Chapter V

Binding Models for Humic Substances

Wolfgang HUMMEL
Waste Management Laboratory
Paul Scherrer Institut
CH-5232 Villigen PSI (Switzerland)

V.1. Introduction

Humic substances are the largest fraction of natural organic matter in water. They are important for water quality, for chemical weathering in natural environments, and as complexing agents for trace metals. The latter property requires that humic substances are included in thermodynamic modelling of aqueous systems. However, in general thermodynamic databases, do not contain equilibrium constants for complexation of metal ions with humic substances. Any attempt to remedy this omission inevitably pulls the modeller into a veritable jungle of humic binding models, published in a plethora of journal articles. Obviously there must be some differences between metal ion binding by “ordinary” or “simple” ligands like carbonate or acetate, which is described in terms of “classical” equilibrium thermodynamics, and binding of metal ions by humic substances.

This chapter is intended to guide the modeller through the multitude of humic binding models by emphasising the differences between complexation models of simple organic ligands and binding models of humic substances. The modeller should understand (1) why, from a thermodynamic point of view, humic substances cannot be treated the same way as simple organic or inorganic complex forming ligands; (2) why and for what purpose the various binding models were developed; and (3) what problem solving strategy could be followed in a particular modelling problem. As all current humic binding models are just fitting models, consistent treatment of experimental data is emphasised as a prerequisite to deriving a reliable set of model parameters tailored to the problem at
The general discussion of humic binding models will be useful in modelling metal-humic interactions in any aquatic system. The example discussed in detail throughout this chapter is taken from ongoing work in the assessment of radionuclide behaviour in the environment. Likewise, the problem solving strategy proposed in the last part of this chapter focuses on this topic, although it is not at all limited to radioactive waste problems.

V.2. What are humic substances?

Humic substances occur in rotting vegetable matter and can be detected in the black slime of an ordinary compost pit in a home garden. They are found in the brown organic matter of a variety of soils, as well as in peat, lignite and brown coals. The concentration of humic substances in natural waters varies over three orders of magnitude [85THU]: Ground waters and marine waters are lowest in concentration with 0.03 to 0.6 mg/l of humic substances expressed as dissolved organic carbon (DOC). Streams, rivers, and lakes vary from 0.5 to 4.0 mg/l. Tea-colored waters, such as marshes, bogs, and swamps vary from 10 to 30 mg/l DOC as humic substances. As a group humic substances account for approximately 30 to 50 percent of the DOC of most natural waters, except in colored waters, where they contribute 50 to 90 percent of the DOC.

What is the chemical composition of these “humic substances”? This is a difficult question. Humic substances are the product of decomposition chemistry, not the ordered chemistry of biological products. Thus, no chemical labeled “humic substances” exists, and there are no simple methods of analysis for humic substances. The first problem is to define, in some limited yet useful way, what humic substances are. Humic substances may be defined operationally [85THU]: They are colored, polyelectrolytic, organic acids isolated from water on XAD resins1, weak-base ion-exchange resins, or a comparable procedure. Alternatively, they are extracted from soil by sodium hydroxide (typically 0.1 M). In both cases a further fractionation divides humic substances into two classes, which are humic and fulvic acid. Humic acid is the fraction that precipitates at pH 2.0 or less, the fraction remaining in solution is fulvic acid. Other classification schemes emphasise the origin of humic substances (soil, aquatic, sediment, etc.) rather than pure operational classifications. For an in-depth discussion of this topic see [88BUF].

The knowledge concerning the structure of humic substances may be summarised according to Thurman [85THU] as follows. Fulvic acids have a range of molecular weight from 500 to 2000 g/mol, whereas humic acids are larger and often colloidal, with molecular weight from 2000 to 5000 g/mol, and sometimes much larger, up to 100,000. The major

1 XAD resins are nonionic methylmethacrylate polymers that adsorb organic matter from water by hydrophobic bonding. The pH of the water is lowered to 2.0, and the humic substances adsorb onto the XAD resin. Then, the humic substances are desorbed quantitatively with base and studied by various techniques. Because approximately 30% of the dissolved organic carbon of a natural water are organic acids that are not retained by XAD resins at pH 2.0, they have been called the “hydrophilic acids”. Little is known about the nature of these hydrophilic acids and their study has only begun.
functional groups include: carboxylic acids, phenolic hydroxyl, carbonyl, and aliphatic hydroxyl groups. On the average, fulvic acid contains 5.5 mM of carboxyl groups per gram. This corresponds to one carboxylic acid group per 6 carbon atoms, or one group per aromatic ring, if distributed evenly. If not, there may be as many as two or three carboxylic-acid groups on some aromatic rings, and none on others. The $^{13}$C-NMR spectra indicate that the aromatic to aliphatic ratio is 1:2. Hence, approximately 65 percent of the carbon is aliphatic, and many of the carboxyl and hydroxyl groups are on aliphatic carbons. The average phenolic content in fulvic acids is 1.2 mM/g based on NMR and titration data, this is 1 phenolic functional group for every 30 carbon atoms, or only two phenolic groups per fulvic acid molecule, as the molecular size of less than 2000 suggests that up to 60 carbon atoms are involved in the structure with probably 3 to 4 aromatic rings. This is not a large molecule, rather, it is a medium-sized, water-soluble acid. Hydroxyl and carbonyl groups, summed together, are as abundant in fulvic acid as carboxyl groups. This information is based on $^{13}$C-NMR spectra of several samples. The amount corresponds to 5 to 7 mM/g. This suggests that the fulvic acid mixture contains molecules with either carboxyl, carbonyl, and hydroxy groups for every 3 carbon atoms. Fulvic acid from water is probably a mixture of many different molecules, with the average characteristics listed above. The number of compounds that constitute the fulvic acid fraction may be 10, 100, 1000 or more compounds, and the structure of fulvic acid remains an interesting unresolved question. Humic acid is less soluble than fulvic acid. On the average, it contains fewer carboxyl groups than fulvic acid, but a somewhat larger phenolic content. Degradation experiments do not show radically different products for humic and fulvic acid, suggesting that the cores of both humic and fulvic acid are similar. Therefore, in the following discussion of binding models the term “humic substances” comprises both, humic and fulvic acid.

This short summary of knowledge about the nature of humic substances foreshadows the difficulties encountered when their binding properties with metal ions are studied experimentally, and when the experimental results are subsequently modelled by means of thermodynamic approaches [88BUF].

V.3. Metal ion binding of humic substances

V.3.1. The experimental data

The minimal set of experimental data needed to describe the interaction of a metal ion, M, with a humic substance, HS, comprises [MHS], the concentration of metal bound to a certain humic substance, [M], the concentration of free metal in the aqueous phase, and (HS)$_{total}$, the total concentration of humic substance. [MHS] and [M] can be quantified on the molar scale [mol/l], but (HS)$_{total}$ is known only as mass per unit volume (g/l). Note, that [ ] is used in the following for molarity units and ( ) for mass per unit volume. One of the two molar concentrations, [MHS] or [M], is usually derived directly from measured quantities, whereas the other is calculated from mass balance equations involving the total concentration of metal in the system, [M]$_{total}$, and the concentration of aqueous metal.
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complexes formed. The experimental procedures to measure these quantities and the subsequent mass balance calculations also contain some model assumptions; but these, like the complexation behaviour of the metal ion with ligands other than HS, can be checked independently of the humic binding model which is used to interpret the experimental data.

This minimal set of experimental information can be described by a constant ‘\( K \)', defined as the number of moles of metal bound per gram of humic substance divided by the concentration of free metal in solution:

\[
\begin{align*}
\text{‘} K \text{'} &= \frac{[\text{MHS}]}{[\text{M}] \cdot (\text{HS})_{\text{total}}} \quad \text{(V.1)}
\end{align*}
\]

The unit of ‘\( K \)’ therefore is volume per mass, usually given as \( \text{L/g} \). The coefficient ‘\( K \)’ closely resembles the well known stability constant

\[
K = \frac{[\text{ML}]}{[\text{M}] \cdot [\text{L}]} \quad \text{(V.2)}
\]

of a metal-ligand complex formation for the reaction

\[
\text{M + L } \rightleftharpoons \text{ ML} \quad \text{(V.3)}
\]

However, there are two fundamental differences between the formally similar Eqs. (V.1) and (V.2).

First, in the case of simple organic ligands, like acetate, oxalate or edta, the molecular structure of the ligand \( \text{L} \) and thus, the nature and number of functional groups \( \text{S} \) is well known. The stereochemistry of the possible metal-ligand complexes can be deduced from this molecular structure information. The complexes predominating within a certain experimentally investigated region of chemical parameter space (component concentrations, pH, ionic strength, \( \text{etc.} \)) are usually determined by data fitting procedures using a number of alternative complexation models characterised by different sets of possible complexes. In cases where there are only small differences between the best fits of these alternative complexation models, additional evidence for verification of the existence of certain species like \( \text{ML}, \text{ML}_2, \text{MHL}, \text{M(OH)L}, \text{etc.} \), may be obtained from spectroscopic studies and crystal structure determinations of the metal-organic compounds. In contrast to these well-defined ligands, “humic substances” serves just as a label for an operationally defined class of a naturally occurring mixture of large size molecules. The molecular structure models proposed so far for humic substances are rather dissimilar and indicate the lack of knowledge and the complexity of the subject (see, for example, “Kleinhempel’s model” [70KLE], also in [88BUF] p.175, a “random molecular model” [83MUR/LIN], a “pseudomicellar structure model” [94ENG/WAN], or a “flexible carbon network structure” [94SCH]). The nature and number of functional groups \( \text{S} \) involved in metal binding by humic substances are, at best, uncertain. That is, the stereochemistry of \( \text{M - HS} \) complexes is largely unknown. By analogy to small molecules, the functional groups involved in binding a metal ion may be called a “ligand”. A 1:1 complex in the case of humic
substances is defined as a metal ion bound to a certain (unknown) number of functional groups within the same humic molecule.

The second difference between Eqs. (V.1) and (V.2), is closely related to the first one, and concerns the concentration of free ligand, $[L]$, and the total concentration of humic substance $(HS)_{\text{total}}$. The latter provides information about experimental conditions; the mass of humic substance added per unit volume of solution. In order to convert this mass number into the total molar concentration of “ligands” or binding sites available for complexation with the metal ion, $[L]_{\text{total}}$, we need to know the number of complexing sites per unit mass of the humic substance. Analytical methods like pH - titration, elemental analysis or radioactive labeling, measure, or at least allow an estimate, of the total concentrations of different kinds of functional groups. These total concentrations, however, only give upper limits for the concentrations of the binding sites $[L]_{\text{total}}$. The only method to directly measure these quantities would involve the metal ion under study as a probe: Suppose we know the stereochemistry of the MHS complex formed and its equilibrium constant, the molar concentration of binding sites could then easily be derived from the measurements. But the stereochemistry, i.e. the nature and number of functional groups involved in metal binding, and their associated complexation strength are the unknowns in this game. The total molar concentration of binding sites, $[L]_{\text{total}}$, cannot be measured independently of the model assumptions. Hence, the concentration of free binding sites $[L]$ is a model dependent parameter.

Summarising laboratory experiments on selected humic substances, the coefficient $'K'$ is found to vary with changes in component concentrations, pH, and ionic strength. These changes are described in the various binding models of humic substances. The different concepts to describe these changes are presented in the following sections in a systematic manner. We begin with variations in component concentrations, i.e. the concentrations of metal ions and humic substances, at constant pH and ionic strength. Then we proceed to pH variations and finally we discuss the treatment of ionic strength effects. Humic binding models may comprise any combination of these concepts. If we attempted to discuss published binding models in a systematic manner, we would end up with a classification scheme consisting of such complicated classes as “discrete heterogeneous non-electrostatic models”, for example. The intent is not to give a detailed review of all humic binding models developed so far but merely to discuss some important aspects of published models, in the hope of providing the reader with a pathway through the multitude of humic binding models.

V.3.2. Variations in component concentration

V.3.2.1. The simplest model

Any useful binding model for humic substances contains a number of assumptions, but relies ultimately on experimental data. This seems to be a rather trivial statement, but while struggling along with the different humic binding models, the reader of the literature in the field may get the impression that a clear-cut distinction between measured data
and more or less plausible model assumptions is all but impossible. In some cases model assumptions intermingle with experimental results; in most cases at least some of the basic assumptions are never explicitly stated. In the hope of clearing this thicket, an effort is made here to clearly state the assumptions and to discuss their plausibility and consequences.

**Table V.1:** List of model assumptions.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Description of assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>{A1}</td>
<td>The metal ion M forms only 1:1 complexes with ligand sites L of the humic molecule. The humic molecule consists of a number of functional groups S. This number is not specified in the model, but is assumed to be fixed within the pH and metal concentration range where the model is applied.</td>
</tr>
<tr>
<td>{A2}</td>
<td>For each metal ion M under study, only one kind of ligand site L predominates within the parameter range where the model is used.</td>
</tr>
<tr>
<td>{A3}</td>
<td>The complexing strength of the ligand sites L is constant, and does not vary with the location within the humic molecule, i.e. the influence of different substituents and varying stereochemistry on L is ignored.</td>
</tr>
<tr>
<td>{A4}</td>
<td>Chemical changes of the humic molecules have no influence on the number of active ligand sites available for metal complexation.</td>
</tr>
<tr>
<td>{A5}</td>
<td>The functional groups S involved in metal binding do not undergo any proton exchange reactions in the pH range of interest.</td>
</tr>
<tr>
<td>{A6}</td>
<td>There are no interactions between functional groups S of the humic molecule, i.e. electrostatic effects that change the binding characteristics of S are ignored.</td>
</tr>
</tbody>
</table>

The simplest version of a humic binding model, based on assumptions {A1} to {A6} (Table V.1), considers metal-humic interactions as a reaction between a metal ion and a unique ligand site L to form a 1:1 complex, as described by Eqs. (V.2) and (V.3). In other words, the simplest humic binding model, sometimes called a "single site model",


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treats humic substance like a simple organic ligand with unknown molecular weight.
The amount of metal bound to the humic substance is then given by

\[ [\text{MHS}] = [\text{ML}] \]  \hspace{1cm} (V.4)

and the total concentration of ligand sites is simply the sum of free ligand sites and metal bound to humic substance

\[ [L]_{\text{total}} = [L] + [\text{ML}] \]  \hspace{1cm} (V.5)

The total concentration of humic substance, \((\text{HS})_{\text{total}}\), is related to the total concentration of ligand sites \([L]_{\text{total}}\) by

\[ (\text{HS})_{\text{total}} \cdot \text{SCC} = [L]_{\text{total}} \]  \hspace{1cm} (V.6)

where the Site Complexation Capacity SCC is the amount of active binding sites per unit mass of humic substance (mol/g). As discussed in Section V.3.1, \([L]_{\text{total}}\) and thus SCC is a model dependent adjustable parameter. According to assumption \{A4\}, the simplest model described here, treats SCC as a constant, independent of the concentrations of metal and humic substance. Combining Eqs. (V.2), (V.5) and (V.6) gives

\[ (\text{HS})_{\text{total}} \cdot \text{SCC} = [L] (1 + K \cdot [M]) \]  \hspace{1cm} (V.7)

Finally, combining Eqs. (V.1), (V.2), (V.4) and (V.7) and rearranging shows the relation between the measured data \(cK\) and \([M]\) and the adjustable model parameters \(K\) and SCC:

\[ cK = \frac{K}{1 + K \cdot [M]} \cdot \text{SCC} \]  \hspace{1cm} (V.8)

Experimental data plotted in a \(\log_{10} cK-\log_{10}[M]\) diagram, which extends over a sufficiently large range of free metal concentration, will give various information: In the region of very low metal loading the free ligand sites predominate, \([L] > [\text{ML}]\) or \(K \cdot [M] < 1\), and Eq. (V.8) reduces to

\[ cK = K \cdot \text{SCC} \]  \hspace{1cm} (V.9)

The model predicts that \(cK\) is constant in the range of trace metal concentrations. In the region of high metal loading close to metal saturation, the ligand sites are to a large extent bonded to metal ions, i.e. \([\text{ML}] > [L]\) or \(K \cdot [M] > 1\), and Eq. (V.8) reduces to

\[ cK = \frac{1}{[M]} \cdot \text{SCC} \]  \hspace{1cm} (V.10)

Thus, in the region of high metal loading, \(\log_{10} cK\) decreases with increasing \(\log_{10}[M]\) by slope \(-1\). As can be seen from Eq. (V.10), in the region of metal saturation \(cK\) no longer depends on the parameter \(K\) but is determined by SCC, the site complexation capacity,
alone. As a consequence of the model assumptions, the site complexation capacity is
defined as the maximum number of moles of metal ions bound per unit mass of humic
substance

\[
\text{SCC} = \frac{[\text{MHS}]_{\text{max}}}{[\text{HS}]_{\text{total}}} \quad (V.11)
\]
at metal saturation \([L]_{\text{total}} \approx [\text{ML}] = [\text{MHS}]_{\text{max}}\). The parameter SCC, in this model, is
therefore usually associated with terms like “total metal-binding capacity” [91BID/GRE],
“complexing capacity” [95MOU/MOU], or “loading capacity” [96KIM/CZE].

