

# Novel Nanoaggregates of Surfactants and Block Copolymers

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**Abstract**—Surfactants self-aggregate spontaneously form micelles in aqueous solution above the critical micelle concentration (CMC). Because of this distinctive property it is widely used in many applications. Polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) block copolymers are nonionic surfactants, where polyethylene oxide forms the end blocks and polypropylene oxide forms the middle block, sold under the trade name Pluronic (BASF). These mixed micelles have been investigated on the aqueous solutions of a mixed surfactant system constituted by various surfactants. Water soluble block copolymers have been found to form nanoaggregates with potential applications.

## 1. INTRODUCTION

In the last two decades, new modern informative research have emerged which is broadly defined as “nanoscale science and technology”. These new trends occupy the capability to formulate, characterize, and manage artificial structures, whose features are controlled at the nanometer level. They hold areas of research as Chemistry, Engineering, Physics, and materials science, etc.

Study in this route has been triggered by the recent availability of novel instruments and approaches that allow the investigation of material characteristics with a resolution very close to the atomic level.

Surfactants self-aggregate spontaneously form micelles in aqueous solution above the critical micelle concentration (CMC). Due to this unique property it is extensively used in manufacturing and commercial applications. Mixed surfactant systems in solution exhibit improved surface activity compared to that of pure surfactant solutions. Due to this reason, mixed surfactants are often used in many formulations.

An industrially and scientifically important class is block copolymers. These molecules have two or more large, homopolymerized segments with different chemical characteristics (that is, one hydrophobic and one hydrophilic), giving them surfactant properties. Polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) also known as

EPE block copolymers are nonionic surfactants with following structure (Fig. 1).

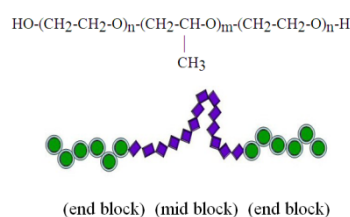


Fig. 1

Amphiphilic block copolymers composed of hydrophilic block and hydrophobic block self-associate in aqueous solution to form a variety of molecular aggregates. These block copolymers widely utilized in a variety of applications such as cosmetics, pharmaceuticals, and petroleum industries. These block copolymers have little toxicity and due to their nontoxic properties and surface-activity, these have found applications in the areas of biomaterials and drug delivery system too. Water soluble block copolymers have been found to form nanoaggregates with potential applications. Aqueous solutions of PEO-PPO-PEO block copolymers exhibit interesting temperature-induced aggregation phenomena as a result of the hydrophobic nature of the PPO block.

At low temperature and concentration, PEO-PPO-PEO block copolymers exist in solution as dissolved monomers but self-assemble at higher concentrations and temperatures into block copolymer micelles (size of several nm) that form under conditions defined by the critical micelle concentration (CMC, at constant temperature) and the critical micelle temperature (CMT, at constant concentration). Highly concentrated solutions of some block copolymers show reversible thermorheological sol-gel transitions. The surface and colloid chemical behaviour of these block copolymers can be tuned by controlling the length of the PEO and/or PPO blocks to observe the desired functional properties.

Block copolymers in solvent free systems form spherical, cylindrical and lamellar morphologies. Temperature induced sphere-rod transitions have also been observed in block copolymers. In some cases worm-like micelles have also been observed.

One novel approach of obtaining nanoaggregates has been through the formation of polyelectrolyte complexes by electrostatic interaction between a double hydrophilic block copolymer and low molecular weight ionic compounds with charge opposite to that on the ionic block of the copolymer. Such complexes resemble amphiphilic polymers as they form nanoaggregates comparable to polymeric micelles. This system is of interest from the standpoint of the development of novel hybrids with organic and inorganic compounds. The morphology and polydispersity of particles produced depends on the molecular characteristic of the copolymer, and on external factors such as temperature, ionic strength and pH. Self-assembly of block copolymers that are made of poly(ethylene oxide), PEO, as the hydrophilic non-ionic block, has been extensively explored. Self-assembled nanoaggregates of amphiphilic block copolymers draw strong research attention due to the large number of promising and potential applications. These include smart nanocontainers for encapsulation, delivery and controlled release of biologically active molecules in nanomedicine, food and personal care products, and agrochemistry. Uptake of heavy metal ions, radionuclides, and toxic organic compounds is being explored for water treatment and environment monitoring purposes. Polymeric nanostructures of diverse and controlled morphologies could work as molecular templates for nanoelectronic devices. The main motivation for studying triblock copolymer is related to the presence of a third nanosized compartment in the micellar structure.

