Quasi Chemical Theory and MC Simulations applied to hybrid systems of surfactants and terminal or bridging organosilica precursors

A. Patti[1], A. D. Mackie[1], F. R. Siperstein[1,2]

(1) Escola Tecnica Superior d'Enginyeria Quimica,
Universitat Rovira i Virgili, Tarragona

(2) flor.siperstein@urv.cat

MC simulations in the NVT ensemble are used to model amphiphilic solutions where terminal (R-Si-$(OEt)_3$) or bridging ($(EtO)_3$-Si-R-Si-$(OEt)_3$)) organosilica precursors (OSPs) are also present. At high surfactant concentrations, these systems are able to form periodic structures, such as hexagonal-ordered rods and lammellas [1], that are key in the synthesis of functional mesoporous materials.
In this work we aim to compare the phase behaviour of bridging and terminal OSPs to understand to which extent they can be used for the synthesis of ordered mesoporous materials, depending on their hydrophobic/hydrophilic nature and solubility in the solvent.
The structures obtained from different precursors are compared on the basis of two factors: (i) the degree of order obtained, and (ii) the distribution of the organic group of the OSPs in the framework walls.
Experimental evidence indicates that it is easier to obtain ordered materials with bridging precursors than with terminal precursors [2]. Our simulations indicate that this is because the surfactant content in the concentrated phase is higher when bridging precursors are used. When hydrophobic terminal OSPs are used, ordered structures are not obtained, regardless of the concentration of surfactant, because of the high hydrophobicity of the organic group in the precursor. Also with hydrophobic bridging OSPs no ordered structures are observed, although non-ordered aggregates are formed in the surfactant-rich phase.
In general, good agreement is observed in the phase diagrams obtained using quasi chemical theory and MC simulations. Quantitative agreement is found when no ordered structures are formed, but some discrepancies are observed in systems with ordered structures, especially when the OSPs are miscible with the solvent.

[1] A. Patti et al. COPS VII, Studies in Surf. Sci. and Cat. **495**,(2006).

[2] B. Hatton et al. Acc. Chem. Res. **38**, 305 (2005).