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Treatment of multi-dentate surface complexes and diffuse layer implementation in various speciation codes

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ABSTRACT

Spectroscopic studies and atomistic simulations of (hydr)oxide surfaces show that ionic aqueous adsorbates can bind to one, two, three, or four surface oxygen atoms (sites), forming multi-dentate species in surface complexation reactions. The law of mass action (LMA) for such reactions can be expressed in several alternative scales of surface concentration (activity). Unlike for mono-dentate surface complexes, the numerical value of the equilibrium constant is not independent of the choice of the surface concentration scale. Here, we show in a number of examples that the different formalisms implemented in popular speciation codes (MINEQL, MINTEQA2, PHREEQC, and ECOSAT) yield different results for the same systems when the same parameters are used. We conclude that it is very important to generate general equations to easily transfer stability constants between the different concentration scales. It is of utmost importance for application of these models to reactive transport that the implementation in both the model fitting and speciation codes, and in the transport codes, is transparent to users.

We also point to the problem that the implementation of the diffuse layer formalism in the various codes is not necessarily generally applicable. Thus, codes like VisualMinteq or MINEQL involve the Gouy–Chapman equation, which is limited to symmetrical ($z:z$) electrolytes, while PHREEQC and ECOSAT use general equations. Application of the former two to environmental problems with mixed electrolytes will therefore involve an inconsistency.

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1. Introduction

The uptake of chemical species on the surfaces of minerals from aqueous solutions, usually termed ‘adsorption’, plays a crucial role in the retention of hazardous cations and anions. The extent of adsorption is strongly dependent upon the local chemical environment, and it is therefore necessary to have realistic models for sorption processes to generate more defensible predictions. Such models can be developed utilising the same thermodynamic approaches as those applied in solution chemistry, using chemical reactions with associated stoichiometry and equilibrium constants, known as surface complexation models (SCMs). Davis and Kent (1990), Stumm (1992) and Kallay et al. (2011) provided a recent overview of the thermodynamics of mono-dentate reactions at solid/liquid interfaces.

Initially, surface reactions were determined on the basis of analogy with the structure of mononuclear aqueous complexes, and equilibrium constants were fitted against the macroscopic (experimental) sorption data. Nowadays, surface complexation reactions are being formulated with the input from spectroscopic studies or from detailed atomistic (mechanistic) models of the mineral–water interface.

With the advent of spectroscopic techniques that probe the structure of surface species (Ponthieu et al., 2006; Sherman, 2009; Sherman et al., 2008; Sylwester et al., 2000; Machesky et al., 2006; Zhang et al., 2004; and refs. therein), many adsorbed cations were found to be coordinated not only to one but to two, three or four surface oxygens, and represented accordingly in SCMs as multi-dentate surface complexes. Such bi-, tri- or tetra-dentate surface species have been identified in many solid/liquid systems, encompassing both cation and anion adsorption to surface functional groups.

The treatment of multi-dentate surface complexes is possible in various ways, and the case of bi-dentate complexes has been

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previously discussed (Benjamin, 2002). Wang and Giammar (2013) give a recent overview for bi-dentate surface complexes and related pitfalls in adsorption modelling. Furthermore, while the present manuscript was under review, Gustafsson and Lumsdon (2014) showed how the incorrect handling of bi-dentate surface complexes could induce unwarranted conclusions. In the present paper, we illustrate that different numerical formalisms have been implemented in available codes, which have been widely used in geochemical modelling. Consequently, it would be helpful if the differences can be made transparent for the user community.

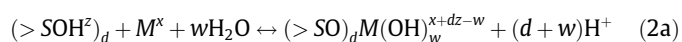
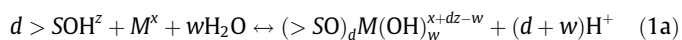
Another subtle detail is in the treatment of the diffuse part of the double layer in electrostatic models. While some codes document the use of the Gouy–Chapman equation (e.g. codes of the MINEQL family (Westall et al., 1986) like FITEQL), other codes have the general treatment implemented (e.g. ECOSAT). The difference is that the Gouy–Chapman equation is valid for symmetrical electrolytes only. This would mean that in general environmental settings, with a mixture of electrolytes, the diffuse part of the double layer cannot be correctly described with the Gouy–Chapman equation. While the effect on the overall calculations of the surface equilibria is probably minor in most cases, it can be of more importance in certain cases.

The aim of the present paper is to make the reader aware of existing differences between codes in treatment of adsorption involving multi-dentate surface species, and to show that the treatment of the diffuse part of the double layer is not necessarily general.