In theory, the parameter SCC can be adjusted in the region of metal saturation
(Eq. (V.11)), whereas the parameter \(K\) may be derived from data in the range of trace
metal concentrations (Eq. (V.9)). In practice, however, the analytical window of a given
experimental technique used to study metal-humic interactions usually does not permit
measurements over many orders of magnitude in component concentration. In the region
of high metal loading especially, metal saturation can only approximately be achieved,
due to coagulation and precipitation of humic substances and Eq. (V.11) cannot be ap-
plied directly. Most studies published so far present data measured over two to three
orders of magnitude in component concentration, and the model parameters \(K\) and SCC
are obtained by fitting these data for given pH and ionic strength values.

For example, Bidoglio et al. [91BID/GRE] interpret their equilibrium titration curves
of the lanthanides Eu(III) and Tb(III) with fulvic acids in terms of this simple model.
They denote the site complexation capacity SCC as \(c\), the total metal-binding capacity
of fulvic acid, and their conditional constant \(K'\) is identical with our parameter \(K\). The
same type of model is used by Moulin and Moulin [95MOU/MOU] to interpret data of
Am(III), Cm(III), Dy(III), Np(V) and U(VI) complexation with humic substances. The
site complexation capacity SCC is named \(W\), the complexing capacity, and the conditional
interaction constant \(\beta\) is identical with our parameter \(K\). The approach used by Kim
and coworkers [96CZE/KIM, 96KIM/CZE] to model data of Am(III), Cm(III), Np(V)
and U(VI) complexation with humic acid looks somewhat different at a first glance. A
loading capacity LC is defined as a dimensionless number, the maximum number of moles
of metal ions bound per moles of humic substance

\[
\text{LC} = \frac{[\text{MHS}]_{\text{max}}}{[\text{HS}]_{\text{total}}} \quad (V.12)
\]

where \([\text{HS}]_{\text{total}}\) is the total concentration of humic substance in mol/l. The conversion
from the analytical concentration of humic substance in g/l, \((\text{HS})_{\text{total}}\), to the molar
concentration, \([\text{HS}]_{\text{total}}\), is operationally defined as

\[
[\text{HS}]_{\text{total}} = \frac{(\text{HS})_{\text{total}} \cdot \text{PEC}}{z} \quad (V.13)
\]

PEC is the proton exchange capacity in mol/g at pH 7, derived from pH titration of the
humic substance. The parameter \(z\) is thought to be the number of functional groups (with
charge minus one) coordinating to a metal ion. Local charge neutralisation is assumed
in the model, i.e. \(z = 3\) for trivalent ions like Am\(^{3+}\), \(z = 2\) for divalent ions like UO\(_2^{2+}\), and
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For monovalent ions like NpO\(_2^+\). The total concentration of ligand sites \([L]_{total}\) is defined in terms of the loading capacity

\[ [L]_{total} = [HS]_{total} \cdot LC \]  \hspace{1cm} (V.14)

Combining Eqs. (V.12) and (V.14), reveals that the total concentration of ligand sites is defined as the maximum concentration of metal ions bound to humic substance, \([L]_{total} = [MHS]_{max}\) in accordance with our model. Thus, the conceptual models used in [91BID/GRE, 95MOU/MOU, 96KIM/CZE] are the same despite some differing definitions of conversion relations and adjustable parameters. The conditional interaction constants \(K'\) or \(\beta\) in all these models are numerically identical if fitted to the same data sets. Note, that \(\beta\) values derived by Kim and Czerwinski [96KIM/CZE] are independent of the actual value of PEC and the number chosen for \(z\). The assumption of local charge neutralisation cannot be verified or falsified by experimental data. The fit of any experimental data set results in the same values of \(\beta\) irrespective of the value chosen for \(z\).

The fitting parameter \(K\) should turn out to be constant over large component concentration ranges if the assumptions of our model are valid. Experimental investigations at relatively high metal loading by Bidoglio et al. [91BID/GRE] and Kim and coworkers [96CZE/KIM, 96KIM/CZE] indeed result in constant parameters \(K\) over the entire range of metal concentration. However, in the range of low metal loading, Moulin and Moulin [95MOU/MOU] report an increase in the fitted \(K\) values with decreasing metal concentration! Contrary to the claim in [96CZE/KIM] this change in \(K\) cannot be ascribed to different definitions of the humic substance concentration, because these differences have no influence on the fitted \(K\) values. Our simple model therefore seems not to be an adequate description of metal-humic complexation behaviour from metal saturation down to very low metal loading. This is not surprising, we cannot expect that humic substances behave just as a simple monofunctional organic ligand.

V.3.2.2. Mixed-ligand models

In the simplest model of metal-humic binding, \{A1\}, we assumed that the metal ion \(M\) only forms 1:1 complexes with ligand sites \(L\) of the humic molecule. However, it is possible that a metal ion bound to a ligand site \(L\) exchanges coordinated water molecules for low molecular weight ligands \(X\), thereby forming mixed-ligand \(L\)-M-\(X\) complexes. If we skip assumption \{A1\}, such complexes may be described by the equilibrium

\[ ML + X \rightleftharpoons MLX \]  \hspace{1cm} (V.15)

where \(X\) is an anion like \(\text{CO}_3^{2-}\), oxalate, etc. The conditional stability constant of this mixed-ligand equilibrium is

\[ K_{mix} = \frac{[MLX]}{[ML] \cdot [X]} \]  \hspace{1cm} (V.16)
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The concentration of metal bound to the humic substance thus is now given by

\[
[MHS] = [ML] + [MLX] \quad (V.17)
\]

and the total concentration of ligand sites is simply the sum of free ligand sites and metal bound to the humic substance

\[
[L]_{\text{total}} = [L] + [ML] + [MLX] \quad (V.18)
\]

The relation between the measured data \(cK\) and \([M]\) and the three adjustable model parameters \(K, K_{\text{mix}}\) and SCC is now:

\[
cK = \frac{K (1 + K_{\text{mix}} \cdot [X])}{1 + K (1 + K_{\text{mix}} \cdot [X]) \cdot [M]} \cdot SCC \quad (V.19)
\]

In the region of high metal loading where the ligand sites are predominantly occupied by metal ions, we have \([ML] + [MLX] > [L]\) or \(K(1 + K_{\text{mix}} \cdot [X]) \cdot [M] > 1\), and Eq. (V.19) reduces to Eq. (V.10) in the previous model. In this parameter range, no influence of the additional ligand X on the experimental \(cK\) values is expected. In other words, in the region of high metal loading experimental data do not allow us to distinguish between metal ions bound via 1:1 complexes only, or mixed-ligand complexes. However, in the region of very low metal loading, the free ligand sites predominate, \([L] > [ML] + [MLX]\) or \(K(1 + K_{\text{mix}} \cdot [X]) \cdot [M] < 1\), and Eq. (V.19) reduces to

\[
cK = K (1 + K_{\text{mix}} \cdot [X]) \cdot SCC \quad (V.20)
\]

Here, we expect an increase of \(cK\) when the concentration of the additional ligand X is increased above a certain threshold, which is given by \([MLX] > [ML]\) or \(K_{\text{mix}} \cdot [X] > 1\). Therefore, only experimental data at low metal loading are appropriate to decide whether mixed-ligand complexes are formed, or not, within a certain range of X concentrations.

Information about the formation of MLX complexes in the literature is scarce. Experimental evidence for the existence of such complexes was first provided by acid-base titrations combined with ion-selective measurement of Cu\(^{2+}\) concentration [73MAN/RAM]. Powell and Town [91POW/TOW] postulated from data obtained by spectroscopic and voltammetric techniques that MLX complexes were formed in significant amounts. However, no attempt was made by the authors to derive stability constants from their data, [91POW/TOW]. Buffe [80BUF] corrected literature data for the complexation of Cu(II) by humic substances in the presence of X by introducing mixed-ligand complexes. He tentatively assumed that the stability constant for the reaction between ML and X is the same as for the addition of X to the metal aqua ion. As a result, the corrected data fit better to the binding models used in that study. Recently, Glaus, Hummel and Van Loon [95GLA/HUM] showed in an experimental study of the complexation of humic substances with Co(II), Eu(III) and U(VI), and carbonate, oxalate, nta and edta as anion X, that MLX complexes are rather weak compared with complexes formed by the low molecular
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weight ligands X alone. In all cases studied so far, $K_{mix} < K_2$, where $K_2$ is the stepwise stability constant for the equilibrium between MX and MX$_2$, i.e.

$$K_2 = \frac{[MX_2]}{[MX] \cdot [X]}$$

(V.21)

If the relation $K_{mix} < K_2$ is valid in general for any metal/ligand combination, it will be possible to estimate the threshold concentration of X, above which mixed ligand complexes become important in metal-humic systems, even for cases where $K_{mix}$ is not known.

**V.3.2.3. Variable stoichiometry models**

If we assume that X is not a low molecular weight ligand, but a second ligand site L of the humic substance that coordinates to the metal ion M, we postulate the formation of classical 1:2 complexes according to:

$$M + 2L \rightleftharpoons ML_2$$

(V.22)

The conditional stability constant of equilibrium (V.22) is

$$\beta_2 = \frac{[ML_2]}{[M] \cdot [L]^2}$$

(V.23)

The concentration of metal bound to the humic substance thus is now given by

$$[MHS] = [ML] + [ML_2]$$

(V.24)

and the total concentration of ligand sites is the sum of free ligand sites and metal bound to the humic substance

$$[L]_{total} = [L] + [ML] + 2[ML_2]$$

(V.25)

The relation between the measured data ‘K’ and [M] and the three adjustable model parameters $K$, $\beta_2$ and SCC is:

$$'K = \frac{K + \beta_2 \cdot [L]}{1 + (K + \beta_2 \cdot 2[L]) \cdot [M]} \cdot SCC$$

(V.26)

This type of model is sometimes called a “multidentate model” [86TUR/VAR]. The term is misleading since we do not know a priori how many functional groups S constitute a ligand site L of a humic substance. If more than one functional group S is coordinating, even a simple 1:1 complex ML is a multidentate complex. We therefore recommend using the term “variable stoichiometry models” for models comprising other than simple 1:1 complexes.

In the region of high metal loading close to metal saturation, the ligand sites are predominantly occupied by metal ions, i.e. $[ML] + 2[ML_2] > [L]$ or $(K + \beta_2 \cdot 2[L]) \cdot [M] > 1$,
but Eq. (V.26) does not simply reduce to Eq. (V.10), as in the cases discussed so far. We have to distinguish two cases. If the 1:1 complex predominates, i.e. if \([ML] > 2 \cdot [ML_2]\) or \(K > \beta_2 \cdot 2[L]\), Eq. (V.26) reduces to Eq. (V.10):

\[
\gamma K = \frac{1}{[M]} \cdot \text{SCC}
\]

If the 1:2 complex predominates, i.e. if \([ML] < 2 \cdot [ML_2]\) or \(K < \beta_2 \cdot 2[L]\), Eq. (V.26) reduces to

\[
\gamma K = \frac{1}{[M]} \cdot \frac{\text{SCC}}{2} \quad (V.27)
\]

Hence, the site complexation capacity is divided by a factor of two as compared to Eq. (V.10), because two complexing sites are involved in the formation of 1:2 complexes. A factor of two in experimental \(\gamma K\) values will in general be within the scatter in the experimental data. Thus, the existence of 1:2 complexes is very difficult to prove unambiguously.

In the region of very low metal loading, the free ligand sites predominate, and \([L] > [ML] + 2[ML_2]\) or \((K + \beta_2 \cdot 2[L]) \cdot [M] < 1\), Eq. (V.26) reduces to

\[
\gamma K = (K + \beta_2 \cdot [L]) \cdot \text{SCC} \quad (V.28)
\]

In this range the concentration of free binding sites is close to the total concentration of binding sites, \([L] \approx [L]_{\text{total}} = (\text{HS})_{\text{total}} \cdot \text{SCC}\), and Eq. (V.28) can be written as

\[
\gamma K = (K + \beta_2 \cdot (\text{HS})_{\text{total}} \cdot \text{SCC}) \cdot \text{SCC} \quad (V.29)
\]

A linear increase with slope one of the experimental \(\gamma K\) values with increasing total concentration of humic substance is predicted in this concentration range if 1:2 complexes predominate. This behaviour differs from that in the simple model discussed above, Eq. (V.9), where experimental \(\gamma K\) values are predicted to be independent of the total concentration of humic substance \((\text{HS})_{\text{total}}\). An increase of experimental \(\gamma K\) values with increasing total concentration of humic substance, can also be interpreted in terms of multiple sites. In this conceptual model, as discussed in detail in the next section, increasing concentration of humic substance at constant total metal concentration results in a decrease in the overall metal loading of the humic substance. As a consequence, the ratio strong/weak complexing sites is shifted towards the (few) strong sites and the overall effect is an increase of experimental \(\gamma K\) values.

In summary, discrimination between models including complexes with variable stoichiometry, and models including (multiple) 1:1 complexes only, can only be achieved by varying both, the total concentration of humic substance and the total concentration of metal, at low metal loading, over several orders of magnitude. Unfortunately, all attempts published so far to model data with 1:2 complexes were made with data sets consisting of either variable metal concentrations but constant humic substance concentration alone,
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or vice versa. No unique model can be obtained from these data sets. The existence and potential importance of 1:2 metal-humic complexes has not yet been shown from experimental data. In addition, the concepts of 1:2 complexes presented by different authors are rather inconsistent. A few representative examples illustrating this unfortunate situation follow.

We begin with an example representing the clearest discussion of variable stoichiometry models found in the literature. Buflle, Greter and Haerdi [77BUF/GRE] measured the complexation properties of fulvic acids with lead and copper ion-selective electrodes. The experimental data consist of metal and pH titrations at constant humic substance concentration (and constant ionic strength). They were interpreted in terms of 1:1 and 1:2 complexes, including proton exchange equilibria (see Section V.3.3.2). The authors [77BUF/GRE] assumed that the fulvic acid molecules contain only one coordinating site, and thus the site complexation capacity parameter, SCC, is inversely proportional to the mean molecular weight, $M_w$, of the fulvic acid: $\text{SCC} = 1/M_w$. As a consequence, the 1:2 complexes are thought to involve two molecules of fulvic acid which "is physically possible since the molecular weight of the complexing molecules of fulvic acid is always low (generally less than 1000 g/mol)." Three parameters were fitted to the metal titration data, the two stability constants for 1:1 and 1:2 complexes and $M_w$. However, the authors were aware of the fact that metal titration data alone cannot prove or disprove the existence of 1:2 complexes. After deriving Eq. (V.29), Buflle, Greter and Haerdi [77BUF/GRE] stated that this equation was checked by plotting $cK/\text{SCC} \text{versus (HS)}_{\text{total}} \cdot \text{SCC}$ for various water samples. "Good straight lines were obtained", but no data or plots of this kind are shown in the paper.

