
<td></td>
<td>diffuse layer, &quot;uncomplexed&quot; sites</td>
</tr>
</tbody>
</table>

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 electrotye ions bound as ion-pairs are "in contact" with the diffuse layer. Note that the TLM has not been utilised in codes such as FITEQ, based on the equations of the original papers, which equate the diffuse layer charge to the charge in the d-plane, whereas the TFM 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; electrotye 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 BSEM. The relation between the capacitance values allows constraints on the optimum couples of C0 and C0. Problems will arise when charges of adsorbed solutes may reach further towards the solution than what is allowed by C0

\[ C = C0 + C1 + C2 \]

(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 functional forms of the acid-base parameters of multi-dentate surface complexes may need to be corrected for the suspension concentration. Most computer programs do not allow for the inclusion of inorganic ions but also organic species; 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 (SO3)2- entities for bidentate. As long as the total amount of bidentates is much lower than the total amount of the generic site the approach is a valid approximation. For mechanistic models with different types of sites the situation becomes more complicated and the by-passer in 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 number of surface complexation capacity 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 Smitt [59]. Smitt invoked very low values for the outer-layer capacitance. The values of about 0.2 Fm2 typically used in the TLM can be significantly lowered. According to work quoted by Smitt this corresponds to experimental observations.

The original Smitt 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 uncomplicated surface groups are present) and another section characterised by the fraction f of the surface sites where ions are formed with the electrolyte. For the two sections separate electrostatic models are introduced: a BSEM (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 C - potential is calculated from the equation given in Figure 5b.

In this model, the overall capacitance of the inner layers varies with pH and it 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 Smitt model (i.e. combination of a BSEM and TLM, 2-πK formalism) are not unique. The compartment principle itself allows a huge amount of such combinations such as a BSEM for adding supplementary compartments when e.g. a sorbing molecule would be introduced. This increases the number of parameters and in view of the number of the number of the number of multidentate 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 is adsorbed to a mineral surface in the presence of an electrotye. Compared to a standard Smitt model (two compartments) used for the acid-base properties of the mineral, the adhesion of the molecule may cause an extensive distance between adsorbed charge (introduced by the molecules) 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 x0 in Figure 5b. The mean plane obtained for the C - potential would shift further towards the solution side of the interface, which would actually lead to a significant effect on the C - 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 C - 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 still 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.
- 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 detail or to compare in a meaningful way.

These particle properties can in principle be determined with some confidence and there is broad agreement. For the morphological 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 optimization to approximate estimations.

3.3.1.2 Modelling (adjustable) parameters
- Capacitance values: All models except purely diffuse layer models involve capacitance values, which can be interpreted with respect to distances between respective surface planes (or for the thickness of a layer):

  \[ C_i = \varepsilon_i \varepsilon_0 / d_i \]  

  (17)

where \( C_i \) is the capacitance of layer \( i \), \( \varepsilon_i \) is the relative dielectric constant of the medium in layer \( i \), \( \varepsilon_0 \) is the permittivity of free space, and \( d_i \) is the thickness of the layer. Usually, \( \varepsilon_i \) is not known, but it may be obtained from dielectric saturation (at surfaces with strong water structural, \( \varepsilon_{sw} \) is about 6) and pure water (78.5).

Worby et al. [61] on various polymorphs of TiO₂ 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 different capacitance values are obtained: 0.9 F/m² for particles with a "smooth" surface and 1.7 F/m² 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 reported for zeta- and x-bands by the same group [47, 62] for samples with and without surface roughness. This would significantly simplify the application of this model to a broader range of parameters for well-characterized sorbents as zeta. For powders with at present no possibility to obtain such estimations on an experimental basis, approximate values are necessary. Also for the well-defined sorbents such approaches would be highly desirable to verify assumptions about amount and reactivity of surface sites.

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 chemistry. A comparable parameter in solution chemistry would be ligand concentration in a metal-ligand system. A potentiometric study of magnetic 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 proton or hydroxyl (e.g. Løvigie et al. [8], Marmier et al. [63], Heem [64]; the data of Marmier et al. [63] is puzzling since the blank titrations appear to be too small). Some groups have assessed the measurement in the pH regions relevant to site saturation because of the expected errors in the evaluation of the activity of the solution since total and free proton concentration become similar and proton uptake is not an important parameter compared to the amount of protonated sites to the system. Site density is an important parameter and results obtained by Gumerov [21] indicate that the site density of zeta 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 causes 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 must be a "conditional" particle property. Surface charge data in 0.6 M sodium chloride medium obtained by coulometric backtitration of suspensions samples suggest no saturation but only a slightly higher uptake (by up to 6%) 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 density estimation from crystallographic considerations for such well-characterized sorbents as zeta. For powders with at present no possibility to obtain such estimations on an experimental basis, approximate values 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 [46] up to three site concentrations and associated affinity constants were 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 titration 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. Schluhbues 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 pKₐ 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 2-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 strength 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. When 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 constants. Since total and free proton concentration become similar and proton uptake is not an important parameter compared to the amount of protonated sites to the system. Site density is an important parameter and results obtained by Gumerov [21] indicate that the site density of zeta 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 causes 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 must be a "conditional" particle property. Surface charge data in 0.6 M sodium chloride medium obtained by coulometric backtitration of suspensions samples suggest no saturation but only a slightly higher uptake (by up to 6%) compared to the continuous
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 unstable. 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. In 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 quarrelsome. It might be interesting to optimize 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.

