New Surfactant Structures: the key for chemical nanotechnology and new processes

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In research, but slowly approaching also in applications, design and employment of surfactants underwent – beside the continuous evolution process- a “silent revolution”. Beside washing and cleaning, surfactants are more and more intelligent key components in a variety of non-classical application fields, e.g. nutrition, cosmetics, agrochems, diagnostics and drugs, pigments, and –maybe most surprising- in large scale materials applications, such as high strength concrete or nanocomposite polymers.

As a minor component, the intelligent use of surfactants creates products with partly highly added value, and one might phrase illustratively that surfactant science shifts from commodity operations (being mainly driven by economy of scale) to key knowledge based activities, i.e. we expect the shapening and creation of more and more “know how” companies, based on the principle of surface structure and process control.

This can be exemplified with a long list of cases: surfactant controlled drug crystals or drug delivery system change pharmacy completely, “nanovitamines” improve the benefits of cosmetics, “nanofoamed” polymers stabilized by special surfactants are essential for heat insulation, nanocolorants give new dye effects and allow new printing resolutions, water based polymer applications increasingly involve special surfactants, etc, etc. In the very heart, the whole chemical nanotechnology cannot live without a new generation of surface active molecules.

The present contribution will mainly focus on those new surfactant applications, and I will try to delineate the new demands on surfactant structures plus the solutions and technologies coming from those demands and problems.

The problems of classical surfactants in nanotechnology

It is trivial knowledge: the smaller structures become, the higher is their interface. Assuming similar shapes, all colloidal quantities scale with the size, e.g. the surface area goes with the inverse of size. Typical oil droplets of 1_m radius (“classical technology”) have a surface area of 3 m²/g, whereas similar 10 nm sized particles simply have 300 m²/g.
By similar principles, the droplet pressure (driving for instance Ostwald ripening) is increased by a factor of 100, the number of droplets has increased by $10^6$, and the mutual droplet distance is lowered by a factor of 100.

This already indicates that the demands onto surfactant properties “explode” with decreasing size.

It is the rare exception that you do the targeted nano-operations with classical surfactants. For instance, a similar surface coverage would simply require 100 times higher surfactant loads, which is usually not feasible. Nevertheless, the following arguments also hold for classical application and size ranges, but are simply not so critical there.

One can indentify two conceptual weaknesses of traditional surfactants:

- The “wrong” polarity design. Most surfactants show something we call the “cohesion energy gap”, that is they are composed of a very polar and a quite unpolar moiety only. This implies that many surfaces and molecules cannot be appropriately addressed, as they found no counterpart in the molecular structures. In addition, self-adjustment to the surface is impossible due to molecular layout.
- The “wrong” geometry design. For “nano”, a layer thickness of 3 nm to be effective is an incredible waste of material. Model experiments with target structures indicate that the same job can be done with 0.3 nm thickness, that is a tenth of surfactant load.

**Biomimetic approaches**

As Nature performed, in modern language, about 500 Myears research and development on the stabilization of nanostructures, we can learn in modesty for her solutions. And: Nature does not use the layout principles of technical surfactants at all! (Only lipids are known, but they are usually used as flexible mechanical construction parts. Employment of lipids a stabilizer always fulfils second thoughts). For us, especially two solutions a worthy of note:

- Flat stiff structures which do not form micelles. Indeed, their effective thickness for surface stabilization is just 0.3 nm, and they are multipolar. This class includes systems as cholic acid (a well known superior cleaning agent!), saponines, deferoxamines, or didesipside. They are excellent “problem solvers” for technology, but their use in consumer applications is critical.
- Short polymeric structures as stabilizers (usually proteins, but also olgosaccharides). Flat polymer adsorption is regarded as the most efficient stabilization motive (as measured in $m^2/g$), whereas “trail adsorption” represents the most stable situation known. In addition, polymers are “multipolar” or adaptive to a variety of surfaces, and – with appropriate design, they decompose into useful (or harmless), non amphiphilic fragments.

