Calorimetry and thermal analysis approach to study Bio-macromolecules. From systems in solution to condensate biomaterials

Dimitrios Fessas
University of Milan, Department of Food, Environmental and Nutritional Sciences
Email: dimitrios.fessas@unimi.it
Celia Duce
University of Pisa, Department of Chemistry and Industrial Chemistry
Email: celia.duce@unipi.it

Calorimetry and Thermal Analysis is widely used for the characterization of bio-systems. The rather well defined general picture of the field implies the use of techniques and theoretical approaches that depend not only on the chemical peculiarities but mainly on the status of the system with respect to the aqueous medium and the co-solutes.
In the case of bio macromolecules in diluted solution/suspension (globular proteins, DNA, membranes, etc.), calorimetric data, once treated according to the formal expressions of thermodynamics and statistical mechanics, allow evaluation of the partition function of the system which includes all the thermodynamic information about the accessible states and their stability, singling out enthalpic from entropic contributions. More specifically, the HS-DSC (High Sensitive Differential Scanning Calorimetry) provides quantitative information about the mechanisms of the conformational transitions and the thermal stability of the energetic domains of the macromolecules, allowing one to separate the contributions relevant to either the solvent or the co-solutes that are responsible for specific interactions. Further details about the thermodynamics of this kind of interaction (affinity constant, interaction enthalpy and entropy, cooperativity, allosteric effects, etc.) can be drawn from ITC (isothermal titration calorimetry) investigations.
The above thermodynamic picture is substantially modified when bio-polymers (polysaccharides, proteins, lipids, etc) are present in a condensate phase. These biopolymers often are thermodynamically incompatible, leading to the formation of several distinct phases in the system (aqueous or not) which may be in thermodynamic equilibrium or not. In this context, thermogravimetry combined with DSC analysis represents one of the most suitable approaches to a comprehensive understanding of the properties of these complex matrices, including their modifications induced by the thermal treatment.
In this lesson we provide elements of the general physical chemistry background of these methods and examples following some case studies, including tips and tricks for practical use.