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Contribution ID: 40

Type: poster contributions

## Hierarchical self-assembly of surfactants and cyclodextrins: from inclusion complexes to responsive supramolecular aggregates

Cyclodextrins (CD) are cyclic oligosaccharides formed by  $\alpha$ -(1-4)-D-glucopyranoses linked units. Their unique shape and the presence of a cavity provide particular physicochemical properties, including the ability to form host-guest complexes [1]. Cyclodextrin-surfactants host-guest complexes are a flourishing research field due to the availability and diversity of surfactants and the tendency to self-organize into highly ordered structures [2]. Among many surfactants, polyoxyethylene alkyl carboxylic acids (CiEjCH<sub>2</sub>COOH) are attractive surfactants to integrate these systems as guests due to their pH and thermo-responsiveness [3]. In the last years, a multi-level assembly involving complex building blocks ordering has raised strong interest in many scientific areas. The lattice self-assembly of inclusion complexes relies on strong and directional intermolecular interactions between the CDs involving a delicate balance of forces, producing rigid and complex structures [4].

The formation of inclusion complexes and thermodynamics of complexation of  $\alpha$ -CD and  $\beta$ -CD with C<sub>12</sub>E<sub>5</sub>CH<sub>2</sub>COOH and C<sub>12</sub>E<sub>10</sub>CH<sub>2</sub>COOH in aqueous solutions was studied by densitometry and isothermal titration calorimetry (ITC), and a comprehensive structural investigation was conducted by small-angle neutron scattering (SANS), differential scanning calorimetry (DSC) and microscopy. The spontaneous formation of the host-guest complexes and their assembly as building blocks of large supramolecular aggregates with rich structural behaviour was verified.

The results pointed to a remarkable dependence of the structures on the mixing ratio, concentration of the components, and temperature. In addition, by exploring the pH responsiveness property of the surfactants, it was possible to fine-tune the structures and, therefore, control the self-assembly process. The formation of well-layered structures exhibited long-range order in the most concentrated systems with the ionized surfactant, at high pH, featuring multilayered hollow cylinders, whereas rhomboidal crystalline plates are obtained in nonionic systems, at low pH [4]. The analysis also allowed an insight into the effect of the number of ethylene oxide units and CDs features in the formation and topology of the novel aggregates.

In an additional approach, the addition of chitosan to the system revealed a novel parameter for self-assembly control. The polymer addition affects the specific inclusion complexation forces, long-range electrostatic interactions, and dispersion forces within the supramolecular aggregates, influencing the CD-CD hydrogen bonding network.

This work delivers a thermodynamic and structural complementary approach that allows designing supramolecular aggregates of the desired properties with potential applications in a variety of formulations.

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