Stevenson [76STE] reports potentiometric titration data for complexes between Cu, Pb and Cd and three humic acids at various ionic strengths but constant humic acid concentrations. The results were interpreted in terms of 1:1 and 1:2 complexes according to Eq. (V.26), including proton exchange equilibria (see Section V.3.3.2). [76STE] states "it should be noted that, in coordination chemistry, 1:1 and 1:2 complex refer to the number of molecules necessary to satisfy the coordination number of the metal ion. As used herein, the relationship denotes the number of ligand sites per metal ion." Although not stated clearly in the paper, further discussions in [76STE] indicate that the author thinks his postulated 1:2 complex consists of two adjacent acidic groups, most probably of the structure type of phthalic or salicylic acid, which is the definition of a two-dentate 1:1 complex. In essence, a conceptual two site model, as discussed in the next section, is formally treated in terms of a variable stoichiometry model. The same misleading terminology, mixing up the concept of variable stoichiometry and multiple sites, is used by Yoon et al. [94YOO/MOO]. They interpret spectroscopic data of Eu(III) - fulvic acid complexation in terms of "two types of carboxylate moieties for the binding of metal ions on fulvic acid which formed 1:1 (EuL$^{2+}$; L = carboxylate) and 1:2 (EuL$_2^+$)." Misleading terminology adds further to the already rather complicated topic and should be avoided.

The interaction of humic and fulvic acids with Eu(III) and Am(III) at trace metal concentration was measured by Bertha and Choppin, [78BER/CHO], using Schubert’s method. The total metal concentration was held approximately constant while the con-
centration of humic substance was varied over about one order of magnitude. The experimental data were interpreted as a 1:m complex, with m between 1.4 and 1.8. Bertha and Choppin [78BER/CHO] therefore assumed that the complex species are ML and ML₂. In addition, they state “since we cannot a priori choose whether these two types of sites are identical or not, we designate the 1:1 sites as X and the 1:2 sites as Y”. In fact, this represents a combination of a variable stoichiometry model with a multiple site model. This model was abandoned in later publications of the same group in favor of a formal variable stoichiometry model. For example, Torres and Choppin [84TOR/CHO], measuring Eu(III) and Am(III) humate complexation by a liquid/liquid distribution method at approximately constant trace metal concentrations but varying pH, state “the experimental data was fitted satisfactorily by a second order analysis leading to values of ß₁ and ß₂ but did not require any further parameter, e.g. ß₃”. This misleading formal treatment of experimental data is still presented in recent publications. For example, Tao, Du and Li [96TAO/DU] report 1:1 and 1:2 stability constants for uranyl-fulvic acid complexation, formally derived from data obtained by an ion exchange method. These models add very little to our understanding of metal-humic interactions.

V.3.2.4. The multi-site models

The conceptual models discussed so far treat humic substances as a simple organic ligand with an unknown molecular weight, which forms primarily 1:1 complexes with metal ions. Variations in experimental ‘K’ values at low metal loading lead either to variable fitting parameters K in the simplest model, Eq. (V.8), or are treated by formally introducing 1:2 complexes as in Eq. (V.26). The following is an alternative to variable “constants” K or the controversial concept of variable stoichiometry, e.g. 1:2 complexes.

For illustration, Eu, Am and Cm data in the pH range 5 - 5.5 and at ionic strength 0.1 M were collected from several publications. These data have been obtained using different experimental methods. All experimental data are expressed in terms of ‘K’ and [M] as a common basis. As can be seen in Figure V.1, the experimental data show a consistent pattern. However, it is not possible to model the entire range of data by the simple single site approach (Eq. (V.8)). If we split the data set into the concentration ranges [M] > 10⁻⁹ M and [M] < 10⁻⁹ M, the single site model nicely fits both data sets separately but with two rather different sets of parameters in Eq. (V.8), namely log₁₀ K = 7.5, log₁₀ SCC = -3.2 (dashed line in Figure V.1) and log₁₀ K = 10.8, log₁₀ SCC = -5.0 (dotted line in Figure V.1).

If we want to describe the entire range of experimental data we have to drop the assumption {A2}, and consider more than one kind of ligand site. The total amount of metal bound to the humic substance is given by the sum of metal bound to different ligand sites i

\[ [\text{MHS}] = \sum_i [\text{ML}_i] \]  \hspace{1cm} (V.30)

As before, the total concentration of a given ligand site i is the sum of the concentration
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Figure V.1: Metal concentration dependence of humic complexation. Eu, Am and Cm complexation with humic and fulvic acids. Symbols: Experimental data in the pH range 5.0 - 5.5 and at ionic strength 0.1 M from several publications. PSI: M.A. Glaus, W. Hummel and L.R. Van Loon, Paul Scherrer Institute (1996) unpublished data. Lines: Model calculations using Eq. (V.8), single site model, with \( \log_{10} K = 7.5 \) and \( \log_{10} SCC = -3.2 \) (dashed line) and \( \log_{10} K = 10.8 \) and \( \log_{10} SCC = -5.0 \) (dotted line), or using Eq. (V.33), two site model, with the same parameters (solid line).

\[
\text{of the free ligand site } i \text{ and of the metal bound to humic substance at site } i
\]

\[
[L]_{\text{total, } i} = [L_i] + [ML_i]
\]  
(V.31)

The total concentration of humic substance, \( (HS)_{\text{total}} \), is related to the total concentration of ligand site \( [L]_{\text{total, } i} \) by

\[
(\text{HS})_{\text{total}} \cdot SCC_i = [L]_{\text{total, } i}
\]  
(V.32)

where SCC\(_i\) is the site complexation capacity of binding site \( i \) in mol/g. The single site model (Eq. (V.8)) is then extended to a multi-site model:

\[
^cK = \sum_i \frac{K_i}{1 + K_i \cdot [M]} \cdot SCC_i
\]  
(V.33)

In essence, the multi-site model, Eq. (V.33), considers humic substance as a mixture of simple organic ligands with unknown molecular weights, where each component of the mixture is characterised by two fitting parameters, \( K_i \) and SCC\(_i\).
The simplest version of Eq. (V.33), a two site model \((i = 2)\) contains the two parameter sets derived above (solid line in Figure V.1). The main feature of this model is that it interprets the experimental data by assuming a high concentration of weak sites and a low concentration of strong sites. The weak sites determine the behaviour of humic complexation at high metal loading, whereas the strong sites, even though their concentration is only in the range of a few percent of the weak sites, determine the complexation strength of humic substances at low metal loading, \(i.e\), at trace metal concentrations.

This type of model is very often used in the literature. For example, Li, Victor and Chakrabarti [80LI/VIC] interpret their data on U(IV) and U(VI) complexation with humic, fulvic and tannic acids by graphical analysis (Scatchard plots) in terms of a 2-site model according to Eq. (V.33). Using the same type of graphical analysis, Mantoura and Riley [75MAN/RIL] interpret their data on complexation of Co, Ni and Zn with humic acids of different origins in terms of a 2-site model. Note that their parameter \(n_i\) is the number of metal binding sites per molecule of humic acid. Although not clearly stated in their paper, they must have used an average molecular weight of 5000 g/mol to convert \((\text{HS})_{\text{total}} \text{(g/l)}\) into \(M_{\text{HA}}\), the molar concentration of humic acid. The stability constants derived by Mantoura and Riley [75MAN/RIL] are identical with the \(K_i\) in Eq. (V.33), however, their \(n_i\) has to be multiplied by 0.0002 to be compatible with the definition of SCC \(i\) used here. The complexation behaviour of humic acid towards Eu\(^{3+}\) is described by Caceci [85CAC] in terms of a 2-site model. The data were fitted numerically to Eq. (V.33). In addition, experimental ‘\(K\)’ data are published, which are called \(K^*\) by Caceci [85CAC]. McKnight et al. [83MCK/FED] investigated the copper-complexing properties of aquatic humic substances isolated from eighteen different environments. They did numerical fits using a model containing two types of Cu(II)-binding sites and found that all data sets could be described by one set of constants according to Eq. (V.33). Note that the site complexation capacity SCC \(i\) is given as \(L_i\), moles of Cu(II) binding sites per milligram carbon of aquatic fulvic acid. The complexation of copper(II) with dissolved organic ligands in seawater is interpreted by Van den Berg [84BER4] in terms of two complexing ligands. He did not determine the mass of the dissolved organic ligands, but rather the concentration of Cu(II) bound to organic ligands and the concentration of free copper. Thus, instead of fitting data to Eq. (V.33), Van den Berg [84BER4] used Eq. (V.34), derived by multiplying Eq. (V.33) by \((\text{HS})_{\text{total}}\). Note, that Van den Berg [84BER4] uses the term ‘complexing capacity’, \(C_{Lx}\), for the total concentration of ligand sites, \([L]_{\text{total}}\).

\[
\frac{[\text{MHS}]}{[M]} = \frac{cK}{(\text{HS})_{\text{total}}} = \sum_i \frac{K_i}{1 + K_i \cdot [M]} \cdot [L]_{\text{total}} \quad (V.34)
\]

These examples show, that even though the same conceptual model is used, great care has to be taken when comparing results. Different terms and definitions are used by different authors, and sometimes the total concentration of humic substance is converted into molar units by more or less plausible model assumptions. All these items have to be ‘translated’ to a common basis before any comparisons of data and models can be made.

The good agreement between the solid line for the two-site model in Figure V.1 and the experimental data may be an artifact. There is no obvious reason why binding of metal
ions by humic substances should be dominated by just two different types of sites. A numerically more accurate fit would probably be based on a multi-site model containing more than two sites. For example, Cabaniss and Shuman [88CAB/SHU] quantitatively model copper binding by Suwannee River fulvic acids using a 5-site model according to Eq. (V.33) with ten adjustable parameters. This model fits the data used to calibrate it, quantitatively describes results from other experiments, and can be used to describe data which cover three orders of magnitude of copper concentration and one order of magnitude of DOC. Cabaniss and Shuman [88CAB/SHU] note that a good fit does not imply that the “sites” determined correspond to chemical reality; the parameters may be useful for equilibrium modelling, but should not be used to make inferences about molecular structure.

A disadvantage of multi-site models is the two added adjustable parameters for each additional site. An approach to reduce the number of adjustable parameters is proposed by Mattigod and Sposito [79MAT/SPO]. They select a number of simple organic ligands which are thought to represent the major types of binding sites of humic substances. Specifically, they used nine organic acids as a model for sludge-derived fulvic acid [79MAT/SPO]. This represents a 9-site model according to Eq. (V.33) where all the $K_i$ values are fixed by the selection of a set of aromatic, aliphatic, and amino acids whose functional groups are expected to simulate closely the metal-complexing groups in the fulvic acid fraction of a sewage sludge. Nine adjustable SCC$_i$ parameters remain. These were fitted to a “reference fulvic acid” and the concentration of each model acid is given in terms of the total concentration of ligand sites, $[L]_{\text{total};i}$. The actual $[L]_{\text{total};i}$ or SCC$_i$ parameters have to be calculated from the reference $[L]_{\text{total};i}$ and reference $(HS)_{\text{total}}$ and the actually measured $(HS)_{\text{total}}$.

At a first glance, a huge difference seems to exist between a 9-site model according to Eq. (V.33) with 18(!) adjustable parameters and the mixture model of Mattigod and Sposito [79MAT/SPO] where all parameters are fixed. However, this difference is only apparent. Choosing the reference ligands out of a large set of simple organic acids only replaces the numerical fit of $K_i$ values with a “fit-by-selection” procedure. And fitting the concentrations of these selected simple organic acids to a reference humic substance is equivalent to a fit of SCC$_i$ parameters to a reference humic substance. The degree of freedom is the same in both approaches, only the technique of parameter fitting is different.

V.3.2.5. The continuous distribution models

The heterogeneous mixture labeled “humic substance” may comprise 10, 100, 1000 or more compounds, all with slightly different molecular structure and stereochemistry of their binding sites. There is no theoretical limit of the number of different ligand sites used to represent the metal binding properties of humic substances. In fact, a very large number of different ligand sites characterised by varying parameters $K_i$ may be envisioned in humic binding models. The discrete distribution of sites in the multi-site model discussed above, characterised by site complexation capacities SCC$_i$, may then be
replaced by a continuous distribution of ligand sites, characterised by a differential site complexation capacity SCC($K$), defined as

$$SCC_i = SCC(K) \, dK$$  \hspace{1cm} (V.35)

In the mathematical description of the binding model, the sum of Eq. (V.33) therefore is replaced by an integral

$$cK = \int_0^\infty \frac{K}{1 + K \cdot [M]} \cdot SCC(K) \, dK$$  \hspace{1cm} (V.36)

The actual evaluation of the differential site complexation capacity SCC($K$) depends on the model assumptions. To begin with, one may assume that one kind of binding site predominates the interactions of a metal ion with humic substances. In contrast to our simplest binding model discussed in Section V.3.2.1, we assume that the complexing strength of the ligand site is not a fixed number, but varies around a mean value due to the influence of different substituents and varying stereochemistry in the large number of different molecules comprising “humic substance”. If we therefore drop assumption {A3} (Table V.1), we expect some sort of single-mode distribution of SCC($K$) as function of $K$. Any analytical form of the distribution can be assumed. Following Perdue and coworkers [83PER/LYT2, 84PER/REU] a normal distribution is described by

$$SCC(\log_{10} K) = \frac{SCC_0}{\sigma_{\log_{10} K} \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\log_{10} K - \log_{10} K_0}{\sigma_{\log_{10} K}} \right)^2 \right]$$  \hspace{1cm} (V.37)

where $\log_{10} K_0$ is the mean $\log_{10} K$ value, $\sigma_{\log_{10} K}$ is the standard deviation for the distribution of $\log_{10} K$ values about the mean value, and SCC$_0$ is a proportionality factor for the site complexation capacities in g/mol. Note, that the distribution is defined in logarithmic units of $K$. Thus, when Eq. (V.37) is substituted in Eq. (V.36), the integration variable has to be changed to $\log_{10} K$ and the integral evaluated from minus to plus infinity:

$$cK = \frac{SCC_0}{\sigma_{\log_{10} K} \sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{10^{\log_{10} K}}{1 + 10^{\log_{10} K} [M]} \times \exp \left[ -\frac{1}{2} \left( \frac{\log_{10} K - \log_{10} K_0}{\sigma_{\log_{10} K}} \right)^2 \right] d\log_{10} K$$  \hspace{1cm} (V.38)

No analytical solution for Eq. (V.38) is known, and a numerical solution has to be found for any given value of [M], and given values for the three adjustable parameters $\log_{10} K_0$, $\sigma_{\log_{10} K}$ and SCC$_0$.

A modified version of the normal distribution model is available which remedies this problem. A distribution function was proposed by Sips [48SIP] which closely resembles
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A normal distribution but has the advantage that it can be integrated analytically. The Sips distribution is given by

\[ SCC(K) = \frac{SCC_s \sin(\pi \alpha)}{\pi K^\alpha / K_s + 2 \cos(\pi \alpha) + K_s / K^\alpha} \]  \hspace{1cm} (V.39)

where \( K_s, \alpha \) and \( SCC_s \) are constants. The distribution represented by Eq. (V.39) has a quasi-Gaussian shape with an apex at \( K_s^{1/\alpha} \). \( K_s^{1/\alpha} \) is thus analogous to the mean \( K_o \) of the normal distribution Eq. (V.37), and the index of heterogeneity, \( \alpha \) (0 ≤ \( \alpha \) ≤ 1), is analogous to the standard deviation \( \sigma_{\log_{10} K} \). If this form of \( SCC(K) \) is substituted into Eq. (V.36), a modified Freundlich binding expression is obtained upon (non-trivial !) integration [48SIP]:

\[ cK = \frac{K_s \cdot [M]^{\alpha-1}}{1 + K_s \cdot [M]^\alpha} \cdot SCC_s \]  \hspace{1cm} (V.40)

When \( \alpha = 1 \), corresponding to identical sites which may be mathematically represented by a Dirac delta function distribution of \( SCC(K) \), Eq. (V.40) reduces to the Eq. (V.8) of the simplest model.

