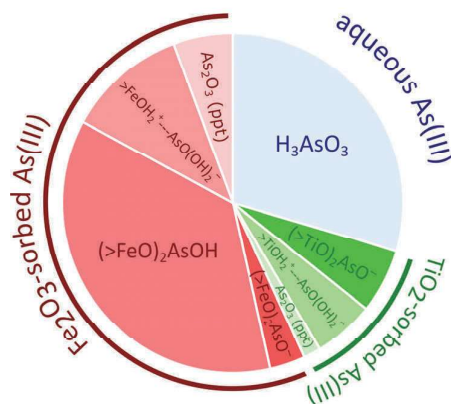


# Surface complexation modelling: building tools to understand and predict adsorption

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Surface complexation models (SCM) are important tools for environmental chemists, allowing us to understand and predict adsorption in complex systems. This Brief introduces SCM, describes how a new modeller gets started and develops their own models, and highlights some advanced SCM applications.

The Langmuir and Freundlich adsorption isotherm models are well known; indeed, they are taught in most undergraduate chemistry courses (1). However, these models describe single-sorbate single-sorbent systems, and are only valid for the specific conditions under which the model's parameters were experimentally determined. Surface complexation models (SCM) provide a more sophisticated description of adsorption, sensitive to changes in environmental conditions including pH, ionic strength and the presence of competitor ions (2). SCMs have important applications, such as determining the mobility of toxic heavy metals and essential micronutrients in groundwater and soil (3), and understanding the performance of synthetic sorbent materials for the remediation of contaminated waters (Figure 1) (4).



**Figure 1.** Predicted speciation of arsenic (III) adsorbed onto a mesoporous  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  composite. Conditions:  $32.1 \text{ mg L}^{-1}$  total As(III),  $1 \text{ g L}^{-1}$  sorbent, pH 7,  $0.01 \text{ M NaCl}$ . Surface complexation model was calculated following Bullen et al. (2020).

## What is a SCM?

Surface complexation models use the analogy of solution phase metal-ligand complexation to describe the adsorption of a dissolved sorbate onto a solid surface. Surface complexation reactions are modelled using equilibrium constants and the activities of reactants M (representing the sorbate) and L (representing the functional groups of the sorbent) and the product (ML):

$$K = a_{\text{ML}} / a_{\text{M}} a_{\text{L}}$$

Electrostatic forces can significantly influence the extent of adsorption. For instance, the attraction between a positive iron oxide surface and negative  $\text{HAsO}_4^{2-}$  anions at neutral pH shifts the equilibrium position towards the products. Electrostatics are accounted for by modifying the intrinsic equilibrium constant with an electrostatic term, yielding an 'apparent' equilibrium constant:

$$K_{\text{apparent}} = K_{\text{intrinsic}} \cdot \exp^{-F\Delta\psi/RT}$$

where  $\psi$  is the surface potential of the sorbent (V) (2).

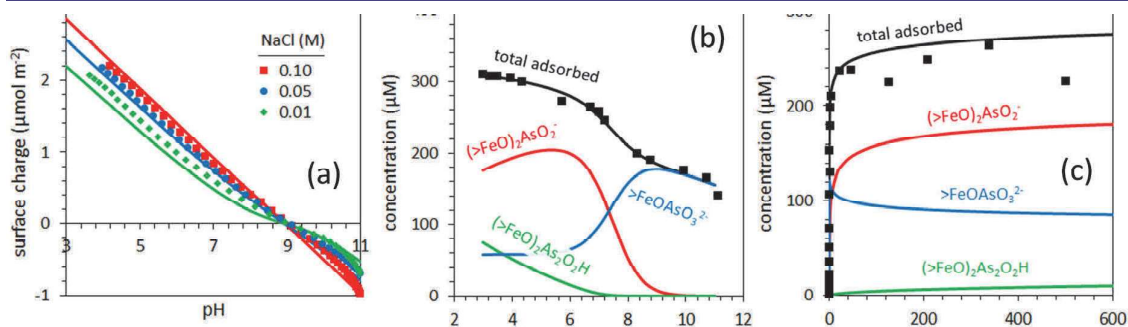
## Running the first model

Several software packages with SCM capabilities are freely available (e.g. Visual MINTEQ and PHREEQC). Both offer introductory tutorials and contain databases of the equilibrium constants needed to model many aqueous phase and surface complexation reactions.