2. Multi-dentate surface complexes

2.1. Formalism

A general surface complexation reaction can be written in two ways



$>\text{SOH}$ denote surface sites, z and x denote charges, and d and w are stoichiometric coefficients. While the mass balance equations associated with both equations would be identical, the mass law equations will differ for “denticity” $d > 1$.

$$K_M^{\text{int},d} = \left[(> \text{SO})_d M(\text{OH})_w^{x+dz-w} \right] \times [\text{H}^+]^{d+w} \times [> \text{SOH}^z]^{-d} \times [M^x]^{-1} \quad (1b)$$

$$K_M^{\text{int}} = \left[(> \text{SO})_d M(\text{OH})_w^{x+dz-w} \right] \times [\text{H}^+]^{d+w} \times [(> \text{SOH}^z)_d]^{-1} \times [M^x]^{-1} \quad (2b)$$

Here, K_M^{int} stands for the intrinsic equilibrium constant; we assume that the activity of water is constant, and use molarities instead of activities for the remaining species. Also we initially ignore the possibility of multi-nuclear complexes (in M^x) and omit the electrostatic factors. The set of Eq. (1) will also be referred to as formalism 1, while the set of Eq. (2) will be referred to as formalism 2.

The important difference between formalism 1 and 2 is that in latter the ratio between concentration terms for surface species does not depend on the denticity d , while for the former it does. The consequence for formalism 1 is that a sorbent concentration term will ultimately appear, which involves correction of the stability constant in an appropriate way. This has been known for a long time and is included in textbooks (Sigg and Stumm, 1989, 1996; Sigg et al., 1992). Interestingly, in the textbook by Stumm

and Morgan (1996), only formalism 2 is mentioned. A detailed derivation can be found in the recent review by Wang and Giammar (2013).

A debate about the formal treatment, i.e. Eqs. (1) vs. (2), still exists. An argument in favour of 1 would be that multiple bonds on the surface must be formed, and that the adsorbing species M^x has various possibilities to coordinate to available function groups on the surface. Such reasoning ultimately requires consideration of the surface structure (i.e. how the binding sites are arranged). Arguments in favour of 2 would come from comparison to ligands like oxalate, where a single oxalate forms a bi-dentate complex with metal ions in solution. This would never involve a square in the respective mass law equation. On the surface, similar to a dissolved ligand like oxalate, the functionalities are pre-arranged. No effect of solid concentration on the stability constant would result from Eq. (2).

In general, any treatment will fail when the surface coverage is high, and the possibilities for forming multidentate surface complexes become restricted. A simple mass law equation/mass balance treatment cannot handle this situation correctly if $d > 1$.

In case of Eq. (1), ultimately a second debate evolves about the best concentration scale to use, including molarities/molalities, mole fractions, or coverage fractions (Kulik et al., 2010; Wang and Giammar, 2013).

2.2. Consequences for the treatment in speciation codes

Formalism 2 is exclusively possible with codes that allow distinction between the mass action law equation and the mass balance coefficients.

Formalism 1, as implemented in a given code, is currently restricted to one of the concentration scales per code, though it could be made more general. For the ECOSAT code, for example, the precise treatment has been described by Venema et al. (1996). In the ECOSAT implementation, the treatment is extended to multidentate surface species involving more than one kind of surface sites. While this seems to complicate the situation, because again various possible ways of defining the stability constants may exist, given that the implementation in the various codes and with respect to published parameters are known, the appropriate corrections can be made (Kulik et al., 2010).

In the present comparison, we apply the codes ECOSAT, FITEQL, PHREEQC, and VISUALMINTEQ (references to the codes can be found in the REFERENCES section). We compare formalism 1 within different codes, starting with a single site model and continuing to the more general case where different kinds of surface sites contribute to a multidentate surface complex. In principle this may also extend to different kinds of surfaces that interact as described by Lützenkirchen and Behra (1996). In particular, we compare the results obtained with the different codes on given examples to illustrate that the codes employ different implementations. In some examples we also involve a comparison between the two formalisms for bi-dentate complexes using FITEQL. Formalism 1 will then be denoted as FITEQL (1) and formalism 2 as FITEQL (2).

3. Diffuse layer potential

3.1. Formalism

In most electrostatic surface complexation models, a distinct treatment of the diffuse part of the electrical interfacial layer (EIL) is included. The simplest treatment involves the Gouy–Chapman equation, which relates the potential of the onset of the diffuse layer (Ψ_d) to the diffuse layer charge (σ_d), as given in Eq. (3).

$$\sigma_d = -(8000eRT)^{1/2} \sin h(zF\Psi_d/2RT) \quad (3)$$

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