A thermodynamic study of heteroaggregation between titanium dioxide nanoparticles and hematite colloids

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A better understanding of the fate and behavior of engineered nanoparticles (ENPs) in aquatic systems is of great significance for their risk assessments [1]. The stability of ENPs are strongly affected by the water properties and natural colloids [2]. The interaction process between ENPs and natural collods, namely heteroaggregation have been investigated in several studies, but the thermodynamics associated to heteroaggregation remain poorly understood. In the present study, we have applied isothermal titration calorimetry (ITC) to quantify the energies of TiO_2 NPs (as a representative of ENPs)-hematite collids interaction in aqueous solution.

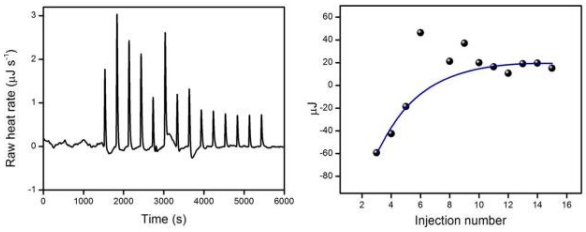

Figure 1: (a) ITC thermogram and (b) integrated heat data for the titration of humic acid(HA)-coated hematite to TiO_2.

The titration of HA-coated hematite (HA/Fe_2O_3) to TiO_2 begins with an exothermic reaction followed by an endothermic reaction. ITC data are well fitted by two types (high- and low-affinity) of binding sites that are distinguished by ~10 fold difference in their k_a values. The association of HA/Fe_2O_3 with a high-affinity site in TiO_2 is achieved by enthalpy changes, while the entropy contribution ΔG is predominant in a low-affinity site. Complementary electrophoretic mobility measurements reveal that the endothermic transition may be related to the formation and growth of HA/Fe_2O_3−TiO_2 heteroaggregates.

[1] Lowry *et al*. (2012) *Environ. Sci. Technol.* **46**, 6893-6899.
[2] Praetorius *et al.* (2014) *Environ. Sci. Technol.* **48**, 10690-10698.