3.3.3 Goodness of fit criteria

In this section we shall make again reference to FITIEQ [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 minimized by FITIEQ is

\[ V_r = (W_SOSO)^{0.5} \]

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

\[ W_SOSO = \sum_{ij} (\varepsilon_{ij}^2)(\chi_{ij}^2) \]

where \( \varepsilon_{ij} = (C_{ij} - C_{ij,calc}) \) is the difference between experimental and modelled concentration at data point \( n \) of a total of \( n \) data points, and \( w_{ij} \) is the error estimate for the component for which C data are available. DF stands for degree of freedom and is defined as

\[ DF = n - m \]

The parameter \( m \) is the number of components for which a simultaneous material balance and free concentration constraint is available and \( n \) is the number of optimised components.

WSOSO/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
unity overinterpret the experimental data. The inverse of the squared experimental error estimates are also called weighting factors. They accommodate a weighting of the experimental data, i.e., if the error of data point \( n \) is estimated larger than that of data point \( n+1 \), minimization of \( Y \) for \( n \) will result in a smaller contribution to the minimization 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, 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 \( C_{\text{obs}} \), 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 spectrosopy) should have been included in a structural model. Violation of such constraints for structural models devitalizes 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 any whether one model is better than another. However, no absolute conclusion about the quality of the model should be drawn with fictious error estimates. This statement applies to the constraint \( 0.1 < V_r < 20 \) in the FITEQ model which is generally misleading.

### 3.4 Limits

Limits exist with respect to the capabilities of the modelling tools and to the models themselves. Surface completion 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 systems. In principle if the sorbent properties cannot be characterized, the model 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 model. One should however note 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 sophiticated 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 agree 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 operate on iron (hydro)oxides [45]. Still the two protonation steps within a narrow range of the doubly coordinated sites obtained in the calculation might faviour 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 FITEQ 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 applications) some warnings about the successful use of sophisticated mechanistic models is appropriate. These latter suggest that

\[
2\text{Fe}^{3+}_{(aq)} + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+}_{(aq)} + 6\text{H}^+ + 3\text{H}_2\text{O}
\]

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
adhesion. 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:

$$2 \text{Fe(OH)}_{24}^{6+} + 2 \text{Fe(OH)}_{24}^{5+} + \text{Fe(OH)}_{24}^{4+} + L^2+ \leftrightarrow$$

$$[\text{Fe(OH)}_{24}^{6+} + \text{Fe(OH)}_{24}^{5+} + \text{Fe(OH)}_{24}^{4+} + L^2+]$$

(22)

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 (hyd)oxides. This section provides some applications of the MUSIC model using the example of the surface complexes of three benzoic carboxylates.

A number of infrared spectroscopic studies have shown that many carboxylates display pH-dependent coordination modes on metal (hyd)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 benzoic carboxylates of different charge are also smaller for ligands of larger charge [51]. Whilst the onset of the edges at high pH (and thus of the outer-sphere complexes) vary with the charge on the benzoic carboxylate, the onset of the inner-sphere complex at circumneutral pH is relatively constant, cf. Figure 9. Thus, while electrolyte 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 bimolecular complex with only singly-coordinated sites of the (110) plane:

$$2 \text{Fe(OH)}_{24}^{6+} + 2 \text{H}^+ + L^2+ \leftrightarrow \text{Fe(OH)}_{24}^{6+} + L^2+$$

(23)

where the charges of L$^+$ 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 zon of positive and neutral sites shown in Figure 7. 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:

$$\text{Fe(OH)}_{24}^{6+} + 2 \text{H}^+ + L^2+ \leftrightarrow \text{Fe(OH)}_{24}^{4+} + 2 \text{H}_2\text{O}$$

(24)

where L$^+$ is a ligand of charge z$^-$. Ab initio infra red frequency calculations further support the concept that

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 either 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.

Figure 8
Surface concentration (μmol/cm$^2$) of phthalate (1,2-benzenedicarboxylate), trimellitate (1,2,4-benzenetricarboxylate), and pyromellitate (1,2,4,5-benzenetetraacarboxylate) on goethite in 0.1 M NaNO$_3$ at 298.2 K. Total ligand concentration = 2.22 μmol/cm$^2$. 