In the region of high metal loading close to metal saturation, the ligand sites are predominantly occupied by metal ions, i.e. \( K_s \cdot [M]^\alpha > 1 \), and Eq. (V.40) reduces to Eq. (V.10) for all \( \alpha \) values. In other words, at high metal loading no difference between a simple single-site model and a continuous distribution model is expected. In the region of very low metal loading the free ligand sites predominate, i.e. \( K_s \cdot [M]^\alpha < 1 \), and Eq. (V.40) reduces to

\[ cK = K_s \cdot SCC_s \cdot [M]^{\alpha-1} \]  \hspace{1cm} (V.41)

At low metal loading \( cK \) reaches a constant value only if \( \alpha = 1 \). In all other cases, \( \log_{10} cK \) varies linearly with varying \( \log_{10} [M] \) with slope \( \alpha - 1 \). This increase in \( \log_{10} cK \) with decreasing \( \log_{10} [M] \) is steeper the smaller the parameter \( \alpha \) is, i.e. the broader the distribution of \( SCC(K) \) as function of \( K \).

For illustration, the data of Figure V.1 are presented in Figure V.2 together with a fitted curve based on Eq. (V.40), the Freundlich type binding expression (solid line in Figure V.2 with \( \log_{10} K_s = 5.2, \log_{10} SCC_s = -3.2, \alpha = 0.7 \)). For comparison, the result of the two-site model of Figure V.1 is added (dotted line). As can be seen, the two-step appearance is gone and a smooth dependence of \( cK \) on free metal concentration is obtained. An infinitely increasing \( cK \) coefficient with decreasing metal loading is predicted by this model. This is clearly in contradiction with chemical reality, as there are no infinitely strong binding

---

2 Actually, the derivation of the Sips distribution went the other way round. Sips started from the observation that adsorption of gas molecules on catalyst surfaces can be described by (purely empirical) Freundlich isotherms. By applying an inverse Stieltjes-Laplace transform to the mathematical expression known as Freundlich isotherm, Sips obtained a distribution function which is now known as Sips distribution and which happened to be very similar to the Gaussian normal distribution function [48SIP].
Figure V.2: Metal concentration dependence of humic complexation. Eu, Am and Cm complexation with humic and fulvic acids. Symbols: Experimental data in the pH range 5.0 - 5.5 and at ionic strength 0.1 M from several publications. PSI: M.A. Glaus, W. Hummel and L.R. Van Loon, Paul Scherrer Institute (1996) unpublished data. Lines: Model calculations using Eq. (V.33), two site model, with parameters given in Figure V.1 (dotted line), or using Eq. (V.40), a continuous distribution model, with $\log_{10} K_s = 5.2$, $\log_{10} SCC_s = -3.2$ and $\alpha = 0.7$ (solid line).

sites. An upper limit of binding strength will be reached at some low metal loading, and beyond this limit $K$ is expected to remain constant. Thus, we have remedied the chemically unrealistic two-site model by creating a chemically unrealistic infinite increase of the $K$ coefficient. If we want to solve this new problem, we have to replace the infinite upper boundary in Eqs. (V.36) or (V.38) by a finite boundary. This adds another adjustable parameter to our model, effectively modifying it to a “truncated” continuous distribution model. But we not only increase the number of adjustable parameters, we also lose the advantage of the analytical expression, Eq. (V.40), as no analytical solutions of truncated SCC($K$) distributions are known.

Until now we have assumed that only one class of binding site predominates, according to assumption {A2} (Table V.1). If we drop this assumption by postulating the existence of more than one class of ligands, we arrive at multiple site continuous distribution models. For the simplest case, a two site model, we expect bimodal distributions of SCC($K$) as function of $K$. A pronounced bimodal distribution is actually reported by Perdue,
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Reuter and Parrish [84PER/REU] as the final result of their statistical model of proton binding by humic substances. They found two maxima of SCC(K) around \( \log_{10} K_0 = 4 \) and \( \log_{10} K_0 = 12 \) by extending Eq. (V.38) to a two-site Gaussian distribution model. This result can be interpreted as representing proton binding by carboxylic and phenolic binding sites. Similar results are reported by Nederlof et al. [93NED/WIT] using a double Freundlich binding expression based on Eq. (V.40). They found two maxima of SCC(K) around \( \log_{10} K_0 = 3 \) and \( \log_{10} K_0 = 10 \), both maxima appearing at the edges of their experimental window. Results for metal binding of humic substances are less clear-cut than proton binding. Perdue and Lytle [83PER/LYT2] report results for copper binding by humic substances and state that the “data sets were fit reasonably well by a single-mode Gaussian distribution model (one class of ligands), although minor improvement in the degree of fit was obtained with the bimodal distribution model”. The free copper concentrations in their measurements range between \( 10^{-2} \) M and \( 10^{-6} \) M. In a recent study, Benedetti et al. [95BEN/MIL] extended the free copper concentration down to \( 10^{-14} \) M and found a pronounced bimodal distribution using a Freundlich type binding expression according to Eq. (V.40). Similar results are obtained for Cd, whereas Ca binding can be described by a monomodal Sips distribution [95BEN/MIL].

All these results depend on a priori assumptions about the distribution function SCC(K). If no assumptions are made beforehand about the type of distribution, the function SCC(K) has to be derived from experimental data. Mathematically, finding SCC(K) implies the inversion of Eq. (V.36), which cannot be achieved analytically. Good results are obtained with numerical methods only for very accurate data that cover the whole range of concentrations of interest. By making some approximations it is also possible to solve Eq. (V.36) analytically for SCC(K). Numerous methods have been proposed and applied to experimental data, such as the affinity spectrum method [83SHU/COL, 86DZO/FIS, 86FIS/DZO], the differential equilibrium function [70GAM, 88ALT/BUF], the logarithmic symmetrical approximation [90NED/RIE], and the site occupation distribution function [90BUF/ALT]. These and some other “semianalytical” methods are compared and discussed in some detail in [86DZO/FIS, 86FIS/DZO, 90BUF/ALT, 92NED/RIE]. In an ideal world of accurate data and infinitely wide analytical windows, these methods would allow the derivation of chemically meaningful SCC(K) distributions, which in turn would provide valuable information for the development or selection of an appropriate humic binding model. In reality, however, all these methods suffer severely from artifacts due to narrow analytical windows and spurious peaks in the distribution function generated by experimental errors. The problem of truncated and error prone data sets was a topic of discussion during the last ten years, as documented in [86FIS/DZO, 86TUR/VAR, 90BUF/ALT, 94NED/RIE]. Despite all efforts made to eliminate these problems by using spline functions to smooth the experimental data [86FIS/DZO, 94NED/RIE], or by introducing new methods [90BUF/ALT], it still remains to be seen if these approaches contribute to our understanding of metal-humic binding and promote the development of chemically more realistic and more accurate binding models.
Variations in pH

A general observation made in investigations of metal-humic complexation is that the experimental $K$ values vary with pH. Different concepts were developed to describe, to explain, and to model this observed pH dependence of $K$ values. The ideas can roughly be divided into concepts assuming variable pH dependent concentration of complexing sites and concepts ascribing the behaviour of $K$ values to variable pH dependent conditional stability constants. This pH dependence of conditional stability constants is modelled by empirical functions, by assuming proton exchange reactions or by introducing electrostatic effects.

Empirical functions

In some models the concentration of complexing sites is identified with the maximum concentration of metal ions bound to humic substances. It is observed that the latter quantity, which is proportional to quantities like “complexing capacity” or “loading capacity”, changes with pH. Consequently, the complexing capacity $W$ [95MOU/MOU] or the loading capacity $LC$ [96CZE/KIM] is evaluated experimentally and used to define the amount of humic substance available for complexation under a given set of experimental conditions. The resulting empirical functions of pH, i.e. $W = f(pH)$ and $LC = f(pH)$, are found to be highly non-linear.

A similar approach is chosen by Choppin and coworkers [84TOR/CHO, 95RAO/CHO] who assume that the site complexation capacity, $SCC$, of a humic substance is proportional to the degree of ionisation, $\alpha$, of the humic substance at a particular pH, i.e. $SCC = f(\alpha)$, or more precisely $SCC = PEC \cdot \alpha$, where PEC is the proton exchange capacity or the “total carboxylate capacity” [84TOR/CHO]. Both $\alpha$ and PEC, are evaluated experimentally by pH titration. $\alpha$ is also an empirical function of pH which is highly non-linear [84TOR/CHO].

These concepts implicitly drop assumption {A4}, that the number of active binding sites is constant under varying chemical conditions. Although not always clearly stated (with the commendable exception of [96CZE/KIM]), the common assumption underlying these concepts, is that metal ions may interact only with deprotonated, or dissociated, functional groups of the humic substance. At a given pH, where the potential ligand sites are only partially dissociated, all proton exchange sites, PEC, are not fully available for metal complexation, and thus the experimental $K$ values vary with pH. Metal-proton exchange reactions of the type $M + HL \rightleftharpoons ML + H$, with strongly complexing functional groups like phenolic or alcoholic OH groups, are not considered in this concept. This means that assumption {A5}, no proton exchange reactions, is valid even at increasing pH.

This model seems to work fairly well at high metal loading close to metal saturation. In this parameter range, where the metal-humic interactions most probably are dominated by weak complexes with carboxylic acid groups, a “stability constant” independent of pH is found when the concentration of complexing sites is defined by the empirical loading
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capacity [89KIM/BUC, 96KIM/CZE] or the degree of ionisation [95RAO/CHO]. At trace metal concentrations, i.e. very low metal loading, however, the “stability constants” are found to change drastically with pH even if the concentration of binding sites is defined by the degree of ionisation [84TOR/CHO]. This is strong evidence that metal-proton exchange reactions play some role in this pH/concentration range.

Nevertheless, the pH dependence of conditional stability constants is sometimes described by empirical functions. For example, Torres and Choppin [84TOR/CHO] found that the pH variation of the conditional stability constants $\log_{10} \beta$ for uranyl-humate complexation, corrected for the degree of ionisation, $\alpha$, is a linear function of this parameter $\alpha$, i.e. $\log_{10} \beta = \text{intercept} + \text{slope} \cdot \alpha$. This model just serves as a simple description of experimental data and no explanation of the empirical linear function in chemical terms was attempted by Torres and Choppin [84TOR/CHO].

V.3.3.2. Proton exchange reactions

All concepts discussed so far assume, {A5}, that metal-proton exchange reactions do not influence the metal complexation behaviour of humic substances. On the other hand, it is well known that the formation of strong metal complexes with small organic ligands like salicylic acid or edta involves proton exchange reactions of the type

$$M + HL \rightleftharpoons ML + H$$  \hspace{1cm} (V.42)

with an equilibrium constant

$$K_{\text{exch}} = \frac{[ML] \cdot [H]}{[M] \cdot [HL]}$$  \hspace{1cm} (V.43)

We drop the assumption {A5} and postulate that proton exchange reactions, e.g. with phenolic OH groups, dominate metal complexation with humic substance within a certain pH range. Within this pH range, all free ligand sites of the humic substance are protonated, i.e. $[L]_{\text{total}} = [HL] + [ML]$, and thus the model described by, Eq. (V.8), is modified to

$$^cK = \frac{K_{\text{exch}} \cdot [H]^{-1}}{1 + K_{\text{exch}} \cdot [M]/[H]} \cdot \text{SCC}$$  \hspace{1cm} (V.44)

In the region of high metal loading, the same behaviour of $^cK$ as in the case of the model described by Eq. (V.10) is expected. In the region of low metal loading the protonated ligand sites predominate, i.e. $[HL] > [ML]$ and we expect an increase of $\log_{10}^cK$ with increasing pH with a slope of one:

$$\log_{10}^cK = \log_{10} K_{\text{exch}} + \log_{10} \text{SCC} + \text{p[H]}$$  \hspace{1cm} (V.45)

Metal-proton exchange reactions are often assumed to be the predominant equilibria in the more complex humic binding models. For example, Stevenson [76STE] includes proton
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exchange in his variable stoichiometry model, which is already discussed in Section V.3.2.3. Chemical equilibria in Tipping’s Model V [92TIP/HUR] are also expressed in terms of metal-proton exchanges. In this model, two classes of binding sites are assumed, single proton-dissociating A sites (monodentate) according to Eq. (V.42), and, when the single groups are sufficiently close, bidentate B sites which are assumed to release two protons when complexing a metal ion. Two separate exchange constants for type A and type B sites, $K_{\text{MHA}}$ and $K_{\text{MHB}}$ respectively, are included in Model V as adjustable parameters.

Experimental results for the complexation of humic substance with Eu, Am and Cm at trace metal concentrations may serve as an illustration of the pH dependence of $cK$. Data measured by different authors on humic and fulvic acids from various sources within the pH range 3.8 to 7 at an ionic strength 0.1 M exhibit a very strong pH dependence, even in the acidic pH range (Figure V.3). In Figure V.3, $\log_{10} cK$ increases with pH with a slope of one, which corroborates the assumption of predominating metal-proton exchange reactions according to equilibrium (V.42). However, the interpretation is not unambiguous. Bulk thermodynamic data alone cannot discriminate between a model describing the observed variability of $cK$ by assuming a proton exchange reaction according to equilibrium (V.42) and a model assuming the formation of ternary complexes with $\text{OH}^-$ according to equilibrium (V.46):

$$M + L + \text{H}_2\text{O} \rightleftharpoons M(\text{OH})L + \text{H} \quad (V.46)$$

There are additional chemical arguments which allow a choice between the two models. These go as follows: In the case of U(VI) one observes an increase of $\log_{10} cK$ with pH with a slope of one below pH 5.5 at trace metal concentration [93HIG/KIN]. According to our own experimental results, the increase of $\log_{10} cK$ by slope 1 extends up to pH 10 for both U(VI) and Eu. The hydrolysis of Eu$^{3+}$ and UO$_2^{2+}$ aquo ions commences at completely different pH values, i.e. above pH 4 for UO$_2^{2+}$ and beyond pH 7 for Eu$^{3+}$. If the formation of ternary hydroxo complexes predominated in the pH range investigated here, one would expect that different hydrolysis behaviour would somehow be reflected in the variation of $\log_{10} cK$ with pH. Since this was not observed, we assume proton exchange reactions according to Eq. (V.42) in both cases over the whole pH range investigated.

This simple model fails if it is applied to other metal ions like Ca or Pb, or transition metals like Ni, Co, and Cu. Experimental results of humic complexation with these metals consistently show a pH dependency of $\log_{10} cK$, but with a slope significantly less than one (see for example [77BUF/GRE] or [93HIG/KIN]). One may argue that the measured bulk properties do not reflect a single metal-proton exchange reaction, but a mixture of many slightly different reactions which may or may not release protons while binding a metal ion. The observed net result is an average number, $x$, of protons released during metal binding

$$M + \text{H}_x\text{L} \rightleftharpoons M\text{L} + x\text{H} \quad (V.47)$$

where $x$ may be a non-integer number. This model contains, besides $K_{\text{exch}}$ and SCC, a
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Figure V.3: The pH dependence of humic complexation. Eu, Am and Cm complexation with humic and fulvic acids. Symbols: Experimental data in the range of trace metal concentration and at ionic strength 0.1 M from several publications. PSI: M.A. Glaus, W. Hummel and L.R. Van Loon, Paul Scherrer Institute (1996) unpublished data. The solid line with slope one corroborates the assumption of metal-proton exchange reactions as the dominating complexation process.

\[
\log_{10} K = \log_{10} K_{\text{exch}} + \log_{10} \text{SCC} + x \cdot p[H]
\]  

(Buffler, Greter and Haerdi [77BUF/GRE] included \(x\) in a variable stoichiometry model (see Section V.3.2.3) and determined its value from the titration of samples at constant concentration of the metal ion. They report values of \(x\) between 0.6 and 0.8 for Cu and Pb.

