

Characterization of ion adsorption with proton-ion titrations

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A large variety of Surface Complexation Models (SCM) is available for describing ion adsorption. Most SCMs are able to describe adsorption data if the choice of the type of species is unrestricted. It is not obvious that these models are a priori able to predict adsorption in multicomponent systems on the basis of monocomponent systems. The predictability may improve by incorporating knowledge from spectroscopy, colloid chemistry and mineralogy in SCMs, as is done in the CD-MUSIC model (2). Recent ATR-FTIR measurements of sulphate on hematite have shown that only one species of sulphate is dominant over a large range of surface coverages (1). Sulphate is therefore a perfect ion to test SCMs because the models should be able to describe the pH dependence of sulphate adsorption with only one sulphate surface-species over a large range of surface coverages and concentrations.

In this contribution we will show that the CD-MUSIC model can describe sulphate adsorption over a large range of conditions in accordance with spectroscopic information. It will be shown that proton-ion titrations are a sensitive tool in the characterization of ion adsorption (for which measurements are in progress for selenate, selenite, arsenate, arsenite, phosphate, chromate and molybdate). The results of modelling will be applied in the evaluation of the effect of outer-sphere ions on

sulphate adsorption. Predictions show that lower basic charging in perchlorate as compared to chloride results in a higher sulphate adsorption in perchlorate as is also found in experiments.

CD-MUSIC Model

Environmental chemists are challenged to translate the knowledge of coordination of surface species on metal-hydroxides from new *in-situ* spectroscopic techniques such as EXAFS, ATR-FTIR and CIR-FTIR to models for chemical equilibria in soil, sediment and water, which can also deal with adsorption reactions. A concept to formulate physically realistic and therefore spectroscopic verifiable surface-species in surface-chemical equilibria has been proposed by Hiemstra and Van Riemsdijk (2). The concept is called the CD-MUSIC model (charge distribution multisite

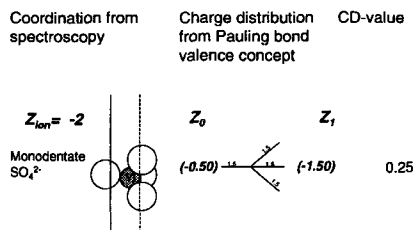


FIG. 1. A schematic representation of the relation between coordination as expected from spectroscopy and the estimated charge distribution as used for modelling sulphate adsorption.

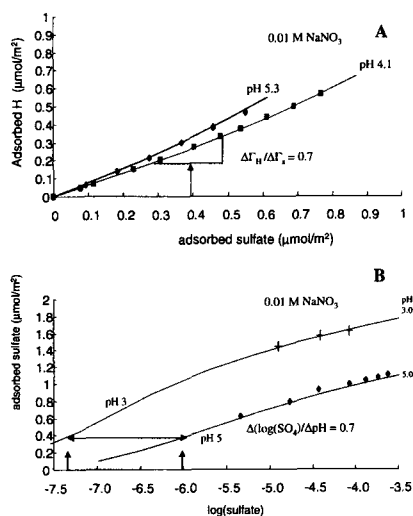


FIG. 2. Relation between proton-sulphate stoichiometry (A) and sulphate adsorption isotherms (B). Points give the data and lines are calculated using the CD-MUSIC model.

complexation). In this model an intrinsic equilibrium constant ($\log K$) and a so-called Charge Distribution (CD) value characterize each adsorbed species.

The concept of charge distribution is based on the bond valence concept of Pauling in which bond valence is the charge (v/CN) shared with another ion and is calculated by the valence (v) of the ion-center divided by its coordination number (CN). This concept enables one to estimate the charge of a surface group, the change of charge on a surface-oxygen by ligand exchange and the charge on the solution-directed ligand. For example the charge on a single coordinated oxygen on goethite before and after protonation is estimated to be $\text{FeOH}^{-0.5} + \text{H}^+ = \text{FeOH}_2^{0.5}$ because the Fe-O bond valence is $v/\text{CN} = 0.5$.

