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SUPRAMOLECULAR SYSTEMS BASED ON CALIX[4]ARENES: A PLATFORM FOR NANOMATERIALS DESIGN BY SELF-ASSEMBLY

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Lower rim thiacalix[4]arenes derivatives in *cone* and *1,3-alternate* conformations have many advantages to create a wide range of precursors for the design of very sophisticated supramolecular architectures.
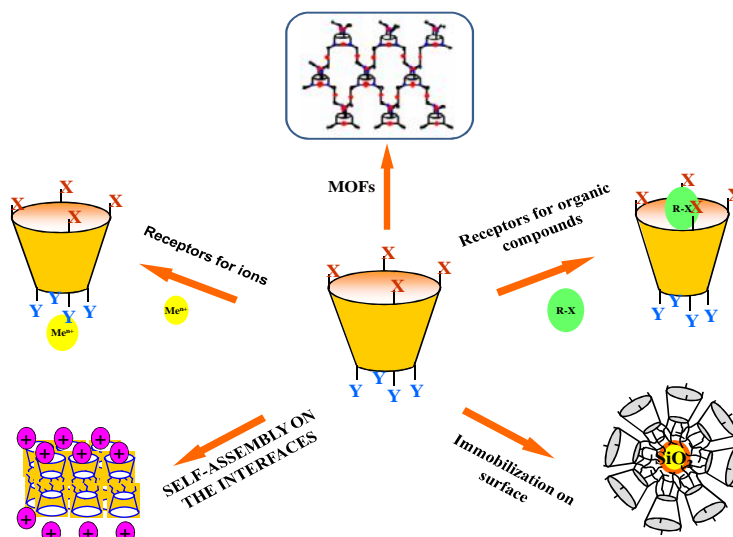
These compounds can be considered as technological platform for nanomaterials design by self-assembly method. Particular attention will be paid to the application of calixarene derivatives for the construction of various supramolecular and nanosystems, devices and smart materials: colloid nanoparticles, catalytic systems, metal-coordinated networks, Langmuir-Blodgett nanolayers, molecular magnets etc.

MOLECULAR THERMODYNAMICS FOR MICELLE-MEDIATED SEPARATION OF BIOCOMPONENTS

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In chemical and biomolecular engineering, micelle mediated separation has become an important tool that is widely used for cloud-point extraction, purification, controlled release and delivery of chemicals [1,2]. Examples are numerous and include applications of micelles formed by surfactants and their formulations as well as block copolymer micelles in cosmetics, pharmacy, medicine, oil industry, etc. [3,4]

Whereas a substantial amount of knowledge has mainly been amassed from experimental experience and voluminous empirical data, the development of a rigorous statistical mechanical theory has been hampered, owing to structural complexity of micellar systems that are strongly nonuniform on the scale of a single aggregate and are not well-suited for coarse graining and application of the theoretical approaches developed for macromolecular systems, including self-consistent field techniques.

Molecular simulations have progressed tremendously within the last 20 years and helped to establish peculiar microscopic features of quite a number of specific micellar systems yet simulations remain generally too time-consuming to be applied for engineering applications. Therefore, the molecular-thermodynamic approaches that have been first proposed in the early nineties and combine accurate empirical correlations with the elements of rigorous statistical mechanics remain the most effective approach for correlating experimental data and predicting the aggregation behavior of micellar systems from the molecular characteristics of components [5].

The core problem is to model the distribution of solute molecules between the micelle and the surrounding solvent depending on the shape (sphere, wormlike, vesicle or other) and size distribution of the aggregates. Description of the liquid-liquid phase split and of the cloud-point curves for a micellar solution is another hard problem that includes modeling of intermicellar interactions and the development of the osmotic equations of state. Theoretical description of the details of solute partitioning in such systems is a particularly challenging task.

In this work we overview the molecular-thermodynamic approaches available for describing the partitioning of solutes in micellar systems formed by surfactants and their mixtures, including classical molecular-thermodynamic aggregation models, mean-field models of block copolymer micelles, COSMOmic [6], single-chain self-consistent field approach [7] and versions of the molecular-thermodynamic models developed in our group. We discuss recent trends in the field and summarize model limitations and challenges.

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HYDRATION AND COUNTERION-BINDING OF SOME COMMON NEUROTRANSMITTERS

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Neurotransmitters (NTs) are a class of small, biologically active molecules essential for signal propagation in living organisms as they transmit signals across the synaptic cleft connecting two neurons or joining a muscle cell and a neuron. In this process the excitation potential moving along the presynaptic nerve triggers NT release from storage vesicles at the end of the axon into the synaptic cleft. The NT then diffuses across this gap and, by binding to specific receptors on the postsynaptic neuron, excites or inhibits the electrical signal carrying information further. Obviously, NT action arises from specific interactions with their receptors. However, in the synaptic cleft these molecules interact with water and other dissolved molecules and ions, which affects their binding behavior, metabolism and reuptake [1,2].

In this contribution, we compare the hydration and -where appropriate- counterion binding of three common neurotransmitters, namely acetylcholine (ACh^+, as chloride salt), γ-aminobutyric acid (GABA), and glutamate (Glu^-, as sodium salt [3]). These three NTs have similar size and shape but either carry a single positive charge (ACh^+), are zwitterions (GABA) or combine a zwitterionic moiety with an additional negative charge (Glu^-). Aqueous solutions at natural pH up to the saturation limit were studied with broadband dielectric relaxation spectroscopy (DRS), statistical mechanics at the 1D-RISM and 3D-RISM level, and dilute-solution conductivity measurements (AChCl only).

For all three NTs DRS-detected effective total hydration numbers, Z_t (ACh^+ ~11, GABA ~11, Glu^- ~40 at c→0), decrease with increasing solute concentrations. Whilst for ACh^+ and GABA this decrease is linear up to the respective solubility limits (~0.6 and ~6.2 M), that for Glu^- (solubility ~1.8 M) is bimodal with a clear break at ~0.25 M. Interestingly, the high-concentration data for Glu^- extrapolate to $Z_t(0) \approx 15$ and thus are again comparable to ACh^+ and GABA. It was possible to split Z_t into contributions of Z_s moderately bound and Z_{ib} "frozen" water molecules hydrating the solute. Except for Glu^- at c < 0.25 M, where apparently also the second hydration shell is affected, comparison of Z_s and Z_{ib} with coordination numbers deduced from RISM suggests that both fractions of DRS-detected bound water are mainly interacting with the ester moiety of ACh^+ or the carboxylate groups of GABA and Glu^-. This is corroborated by the effective solute dipole moments obtained from the relaxation strengths of ACh^+, GABA and Glu^-.

With regard to counterion binding by the ionic species ACh^+ and Glu^-, it appears that the formation of $[Na^+Glu^-]^0$ ion pairs is negligible. On the other hand, with a standard-state association constant of $K_A^\circ = 2.5$ M^{-1} at room temperature, the formation of $[ACh^+Cl^-]^0$ contact ion pairs is weak but not clearly negligible.

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