In the foregoing discussion we dropped assumption \{A2\} by introducing a non-integer stoichiometry coefficient \(x\) for proton release. Alternatively, we may drop assumption \{A3\}, and assume that \(K_{\text{exch}}\) has a continuous distribution of values due to the influence of different substituents and varying stereochemistry. If we further assume a Sips
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distribution, Eq. (V.39), then our original continuous distribution model without proton exchange reactions, Eq. (V.40), is equal to

\[ cK = \frac{K_{s,exch} \cdot [M]^{\alpha-1} [H]^{-\alpha}}{1 + K_{s,exch} \cdot ([M]/[H])^\alpha} \cdot SCC_s \]  

(V.50)

At low metal loading, Eq. (V.50) reduces to

\[ \log_{10} cK = \log_{10} K_{s,exch} + \log_{10} SCC_s + (\alpha - 1) \cdot \log_{10} [M] + \alpha \cdot p[H] \]  

(V.51)

In contrast to the concepts discussed so far, in which \( cK \) is independent of the metal concentration at low metal loading, we now have a coupled dependency of \( cK \) on pH and the metal concentration. If \( \log_{10} cK \) increases with pH by slope \( \alpha \), a variation with \( \log_{10} [M] \) of slope \( \alpha - 1 \) is expected. In other words, the “flatter” the pH dependency becomes, the steeper \( \log_{10} [M] \) dependency would be expected.

So far we assumed that metal-proton exchange reactions predominate over the entire parameter range of interest, resulting in a linear pH dependence of \( \log_{10} cK \) to very high pH values. From a chemical point of view this is a rather unrealistic assumption, because beyond some pH range the predominating functional groups may be deprotonated and metal complexation may take place at free ligand sites. This effect may be accounted for in humic binding models as follows: The equilibrium described by Eq. (V.42) can be interpreted as a competition between a simple metal-ligand formation, Eq. (V.3), and a protonation reaction according to

\[ H + L \rightleftharpoons HL \]  

(V.52)

with a protonation constant

\[ K^H = \frac{[HL]}{[H] \cdot [L]} \]  

(V.53)

The total concentration of ligand sites is now the sum of free and protonated ligand sites and metal bound to the humic substance

\[ [L]_{\text{total}} = [L] + [HL] + [ML] \]  

(V.54)

and the model, Eq. (V.8), extends to

\[ cK = \frac{K}{1 + K^H \cdot [H] + K \cdot [M]} \cdot SCC \]  

(V.55)

At low metal loading, \( \log_{10} cK \) as a function of pH now varies between slope one, if all free ligand sites are protonated, and slope zero, if all free ligand sites are deprotonated. The transition between these two regions is determined by the value of the protonation constant \( K^H \).
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Any shape of the log\(_{10}\)\(\epsilon K\) - pH curves can be obtained if we assume multiple sites and extend our single site model, Eq. (V.55), to a multiple site model

\[
\epsilon K = \sum_i \frac{K_i}{1 + K_i^{\text{H}} \cdot [H^+] + K_i \cdot [M]} \cdot \text{SCC}_i
\]  

(V.56)

However, increasing the number of sites increases the number of adjustable parameters by three for each site.

In order to circumvent this parameter increase, one may try to combine the concept of individual protonation constants, Eq. (V.53), with the concept of continuous distributions of stability constants. In general, the resulting two-dimensional distribution functions of \(K\) and \(K^{\text{H}}\) cannot be solved analytically. The numerical evaluation of these expressions is not an insurmountable technical problem, but puts serious obstacles in the way of evaluating conceptual models in terms of chemical plausibility. Only if we assume that both, \(K\) and \(K^{\text{H}}\), have identical distribution functions, thus reducing the two-dimensional case to a one-dimensional one, and assume a Sips distribution, Eq. (V.39), can we obtain an analytical solution. The derivation of this “multicomponent equation” is discussed in detail by van Riemsdijk et al. [86RIE/BOL].

None of the more complicated approaches to model the pH dependence of \(\epsilon K\), as described by Eqs. (V.50), (V.55), (V.56) or multicomponent equations [86RIE/BOL], has been thoroughly evaluated in the literature. If these approaches are used at all, they are incorporated into even more complex models, e.g. [95BEN/MIL], and the reasons for the usual resulting “good fit of experimental data” is not analysed in terms of individual contributions of conceptual “compartments” of the composite model. Whether the general trend of pH and metal concentration effects, found experimentally for a large set of metal ions over a wide range of pH, can be described consistently by any one of the models discussed above or any plausible combination of them, is still an open question.

V.3.3.3. Electrostatic effects

A completely different concept to explain the observed pH (and ionic strength) dependence of experimental \(\epsilon K\) values emerges if the overall charge of a humic macromolecule is considered. The following reasoning was originally developed for sorption of metal ions on solid surfaces, e.g. [90DZO/MOR], but may be also applied with some small modifications to the complexation of metal ions to humic substances.

The basic idea is that the concentrations of protons and free metal ions in the vicinity of humic binding sites are different from the proton and free metal concentrations of the bulk solution. Energy is required to move ions through potential gradients near charged regions of macromolecules, so the overall charge of humic substance affects the tendency of binding sites to coordinate or dissociate protons and metal ions. With increasing negative charge of the humic molecule, caused by progressive dissociation of protonated functional groups with increasing pH, it becomes more difficult to dissociate protons and metal ions. Although it is impossible to separate the chemical and electrostatic contributions to the total binding energy experimentally, it is useful to separate them theoretically in order to
obtain a specific (i.e., chemical) interaction term that does not vary with overall charge, and a variable electrostatic interaction term \[90\text{DZO}/\text{MOR}\].

The total free energy of complexation, \(\Delta G_{\text{total}}^o\), is separated into its component parts

\[
\Delta G_{\text{total}}^o = \Delta G_{\text{int}}^o + \Delta G_{\text{coul}}^o
\]  
(V.57)

where \(\Delta G_{\text{int}}^o\) is the chemical or “intrinsic” free-energy term and \(\Delta G_{\text{coul}}^o\) is the variable electrostatic or “coulombic” term. In other words, the overall complex formation equilibrium

\[
\text{M} + \text{HS} \rightleftharpoons \text{MHS}
\]

\[
\Delta G^o = -RT \ln K
\]  
(V.58)

is separated into an equilibrium with “local” concentration of metal ions, \([\text{M}]_{\text{local}}\), either at the surface of an impenetrable region, or within a penetrable phase,

\[
\text{M}_{\text{local}} + \text{HS} \rightleftharpoons \text{MHS}
\]

\[
\Delta G_{\text{int}}^o = -RT \ln K_{\text{int}}
\]  
(V.59)

and an equilibrium between this “local” concentration and the bulk concentration of ions

\[
\text{M} \rightleftharpoons \text{M}_{\text{local}}
\]

\[
\Delta G_{\text{coul}}^o = Z \cdot F \cdot \psi
\]  
(V.60)

The theoretical expression for the coulombic term, Eq. (V.60), is derived from the electrostatic work in transporting ions through the interfacial potential gradient. Combining Eqs. (V.57) to (V.60) we get

\[
K = K_{\text{int}} \cdot \exp(-\Delta Z F \psi / RT)
\]  
(V.61)

where \(R\) is the gas constant, \(T\) the absolute temperature, \(F\) the Faraday constant, \(\psi\) the electrostatic potential, \(K_{\text{int}}\) an intrinsic (adjustable) equilibrium constant which is assumed not to depend on the overall charge of the humic molecule, and \(\Delta Z\) the change in the charge of the binding site due to the complexation reaction. In the case of simple metal ion coordination, Eq. (V.58), \(\Delta Z\) is simply the charge \(Z\) of the free metal ion. In the case of metal-proton exchange reactions, \(\Delta Z\) is the difference between the charge of the metal ion and the number of protons released.

Eq. (V.61) is the basic expression in all electrostatic models, and all further problems are related to the question of how to evaluate the electrostatic potential \(\psi\). This question is discussed in detail by Bartschat, Cabaniss and Morel \[92\text{BAR}/\text{CAB}\] and the following short summary follows their reasoning. The key variable for calculating the coulombic effect on the free energy of a reaction, the electrostatic potential \(\psi\), is usually obtained as the solution of a Poisson-Boltzmann equation.

When the potential \(\psi\) is small, so that \(\exp(F \psi/RT) \approx 1 + F \psi/RT\), the Poisson-Boltzmann equation can be linearised to an equation with analytical solutions for planar,
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cylindrical, and spherical geometries. The impenetrable sphere concept was first used by Debye and Hückel to derive their well-known limiting laws for the activity coefficients of strong ions in solution. More recently, the Debye-Hückel equation\(^3\) was applied to humic substances by Tipping, Reddy and Hurley [90TIP/RED] and Falck [91FAL]. This Debye-Hückel equation contains three adjustable parameters, the radius of the humic molecule, the distance of closest approach of a small ion to the humic molecule, and the charge in mol/g of the humic molecule. The latter parameter may be estimated from the total charge of the humic substance, measured by pH titration, and the average molecular weight of the humic substance. Whereas the distance of closest approach of small ions is expected to vary little from ion to ion, the radius and molecular weight of a humic molecule are essentially two fitting parameters in the Debye-Hückel equation. The effects of varying these parameters when fitting proton dissociation data of humic substances is discussed in some detail by Tipping, Reddy and Hurley [90TIP/RED].

However, when \(\psi\) is large, as may be the case when considering humic molecules with many deprotonated functional groups at high pH, the linear approximation might be inappropriate.

Unfortunately, the only nonlinear Poisson-Boltzmann equation for which an analytical solution has been found is for an infinite plane with equally distributed charges. This solution was used by Gouy and Chapman in their original theory, which is the basis of surface complexation models describing sorption of ions on mineral surfaces [90DZO/MOR]. The charge on a surface is determined by proton transfer reactions and by surface coordination reactions with other cations and anions. If a diffuse layer of counterion charges is assumed to be located on the solution side of the interface, the relationship between surface charge and potential is fixed by the electrical double-layer theory. According to the Gouy-Chapman theory (for a symmetrical electrolyte with valence \(z\)), the surface charge density \((\sigma, \text{ in C/m}^2)\) is related to the potential at the surface \((\psi, \text{ in volts})\) at 25°C by

\[
\sigma = 0.1174 \cdot \sqrt{c} \cdot \sinh(z \cdot \psi \cdot 19.46)
\]

where \(c\) is the molar electrolyte concentration [90DZO/MOR]. A more general discussion of charge density expressions including asymmetrical electrolytes is given by de Levie

---

\(^3\) Note some potential pitfalls when dealing with equations referring to electrostatic effects. In the older literature, e.g. in Tanford's comprehensive textbook [61TAN], the Debye-Hückel equations and variants thereof are derived in CGS electrostatic units (esu). This not only involves a factor of 4\(\pi\) in the equations, but also the fundamental physical constants like \(\varepsilon_0\), \(\varepsilon\), and \(k\) have different units and different numerical values than in the SI system (see Table II.6). Tipping, Reddy and Hurley [90TIP/RED] and Falck [91FAL], however, just take equations from [61TAN] without stating this fact. In addition, in both publications the formula for the Debye parameter \(\kappa\) is wrongly copied from [61TAN]. Tipping, Reddy and Hurley [90TIP/RED] present an equation (2) for \(\kappa\) which does not refer to the ionic strength \(I\), but to \(N\) ions per cubic centimeter (Eq. 26-16 in [61TAN]). Falck [91FAL] presents an equation (6) for \(\kappa\) where a scaling factor of \(\sqrt{1000}\) is dropped (Eq. 26-32 in [61TAN]) and thus \(I\) is implicitly defined in mol per cubic centimeter. In addition, the numerical value of the Debye parameter at 25°C (in SI units !) is wrong in [91FAL], probably by a factor of \(\sqrt{10}\). In summary, great care has to be taken when considering electrostatic theory from the older literature, otherwise one may easily introduce numerical errors of many orders of magnitude in binding models.
The surface charge density $\sigma$ cannot be measured directly, but is an adjustable parameter in binding models that include the Gouy-Chapman electrostatic term. In principle, $\sigma$ can be evaluated by two methods. The first, more empirical one, considers the total charge of the humic substance, measured as a function of pH by titration. The second method, employed in surface complexation models, calculates the net charge on the surface by mass balance equations of (postulated) surface complexation equilibria [90DZO/MOR]. Both methods need the specific surface area $A$ (m$^2$/g) to convert the total charge of the surface into the surface charge density $\sigma$. In the case of sorption of ions on mineral surfaces some methods are proposed which allow an estimate of the specific surface area within one order of magnitude, at least for pure metal oxides [90DZO/MOR]. The specific surface area $A$ of humic substances has to be treated as an empirical fitting parameter. Due to conformational changes of humic molecules with varying chemical conditions, $A$ is probably not a constant, even for a specific sample, but may vary with pH and the ionic strength.

Modeling humic substances as infinite planes seems to be justified for large humic acid molecules, but is a poor approximation for the smaller size fraction of fulvic acids.

A completely different concept for electrostatic interactions is promoted by Marin-sky and coworkers [86EPH/ALE, 86EPH/MAR, 86MAR/EPH, 89CAB/MOR]. Humic substances are treated as a microphase gel [84MAR/RED2] based on a macroscopic two-phase gel model originally developed for the physicochemical description of synthetic cross-linked polyelectrolytes like ion exchange resins [84MAR/RED]. It is assumed that enough counterions accumulate in the charged gel phase to neutralise it, and based on this electroneutrality assumption, the distribution of protons and metal ions between the gel phase and the bulk solution can be described by Donnan potentials. The Donnan potential term, the ratio of the metal ion activities in the two phases, i.e. $\left\{M\right\}_{gel}/\left\{M\right\}_{solution}$, is used to evaluate the exponential term in Eq. (V.61). For low ionic strength the concentration of counterions in the gel phase is approximately equal to the concentration of charge of the humic substance, and $\psi$ is related to $\rho_0$, the volume charge density of the gel, by Bartschat, Cabaniss and Morel [92BAR/CAB]:

$$\frac{-\rho_0}{I} = \exp\left(-\frac{F\psi}{RT}\right)$$

The concentration of counterions in the gel phase, which, by the electroneutrality assumption, is equal to the volume charge density of the gel, cannot be measured. To calculate this quantity, the total charge of the humic substance, measured by pH titration in mol/g, and the specific volume, $V_{gel}$, of the gel phase in l/g are needed. In the case of macroscopic two-phase gels, the density of the gel can be measured in a pycnometer [84MER/MAR], or the volume of the remaining solution can be measured with a spectrophotometer after adding a macromolecular dye which cannot diffuse into the gel phase [84ALE/ESC]. Both methods lead to an independent determination of $V_{gel}$. In the case of a peat, the volume of the gel phase could only be estimated by assuming that it corresponds to the quantity of water contained by the fully hydrated sample ("wet peat") [80MAR/WOL]. In contrast to ion exchange resins and similar cross-linked synthetic polymers, simple linear
polymers and humic substances are one-phase solutions, and do not exhibit a macroscopic gel phase. However, one may envision the large molecules of linear polymers and humic substances as microparticle gels. The phase boundary of these microparticle gels must be defined arbitrarily [80SLO/MAR]. In other words, the specific volume of a humic substance, \( V_{\text{gel}} \), is a model-dependent adjustable parameter, like the specific surface area, \( A \), in the Gouy-Chapman theory discussed above. Within the scope of Marinsky’s gel model for humic substances, the exponential term in Eq. (V.63), named the “electrostatic deviation term (\( \Delta pK \))” [86EPH/AL, 89EPH/BOR]

\[
\Delta pK = -\frac{F \psi}{RT}
\]  

is derived from experimental data in the following manner: At high ionic strengths (1 M and higher), experimental titration data are found to be insensitive to ionic strength. It is assumed that in this region the electrolyte concentration in the bulk solution and in the gel phase are the same, i.e., the Donnan potential vanishes and thus \( \Delta pK \) is zero. Therefore, the experimental data at high ionic strength are taken as a “reference line” and all deviations of experimental data at lower ionic strength are interpreted as due to the electrostatic deviation term \( \Delta pK \) (see Figure 24 in [86EPH/AL] or Figure 4 in [89EPH/BOR]). In other words, although it is never clearly stated in the publications of Marinsky and coworkers, the specific volume, \( V_{\text{gel}} \), of a humic substance “gel” is considered to be an empirical function of pH and ionic strength and is used to express the deviation between the experimental data at lower ionic strength from the “reference line” at high ionic strength.

