The influence of internal charge on the sorption properties of clays

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The surface complexation model (SCM) has been used successfully to describe the adsorption properties of oxides and other solids, such as carbonates and sulphides. This model describes adsorption as a superposition of the electrostatic interactions at the solid-water interface with chemical reactions of solutes with reactive groups at the surface of the solid. The activities of the species at the interface depend on the electrostatic potential of the surface, and are calculated from a so-called 'coulombic term' whose exact form depends on the electrostatic description of the interface (e.g. double layer or triple layer).

The surface complexation model has been used to model two kinds of experimental data: acid-base titration curves and metal or ligand sorption edges. It predicts that as the ionic strength, I, decreases, the absolute surface charge density also decreases at a given pH. At low ionic strength, the surface charge is less efficiently shielded and accumulation of charge on the surface is energetically more difficult. In the absence of any strongly binding ion, the SCM also predicts that the titration curves at various I intercept at the same pH, the zero proton condition (ZPC), where the concentrations of adsorbed H^+ and OH^- at the surface are equal. Sorption edges of a cation M^{n+} usually show a strong increase of adsorption with pH, as the competition of H^+ with the cation for the surface sites decreases. The slope of the $[M^{n+}]$ adsorbed vs pH curve reflects the net number of H^+ ions displaced by the adsorption of M^{n+} which depends on the stoichiometry of the reaction and the variation of the surface potential with pH.

In spite of the success of the SCM in describing sorption properties of oxides, its application to clays has not been straigthforward. In particular, some titration data on clays such as kaolinite and montmorillonite show an increase in the ZPC as ionic strength decreases; concomitantly, at low pH, the charge density is higher at low ionic strength, contrary to what is usually observed on oxides. Furthermore, fitting metal sorption on clays with the SCM has proven difficult (Bradbury and Baeyens, 1997). Here, we propose that the different sorption properties of clays compared to oxides may be explained by the porous character of clays, whose interlayers are permeable to water and electrolyte ions, together with their fixed internal charge resulting from isomorphic substitution.

The electrostatics of a system consisting of a homogeneous porous solid bearing a fixed internal charge and immersed in a 1:1 electrolyte solution can be described by the Poisson-Boltzmann equation, leading to a generalization of the Gouy-Chapman theory. We thus obtain expressions for the internal and surface potential as a function of ionic strength, internal charge density and surface charge density.

TABLE 1. Model parameters

Model parameters	Fig. 1	Fig. 2	Fig. 3
pK_{a1}	4.6	5.0	5.6
pK_{a2}	8.6	8.5	8.7
Surface area (edges) (m^2/g)	na	31.53	35
Relative permittivity of the porous solid ε_s	78.5	78.5	78.5
Concentration of acid-base species (mol/Kg)	0.015	0.028	0.08
Fixed internal charge density ρ_{fix} (eq/l)	−0.046	−1.02	−1.15
Dry solid concentration (g/L)	20	5	1.24
Ratio of solution volume inside the solid to total solution volume	2.10^{-2}	5.10^{-3}	$9.4.10^{-4}$

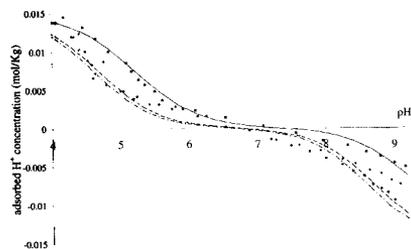ρ_{fix} is in equivalents per liters of solution inside the clay.

FIG. 1. Acid-base titration of H-kaolinite. Squares and full line: I = 0.01 M; diamonds and dotted line: I = 0.1 M; circles and semi-dotted line: I = 1M. The fitting parameters for the calculations (lines) are given in Table 1. The data (symbols) are taken from Schindler *et al.* (1987).

