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ADSORPTION OF CALIXARENE-BASED SUPRAMPHIPHILES AT THE SOLID-LIQUID INTERFACE MONITORED BY QCM-D

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Surfactants or amphiphiles are molecules that consist of a polar or ionic hydrophilic head group and a hydrophobic tail, often a long-chain aliphatic hydrocarbon group. Surfactants can be classified as anionic, cationic, nonionic and amphoteric based upon the nature of the hydrophilic head. Surfactants have widespread applications in industry as emulsifiers, foaming agents, wetting agents, dispersants and detergents. Pharmaceutical and biotechnology industries use surfactants for a variety of applications including stabilization of protein therapeutics.

Amphiphilic surfactants do not feel “at ease” in any solvent, be it polar or non-polar, since there is always one of the groups that does not like the solvent environment. Thus, these molecules do have strong tendency to migrate to interfaces or surfaces to orient themselves [1].

Self-assembly, making use of amphiphiles as building blocks, is an important topic in supramolecular chemistry. Besides the vast amount of synthetic conventional amphiphiles, there has been great interest in supramolecular amphiphiles (supramphiphiles) in which noncovalent interactions are used to promote their formation. Interactions between the hydrophilic and hydrophobic components may result from hydrogen bonding, electrostatic attraction, coordination interactions, charge transfer, π - π stacking and *host-guest* interactions [2, 3]. These systems can aggregate to form micelles, bilayers, vesicles.

In the present communication we report on interface adsorption studies of supramphiphiles formed by a p-sulfonatocalix[4]arene (*host*) and cationic *guests* that differ for the length of the hydrophobic tail or for the polar head; the process is monitored by Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). Deposition of a thin, rigid and uniformly distributed layer on the quartz surface causes a decrease of the crystal oscillation frequency; however, when a soft or thick layer is bound to the crystal, dissipation changes [4].

The study at the solid-liquid interface compares the absorption features of conventional amphiphiles [5,6] with those of supramphiphiles. The adsorption of both conventional and supramolecular surfactants is strongly affected by the length of the apolar tail and, partially, by the nature of the polar head. Although supramolecular systems have critical micellar concentration (CMC) values much lower than the analogous uncomplexed surfactants [7], the absorbed amount at the interface is somehow comparable thus highlighting the key role played by the calixarene scaffold. Indeed, absorption isotherms may be satisfactorily obtained also when dealing with fairly diluted surfactant solutions. Furthermore, the presence of the calixarene moiety inhibits the “bulk” effect observed for surfactants with

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large CMC value. Finally, kinetic adsorptions curves revealed significant insights on the rate as well as the mechanisms of the adsorption processes.

References

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