All treatments of electrostatic effects discussed so far can be considered as limiting cases, or special solutions of the Poisson-Boltzmann equation, limited to small potentials as in the Debye-Hückel theory, or to infinite flat interfaces as in the Gouy-Chapman flat plate model or Marinsky’s gel model. Unfortunately, all more general cases of the Poisson-Boltzmann equation do not have analytical solutions and we must resort to numerical methods for their solution. The case of rigid impenetrable spheres of arbitrary electrostatic potential is described by de Wit et al. [90WIT/RI], and both penetrable and impenetrable spheres and their limiting cases are discussed in detail by Bartschat, Cabaniss and Morel [92BAR/CAB]. In the case of an impenetrable sphere, the relevant charge parameter is \( \sigma \), the surface charge density on the sphere, which is assumed to be uniform. In the case of a penetrable sphere, the relevant charge parameter is \( \rho_0 \), the density of the charge contained in the volume of the sphere in the absence of counterions. In both cases the charge parameters can be evaluated from experimental titration data by assuming an average radius and an average molecular weight of the humic substance. If size distributions are to be considered, a third model-dependent parameter enters the game, to describe the relationship between the size of the humic molecule and the charge parameter, \( \sigma \) or \( \rho_0 \). If it is assumed that the number of charged sites is proportional to the molecular weight and that the molecular weight of the molecule is proportional to its volume, the volume charge density \( \rho_0 \) of the penetrable sphere will not vary with size. In the case of the impenetrable sphere, the surface charge density \( \sigma \) will increase in direct proportion to the radius of the humic molecule. However, additional assumptions are
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hidden here not stated by Bartschat, Cabaniss and Morel [92BAR/CAB], namely that proportionality between the number of charged sites and the volume holds also for an impenetrable sphere and that all these charged sites contribute to the surface charge. By contrast, if we assume that the number of charged sites is proportional to the surface area of the humic molecule, the surface charge density $\sigma$ will not vary with size. As is shown by Bartschat, Cabaniss and Morel [92BAR/CAB], both the penetrable and impenetrable sphere models can elegantly describe the effect of size distributions and provide an intermediate solution for medium sized molecules not described well by either Debye-Hückel or polyelectrolyte models. The behaviour of such molecules is of the Debye-Hückel type for small-sized molecules, and is described as either the Donnan model (penetrable spheres) or the Gouy-Chapman model (impenetrable spheres) when their radius becomes very large. As in all other approaches towards more “realistic” humic binding models discussed in the preceding sections, the advantage of considering size distributions of humic molecules is offset by the increase of the number of empirical fitting parameters in the model.

A more general problem inherent in all the electrostatic concepts is the question, “What is the ‘surface’ or the ‘volume’ of a humic molecule?”. From the viewpoint of macroscopic properties, e.g. the filtration behaviour of humic colloids, envisioning humic substance as composed of spherical particles is perfectly valid. On the microscopic level, metal-humic bonding is described using functional groups, or “local” molecular properties. Electrostatic effects on macromolecules are described on a scale between these two extremes. The geometrical distribution of charges in the near and intermediate neighborhood of a chosen local reference point influences the binding properties of this functional group. As the molecular structure of humic substance is not known, we cannot infer the geometrical distribution of charges in the intermediate neighborhood from local functional groups. What may appear to be spheres from a distance will blur when we “approach” our objects of research, and finally might look more like cotton wad than like billiard-balls. In fact, humic substances may be described in terms of fractal geometry over about two orders of magnitude in size [93RIC/LIN, 94OST/MOR]. Fractals are geometric representations of strongly disordered systems with structures that can be described by non-integral dimensions [94SEN]. A fundamental tenet of fractal geometry is that disorder exists at any characterisation scale used to examine the substance. Regardless of the “magnification” used, the disorder of a fractal object cannot be resolved. From this perspective, disorder is seen as an inherent characteristic of a fractal material rather than as a perturbation phenomenon forced upon it. Experimental results show [93RIC/LIN, 94OST/MOR] that humic substances can be described as fractal materials exactly in the size range that causes electrostatic effects on metal-humic binding. Thus, the mental construct of humic molecules as simple geometrical objects having well-defined “surfaces” and “volumes” may be quite inappropriate. But no attempt has yet been made to model electrostatic effects in terms of fractal geometry.

To circumvent the geometrical problems, one may resort to a purely empirical treatment of electrostatic effects. In an early approach of this type Wilson and Kinney [77WIL/KIN]
used the empirical relation

\[ 2\omega Z = F\psi/RT \]  \hspace{1cm} (V.65)

where \( \omega \) is the electrostatic interaction factor and \( Z \) is the average charge on a humic molecule at a given pH. The average charge \( Z \) cannot be evaluated without knowledge of the average molecular weight of the humic molecules. If one assumes that protons are the only cationic species in solution and that only one type of carboxylic acid groups is present, the molecular charge at a given pH can be represented as

\[ Z = -\alpha \cdot n_{\text{COOH}} \]  \hspace{1cm} (V.66)

where \( n_{\text{COOH}} \) is the (not measurable) total number of carboxylic acid groups per molecule, and \( \alpha \) is the (measurable) fraction of species dissociated. As a consequence, the product \( \omega \cdot n_{\text{COOH}} \) can be derived as an empirical fitting parameter from titration curves [77WIL/KIN]. However, the product cannot be resolved further without additional model assumptions, e.g., of the average molecular weight.

More recently, Tipping used the empirical relation, Eq. (V.65), in his Model V [92TIP/HUR], and defined the electrostatic interaction factor \( \omega \) as

\[ \omega = P \cdot \log_{10} I \]  \hspace{1cm} (V.67)

where \( I \) is the ionic strength and \( P \) is an adjustable parameter for optimisation. In contrast to the product, \( \omega \cdot n_{\text{COOH}} \), in [77WIL/KIN], we have now two independent fitting parameters in Model V [92TIP/HUR], the average molecular weight of the humic molecule and the purely empirical parameter \( P \).

A final remark on electrostatic effects: Pure polyelectrolyte models assume a single repeated functional group, i.e., assumptions \{A1\} to \{A5\} are valid, and all measured pH variations of \( \cdot K \) are thought to be due to electrostatic interactions. This is a valid description of synthetic polyelectrolytes, but humic substances are more complex. Therefore, humic binding models usually combine electrostatic effects with functional group heterogeneity in one way or another. A few examples may illustrate this point. In Morel’s "oligoelectrolyte model" [92BAR/CAB] electrostatic terms are combined with a multiple site model. Tipping’s “Model V” [92TIP/HUR] contains electrostatic terms and discrete distributions of two classes of metal-proton exchange sites. Van Riemsdijk and coworkers [90WIT/RIE] propose a humic binding model which comprises electrostatic interactions and continuous (Sips) distributions of binding sites.

V.3.4. Variations in ionic strength

The variation of experimental \( \cdot K \) values with ionic strength is a general observation made in investigations of metal-humic complexation. The ideas developed to model the measured ionic strength effects can be divided into concepts assuming that the concentration of complexing sites is dependent on ionic strength and concepts ascribing the behaviour of
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\(K\) values to conditional stability constants that depend on ionic strength due to electrostatic effects. All models that account for both pH and ionic strength effects have already been discussed in the preceding section. Here we focus solely on the special ionic strength aspects of these models.

V.3.4.1. Empirical functions

In some of the models the concentration of complexing sites is identified with the maximum concentration of metal ions bound to humic substance. It is observed that this is proportional to quantities like “complexing capacity” or “loading capacity”, and changes with varying pH and ionic strength. Consequently, the complexing capacity \(W\) \cite{Moulin} or the loading capacity \(LC\) \cite{CZE} is evaluated experimentally and used to define the amount of humic substance available for complexation under a given set of experimental conditions. The resulting empirical functions of pH and ionic strength, \(W = f(pH, I)\) and \(LC = f(pH, I)\), are found to be non-linear in pH, but little was known about their ionic strength dependence until recently.

Measurements are reported for the complexation of Cm(III) with humic acid in 0.1 M and 0.001 M NaClO\(_4\) at pH 5. \(W\) values of 1.2 and 1.6 meq/g, and \(\log_{10} β\) values of 8.5 and 8.01/l eq, respectively, were found by Moulin et al. \cite{Moulin}. All other measurements of Moulin and coworkers were carried out in 0.1 M electrolyte medium \cite{Moulin}. Additional data have been reported for the complexation of Am(III) with humic acid in 0.1 M and 1.0 M NaClO\(_4\) at pH 6 \cite{KIM}. Two almost identical complexation constants were derived from these two data sets. Almost all later investigations of Kim and coworkers were made only in 0.1 M NaClO\(_4\), but the claim of the complexation constants “being independent of ionic strength” is repeated also for other metal ions like neptunyl and uranyl without experimental verification \cite{SEK, BUC}. Recently, the effect of ionic strength on the complexation of Am(III) and Cm(III) by humic acid was investigated at pH 6 \cite{CZE}. The ionic strength \(I\) was varied from 0.001 M to 5.0 M NaClO\(_4\) and the loading capacity \(LC\) was found to change with \(I\) according to \(LC = \text{intercept} + \text{slope} \cdot \sqrt{I}\). In contrast to earlier claims, an ionic strength dependence of the complexation constants was observed which is larger than the scatter of the experimental data.

V.3.4.2. Electrostatic effects

All electrostatic model concepts discussed in Section V.3.3.3 were developed mainly to “correct” measured data for ionic strength effects. Authors of the different electrostatic models regard concomitant pH effects as less important. The reason for this emphasis on ionic strength effects is the hope, that the “intrinsic” stability constants, \(K_{\text{int}}\), of Eq. (V.61) will turn out to be independent of ionic strength (and pH) at the end of successful modelling, so that they can be treated in the same way as the thermodynamic stability constants, \(K^\circ\), of simple metal-ligand equilibria. This hope has failed so far for two reasons.
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First, at constant pH the Gouy-Chapman flat plate model and the Donnan gel model predict that the apparent stability constant \( \log_{10} K \), Eq. (V.61), is proportional to \( \log_{10} I \)

\[
\log_{10} K = \text{const} - \Delta Z \cdot \log_{10} I \quad (V.68)
\]

provided that the geometric parameters of these models do not vary greatly with ionic strength. The same relation holds for spherical models as long as the spheres have a sufficiently large radius. The model approaches Debye-Hückel behaviour only for small spheres, and, under those conditions, the variation of \( \log_{10} K \) with \( \log_{10} I \) becomes less pronounced [92BAR/CAB]. In general, experimental data do not behave according to this model prediction. For example, Ephraim et al. [86EPH/ALE] modified their Donnan gel model by introducing a purely empirical “fractional contribution of end and charged surface effects in the molecule” in order to explain, why they found a much smaller variation of \( \log_{10} K \) with \( \log_{10} I \) for protonation equilibria of fulvic acid than predicted by the model. The same problem in copper binding data, but combined with large ionic strength variations, was described by Bartschat, Cabaniss and Morel [92BAR/CAB] assuming that the protons bind to small molecules, and copper ions bind to large molecules of the same fulvic acid sample. Their conclusion from this modelling exercise is that “if proton and metal binding are dominated by different size fractions (and this seems to be the only way to explain the data sets), it is futile to try to apply electrostatic information extracted from a pH titration (such as conclusions about size and charge of molecules) to a metal titration”. This is in marked contrast to Tipping’s Model V [92TIP/HUR], where pH titration data are used to “calibrate” the model. When modelling metal complexation data, these parameters remain fixed and only two intrinsic stability constants per metal ion are fitted. In summary, according to [92BAR/CAB] and [92TIP/HUR] there are insufficient data available to properly evaluate ionic strength effects and to resolve the above mentioned contradictions. The “intrinsic stability constants” reported by various authors still have to be regarded as model dependent adjustable parameters rather than “true” thermodynamic constants.

Even if this problem could be resolved, a second obstacle prevents a direct comparison of “intrinsic” stability constants, \( K_{\text{int}} \), with thermodynamic stability constants, \( K^\circ \), of simple metal-ligand equilibria. As discussed by Bartschat, Cabaniss and Morel [92BAR/CAB] the remaining important difference is the reference state for the binding constants. In the Debye-Hückel theory the electrostatic potential \( \psi \) has a finite value at zero ionic strength, and this value is included in the “intrinsic” binding constant, \( K^\circ \), by defining activity coefficients of exactly 1 at ionic strength zero. In the case of the impenetrable sphere model [92BAR/CAB], one also could define constants that use zero ionic strength as a reference state. However, this is impossible for other geometries, infinite planes and cylinders, for which the surface potential approaches infinity as the ionic strength approaches zero. Therefore, electrostatic models for macromolecules do not “subtract out” the contribution at zero ionic strength. Hence, the reference state for the macromolecule is the condition where \( \psi \) is actually zero. Then, and only then the apparent binding constant \( K \) of Eq. (V.61) equals the intrinsic binding constant \( K_{\text{int}} \). In order to be able to compare \( K_{\text{int}} \) values with stability constants of simple ligands, the latter have to be transformed
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to a reference state of zero potential. From a mathematical point of view, the reference state of zero potential is reached as the ionic strength approaches infinity. Consequently, Bartschat, Cabaniss and Morel [92BAR/CAB] propose to “correct” thermodynamic constants, $K^\circ$, with activity coefficients calculated by the Debye-Hückel equation at infinite ionic strength. Although mathematically correct, this procedure ignores the fact that the electrostatic theory fails at high ionic strength due to the increasing importance of non-coulombic interactions. The difficult problems of ionic strength corrections beyond the “Debye-Hückel concentration range” are discussed in detail in Chapter IX. From a practical point of view, the apparent binding constant cannot be distinguished from the intrinsic binding constant, $K_{\text{int}}$, at sufficiently high ionic strength. What is “sufficiently high”? In the scope of Marinsky’s gel model, an ionic strength of 1 M is used implicitly as reference state [86EPH/ALE, 89EPH/BOR], but the topic is not discussed any further. In summary, the problem of reference states seems to be largely ignored. Apart from the above mentioned proposals no discussion of this topic has been found in the literature concerning humic binding models.

V.3.5. What is the best humic binding model?

At the end of this survey of concepts and approaches to the binding of metal ions with humic substances, the reader might like some recommendations concerning the “best” humic binding model. Papers presenting reviews and extensive numerical testing of different models usually conclude that the problem of metal-humic complexation is not yet solved in a satisfactory manner, and that a better humic binding model still waits to be developed. This ideal model should be chemically correct, numerically accurate and simple to use in predictive modelling. Is there any hope that we may see this ultimate humic binding model? The answer is simply no! This unconditional no is based on the idea that there exists a kind of “uncertainty principle” for humic binding models which may be stated as follows:

It is not possible to achieve an accurate and simple description of metal-humic binding.

Accurate in this context does not only mean the numerical accuracy of fitted and predicted results, but also the chemical correctness of the conceptual model. The term “simple” means simplicity when using the model for solving “real world” problems. This has two aspects: the amount of experimental data needed to calibrate a model with respect to the special problem under study, and the mathematical simplicity of the model. The often debated issue of mathematical simplicity of a model is judged to be a problem of decreasing importance in the age of powerful personal computers. Even the most complicated mathematical model needs to be integrated into user-friendly software just once. Then the user is not forced to bother with computational details anymore. On the other hand, if a model requires many site-specific data that requires an elaborate time and money-consuming effort to collect, the model cannot be termed “simple” regardless of its degree of mathematical simplicity.
The ultimate microscopic chemical model of humic bonding requires a detailed description of the molecular structures of site-specific mixtures of large but varying numbers of natural organic compounds. To attain this level of knowledge is hardly feasible, even in a very ambitious research program. Ignoring reality for a moment, we may dream of reaching this utopian goal by some not yet developed experimental techniques. Then we would end up with the most complicated humic binding models, because we would have to redo the entire sequence of site-specific molecular structure determinations for each and every case under study in order to apply this “detailed molecular binding model” in its full beauty and accuracy. Any attempt to decrease the load of experimental work needed to calibrate this model would lead to an “averaged molecular binding model” in which the individual molecular features are replaced by averages within certain parameter ranges. The prize for this decrease in experimental cost, which is a gain in terms of simplicity, is a concomitant loss in chemical and numerical accuracy of the model.

