

Calorimetric study of binding interactions between metal ions and natural organic matter

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The complexation of metal ions with natural organic matter (NOM) greatly influences metal speciation, bioavailability, and toxicity in the environment. Consequently, many researchers have studied the affinity of metal ions and NOM using ion-selective electrodes or potentiometric titration to determine equilibrium constants. However, the mechanisms of metal complexation remain poorly understood [1]. In the present study, we have applied isothermal titration calorimetry (ITC) to investigate the thermodynamics of metal-NOM interaction in aqueous solution.

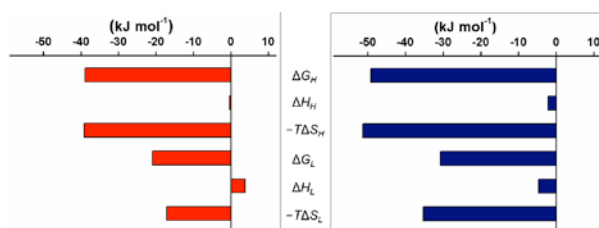


Figure 1: Thermodynamic parameters for metal binding to HA (Ca²⁺: left; Cu²⁺: right).

ITC data for Ca²⁺ and Cu²⁺ association with humic acid (HA) are consistent with the presence of two types (high- and low-affinity) of binding sites, as commonly observed in previous studies [2]. Metal binding to these sites in HA is achieved by entropy changes, demonstrating the importance of dehydration of metal ion and HA upon their association. However, Ca²⁺ and Cu²⁺ exhibit different trends in binding enthalpies that suggest differences in the macromolecular interactions with these metals. Complementary atomic force microscopy (AFM) studies reveal differences in the ability of these ions to flocculate NOM.

[1] Bryan *et al.* (1998) *J. Chem. Soc. Faraday Trans.* **94**, 95-100. [2] Lamelas & Slaveykova (2007) *Environ. Sci. Technol.* **41**, 4172-4178.