Soft Catanionic Vesicles for Hard Nanomaterial Synthesis

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We have summarized the role of self-assembled structures of catanionic surfactants in various templated nanomaterial syntheses. Three basic self-assembly of this recently developed surfactant system have been addressed in this review. The effect of these different catanionic systems on the shape and dimension of synthesized nanomaterials have also been discussed here. So far catanionic systems have been used for synthesis of highly crystalline and well dispersed metallic and metal oxide nanoparticles. However other different nanomaterials along with polymeric nanoparticles are also been considered by different groups to be synthesized within the catanionic vesicular templates and we therefore felt the importance to sum up the works done so far in this regard.

Introduction:

Surfactants have become a very important substance family, demonstrated by their widespread applications in all fields of chemical, pharmaceutical and agricultural industries. Their attractiveness lies in their amphiphilic nature, i.e. they possess a hydrophilic part, also called polar headgroup on the one side, and a lipophilic part on the other side [1].In general,with increasing concentration surfactants assemble to form micelles above the system-specific critical micelle concentration(cmc), followed by the formation of various mesophases and, finally, crystal formation. But depending on the different parameters like temperature, pressure, ionic strength, nature of the counterions, area size per surfactant head group, and length and number of alkyl chain per surfactant micelles grow and take a shape distinctly different from spheroids [1,2]. There are several types of surfactants distinguished by the nature of the headgroup. Generally ionic surfactants (cationic, anionic) have positively or negatively charged headgroups, unlike non-ionic surfactants without any headgroup charges. Surfactants with two opposite charges are called zwitterionic [3]. Mixtures of anionic and cationic surfactants in water produce the so-called ''catanionic'' mixture which has been in the centre of attention of scientists in recent days [4-9]. Catanionic surfactants, which are associations of oppositely charged surfactants, can therefore be seen as a particular case of polycatenar surfactants. The co-adjustment of electrostatic effects and surfactant molecular geometry allows a rich diversity of phase behaviour. It has been reported that catanionic surfactants can self-assemble into variety of microstructures such as equilibrium vesicles [10-13], worm-like micelles [14], disks [15] or regular hollow icosahedra [16] depending upon the composition of the aqueous system.Among different soft drug delivery systems, catanionic vesicles have recently attracted attention towards vectorised hydrophilic and hydrophobic substances and likewise insure protection of encapsulated drugs, reduction of their toxicity and improvement of their efficiency with duration. In this regard it is worth mentioning that in the present social, economical and environmental

situation, designing of sustainable and cheaper material and processes are more and more encouraged. So, preparing nanomaterials within the mixture of heterogeneous molecules which can self-assemble easily is considered quite fascinating rather than the homogeneous system. Due to the strong synergism between the oppositely charged head groups,catanionic surfactants can self-assemble both at the air/water interface and also in the bulk solution [4,17-20] with no chemical modifications or reactions [20,21].In last ten years we have seen an enormous change in the approach towards nanomaterials synthesis. Soft chemical synthetic procedures easily outperformed the conventional solid reaction process to realize precise control over i) synthesis procedure, ii) shape, size and dimension, and iii) properties of the synthesized nanomaterials [22,23]. Generally in soft chemical approach, micelles of normal surfactants (both ionic and non-ionic) and polymers with and without micelle forming ability have been employed for shape controlled nanomaterial synthesis [24-26]. These templates have the ability to direct the shape and size of nanomaterials by restricting the aggregation of particles and also by modifying various reaction parameters like temperature, pH, solvent, acidity, reaction time etc. Soft templates basically allow the delicate building of novel nanostructures with tunable properties and surface chemistry. The use of catanionics or coacervates as templates is increasing rapidly due to their fascinating different phases in aqueous and non-aqueous media. A slightest change in the composition can produce various microstructures with characteristic geometries ranging from spherical to cylindrical to planar structures. Different phases can be achieved by a single catanionic mixture which is unattainable through a single conventional surfactant. Among the different phases scientists exploited mainly bilayer lamellar phases, wormlike micellar phase and vesicle form. This soft chemical methodology has triggered substantial interest due to its self-assembling tunability and bio-mimetic approach.