FIG. 2. Acid-base titration of montmorillonite. Diamonds and full line : I = 0.005 M; squares and dotted line: I = 0.05 M; triangles and semi-dotted line: I = 0.5 M. The parameters for the fits (lines) are given in Table 1. The data (symbols) are from Wanner *et al.* (1994).

As is the case in surface complexation model, this expression is then coupled to a chemical representation of the sorption reactions on and in the solid to yield a complete thermodynamic description of the system.

We hypothesize that our model for porous solids may provide a satisfactory first-order description of the sorption properties of clays: the clay structure is taken to be analogous to the porous solid, the interlayers to the pores, and the edges to the interface with the solution. In the case of kaolinite, we neglect the acid-base groups on the edges and only consider those in the interlayers. When the corresponding sorption model is solved with the appropriate physical and chemical parameters (see Table 1), acid-base titration curves on H-kaolinite previously published by Schindler *et al.* (1987) are adequatly fitted (see Fig. 1). In particular, the increase in the ZPC with decreasing I is correctly predicted, as well as its amplitude. Likewise, the higher charge density at low pH for a lower ionic strength is successfully reproduced. Both effects are due to the fixed internal charge inside the solid, which results in a negative potential that tends to attract H^+ and repulse OH^-; as I decreases, this potential becomes more negative, resulting in a stronger stabilization of sorbed H^+. In this case, this effect is dominant over decreased shielding of the positive charge created by the acid-base groups.

In the case of montmorillonite, we assume that the siloxane sheets in the interlayers do not have acid-base properties, and that all the acid-base groups, $\equiv SOH$, are located at the interface (i.e. on the edges). Again, a fixed negative charge is distributed uniformly inside the solid. Metal sorption thus results from i) cation exchange inside the solid, ii) surface complexation on acid-base groups. Model calculations with the appropriate parameters (see Table 1), provide an acceptable fit of the acid-base titration data obtained by Wanner *et al* (1994) on Na-
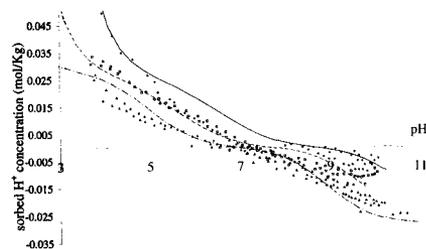
montmorillonite (see Fig. 2). Although the structure of the clays and of the models are different, the same basic features are observed and correctly modeled on montmorillonite and on kaolinite : increase in the ZPC as I decreases and higher charge density at low pH when I decreases. Again, these features are the result of an increasingly negative potential inside the clay as I decreases, which results in a stabilization of sorbed H^+ at the surface. The sharp increase in sorbed H^+ on montmorillonite at low pH is due to sorption by cation exchange, which becomes dominant over surface complexation at low I. One may also notice the relative lack of 'flattening' of the acid-base curves as I decreases, also observed on kaolinite.

Once the intrinsic pKa's of the acid-base groups have been determined independently from acid-base titration data, the zinc sorption edge published by Baeyens and Bradbury (1997) (see Table 1) on Na-montmorillonite cannot be simply fitted in the framework of a surface complexation model, because the slope of $[Zn^{2+}]$ adsorbed *vs* pH curve is too small. If, however, one models Zn adsorption by taking into account the presence of a fixed negative charge density and assuming the formation of a $\equiv SOHZn^{2+}$ species, a good fit of the Zn isotherm is obtained. As a result of the fixed negative charge in the bulk solid, the surface potential decreases less with increasing pH and the increase in adsorption of Zn^{2+} with pH is smaller.

References

Bradbury, M.H. and Baeyens, B. (1997) *J. Cont. Hydro.*, **27**, 223–48.

Baeyens, B. and Bradbury, M.H. (1997) *J. Cont. Hydro.*, **27**, 199–222.

Schindler, P.W., Liechti, P. and Westall, J.C. (1987) *Neth. J. Agr. Sci.*, **35**, 219–30.