If this (hypothetical) process of averaging of molecular properties is driven far enough, we finally reach the realm of the humic binding models in use today. The common feature of these models is that they describe the heterogeneity of humic substances by empirical distributions of molecular properties. The distributions are considered in terms of distributions of equilibrium constants leading to “affinity spectra” or “differential equilibrium functions”, or in terms of molecular size distributions influencing “electrostatic terms” etc., as already discussed in the preceding sections. Compared to our hypothetical “detailed molecular binding model” these models are already far from chemical and numerical accuracy but the experimental effort needed to calibrate them is on the verge of current technology. Thus, leaving utopia and coming back to reality, these “site specific distribution models” are at present those of highest accuracy and “best value for invested research money”.

If we are heading towards simpler models, the process of averaging must go on. This can be done in different ways. The continuous distributions may be replaced by discrete values. Alternatively, some sort of “averaged distribution functions” may be used, which to a certain degree level out the heterogeneity of samples of different origin. Of course, any combination of discrete values and continuous distribution functions may be used as well. In any case, the simplicity of the model is increased at the expense of accuracy. Reaching the extreme case of averaging, all adjustable parameters of the humic binding model are fixed, and we describe some sort of “global average humic substance”. Now the simplicity is at its maximum, but the chemical and the numerical accuracy are both very low.

In summary, there is no such thing as the “best humic binding model”. We always struggle with the tradeoff between accuracy and simplicity. The choice of the “best model” depends on the intention of the modeller, and the purpose of the model. In the following, problem solving strategies are outlined for two cases: models used as research tools, and models used as tools to assess behaviour in nature.
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V.4.1. Models used as research tools

Scientific research projects on humic substances usually aim at increasing our understanding of chemical features and processes governing metal-humic interactions. Within such projects binding models are important research tools. In an ideal case, several different models may be analysed theoretically and tested by comparison with measurable quantities. Hence, experimental data may validate or refute the various model assumptions. In an iterative process, model assumptions and experimental procedures are refined until a satisfactory description of metal-humic interactions is reached. In the real world of limited funding, however, this iterative process is usually stopped by practical constraints. In addition to economic limitations there are two other potential obstacles to progress. First, many scientists adopt a favorite idea at some stage of their work and dwell upon this idea in their further research. Different “schools” develop this way. If these schools tend to ignore each other instead of engaging in open scientific dispute, there is a real danger that progress will be limited. Second, the result may be ambiguous if too small a data set is used to test the various models. A typical example is found in [84CAB/SHU], where eight different models were used to analyse the experimental results of a copper-into-ligand titration of estuarine dissolved organic matter. The metal titration was carried out at a single fixed pH and ionic strength. As it is shown by Cabaniss, Shuman and Collins [84CAB/SHU], the eight models all fit this small data set well, in spite of their being based on contradictory assumptions.

In summary, in order to achieve a deeper understanding of metal-humic binding, a thorough analysis of contradictory conceptual models is needed based on large experimental data sets, comprising different metal ions with sufficient variation in key parameters like metal concentration, pH and ionic strength. Using humic binding models as research tools in this way leads to chemically and numerically more accurate descriptions of metal-humic binding at the expense of simplicity. Examples of this type of research tools are the “differential equilibrium function” approach of Buffle [88ALT/BUF] designed to explore the distribution of binding sites, Marinsky’s “unified physicochemical description of complexation equilibria of natural organic acids” [86EPH/ALE, 86EPH/MAR, 86MAR/EPH] aiming at a consistent description of binding site heterogeneity and electrostatic effects, the “oligoelectrolyte model” of Morel [92BAR/CAB] emphasising the molecular size heterogeneity of humic substances, or models such as the recently published Non-Ideal Competitive Adsorption (NICA) model [95BEN/MIL] developed by van Riemsdijk’s group to explore the chemical heterogeneity of humic substances with respect to competitive binding processes.

Tipping’s Model V, “a unifying model of cation binding by humic substances” [92TIP/HUR, 94TIP] is a research tool on the verge of being an assessment tool. The model includes something of each of the concepts discussed in Section V.3: binding site heterogeneity, metal-proton exchange equilibria, electrostatic terms accounting for charge, and ionic strength effects and counterion accumulation. In addition, metal ion competi-
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tion effects can be explored with this model [93TIP]. As a research tool, Model V contains a large number of adjustable parameters. However, in order to cope with the limited experimental data available, most of these parameters are fixed at “reasonable” values. The remaining parameters are adjusted by analysing large numbers of experimental data sets [92TIP/HUR, 93HIG/KIN, 93TIP2] with the hope of extracting from them a data base of “best values” defining a sort of “global average humic substance”. Whether this approach will finally result in a valuable assessment tool or not, remains to be seen.

V.4.2. Models used as assessment tools

Assessment of metal behaviour in the environment is a task rather different from basic research. Here, the metal-humic interaction is just one feature out of many others to be considered in assessing the behaviour of environmental systems. For example, to develop concepts for the remediation of metal-polluted areas or to assess the performance of future waste repositories, models which predict orders of magnitude are generally sufficient. Of course, models predicting metal-humic interactions with higher accuracy might be welcome, but if the amount of site-specific data needed to calibrate these models exceeds a certain limit they cannot be used in assessments of environmental system behaviour. In the case of large metal-polluted areas important geochemical parameters, like pH, DOC and metal concentrations, may show considerable spatial variations. A time and money-consuming experimental program to characterise in detail the properties of humic substances in such areas is usually not feasible, if there is no convincing evidence that humic substances have a strong impact on the environmental system behaviour. Likewise, in the first phase of the performance assessment of future waste repositories, site-specific data are usually scarce and imprecise. Economic constraints require a concentration of efforts on the main features governing the safety of the planned repository. However, decisions on which types of data collection one should spend most time and money must always to be made on the basis of incomplete data. A problem-solving strategy concerning the possible impact of metal-humic interactions on the safety of a repository of toxic chemical or radioactive waste is outlined in the following.

V.4.2.1. The “conservative roof” approach for performance assessment

In performance assessment the ultimate goal is not to develop the most realistic model of a system or of certain effects, e.g., of humic substances on metal speciation, but to estimate the maximum negative influence of the process on a property of the system, such as the safety of a waste disposal site. In other words, we are interested in a conservative estimate

4 The meaning of the term “conservative” strongly depends on the scenario (the type of physical/chemical system) being considered. In performance assessments, we take a “conservative” estimate to be one that leads to an overestimate of the total concentration of a metal in the liquid phase, leading to a maximum value for the mass being transported. If only the mobile fraction of the humic substances is taken into account, and the total metal concentration in the liquid phase is controlled by either the solubility of a solid phase or by sorption on mineral surfaces, an overestimate of the amount bound to humic substances will lead to an overestimate of the amount in the liquid
of the influence of humic substances on the speciation of toxic metals or radionuclides. Therefore, it is not necessary that binding models for performance assessment reflect every subtle detail of metal-humic interactions. Even if they are wrong by orders of magnitude, they may still be useful in safety analyses, as long as it can be shown that the models overestimate the influence of humic substances on metal ion speciation.

Going back to the example of humic complexation with trivalent lanthanides and actinides, a synopsis of experimental data transformed to a common basis of $\log_{10} K$ values reveals a consistent picture of the variation of $\log_{10} K$ with metal concentration and pH (Figure V.4). In the range of low metal loading, $\log_{10} K$ increases with decreasing free metal concentration and seems to approach constant values at very low metal loading. The effect of pH is quite pronounced in this region (see also Figure V.3), whereas in the range of high metal loading the influence of pH is negligible. If we are interested in a very simple mathematical description of these data, a single site model including a metal-proton exchange reaction would be appropriate (Eq. (V.44)). This model can be calibrated with a minimum number of experimental data: (1) The site complexation capacity, SCC, is derived from data at high metal loading in Figure V.4 by applying Eq. (V.10), and (2) the exchange constant $K_{\text{exch}}$ is determined at trace metal concentration (Figure V.3) using Eq. (V.45). In both cases we adjust these parameters to reproduce maximum values rather than mean values of the available experimental data, in order to get conservative estimates. As a result of this procedure, the conservative estimates cover the experimental data like a “roof”. Actually, the expression “the conservative roof” approach was born when for the purpose of visualising Eq. (V.44) a three dimensional plot of the log $K$ surface as function of pH and log $10[M]$ was created the first time (Figure V.5). All measured data are located at, or somewhat below, the surface of the conservative roof. At trace concentration levels and in the range of high metal loading, the conservative roof is very close to the observed experimental data. In the range of intermediate metal concentration, the simplistic model overestimates the experimental data by up to two orders of magnitude at pH 4 and 5. Hence, a similar overestimation is also expected at higher pH regions of parameter space.

Because the conservative roof approach is intended for use in performance assessment, its main feature is a conservative estimate of the metal-humic binding. Which detailed humic binding model is used to reach this goal is immaterial, as long as it remains simple enough to be “conservatively” calibrated with the (usually few) available experimental phase, which is conservative. The “conservative roof” approach is based on this scenario. On the other hand, if the total metal content in the liquid phase is limited by the amount available for transport, i.e. if its concentration is not solubility-limited and sorption is negligible, the amount of metal-humic binding, or of complexing with any other substances in the liquid phase, will not affect the amount being transported. Likewise, if only the immobile fraction of the humic substances is considered, and the metal concentration is solubility controlled, metal-humic binding will not influence the amount in solution. In both scenarios the term “conservative” is meaningless. By contrast, if the metal concentration is not solubility limited and only the immobile fraction of the humic substances is considered, an increase in metal-humic binding will lower the amount available for transport in the liquid phase. An overestimate of the amount of metal-humic binding in this case will not be conservative.
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Figure V.4: A synopsis of experimental data of Eu, Am and Cm complexation with humic and fulvic acids at ionic strength 0.1 M. In the range of low metal loading, $cK$ increases with decreasing free metal concentration and seems to approach constant values at very low metal loading. The effect of pH is quite pronounced in this region (see also Figure V.3), whereas in the range of high metal loading the influence of pH is negligible.

![Graph showing the relationship between pH and complexation constant (cK) with metal concentration (log [M]). The graph includes data points for pH 3 to pH 7, showing trends for different pH values.](image)

...data. The example shown above is a well investigated case. For most other metals of interest experimental data are scarce, especially at trace concentrations and at high pH. For a sound calibration we need some data in the range of high metal loading and at trace concentration levels. Calibration at high concentrations alone is not enough, because the resulting model predictions will certainly underestimate humic complexation at trace level (and at neutral to slightly alkaline pH) by several orders of magnitude. This can easily be seen from Figure V.5, if the calibration had been done only with data from the “island” at low pH and high metal loadings!

Speciation calculations using any well-calibrated conservative roof model reveal the maximum effect of humic substances on the speciation of toxic metals or radionuclides. If no significant influence is predicted by the first exploration using a conservative roof model, the calibration procedure proposed for “conservative roof” - type models, using a site complexation capacity obtained for high metal loading and adjusting an exchange constant at trace metal concentration, is inconsistent from the viewpoint of models used as research tools which aim at a deeper understanding of humic binding. However, for the purpose of estimating maximum effects of humic binding in performance assessment any set of parameters is appropriate, as long as it ensures a conservative calibration of the chosen model.

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5 The calibration procedure proposed for “conservative roof” - type models, using a site complexation capacity obtained for high metal loading and adjusting an exchange constant at trace metal concentration, is inconsistent from the viewpoint of models used as research tools which aim at a deeper understanding of humic binding. However, for the purpose of estimating maximum effects of humic binding in performance assessment any set of parameters is appropriate, as long as it ensures a conservative calibration of the chosen model.

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Figure V.5: The “conservative roof” approach for performance assessment. A single site model including a proton-exchange reaction (Eq. (V.44)) is calibrated with the experimental data in Figure V.4. The parameters $\log_{10} K_{\text{exch}} = 4$ and $\log_{10} \text{SCC} = -3$ are adjusted in such a way that Eq. (V.44) reproduces maximum values rather than mean values of the available experimental data. All measured data (dark areas) are located at, or somewhat below, the surface of the conservative roof.
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model in the pH and metal ion concentration ranges of interest, humic substances can safely be ignored when describing the properties of the system.

However, if the particular conditions are such that the conservative roof model predicts a significant influence of the humic substances, the situation must be examined further. If enough experimental data are available, a more sophisticated humic binding model may be used, resulting in a more complicated but less conservative roof. In the (usual) case the lack of data can be constrained by a few well designed experiments in this critical region of the parameter space, which subsequently may also lead to a more sophisticated conservative roof model. In both cases, limited experimental effort will identify and constrain the problem, and any decision how to proceed would be based on a sound evaluation of all available information.

Unfortunately, real world systems tend to show much more complicated behaviour than simple laboratory systems. In performance assessment one has to consider all relevant features and processes, not just the few thoroughly investigated in laboratory experiments. In the following, we take some cautious steps out of the well illuminated laboratories into the darkness of real world groundwater systems.

V.4.2.2. Competition of other complexes

The interaction of metal ions with humic substances is usually treated within the scope of equilibrium thermodynamics. Therefore, in principle, all other equilibria in the chemical system are expected to influence these interactions. The predicted magnitude of the competitive effects depends not only on equilibrium constants and the chemical composition, but also on the binding model chosen. This model dependence of predicted competitive effects represents a major difference from chemical equilibrium problems comprising only small ligands. The latter problems are usually solved by classic speciation calculations and the uncertainty of the results depends solely on the completeness and accuracy of the set of stability constants used in the calculations. Binding models for humic substances, on the other hand, include a number of assumptions in addition to those of the standard thermodynamic equilibrium model. These additional assumptions, characterising the different binding models, cause a substantial spread in the predicted effects of competition. In extreme cases, as is discussed in the following, one binding model predicts large effects, whereas another model predicts no competition at all.

From the viewpoint of basic research, the discussion of competitive effects could stop here with the rather general statement: “It depends.” From the viewpoint of performance assessment, however, the situation is not without promise. Here, it is enough to demonstrate that a certain class of competition reactions may decrease metal-humic interactions in all cases, independent of the binding model, if competition has any influence at all. A conservative binding model may then safely ignore this, if not enough experimental data are available to include the effects in a proper way into the model.

In the following, the main competitive effects are divided into three classes, although all of them are coupled: Direct competition of other cations, competition of other anions with binding sites, and competition of mineral surface sites with organic binding sites. As we
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discuss these effects separately, a more and more complex picture of coupled interactions will emerge.

V.4.2.2.1. Competition of other cations like Ca$^{2+}$ and Al$^{3+}$ with toxic metal ions

The most obvious competitive effect is the competition of toxic metal ions with other cations like Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, and Al$^{3+}$. These cations are major constituents of common groundwaters and they are known to form rather stable aqueous complexes with small organic molecules. Therefore, they have also to be considered as effective competitors for the binding sites of humic substances. The predicted effect of varying the concentrations of these cations on metal ion uptake by humics depends strongly on the binding model chosen. For a single site model, which treats humic substances as similar to small organic ligands, direct competition of, for example, Ca$^{2+}$ with all other metal ions is expected. In groundwaters the concentration of Ca usually exceeds toxic metal concentrations by several orders of magnitude, and an increase in Ca concentration may substantially decrease the uptake of these metal ions by humic substances. If a multiple site model is used, the predicted effect depends on the affinities of the various sites for Ca and other metal ions. In an extreme case, the humic substance may be thought of as a mixture of highly specific organic ligands, some exclusively binding toxic metal ions, others only attracting Ca. Then, the influence of a varying Ca concentration on the uptake of other metal ions may vanish.

The theoretical predictions of competitive effects of cations thus range from very strong to zero. The question now arises, is there any way to obtain more precise predictions? Yes, there is, if we consider chemical systematics, especially linear free energy relationships. For a detailed discussion of linear free energy relationships and other correlations see Chapter III.