A comprehensive understanding of thetemplating roles of softcatanionic vesicles is emphasised,including detailed procedures of vesicle templating,the confirmation of synthetic mechanisms, and the properties of the expected materials, which we expect to further promote using soft matter in hard materials applications.

Synthesis of Hard Nanocrystals within the Vesicular templates:

Vesicles are very popular amongst scientists as one of the most convincing model for biological membrane systems and their growing practise in pharmaceutical industry for their outstanding ability towards vectorization of hydrophilic and lipophilic substances [27]. Vesicles have generally spherical, enclosed and hollow structures with a curved bilayer comprising of both hydrophobic and hydrophilic region. The most well-known vesicle is liposomes, mainly comprised of phospholipids (phosphoglycerides and sphingolipids) and cholesterol. However poor physical and chemical stability of the liposomes due to aggregation/flocculation, fusion/coalescence, and lipid ester bond hydrolysis affect the shelf life of liposomes and these factors lead to the formation of unusable large-sized objects and leakage of encapsulated drugs. It is also worth mentioning that synthetic procedures of liposomes require organic solvents which might induce toxicity in the system [27-33]. But in case of catanionic surfactant, when both cationic and anionic surfactants pair with each other the packing parameter$P$ (V/a_0L, where$V$is the volume of thehydrophobic part of thesurfactant, a_0 is the

equilibrium surface area per molecule at the aggregate interface and L is the length of the hydrophobic chain) gets substantially reduced and along with that the bending energy of the catanionic bilayer shows two deep minima on each side of equimolarity. So, vesicles can be formed very easily with low curvature. The modulus of P suggests the type of structure/shape that surfactants tend to assume upon aggregation. Vesicles form when the packing parameter reaches an optimal value leading to the formation of a close double layer [34-37]. In the field of materials chemistry confined compartments of catanionic vesicles (mimicking the confinement in cells or in the extracellular space) are becoming more popular for nanomaterial synthesis [38]. Nanomaterials can be synthesized within the three regions of a catanionic vesicle, i) hydrophilic core, ii) membrane restricted bilayers and iii) hydrophilic outer surface. For hydrophilic core region, the water pool within the core is quite different than the bulk aqueous phase. One of the first reports in nanomaterial synthesis within the vesicle chamber was by Bose et al. in 1995. They produced magnetic $\tilde{a}$-ferrite within the catanionic vesicle of cetyltrimethylammonium bromide (CTAB) and dodecylbenzene sulfonic acid (HDBS) [39]. However in presence of CTAB and sodium octyl sulphate (SOS) a less control was achieved as Fe_3O_4 was formed both within the core and also in bulk solution, as evident from TEM pictures [40]. For the synthesis of nanomaterials within the constrained chamber of catanionic vesicles one must take into account two major concerns. First of all the cations should be removed or desalted from the external environment of the vesicles through dialization or ion exchange process. This procedure result in an immediate osmotic swelling of the oppositely charged ions (anions) into the core region of the vesicles to produce desired nanoparticles.The second point is that the formed vesicle should be stable enough to maintain its morphology and structure during the pool. This strategy has not a handful of references. Although there are some reports available based on lipid vesicles [38,41-44], the chamber of catanionic vesicles are yet to receive proper attention as the microreactor for nanomaterial synthesis. We believe unilammelar vesicles composed of catanionic surfactants are rational choice for adopting the above strategy.
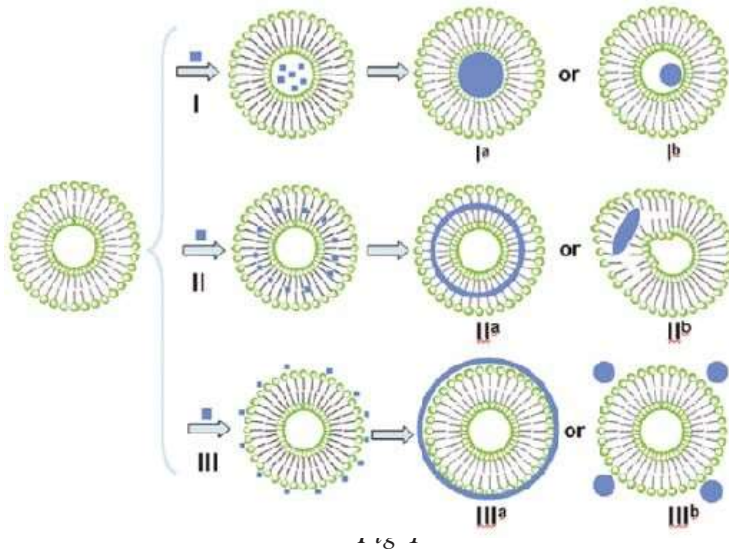