**Amphiphilic Copolymers**
From those two solutions, the present contribution will mainly focus on the second class of stabilizers, the amphiphilic polymers. The high efficiency can be quantified in model experiments, e.g. in emulsion polymerisation of for the formulation of nanoemulsions. The high selectivity and the ability to adopt surfactant structure to practically all solvens/dispergendum problems (“generalization of amphiphilicity”) is shown in the light of examples of very non-traditional surface stabilization problems, namely hydrophilic - hydrophilic stabilization hydrophilic-biophilic.

Double hydrophilic copolymers

A “double hydrophilic” stabilization problem of largest industrial importance is the surface control of polar crystalline materials in general or –specifically- inhibition of mineral scales. Scale inhibitors are already an indispensable part of modern detergent formulations, but their efficiency is quite low. Optimized structures on the base of double hydrophilic copolymers can do the same job at much lower concentrations (ca. 10 % of the classical value), but also with higher structural definition. Figure 1 illustrates the structure of calcium carbonate scale in the presence of classical ligating agents (EDTA, resp polyacrylic acid EDTA) and in presence of an optimised polymer amphiphile:

Fig.1. Morphological results of CaCO$_3$ mineralization in presence of EDTA (a), PAA (b), and a double hydrophilic surfactant (c)

Such techniques can obviously not only used for inhibition, but also for synthetic purposes of well defined powders.

Hydrophilic-“biophilic” stabilization or “chimera” polymers

Another interface of enormous importance is the one between biological objects and the synthetic world. This interface is not only characterized by a structure and polarity, but also by active biological mechanism which have to be considered in the surfactant design. Promising results to actively address this interface have been obtained by so called “chimera”-polymers, structures which are partly composed of biological matter, partly of synthetic polymers.
Fig.2: two examples for “chimera polymers”: the structure is composed of a synthetic polymer part (grey) plus biological fragments, here an α-helix (a) or side chain binding sites (b).

Such polymers are able to mediate between implants and the cell tissue, can transport drug particles within the body in stealth. Other structures made by a variety of groups can dissolve or refold proteins (such as prions), that is they are indeed very powerful. As such structures use the language of living cells, they have to be applied with great care.

A model case for new technology based on surfactants: mini- or nanoemulsions

As a last case for potential innovation, the so-called miniemulsions are presented. In miniemulsions, insufficient surface coverage is bypassed by an osmotic agent to counterbalance Ostwald ripening, so that even classical surfactants can be employed with higher efficiency. With this technique, reverse and inverse emulsions with droplet diameters between 50 – 500 nm can be generated. These emulsions are useful as they are, but can be also employed to realize previously hardly or even impossible procedures and reaction schemes, e.g. the reactions between hydrophilic and hydrophobic components in a two-phase situation.

This is especially important for the synthesis of surface active structures and the application of enzymes onto hydrophobic substrates. This will be illustrated by the synthesis of polyester nanoparticles by enzymatic polymerisation of lactones and the cleavage of fats.

Here, relative reaction rates are of the order of the natural processes, i.e. unusually high for the technical employment of enzymes in non-aqueous media.

Fig.3: polyester grains obtained by direct enzymatic polymerisation of lactone miniemulsions
Conclusion and Outlook

With its key role in chemical technology and biology, we regard the handling of surfaces with appropriate molecules for all purposes as key “know-how” for the next generation of colloid chemical experiments and products. It was shown that “new” surfactant structures carry the promise to expand the performance profile of nowadays surfactants to handle also more critical surface stabilization problems, e.g. the efficient stabilization of very large surfaces or the closure of the “cohesion energy gap” by multipolarity and adaptive construction.

It is with good reason foreseeable that such surfactants will allow to shape new “world scale” applications, such as nutrition, building materials, nanocomposites, insulating nanofoams, or in the redesign of pharmaceutical actives. Chemical nanotechnology is deep down based on the handling of interfaces, and surfactant science will have its significant share.