The bond valence concept can be also applied to ion adsorption. The charge of the surface-oxygen is (partly) neutralized by adsorption of protons or other ions for instance sulphate. The charges on the ligands of sulphate are estimated from S-O bond valence $v/\text{CN} = 6/4 = 1.5$. ATR-FTIR shows that adsorbed sulphate shares one of its ligands with the surface and three ligands are directed to the solution (1), which causes a spatial charge distribution at the mineral-solution interface.

CD-value

The simplest way to incorporate the spatial charge distribution of adsorbed species in surface-chemical equilibria is to partition the charges over two electrostatic planes. Necessary is an electrostatic double layer model with at least two electrostatic planes: one plane in which the surface-oxygens and protons are located and a second plane in which the solution-oriented oxygens are located. The CD-value (charge distribution) is defined as the fraction of charge of a central ion that is shared with surface-oxygen while the other fraction of charge is shared with solution-directed ligands, as is illustrated in Fig. 1.

Monodentate innersphere coordinated sulphate

The CD-MUSIC model is used in to describe sulphate adsorption and the proton-sulphate stoichiometry as is shown in Fig. 2. The proton-stoichiometry is able to characterize the pH dependency of adsorption-isotherms at very low adsorption coverages. This is easily seen from the thermodynamically derived equation:

$$(\delta\Gamma_{\text{H}}/\delta\Gamma_{\text{SO}_4})_{\text{pH}} = (\delta(\log(\text{SO}_4))/\delta(\log(\text{H})))_{\Gamma_{\text{SO}_4}}$$

which was described by Perona and Leckie (3). The equation gives the relation between proton-ion titrations at pH-STAT and the relative position of the adsorption-isotherms at different pH values. The slope in Fig. 2 of the proton-sulphate titrations illustrates the proton-sulphate stoichiometry. For example: the proton-sulphate stoichiometry at $0.4 \mu\text{mol}/\text{m}^2$ gives the change of the sulphate concentration (at log-scale) as function of the pH at $0.4 \mu\text{mol}/\text{m}^2$. Determination of low ion-concentrations is often not possible with conventional techniques, since in case the sulphate equilibrium concentration at an adsorption of $0.4 \mu\text{mol}/\text{m}^2$ (pH 4) is much lower than the detection limit of ICP-AES.

Outer-sphere coordinated ions

Outer-sphere coordination on metal-(hydr)oxides is expected for chloride, nitrate and perchlorate. Outer-sphere ion formation can be characterized by modelling acid-base titrations of metal(hydr)oxides. A more direct approach would be to determine the adsorption of electrolyte ions at the PZC as Sprycha (4) did for anatase. Adsorption of electrolyte ions is however much smaller on goethite (5). We will show here that a combination of acid-base titrations and sulphate adsorption in different salts can characterize outer-sphere ions. Differences between acid-base behaviour in for instance NaCl and NaClO₄ are hardly mentioned in literature and sometimes ignored. Fig. 3 shows the acid-base behaviour of goethite at a concentration of 0.1 M in two salts. Chloride seems more able to screen the positive charge of the goethite particles and perchlorate is a rather inert anion.

The information in Fig. 3 can be used to predict the effect of the type of electrolyte on sulphate adsorption. Several approaches can be followed. If no outer-sphere formation is assumed for chloride and perchlorate it will lead to the prediction of a lower sulphate adsorption in perchlorate and a higher sulphate adsorption in chloride because in chloride more charging of the goethite occurs (see Fig. 3). However in the case of outer-sphere formation the opposite effect is predicted. In case of outer-sphere formation there will be competition between the outer-sphere ions and sulphate. This will lead to the highest sulphate adsorption in the system with the weakest outer-sphere bonded ions. This prediction is given in Fig. 4 together with data. The results support the suggestion of outer-sphere formation. It should be mentioned that all adsorption data of sulphate in Fig. 2 and Fig. 4 are calculated using one and the same affinity constant for sulphate.