Fig. 1

Figure I: Schematic routes of the three principal uses of soft vesicles in the synthesis of hard materials: I, reaction compartmentalization; II,membrane-restricted microreactor; III, surface-reactive templating and synthesis.

Another procedure involving restricted catanionic bilayers has gained immense interest for the synthesis of hydrophobic nanomaterials. This strategy is mainly becoming popular as it can act both as a constrained reactor for polymerization reaction and for hollow silica nanospheres. In the hydrophobic bilayer the monomers are well distributed to form well defined polymer networks to yield hollow polymer capsules. The stability and the spacing of the bilayers were found to be the major controlling factor. Spontaneous formation of bilayers loaded with the monomers and monomers loaded by diffusion within the bilayer resulted in the hollow polymer nanocapsules with same dimension and morphology [45,46]. Vesicle bilayer has been used for preparing silica materials for very long time. In this procedure silicon alkoxides {generally tetramethylorthosilicate (TMOS)} are hydrolyzed, and the resulting silicic acid polymerizes upon condensation to form silica.However so far, scientists generally emphasized on the vesicles made of diblock copolymers for this purpose [23,47]. Very recently there are few reports, which have been published where catanionic vesicle bilayer have been used [48-57]. The hydrophobic interaction gets the water insoluble silicon precursor to get totally solubilized within the bilayer and then the bilayer surfacedirects silica deposition by orienting nucleation andgrowth of silica from the surrounding solution. Variation of the ratio of the cationic and anionic surfactant also can result in different silica structures except the hollow one.

The outer surface of catanionic vesicles have also been proved as potential templates for nanomaterials. These active external layers are generally used for hollow oxide synthesis. Hollow structure can be achieved if the ions are evenly distributed around the outer surface of the vesicle and which is only possible for charged vesicular surface. In this particular approach catanionics surpass the conventional lipid vesicles and depending on the morphology of the vesicles one can easily modulate the shape of the hollow structures as here vesicle act as a filler material [58,59]. However without proper precision different structures are developed apart from the hollow ones [60].

Conclusion:

This report narrates recent developments in the use of soft catanionic vesicles for hard nanomaterial fabrication and characterization. Understanding the ways to control the vesicle templating system is very important to study the physical chemistry of hard materials/softmatter organization. Vesicles have provided various means tosynthesize different functional materials. However, success in this templating area hinges largely on the stability of the vesiclesemployed. Therefore, the study of the different factors (including solvent selection, composition,temperature, pH, the presence of salts, and pressure) that influence thephase behavior of amphiphilic molecules is another important issue. In fact,using amphiphilic molecular aggregates as templates for material synthesis is also a study of the phase behavior of amphiphilic molecules.As stated succinctly by Kaleretal.,"Template

synthesis is not only a powerful means for materials synthesis, but it can also contribute to the determination and analysis of self-organized morphologies [48]."

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