Phthalate (z=2), Trimellitate (z=3), Pyromellitate (z=4)
the inner-sphere complexes are mononuclear chelates, and not binuclear bidentate complexes [77]. In the MUSC framework, this species can only form at terminations of acicular goethite particles (e.g. the [012] 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 complex 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

```plaintext
\[ \text{formation constant, } K_{\text{in}} = \frac{\Delta G_{\text{in}}^0}{RT} \]
```

where $K_{\text{in}}$ is the intrinsic formation constant for reaction 24. For an outer-sphere complex with $\Delta H = 0$ and $\Delta S = -2$, larger (smaller) values of $C_1$ ($C_2$) contribute in decreasing both right and side terms of this equation, thereby decreasing the value of $K_{\text{in}}$. In other words the slope of the adsorption edge is smaller for larger (smaller) values of $C_1$ ($C_2$). Therefore, pyromellitate ($\zeta = -4$) requires a larger (smaller) value of $C_2$ ($C_1$) than phthalate ($\zeta = -3$) and phthalate ($\zeta = -2$), and trimellitate requires a larger (smaller) value of $C_1$ ($C_2$) than phthalate (Figure 10). Larger values of

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]. Some experimental conditions as in Figure 2.

Figure 10
Bound proton concentration in a goethite suspension, expressed in terms of \( \text{\textmu mol/m}^3 \) (i.e. encompassing adsorbed and solution concentrations of protons) calculated as $C_{\text{H}^+}$, $C_{\text{H}^+}^{\text{ads}}$, $C_{\text{H}^+}^{\text{surf}}$, where $a$ is the total surface area (m$^2$). 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 \( \mu \text{mol/m}^3 \), otherwise same experimental conditions as in Figure 8.

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 adsorbrates. 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:

(i) phthalate adsorption promotes the formation of even more Fe(III) chelate sites: by virtue of Le Chatelier’s principle of favourable electrostatic conditions.

(ii) phthalate surface complexes are protonated.

Scenarios (i) and (ii) could be distinguished with infrared spectroscopy. In [79,80] all benzenehexahydroxyl 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 (ii). 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) capacitances, $C_{\text{in}}$ with Eq. 16, where values of $C_3$ ($C_4$) were larger (smaller) for ligands of larger charge. The effect of these capacitance values on the apparent formation constant, $K_{\text{app}}$ can be understood with:

\[ \ln K_{\text{app}} = \ln K_{\text{in}} - \frac{\Delta G_{\text{in}}^0}{RT} \]

where $K_{\text{app}}$ is the intrinsic formation constant for reaction 24. For an outer-sphere complex with $\Delta H = 0$ and $\Delta S = -2$, larger (smaller) values of $C_1$ ($C_2$) contribute in decreasing both right and side terms of this equation, thereby decreasing the value of $K_{\text{in}}$. In other words the slope of the adsorption edge is smaller for larger (smaller) values of $C_1$ ($C_2$). Therefore, pyromellitate ($\zeta = -4$) requires a larger (smaller) value of $C_2$ ($C_1$) than phthalate ($\zeta = -3$) and phthalate ($\zeta = -2$), and trimellitate requires a larger (smaller) value of $C_1$ ($C_2$) than phthalate (Figure 10). Larger values of
An, also decrease $K_{eq}$ 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, $d_0$ (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 $d_{phthalate} > d_{trimellitate} > d_{pyromellitate}$. Unfortunately, the framework of the calculations does not allow an unambiguous inference to be made on $d_0$ 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 than 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 FeOOH(001), 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 electrochemical 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 the electrochemical/physico-chemical relevance, work that is actually under progress. Albeit this, interpreting the infrared spectra, in combination with $C_2$ 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 absorbed proton and benzenecarboxylates is positive) and that all surface complexation models predict positive surface potentials (Figure 12). However, while phthalate only yields positive $C_2$ 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 perpendicular to the surface. From here, the trends in $d_0$ 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 carboxyl groups is also supported by the significantly larger $K_{eq}$ of the outer-sphere complex of pyromellitate.

The negative $C_2$ 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 TPD, yielding the Four Plane Model (FPM) shown in Figure 12b [60]. The same and only difference of this model is that the unbound carboxyl groups of trimellitate and of pyromellitate are set in the 3-plane and the capacitance is optimized to yield a good fit to the $C_2$ - potential data. This approach is successful at predicting $C_2$ - 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 SCM 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...
References


Chem. Scand. A, 6, 301.


325.


Interface Sci., 99, 121.


Sci., 148, 517.


[14] Hunter, R.J. 1981, Zeta Potential In Colloid Science,


[16] Rowlands, W.N., O'Brien, R.W., Hunter, R.J., and

Technol. 22, 602.

201, 71. Pang, G. and Liu, P.S. 1998, J. Colloid Interface
Sci., 201, 77.

Interface Sci., 169,284.

Technol. 12, 2519. Roberton, A.P., and Lechtle, J.O.


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Adsorption of metal ions on activated carbons in aqueous solutions

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ABSTRACT

Adsorption studies of Na(I), Co(II), 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 metal 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.