

Isothermal titration calorimetry (ITC) meets soft-matter colloid science

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Isothermal titration calorimetry (ITC) is a method that has found wide use in biochemistry and biophysics in the last 50 years. It is based on the titration of a solution containing a “biological macromolecule” with repeated minute amounts of another solution containing a suitable “substrate”. Simple models have been devised to fit the thermograms and obtain important thermodynamic information on the “binding”. ITC is a powerful method, but it is severely limited in the absence of knowledge of the structure of the system and the processes actually taking place. This has hindered its widespread application in colloid science, in particular in its soft-matter branch, where significant structure variations can happen in a solution over a single titration.

In the present seminar, three specific problems will be discussed, each illustrating the qualitative value of the method and the great quantitative advances, if added structural and/or modelling information is available.

First, we will examine heat interactions taking place in a liquid-liquid extraction (LLE) system. LLE used for metal separation is based on the transfer of several species (most importantly water, salts and acids) between two different phases in pseudo-ternary phase diagrams. Since several different processes take place at an extraction step, it is difficult to decompose the enthalpy of the total extraction process into individual contributions associated with fundamental processes. Previous results obtained by calorimetry could not distinguish complexation enthalpy from enthalpy of transfer, since the phase diagram, the colloidal microstructures existing in both phases, and the equality of chemical potential of water and acid species co-extracted with the salts were generally not taken into account [1-3]. We show here that combining mixing calorimetry and isothermal titration calorimetry in several identified compositions in peculiar positions in the pseudo-ternary phase diagrams allows to distinguish the partial complexation enthalpy and the enthalpy of transfer for a lanthanide salt, water and co-extracted acids [4]. In addition, analysis of the ITC results using a microdroplet model of the oil phase provides estimates of the total enthalpy of the reversed micelles formed in the oil phase and of the intermicellar interactions.

A second application involves the qualitative measurement of the heat of interaction of lanthanide salts with zwitterionic micelles. It will be shown that salts of the same metal with different anions actually produce different heat effects, and that at the limit of low salt concentration the interaction between salt and surfactant (despite complexation) is endothermic, which can be attributed to hydration [5].

Finally, ITC has been widely used to determine the critical micellar concentration of many surfactant systems and other micellar properties [6]. It will be shown that careful modelling of a large database of heats of micellization may actually lead to new insights on the micellization phenomenon, since the change in enthalpy and free energy of micellization may become available as functions of the aggregation number. Many surprising results, such as the importance of premicellar aggregates, “a correspondence law” for different micellar systems, and the extraction of size distributions from calorimetry data are demonstrated.

- [1] T. Zemb, C. Bauer, P. Bauduin, L. Belloni, C. Déjugnat, et al., Colloid Polym. Sci. 2015, 293, 1.
- [2] M. Špadina, K. Bohinc, T. Zemb, and J.-F. Dufrêche, Langmuir 2019, 35, 3215.
- [3] M. Špadina, J.-F. Dufrêche, S. Pellet-Rostaing, S. Marčelja, and T. Zemb, Langmuir 2021, 37, 10637.
- [4] A. El Maangar, L'extraction raisonnée de métaux stratégiques par des hydrotropes, 2022, PhD thesis, ICSM
- [5] C. Sofroniou, I. Chazapi, E. Leontidis, J. Colloid Int. Sci. 2019, 557, 568.
- [6] Ž. Medoš, M. Bešter-Rogač, Langmuir 2017, 33, 7722.