The research interest in PEO-containing block copolymers was motivated, to a great extent, by potential biomedical applications, which rely on the finding that PEO moieties are biocompatible. Because amphiphilic block copolymers of PEO and poly(propylene oxide) PPO (pluronics) are produced on an industrial scale, research on these nonionic polymeric surfactants resulted in many technological applications. Both PPO and PEO are thermoresponsive, having a low solution critical temperature (LSCT), so nanostructures formed from pluronics also show thermoresponsive features. Unfortunately, they do not show a pronounced response to salt or pH changes in the solution. <sup>[1-12]</sup>

Structures formed by amphiphilic block copolymers composed of a hydrophilic block with ionic and, in particular, pH-sensitive (weak polyelectrolyte) segments, linked to a hydrophobic block, are more responsive. This is because the strength of repulsive Coulomb interactions between the polyelectrolyte (PE) segments can be efficiently tuned by variations in pH or/and ionic strength in the aqueous solution,

while their thermo responsive nature can be maintained if the hydrophobic block is well chosen. <sup>[13]</sup>

In this article, I have center on surfactants efficiency, effectiveness, synthesis, stabilization of nanoparticles, case example, and future prospects of about nanoaggregates form due to interaction of surfactants and block copolymers.

## 2. SURFACTANT EFFICIENCY AND EFFECTIVENESS

Surfactants adsorb at interfaces and reduce the surface or interfacial tension. However, to better realize this, and to evaluate different surfactant structures, it is useful to compute the degree to which they lower interfacial tension. This is skillful by introducing efficiency and effectiveness. Efficiency defines how much surfactant is required to induce a given decrease in surface tension. Effectiveness refers to the maximum reduction in surface tension that can be achieved for a given surfactant, regardless of concentration. It is interesting to note that the most effective surfactants are often not the most efficient, and vice versa. Efficiency is primarily determined by thermodynamics i.e. how much more preferable it is to have material adsorbed at the interface rather than in the bulk, and so, larger hydrophobic tails tend to increase surfactant efficiency. Effectiveness is mainly related to the optimum surfactant packing at the interface and thus is determined broadly by the chemical structure/molecular shape of the surfactant.

## 3. SURFACTANTS IN SYNTHESIS AND STABILIZATION OF NANOPARTICLES

These nanoparticles are commodity chemicals, generated on megaton scales, and are used as additives in lubricant oils: as such, these lubricant detergents stand for an important case study for commercialization of nanotechnology. These oil-additive nanoparticles maintain to be used as vital components in today's lubrication oils.

Commercial surfactants are key components in these systems, fulfilling two functions: as reaction control additives limiting the growth of the inorganic particles and as the essential stabilizer of the inorganic solid-hydrocarbon oil interface, for efficient and effective colloidal dispersion in the diluent oil. The purpose of these nanodetergents is primarily acid neutralization: fuel combustion yields many by-products, including inorganic and organic acids formed by oxidation of sulfurous and nitrogenous impurities in the fuel and oxidative degradation of the lubricant to form organoacids. These acids would cause severe corrosion especially under engine start-up conditions. Since these  $\text{CaCO}_3/\text{Ca(OH)}_2$  nanoparticles are relatively insensitive to temperature, they act as slow-release acid neutralizers. The nanodetergents are also effective oxidation inhibitors and provide protection against rust, promoting engine cleanliness, fuel efficiency, and extended

trouble-free operation. Different commercial surfactants are used to stabilize the particles, typically long-chain carboxylic acids, glycols, alcohols, sulfonates, salicylates, or phosphonates. Research into nanoparticles has grown progressively and continues to draw attention, due to the special characteristics of nanomaterials compared to bulk metals, especially with respect to their photochemical and semiconductor properties. Noble metal nanoparticles have attracted significant interest due to potential applications in catalysis, medicals and electronics properties. Reverse micelles and W/O microemulsions are very convenient compartmentalized “nanoreactors” for nanoparticle synthesis, as the magnitude of the polar domains can be controllably adjusted simply by composition, over a range of 1-10 nm. Precursors, such as inorganic salts, can be readily dispersed in the microemulsion medium by dissolution inside water pools. Microemulsions are dynamic systems, and the droplets collide as a result of Brownian motion, facilitating exchange of materials, hence allowing the nanoreactions to take place (Fig. 2). Control can be achieved by variation of the surfactant chemical structure and temperature, to increase (or decrease) the exchange rate of internally dispersed reactant materials.<sup>[14, 15]</sup>

Another approach, used typically for generating metallic nanoparticles, involves preparation of a microemulsion containing an inorganic salt and then controlled mixing with another separate microemulsion carrying a chemical reducing agent.

