

**O4 SES1**

**SUPRAMOLECULAR AMPHIPHILES: FROM HOST-GUEST COMPLEXES TO CATIONIC MIXTURES**

R. Migliore<sup>1</sup>, C. Sgarlata<sup>1</sup>, G. Arena<sup>1</sup>, M. Gradzielski<sup>2</sup>

<sup>1</sup>*Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Catania, Italy*

<sup>2</sup>*Stranski-Laboratorium für Physikalische Chemie und Theoretische Chemie, Institut für Chemie, TU Berlin, Berlin, Germany*

Amphiphiles have many applications in several fields, such as cosmetics and drug delivery etc. Thanks to their surface active properties these compounds are also named surfactants. Conventional surfactants consist of a hydrophobic alkyl chain and a hydrophilic head group, linked by covalent bonds. A new class of amphiphilic systems, the so-called supramolecular amphiphiles or supramphiphiles, has gained increasing attention in recent years. In this case the hydrophilic and hydrophobic components are held together by non-covalent interactions. Several strategies can be used to obtain supramolecular amphiphiles including host-guest, hydrogen bonding, charge-transfer,  $\pi$ -stacking, and Coulombic interactions [1,2]. Sulfonatocalix[n]arenes (SCn) are water-soluble macrocyclic host molecules formed by n 4-hydroxybenzenosulfonate units linked by methylene bridges in the *meta* position. With  $\pi$ -rich hydrophobic cavities and an upper rim decorated with negatively charged sulfonate groups, these hosts display high affinity and selectivity for positively charged organic species [3]. Besides simple host-guest complexes, SCn's were found to be very effective hosts for the construction of supramolecular amphiphiles owing to their special ability to induce the aggregation of suitable guest molecules. Self-assembled soft materials based on SCn are particularly attractive for biological/biomedical applications due to their low toxicity, water solubility and relatively simple synthesis yielding material on a multigram scale [4]. However, despite the interest in calixarene-based supramphiphiles, a quantitative characterization of the binding features and driving forces of the host-guest formation as well as the aggregation processes occurring in neutral aqueous solution has not been reported yet [5]. In this work, complex species, binding constants and forces driving the formation of supramphiphiles made of a p-sulfonatocalix[4]arene and positively charged long-tailed guests in neutral (buffered) aqueous solution have been determined by isothermal titration calorimetry (ITC) in order to find out the best systems and conditions for the assembly of efficient micellar-like aggregates. The aggregation features of the most promising host-guest complexes have been also studied by ITC in neutral aqueous solution. CMC and  $\Delta H_{mic}$  values of the micellar-like aggregates formed by different supramolecular surfactants highlight the crucial role played by the calixarene scaffold in the formation of efficient self-aggregating systems. Furthermore, mixed systems formed by the supramolecular amphiphiles and selected cationic surfactants have been studied. The synergistic properties and the structural changes of the resulting intrinsic cationic mixtures have been evaluated [6].

**O4 SES1**

**References**

- [1] He Q., Ao Y. F., Huang Z. T. and Wang D. X., *Angewandte Chemie*, 2015, 127(40), 11951.
- [2] Duan Q., Cao Y., Li Y., Hu X., Xiao T., Lin C., Pan Y. and Wang, L., *Journal of the American Chemical Society*, 2013, 135 (28), 10542.
- [3] Bonaccorso C., Migliore R., Volkova M. A., Arena G. and Sgarlata C., *Thermochimica Acta*, 2017, 656, 47.
- [4] Coleman A. W., Jebors S., Cecillon S., Perret P., Garin D., Marti-Battle D. and Moulin M., *New Journal of Chemistry*, 2008, 32(5), 780.
- [5] Basilio N., Francisco V. and Garcia-Rio L., *International Journal of Molecular Science*, 2013, 14, 3140.
- [6] Wolf C., Bressel K., Drechsler M. and Gradzielski M., *Langmuir*, 2009, 25(19), 11358.