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Polyelectrolyte-surfactant complexes (PESCs) composed of oppositely charged components

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Recent developments in the field of oppositely charged polyelectrolyte-surfactant complexes (PESCs) have been reviewed. Among the many developments in that field in particular very interesting is certainly the discovery of still new types of structural arrangements that arise from the complexity of the prevailing interactions, both in terms of electrostatics, as well as steric and specific interactions. More complex structures often arise from the architecture of the polyelectrolyte, such as the use of block copolymers or hydrophobically modified polyelectrolytes. However, also the surfactant plays a role in the PESC structure and for instance bilayer forming surfactants can be induced by polyelectrolyte to form multilamellar assemblies. Of course, PESCs may exhibit responsiveness to changes of pH, temperature, chemical environment etc. and this even in a complex fashion as the polyelectrolyte and surfactant may respond here in a different fashion. Interesting observations also concern the control of rheological properties by PESCs that depend strongly on the properties of the polyelectrolyte and the extension of the formed mixed aggregates, as well as their bridging. An old topic is coacervate formation in such systems, but one that currently receives renewed attention, as various aspects here are still not fully understood and at the same time they are very promising for further applications in separation/sequestration. Often overlooked is the fact that PESCs are typically not static entities but instead highly dynamic systems and recent neutron spin-echo (NSE) measurements indicate that the local dynamics of polyelectrolyte chains is only little affected by the incorporation within such aggregates. Therefore PESCs are still a highly fascinating class of self-assembled structures, where a large number of interesting developments may still be expected in the future.

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Abbreviations: cat-HEC, cationically modified hydroxyethyl cellulose; CGM, carboxymethyl guar; CTAB, cetyltrimethylammonium bromide; DDAB, didodecyldimethylammonium bromide; DDM, dodecyl maltoside; DPCl, *N*-dodecylpyridinium chloride; DB, decyl betainate; DLS, dynamic light scattering; HEC, hydroxyethyl cellulose; MRI, magnetic resonance imaging; NMR, nuclear magnetic resonance; NaPA, poly(sodium acrylate); NaPSS, poly(sodium styrenesulfonate); PAA, poly(acrylic acid); PAAm, poly(acrylamide); PAMPS, poly(sodium 2-(acrylamido)-2-methylpropane-sulfonate); PDADMAC, poly(diallyl-dimethylammonium chloride); PDMAEMA, poly 2-(dimethylamino)ethyl methacrylate; PE, polyelectrolyte; PEI, poly(ethylenimine); PEO, poly(ethylene oxide); PESC, polyelectrolyte surfactant complex; PHOS, poly(4-hydroxystyrene); PMAA, polymethacrylic acid; PNIPAM, poly(*N*-isopropyl acrylamide); PSCI, poly(sodium 2-sulfamate-3-carboxylate isoprene); PTMAEMC, poly(2-methacryloxyethyltrimethylammonium chloride); SANS, small-angle neutron scattering; SAXS, small-angle x-ray scattering; SDBS, sodium dodecylbenzene sulfonate; SDeS, sodium decyl sulfate; SDS, sodium dodecyl sulfate; TEM, transmission electron microscopy

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1. Introduction

Complexes of oppositely charged polyelectrolytes (PEs) and surfactants (PESCs, often also called SPECs: surfactant polyelectrolyte complexes) are formed rather easily and the main driving force for their formation typically is the release of the counterions. As polyelectrolytes and surfactants are already rich with respect to their mesoscopic structural organization, it is evident that their combination then naturally leads to a very rich variety of potential structures that can be formed [1–3].

The interaction of oppositely charged surfactants with polymers in aqueous solution and therefore also the formation of PESCs have been a topic in colloid research for >40 years, early on for instance investigated with respect to the structures formed for the case of sodium dodecyl sulfate (SDS) and cationically modified cellulose [4] or for sodium decyl sulfate (SDeS) and cationic polyamino acids [5]. Corresponding comprehensive reviews about these investigations are available [3,6,7•]. Accordingly, in this review we will focus on some particular aspects that have gained the interest of researchers in this field in recent years and which have changed and improved our understanding of this interesting class of self-assembled systems, which are:

- structural organization
- responsiveness and formation of PESCs
- oppositely charged PESCs for the control of rheological properties
- phase behavior and strength of interaction
- PESCs at interfaces
- coacervate formation

The focus of this review is on aqueous systems with PESCs dispersed in a colloidally stable fashion, while it might be noted that stable PESCs can also be formed in nonaqueous media. In addition, there are, of course, many investigations on precipitated, solid PESCs, which constitute an interesting class of materials, which however, will not be covered here.

