Agglomeration mechanisms and thermodynamic properties of TiO_2 nanoparticles interacting with natural organic matter: an isothermal titration calorimetry study

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Interaction between engineered nanoparticles and natural organic matter is investigated by measuring the exchanged heat during binding process with isothermal titration calorimetry[1,2]. TiO_2 anatase nanoparticles and alginate are used as engineered nanoparticles and natural organic matter to get an insight into the thermodynamic association properties and mechanisms of adsorption and agglomeration. Changes of enthalpy, entropy and total free energy, reaction stoichiometry and affinity binding constant are determined or calculated at a pH value where the TiO_2 nanoparticles surface charge is positive and the alginate exhibits a negative structural charge. Our results indicate that strong TiO_2-alginate interactions are essentially entropy driven and enthalpically favorable with exothermic binding reactions. The reaction stoichiometry and entropy gain are also found dependent on the mixing order. Finally correlation is established between the binding enthalpy, the reaction stoichiometry and the zeta potential values determined by electrophoretic mobility measurement. From these results two types of agglomeration mechanisms are proposed depending on the mixing order. Addition of alginate in TiO_2 dispersions is found to form agglomerates due to polymer bridging whereas addition of TiO_2 in alginate promotes a more individually coating of the nanoparticles.

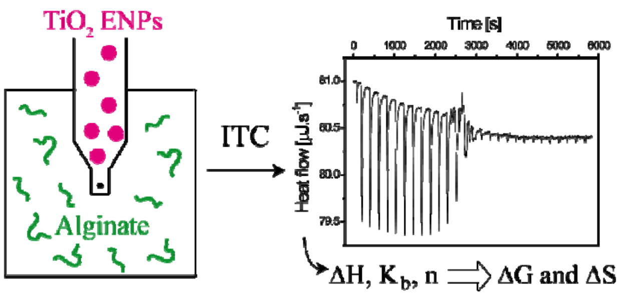

Figure 1 Isothermal titration calorimetry allows the determination of important thermodynamic parameters and assess, when associated with light scattering techniques, the mechanisms of agglomeration.

F. Loosli, L. Vitorazi, J.F. Berret and S. Stoll, *Water Res.*, 2015, **80**, 139.
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