Electrokinetic and potentiometric insight into malonate arrangement at hematite/water interface

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The aliphatic low-molecular-weight carboxylic acids, released by plants roots or microbes to the rizosphere, improves the solubility of nutritient cations from soil minerals and rock fragments, and increases their bioavailability [1]. The incorporating of iron in nature and its bio-availability is controlled by adsorption-desorption processes. To understand the role of carboxylic acids in hematite dissolution and reactivity, we need to gain an insight into the nature of pH-dependent iron oxide surface chemistry [2].

By combining measurements of surface and diffuse potential at hematite/water interface with the potentiometric titration of suspension we were able to precisely describe the electrical double layer properties of the hematite/malonic solution interface. We observed that malonate adsorbs in a broad pH range from 3 to 8.3, however, the mode of coordination depends on actual pH value. We distinguished two different types of malonate complexation to the hematite surface: as innerspherical complexes at pH below 4, and as outer-spherical complexes above pH 5. The transition from the inner to the outer sphere geometries is smooth, suggesting that both types of complexes geometries exist simultaneously, but with a ratio depending on the pH. Our findings are relevant for understanding how organic matter interacts with minerals, a key phenomenon in the chemical weathering processes.

[1] Strobel B.W. (2001) Geoderma, 99, 169-198

[2] Duckworth O.W. et al. (2001) Geochim. Cosmochim. Acta. 65 4289-4301