Again using the example of trivalent lanthanides and actinides, linear free energy relationships correlating the stability constants of small organic ligands of Eu with Al and Ca reveal a rather consistent picture. The stability constants of Eu and Al organic complexes are found to be of the same order of magnitude. The general conclusion drawn from this observation is that the complexation strength of these two cations is expected to be of comparable magnitude in humic substances as well. We do not expect grossly differing affinities for Eu and Al, even when the nature and stereochemistry of functional groups in humic substances vary. Therefore humic binding models will not only predict direct competition of Eu with Al, but also complexation effects of the same order of magnitude for both cations. This result is experimentally confirmed by a rather detailed study of Eu - Al competitive effects [91BID/GRE]. In contrast to Al, stability constants of Ca organic complexes are always found to be several orders of magnitude smaller than the Eu constants. Hence, we expect a significant competition of Ca only if its concentration exceeds Eu by several orders of magnitude. In the case of multiple site models, the predicted Ca competitive effect may be even weaker than for the limiting case of a single site model. The binding of Eu may be considered in a multiple site model mainly as a
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proton exchange reaction with rather strong binding sites of the humic molecule. Ca, however, may not participate in this type of exchange reaction, due to its generally much smaller stability constants. The multiple site model then predicts very different affinities for the two cations and, as a consequence, no competition at all. An experimental study of competitive effects of Ca with trace concentrations of Dy, another rare earth element with similar complexation behaviour to Eu, revealed no influence of Ca on the Dy-humic acid complexation up to a concentration of 0.004 M Ca [95MOU/MOU2], corroborating the validity of our chemical reasoning.

The extent and nature of competition effects will be completely different when considering for instance mercury instead of trivalent lanthanides and actinides. Soft cations like Hg, Pd, Ag, Cd, Tl, Pb are expected to interact with other binding sites of humic substances than hard cations like Ca and Al. Hence, very weak or no competition at all is predicted between these different classes of metal ions by chemical reasoning. For a detailed discussion of qualitative features of complex formations reactions, including the classification of soft and hard metal ions, see Chapter III.

V.4.2.2.2. Competition of other anions like $CO_3^{2-}$ with humic binding sites

In contrast to competition by cations, competition by anions like $CO_3^{2-}$, $F^-$, $SO_4^{2-}$ or $PO_4^{3-}$ takes place in an indirect way. The model dependence of this effect is also less obvious than in the case of cations. It is shown in the following that the predicted competition of anions with organic binding sites depends on the type of complexes assumed to be formed in the binding model.

If the cations are assumed to form only binary complexes with humic substances, the competition of anions remains to a large extent in the realm of classic mass action and mass balance equations. For example, at constant toxic metal concentrations, increasing concentrations of anions and, thus, increasing formation of metal-anion complexes, cause decreased metal binding by humic substances.

This effect may be buffered to some extent by a concomitant increase of the complexation of anions with other competing metal ions, which in turn influences the competition of these metal ions for the humic binding sites. The closed circle of mutual interactions of thermodynamic equilibria is shown schematically in Figure V.6.

An additional buffering effect arises from the heterogeneity of the humic binding sites. At trace concentrations of metal ions, an increase in anion concentration decreases the metal loading of humic substances. With decreasing metal loading, the stronger binding sites of the humic substances predominate, which in turn weakens the anion competition. The prediction of this second buffering effect strongly depends on the chosen humic binding model.

If the binding model for humic substances includes mixed or ternary complexes in addition to binary complexes, the predicted influence of anion competition becomes more complicated. The formation of ternary complexes can be envisioned either as the uptake of metal-anion aqueous complexes by humic substances, or as the binding of anions to
Figure V.6: Schematic representation of competitive effects in metal-humic binding models: The closed circle of competition of other anions with humic binding sites, combined with cation competition. Competing metal-ligand equilibria are indicated as solid lines.

metal cations which are already bound by humic substances. The influence of ternary complexes is schematically shown in Figure V.7 as bent lines, connecting humics, toxic metal ions, and anions, and connecting humics, competing cations, and anions.

Ignoring ternary complexes in modeling natural groundwater systems may lead to significant underestimation of metal-humic complexation. Why? The two most powerful complexing anions in common groundwaters are hydroxide and carbonate. Whereas the pH effect cannot be excluded when studying complexation in aqueous systems, most studies are undertaken in carbonate free environments. If binding models are calibrated with data measured in carbonate free systems, and subsequently applied to groundwater systems with high carbonate concentrations, strong competition of metal-carbonate complexes is predicted. In reality, however, the effect of anion competition may be significantly weaker than predicted due to the formation of ternary metal-carbonate-humic complexes. As a result, the effects of metal-humic complexation are underestimated in the presence of carbonate. The formal inclusion of ternary complexes in humic binding models, the available experimental results and a possible general treatment of these effects [95GLA/HUM] are discussed in Section V.3.2.2.
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Figure V.7: Schematic representation of competitive effects in metal-humic binding models: The closed circle of competition of other anions with humic binding sites, combined with cation competition. In addition to Figure V.6, the influence of ternary complexes is shown as bent lines, connecting humics, toxic metal ions, and anions, and connecting humics, competing cations, and anions.

V.4.2.2.3. Competition of mineral surface sites with binding sites

Interactions of metal ions with surface sites, usually summarised as sorption phenomena, are important mechanisms of metal retention in the geologic environment of a repository for toxic chemicals and radioactive waste. Competition of the surface sites with binding sites of humic substances should therefore be discussed in terms of reducing metal ion sorption by complexation with humic substances. In order to emphasise the importance of surface phenomena, the mineral surface sites are placed in the very center of the sketch of metal ion interactions (Figure V.8). On the other hand, as the interaction of humic substances is the topic of our present discussion and not sorption phenomena on mineral surfaces (which are discussed in detail in Chapter VII), we will focus on humic substances and treat surface sites as competitors for humic binding sites.

If interactions of humic substances (HS) with mineral surface sites (Surf) are neglected, then “pure inorganic” sorption remains as competitive effect (Figure V.8). The competing equilibria RN-HS and RN-Surf are shifted towards RN-Surf by increasing the strength of surface interactions and/or increasing area of active mineral surfaces. This type of indirect
Figure V.8: Schematic representation of competitive effects in metal-humic binding models: Competition of mineral surface sites with humic binding sites. Sorption of toxic metals on surface sites, organic coating of mineral surfaces and the formation of ternary metal-humic-surface complexes is shown.

The competition is very similar to the competing effects of anions, as already discussed, if only binary complexes are considered. The resulting binding models, however, are more complex than models dealing with humic substances only. They should include surface complexation and ion exchange to account for interactions of metal ions with humic substances and surface interactions at the same time.

If humic substances sorb at surface sites, they may form an organic coating on the mineral surface. This coating may significantly alter the sorption capacity of the immobile phase. In the hypothetical case of “pure” coating, sorption decreases because parts of the active mineral surface sites are not accessible to metal ions any more, due to the organic coating. On the other hand, the coating itself is expected to interact with metal ions in the same way as humic substances in solution, but now forming immobile ternary complexes of the type RN-HS-Surf (Figure V.8). Compared with the scenario of a “pure” organic coating, sorption of metal ions increases again due to the formation of ternary complexes. In addition, a second type of ternary complexes, HS-RN-Surf, may be formed (Figure V.8), where the humic substance is “glued” to mineral surfaces via metal cations forming bridges between humic binding sites and surface sites. This type of ternary complexes can be envisioned as sandwich structures. The net effect of organic coatings and formation of immobile ternary complexes on the sorption of radionuclides is hard to predict. It depends on the ratio of the complexation strengths of radionuclides with organic binding sites and
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Figure V.9: Complete sketch of mutual interactions of toxic metals, humic substances, other cations and anions, and mineral surface sites. Straight lines indicate binary interactions, whereas bent lines represent ternary complex formation.

surface sites, and is in addition expected to show a strong pH dependence. If both, the humic acid molecule and the mineral surface are negatively charged, weak interaction is expected due to strong electrostatic repulsion. Strong interaction may only occur within a pH region where the mineral surface is positively charged and the humic molecule still is sufficiently deprotonated. In addition, competing cations and anions further complicate the picture, as shown in our final sketch of competition effects (Figure V.9).

Many of the more complex interactions, schematically shown in the center of Figure V.9, are expected to predominate only within very limited ranges of pH and component concentrations. The most prominent competitive effect, sorption of metal ions by mineral surface sites, may significantly reduce the uptake of these metals by humic substances. An experimental study investigating the uptake of Am by silica colloids in the presence of humic and fulvic acids corroborates this qualitative prediction. This study showed that the humic substances control the cation behaviour in solution leading to a strong decrease of the retention by the inorganic binding sites [95MOU/MOU2].

V.4.2.3. Application of laboratory data in performance assessment

In the following, the major effects influencing metal-humic interactions are summarised from a performance assessment point of view. It is assumed that “average” laboratory data concerning metal-humic binding are used to calibrate the binding models which subsequently are used as assessment tools in a “conservative roof” approach. Plus signs
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indicate an increase of metal-humic interaction with respect to binding models calibrated with the “average” laboratory data. If these topics are ignored in humic binding models, the influence of humic substances on metal speciation may be underestimated. Minus signs indicate a decrease of organic interactions and may thus cause an overestimation of humic binding if ignored in the model structure.

+++ Metal concentration Binding models calibrated with standard metal titration data alone tend to grossly underestimate metal-humic interaction when applied to trace metal concentrations in real world assessments. Experimental data at trace concentration level are needed to properly calibrate any humic binding model.

+++ pH effect Major influence of increasing pH is expected on metal-humic complexation at trace concentration levels of metal ions. In addition to data gathered in the acidic region, experimental data in the neutral and alkaline pH region are needed in order to calibrate humic binding models properly.

++ Ternary complexes Formation of ternary complexes consisting of metal ions, humic binding sites, and small anions may increase the influence of humic substances at high concentrations of these anions, compared with predictions of binding models ignoring ternary complexes. Mixed complexes with carbonate may be important in certain groundwaters. Therefore, at least some rough estimates about the possible formation of ternary complexes with carbonate are necessary.

− + Organic coating Organic coating may reduce the concentration of soluble humic substances and/or may immobilise metal ions by “gluing” them to surfaces. Metal uptake by humic substances in solution, may therefore decrease or increase somewhat. The effects are expected to be limited to certain pH and concentration ranges. They may be neglected as second order effects as long as only the order of magnitude of metal-humic interactions has to be assessed.
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- **Ionic strength**
  Increasing ionic strength in general decreases metal-humic interactions. Most available experimental data refer to an ionic strength of 0.1 M. Binding models calibrated with such data will slightly overestimate metal-humic interactions in more saline waters. Thus, a “conservative roof” approach using binding models which do not explicitly treat ionic strength effects should be calibrated with low ionic strength data. As the ionic strength of common groundwaters rarely drops below 0.01 M, data measured in this range can be used.

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- **Competing anions**
  Complexation of metal ions by inorganic and small organic anions is the realm of NEA TDB reviews. Including this type of competition in humic binding models requires complete and properly reviewed thermodynamic data of small ligands.

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- **Competing cations**
  Competing cations may decrease the influence of humic substances on toxic metal complexation. The predicted effects of cation competition are strongly model dependent. In the absence of reliable experimental data for calibration of humic binding models, cation competition can be neglected for conservative estimates of the influence of humic substances in performance assessment.

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- **Sorption**  
  Sorption is the main topic in performance assessment of the behaviour of trace metals in the environment of a repository. Sorption on mineral surface sites may decrease the uptake of metal ions by humic substances. In order to predict effects of metal-humic interactions on sorption, such models have to be included in humic binding models. As long as the two fields of modeling are not coupled, sorption effects can be neglected for conservative estimates of the influence of humic substances in performance assessment.

We conclude our review of humic binding models by presenting some scoping calculations of humic complexation with trivalent lanthanides and actinides, the illustrative example used throughout this chapter.
Figure V.10: Scoping calculations of humic complexation with Eu at trace concentration level. The surface represents the concentration of humic substance (in $\log_{10} \text{g/l}$) necessary to bind 90% of the total dissolved metal by humics. The surface is calculated as a function of pH and $p_{\text{CO}_2}$ at ionic strength 0.1 M.

The speciation model of Eu - humic complexation comprises:

- the binary Eu - humic binding represented by the “conservative roof” (Figure V.5), which takes account of the effects of metal concentration and pH,

- a maximum value for the ternary Eu - humic - carbonate complexation constant, represented by $K_2$ of Eu - carbonate complexes as discussed in Section V.3.2.2 (Eq. (V.21)), and

- the complexation of Eu by hydroxide and carbonate, the major competing anions in groundwater.

The concentration of humic substance (g/l) necessary to complex 90% of the total concentration of Eu is shown in Figure V.10 as a function of pH and $p_{\text{CO}_2}$ at $I = 0.1$ M.

At low pH and low $p_{\text{CO}_2}$ there is no competition of Eu hydroxide or Eu carbonate complexes. In this range of the pH-$p_{\text{CO}_2}$ parameter space the observed increase in complexation strength with increasing pH (Figure V.5) causes a concomitant decrease in
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Humic substance concentration needed to complex 90% of Eu. Note, that in a region of the parameter space where anion competition and the formation of ternary complexes is negligible, a simple relation between $K$ and $(HS)_{total}$ of Eq. (V.1) holds

$$\log_{10}(HS)_{total} = \log_{10}(n/(100 - n)) - \log_{10} K$$

(V.69)

where $n$ is the percent of total concentration of metal complexed by the ligand, $0 < n < 100$.

The decrease in humic substance concentration with increasing pH proceeds until at pH > 8 and low $pCO_2$. Eu hydroxo complexes act as competitors, or, in the region where both pH and $pCO_2$ increase, the Eu carbonate complexes dominate and Eu hydroxo complexes become minor species. In these ranges a dramatic increase in humic substance concentration is required to maintain 90% Eu - humic complexation.

If the three-dimensional surface of Figure V.10 is projected onto the pH-$pCO_2$ plane, contour plots can be drawn, as is shown in Figure V.11. In addition, pH-$pCO_2$ data derived from almost 1000 Swiss groundwater analyses are added. As can be seen in the contour plot, all groundwater data cluster along the iso-concentration line of $10^{-6}$ g/l humic substance with a maximum spread of ± one order of magnitude.

Ionic strength variation has a significant influence on the Eu - humic complexation strength. According to Ephraim, Marinsky and Cramer [89EPH/MAR] and our own experimental results, an increase of one order of magnitude in $K$ is observed when the ionic strength decreases one order of magnitude. This effect is reflected in a significant shift of the iso-concentration lines in Figure V.11 at low pH. However, ionic strength effects are very small in the pH-$pCO_2$ range of groundwaters, as the concomitant variations of humic and carbonate complexation constants with ionic strength are in the same direction and of the same order of magnitude, resulting in an almost zero net effect.

Competition by other cations is not included in the scoping calculations of Figure V.11. No influence of Ca was observed by Moulin et al. [95MOU/MOU2] on the complexation of humic acid with trace concentrations of lanthanides up to a concentration of 0.004 M Ca. Thus, only in Ca-rich groundwaters some (weak) influence of Ca competition on Eu - humic substance complexation is expected. Al is known to exhibit complexation effects of the same order of magnitude as Eu [91BID/GRE], whereas Fe(III) is expected to form much stronger complexes with humic substances than Eu. Both cations therefore may act as powerful competitors to Eu in acidic surface waters at pH < 5. However, in the pH region of groundwaters strong hydrolysis of Al and Fe(III) may prevent both cations from playing any role as competitors to Eu - humic substance complexation.

In summary, our scoping calculations indicate that the complexation of trivalent lanthanides and actinides with humic substance in groundwater can be considered in performance assessments as independent of pH, $pCO_2$ and ionic strength. Competition by other cations is expected to be very weak, and thus, a conservative estimate of humic complexation effects shows that a concentration of $10^{-6}$ g/l (or 1 ppb) of dissolved humic substance is sufficient to dominate the speciation of trace concentrations of trivalent lanthanides and actinides in groundwater.
Figure V.11: Contour plot of the concentration of humic substance ($\log_{10} \text{g/l}$) necessary to bind 90% of the total dissolved Eu. The solid lines show projections of the $\log_{10}$ [humic substance] levels in Figure V.10 at ionic strength 0.1 M. The dashed lines are the analogous contour lines at ionic strength 0.02 M. The symbols correspond to pH and $p_{CO_2}$ values of almost one thousand Swiss groundwater analyses.