

## **Ion Binding to Complex Molecules or Surfaces: Speciation Modelling Revisited**

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Ever since the creation of numerical codes that can calculate the equilibrium distribution of various species in complex (environmental) systems, environmental scientists have been using these codes to calculate the equilibrium state of systems of their interest. For simple systems, e.g. cadmium present in a sodium chloride solution the free energy of each individual chemical species is known and using this thermodynamic information in computer codes like MINEQL, ECOSAT or WHAM, calculations are straightforward.

However, macromolecules or particle surfaces cannot be characterised with the same detail as simple solution species. The number of possible states the surface can be in even for very simple cases is huge. Even a small oxide particle already may have 7000 reactive sites per particle that can react with protons. The affinity of the surface for protons changes with a change in the amount of protons adsorbed. The change in the affinity with surface coverage can be handled in modelling assuming chemical heterogeneity and/or assuming that the affinity changes due to the changing electric field near the surface as a result of the ion adsorption. In these modelling approaches one does not define explicitly the free energy of all possible surface states, but instead the average degree of protonation of the surface as a function of pH is calculated, using 'adsorption models'.

Modelling ion binding to humics also faces the problem that it is impossible to define all chemical states exactly. Ion binding models for humics like NICA and Model VI therefore only define the average chemical state of the molecules in a statistical sense accounting for the heterogeneity of the molecule. One main difference between Model V/VI and NICA is that the NICA model has a relatively simple analytical expression for the average state of the molecules once the local potential is known.

Humics do not only react with protons or dissolved metal ions, but they also react with sites on mineral surfaces leading to chemical binding to surfaces. A major feature of the interaction of humics with surfaces is that the average state or free energy of the molecules changes upon adsorption. Very recently the SPADE (Species Adaptation Distribution Equilibrium) approach has been presented which can handle this problem. The SPADE approach has been incorporated into the LCD (Ligand and Charge Distribution) model that has been developed earlier. Some results of this new approach will be presented.