These databases firstly define a selection of components or master species. Each component is like a Lego block: components such as  $\text{AsO}_4^{3-}$  and  $\text{H}^+$  can be combined in different ways to yield different chemical species, including  $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}^+$ , and  $\text{OH}^-$ . The surface hydroxyl component,  $>\text{SOH}$ , can be similarly combined to yield surface complex species such as  $>\text{SOH}_2^+$ ,  $>\text{SO}^-$ ,  $>\text{SOAsO}_3^{2-}$  and  $(>\text{SO})_2\text{HAsO}_2$ .

The SCM also requires several physical parameters: (i) the sorbent surface area, and (ii) the site density (the number of surface functional groups per square nanometre) are needed to calculate the total adsorption capacity. Many SCMs also require (iii) a value for the capacitance of the electrical double layer (EDL). Like the equilibrium constants, these parameters can be obtained from the literature when running your first model.

After defining the SCM parameters, the user enters the pH and concentrations of the sorbent, sorbate, electrolyte



**Figure 2.** Development and validation of surface complexation model for the adsorption of arsenic(V) ( $\text{AsO}_4^{3-}$ ) onto goethite ( $\text{FeOOH}$ ). Figures based upon Bullen et al. (2020)

and any competitor sorbates. Running the program calculates the speciation of the system (e.g. **Figure 1**).

When performing an experiment, the user often wants to know how one variable influences another. This is achieved using the sweep function in Visual MINTEQ and by programming loops (using Visual Basic) within PHREEQC.

### Building your own model

Sometimes it is necessary to calculate SCM parameters – if the user cannot find their specific sorbate-sorbent combination in the literature, or previous models are out-of-date (e.g. using disproven surface complexes). SCM parameters are best calculated from experimental data using non-linear regression: an initial guess is made for each parameter, and an algorithm varies these values until the sum of squared residuals between experimental data and the model's output has reached a minimum (5). Software such as FITEQL and Visual MINTEQ offer this functionality.

However, these algorithms can only optimise a limited number of parameters per experiment and it is therefore best to develop our model in stages:

1. Physical parameters must be defined. The surface area of the sorbent is best determined experimentally (BET analysis). Site densities are difficult to determine experimentally and may be estimated from adsorption data or optimised to fit the model (2).
2. Surface charge is heavily controlled by the pH-dependent (de)protonation of surface hydroxyls. Equilibrium constants for these reactions are normally calculated by optimising the model to fit experimental potentiometric titration data (**Figure 2a**).
3. Many sorbates form a pH-dependent variety of surface complexes. Consequently, equilibrium constants for the adsorption of our analyte are best calculated by fitting the model to experimental pH adsorption edges (**Figure 2b**).
4. Finally, it is important to validate the model by predicting new chemical behaviour and comparing the results with unseen experimental data. The compari-

son of SCM-predicted adsorption isotherms with experimental data is often a good way to validate the model (**Figure 2c**).

### The potential of SCM

SCMs are versatile. Multi-sorbate SCMs predict competitive adsorption in complex solutions. Component additive models (CA-SCM) predict adsorption onto new composite materials as a function of their surface composition (4). SCMs are easily integrated with other models, e.g. Visual MINTEQ provides the databases and calculations necessary to simultaneously model (i) adsorption onto minerals, (ii) ion exchange with clay minerals, and (iii) soil organic matter complexation (6). Finally, SCMs can provide new insights into adsorption mechanisms, e.g. helping identify multilayer adsorption or the formation of ternary surface complexes.

If you like to learn surface complexation modelling, Visual MINTEQ and PHREEQC are good places to start:

<https://vminteq.lwr.kth.se>

<https://www.usgs.gov/software/phreeqc-version-3>

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