

## The structure of the double layer near goethite in the presence of mono and bivalent electrolyte ions

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The charging of metal (hydr) oxides is to a large extent influenced by the electric field that is created due to the charging of the particles. It is customary to study the charge as a function of pH in the presence of a so-called background electrolyte, often a 1:1 salt solution. The data are usually described with a variable charge model that combines a site-binding model with an electrostatic model. It allows calculation of the potential as a function of distance from the surface. The strongest interaction between ions and the surface occurs when the ions form a coordinative bond with the surface via a ligand exchange mechanism. The formed surface complex is called an innersphere complex and the distance between the surface and the adsorbed ion is quite small in this conformation. The minimum distance of approach to the surface for ions that do not form innersphere complexes is in general larger than for the innersphere complexes. Spectroscopic techniques try to elucidate the type of surface complex including its geometry. Unfortunately, it is not yet possible to get all the required information from spectroscopy. Even when there is relevant spectroscopic interpretation available, it is still a challenge to use this information to calculate the macroscopic charging behavior. It has been shown that in order to link the microscopic and the macroscopic interpretation, one should not treat the ion that forms an innersphere complex as a point charge in the model. Distribution of the charge over the surface plane and the next electrostatic plane is required, which has led to the development of the CD-MUSIC model. In this contribution, we will show a set of consistent data for the pH dependent charging of goethite in the presence of different electrolytes, which is aimed to get a better insight in the structure of the double layer close to the surface. The ions studied are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{NO}_3^{-1}$ ,  $\text{Cl}^{-1}$ ,  $\text{ClO}_4^{-1}$  and  $\text{SO}_4^{-2}$ . We will demonstrate a new approach to analyze the data to get insight in the location of these ions near the interface. This new approach is an extension of the present CD-MUSIC model.

## Predicting the impact of the environment on the structure and chemistry of metal oxide surfaces

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Metal oxides such as hematite, ( $\alpha\text{-Fe}_2\text{O}_3$ ) play an important role in contaminant sequestration and speciation in groundwater aquifers and soils. A key factor in understanding the reactivity of metal oxides, is how bulk water interacts with the surfaces. Yet, despite considerable experimental and theoretical efforts on the clean hematite surface, little is known regarding the surface structure and even the surface stoichiometry under environmental conditions. The gap between conditions accessible to UHV surface science and what is observed in nature has made it difficult to understand why the hematite (0001) surface reacts with water vapor at a far lower threshold vapor pressure than corundum,  $\alpha\text{-Al}_2\text{O}_3$  (Liu, 1998), but yet is much more stable with respect to weathering and solubility. Theoretical predictions and modeling can provide a powerful means to evaluate fundamental chemical processes with atomic resolution, but also face the challenge of including the effects of a complex environment. We employ the method of *ab initio* thermodynamics (Wang, 2000) that enables us to link 0K density functional theory electronic structure and vibrational calculations to finite temperatures and pressures to calculate the free energy of a surface in equilibrium with multiple species in the environment. We will show how this technique has led to an understanding of the differences in surface structure, reactivity, and solubility between hematite and corundum upon exposure to water in the vapor and liquid phases. (Trainor, 2004)

### References

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