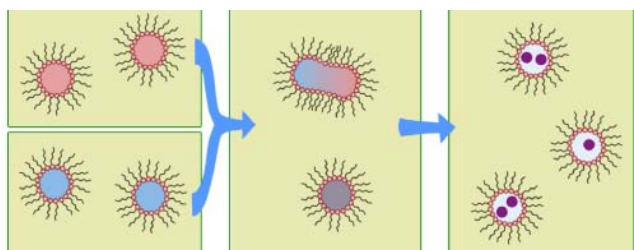


Fig. 2

[Mechanism of nanoparticle preparation]

#### Case of Nanoaggregates of surfactants and block copolymers

Surface active block copolymers are known to interact with normal surfactants such as sodium dodecyl sulfate (SDS). Hecht et al.,<sup>[16-18]</sup> first showed that gradual addition of SDS interfered with and eventually suppressed the micelle formation of the triblock copolymer commonly known by BASF as F127 having a structural formula EO<sub>97</sub>PO<sub>69</sub>EO<sub>97</sub> (MW ) 12500). The basic surface active components of most detergent products are ionic and nonionic surfactants. Most successful practical applications of surfactants employ binary surfactant mixtures because of their superior performances in

comparison to single components. This arises through synergistic interactions between the surfactants.

An attempt has been made to study LS, EMF, ITC, and DSC measurements to examine how the cationic surfactant tetradecyltrimethylammonium bromide (TTAB) interacts with F127. In general, the interactions between cationic surfactants and water soluble nonionic polymers are much less simplistic than the corresponding interaction between the same polymer and SDS.<sup>[19]</sup>

In a recent study, experiment showed that SDS binds strongly to a diverse range of neutral polymers. For example, if we consider the separate EO. and PO blocks of F127, SDS interacts strongly with PPO and PEO whereas TTAB only interacts weakly with PPO.<sup>[20]</sup> In comparison, cationic surfactants are more choosy and only interact feebly with those polymers which have specific hydrophobic groups.<sup>[21]</sup>

On the other hand, a preliminary DSC measurement showed that cationic surfactants readily form mixed micelles with F127 and also moderate its micellar properties.<sup>[22]</sup> This investigation should therefore clarify the binding behavior of TTAB to F127 in its monomeric and micellar form.

#### 4. FUTURE PROSPECTS

Surfactants have contributed toward many advances in colloid and interface science and at the present time nanoscience. Because they are so efficient at performing the vital functions of surface tension reduction, particle stabilization, and control over fluid physicochemical properties through aggregation. Surfactants will continue to play a central role in nanoscience for years to come.

Another important dimension of surfactants is the opportunity for wide chemical structural variations, through design and synthesis of molecules targeted for specialist place applications. Surfactants will play a role in reducing volatile organic solvents in industrial processes. Hydrofluorocarbon (HFC) solvents are attractive alternatives to environmentally hazardous fully fluorinated and chlorocarbon-fluorocarbon solvents (CFCs), due to lesser ozone depletion and toxicity. Recently, there has been a thrust to replace CFCs by HFCs as refrigerants, propellants in metered-dose inhalers and drug delivery devices. The success of this approach points to a future role for surfactants in the pharmacy and related medical sciences, in the development of “nanomedicine.”<sup>[23]</sup>

#### 5. CONCLUSIONS

Knowledge of controlled interaction of Surfactants and block copolymers find powerful applications and will led to structural investigations by sophisticated methods such as light, X-ray or neutron scattering, and nuclear magnetic resonance. The chemical and thermodynamic rules governing

self-assembly are well understood and documented, and theories are now well advanced. Future research directions in this field will be towards expanding the scope of surfactants in facilitating new nanosciences in diverse fields such as nanomaterials, drug delivery, energy efficiency, and environmental cleanup.

## 6. ACKNOWLEDGEMENTS

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