2. Structural organization

Due to the richness in structure and properties of both, polyelectrolytes and surfactant assemblies, their combination leads to a vast richness of potential structures that can be formed in polyelectrolyte-surfactant complexes (PESCs) [3,6,7•]. The mesoscopic structure of PESCs depends largely on the structural parameters of polyelectrolyte and surfactant. Key parameters with respect to the polyelectrolyte are its chain stiffness (as characterized by the persistence length), the charge density along the chain, but also the proximity of the charge to the backbone (controls accessibility and thereby strength of interaction), and its molecular weight. For the surfactant the main quantity is its packing parameter which determines the type of aggregate preferentially formed (spherical or rodlike micelles, bilayers, e.g. in the form of vesicles, etc.) but also the type of head group as here one may also observe more specific interactions and its hydrophobic group. Accordingly, already a rich diversity of structures of soluble PESCs has been described [3,6,7•] but there are constantly new observations reported regarding the mesoscopic arrangements possible in such PESCs. The typical structural evolution upon binding surfactant to oppositely charged polyelectrolyte is depicted in Fig. 1.

2.1. PESCs containing densely packed micelles

For instance the formation of PESCs with densely packed micelles obtained by combining spherical micelles with oppositely charged polyelectrolyte [8] or double-hydrophilic (containing one neutral block) copolymers [9] has been observed already a long time ago. These densely packed micelles may exhibit a liquid crystalline cubic ordering (typically Pm3n) as seen a longer time ago for copolymer gels [8] or precipitates [10], but more recently such behavior was also observed for soluble complexes in mixtures of *N*-dodecylpyridinium chloride (DPCl) and poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO705–PMAA476) for an excess of surfactant charge [11]. Subsequent stopped-flow small angle x-ray scattering (SAXS) experiments then indicated that the formation of these ordered domain PESCs occurs via a two step-process, where the initial step of formation takes place with a time constant of <50 ms followed by a slow "aging" process on the time scale of seconds [12]. For the case of poly(sodium acrylate)-*block*-poly(acrylamide) (NaPA-*b*-PAAm) copolymer complexes with dodecyltrimethyl ammonium cations (DTA^+) the formation of stable hierarchical aggregates with a dense core and a diffuse shell was reported. Here the micelles in the core exhibit a liquid crystalline cubic ordering of Pm3n symmetry, as seen from SAXS experiments [13]. Upon mixing oppositely charged surfactant and PE one can form microcapsules due to the precipitation of the PESC. A recent investigation using cetyl trimethyl ammonium bromide (CTAB) and the block copolymer NaPA-*b*-PAAm showed that, depending on solution pH and temperature, these capsule walls will have different liquid crystalline nanostructures and this interfacial structure controls also the release rate of a hydrophilic agent (as a model Rhodamine B was employed) through this capsule wall [14]. In that context it should be noted that a very interesting structural arrangement in PESCs was reported a while ago for dilute mixtures of high molecular weight poly(acrylic acid) PAA (450 kDa) with cetyltrimethyl ammonium hydroxide (CTAOH). Here not only highly ordered micelles within a polyelectrolyte matrix can be formed, but by addition of the nonionic surfactant $C_{12}E_5$ one can switch this ordered structure from hexagonal to bicontinuous cubic with an Ia3d space group. This was the first time that such a bicontinuous cubic phase had been observed in such a PESC and similarly interesting its arrangement can be shifted to Im3m by reducing the temperature from 25 to 15 °C. Furthermore, the PESCs here had a hydrodynamic radius of 90–140 nm, depending on composition and were stable in time [15]. While in this case the structural arrangement was tuned by admixing a nonionic surfactant, this is also possible by addition of a medium chain alcohol, like octanol or decanol. Its presence increases the packing parameter of the micellar aggregates thereby with increasing alcohol content leading to a hexagonal or lamellar arrangement within the PESC core

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