



Historical perspective

## Co-assembly in chitosan–surfactant mixtures: thermodynamics, structures, interfacial properties and applications



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## ABSTRACT

In this review, different aspects characterizing chitosan–surfactant mixtures are summarized and compared. Chitosan is a bioderived cationic polysaccharide that finds wide-ranged applications in various field, e.g., medical or food industry, in which synergistic effects with surfactant can play a fundamental role. In particular, the behavior of chitosan interacting with strong and weak anionic, nonionic as well as cationic surfactants is reviewed. We put a focus on oppositely charged systems, as they exhibit the most interesting features. In that context, we discuss the thermodynamic description of the interaction and in particular the structural changes as they occur as a function of the mixed systems and external parameters. Moreover, peculiar properties of chitosan coated phospholipid vesicles are summarized. Finally, their co-assembly at interfaces is briefly reviewed. Despite the behavior of the mentioned systems might strongly differ, resulting in a high variety of properties, few general rules can be pointed out which improve the understanding of such complex systems.

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## 1. Introduction

Complexes of polyelectrolytes and surfactants are highly interesting systems and accordingly have been studied in detail so far. However, due to the large number of possible polyelectrolytes and surfactants that can be combined, basically an endless number of mixtures can be envisioned and a rich structural behavior has been observed in these systems. Pronounced synergistic effects are found when surfactants and polyelectrolytes are oppositely charged. These mixtures are used both in the solid state, as they provide an easy route for the preparation of highly structured materials [1–3] and in solution, due to the high structural variety and the often present stimuli-responsiveness of such supramolecular complexes [4–6].

For the interesting system of oppositely charged polyelectrolytes/surfactants the driving force for their assembly is the entropic gain due to release of the small counterions and water molecules. Typically around charge equimolarity insolubility of the formed complexes is observed [5,7]. Such complexes, due to their ability to modify rheological properties and also their ability to incorporate active agents, are interesting for many applications, for instance in the field of cosmetics and pharmaceutical formulations.

A particularly interesting class of polymers are biopolyelectrolytes, which means that they are either directly biopolymers or ones that are obtained from them by simple chemical modification. Within the class of biopolyelectrolytes, charged polysaccharides, play a predominant role. These polymers are in general rather biocompatible, they derive from renewable resources and most of them are available in large quantities and at low cost, making them attractive for industrial purposes [8]. For a general overview of the aspects characterizing ionic polysaccharides and their mixtures with soft colloids we address the reader to some recent reviews [6,9–12]. A general feature of biopolyelectrolytes is that their backbone is based on carbohydrates, e.g., cellulose based polyelectrolytes. This carbohydrate backbone is

substantially stiffer than that of synthetic polyelectrolytes that are typically based on vinyl building blocks.

The group of ionic polysaccharides is rather large and most of them are negatively charged. In our review we will focus on chitosan, which is a biopolymer in acidic conditions. The term chitosan is generally referred to the random block copolymer of glucosamine (GlcN) and N-acetyl glucosamine (GlcNAc), linked by  $\beta$ -(1–4)-glycosidic bonds. The fraction of N-acetyl glucosamine determines the degree of acetylation (DA). In most cases, chitosan is obtained by alkaline or enzymatic deacetylation of chitin, poly N-acetyl glucosamine (see Fig. 1). The density of chargeable groups along the polymer backbone is determined by the degree of deacetylation. Chitosan is rather well biodegradable and can easily become chemically modified by reactions on its amino and hydroxylic side groups [13–15]. The ease of modification, in addition to its antibacterial, antiinflammatory and mucoadhesive properties are reasons why this biopolymer has found applications in a wide range of fields. For instance it is interacting well with skin and hair and therefore is employed in different types of cosmetic formulations or for food processing [16]. In the medical field chitosan has shown outstanding performance in the field of wound covering and healing [17]. The polyelectrolyte properties of chitosan itself have for instance been employed for purposes of coagulation/flocculation processes, which is a relatively eco-friendly approach compared to methods employed so far [18–20]. Another environmentally relevant application of chitosan is the removal of heavy metal ions [21–23].

In this review we focus on complexes of positively charged chitosan. Particular attention will be put on the thermodynamic driving forces governing the co-assembly with surfactants and on the resulting structures. The main focus is on what structural control can be exerted in surfactant/chitosan mixtures and how by that control the properties of such systems for applications can be tailored. By analyzing the behavior of chitosan mixtures with cationic, anionic and nonionic surfactants as well as with phospholipid vesicles, some aspects common to all system will be pointed out.

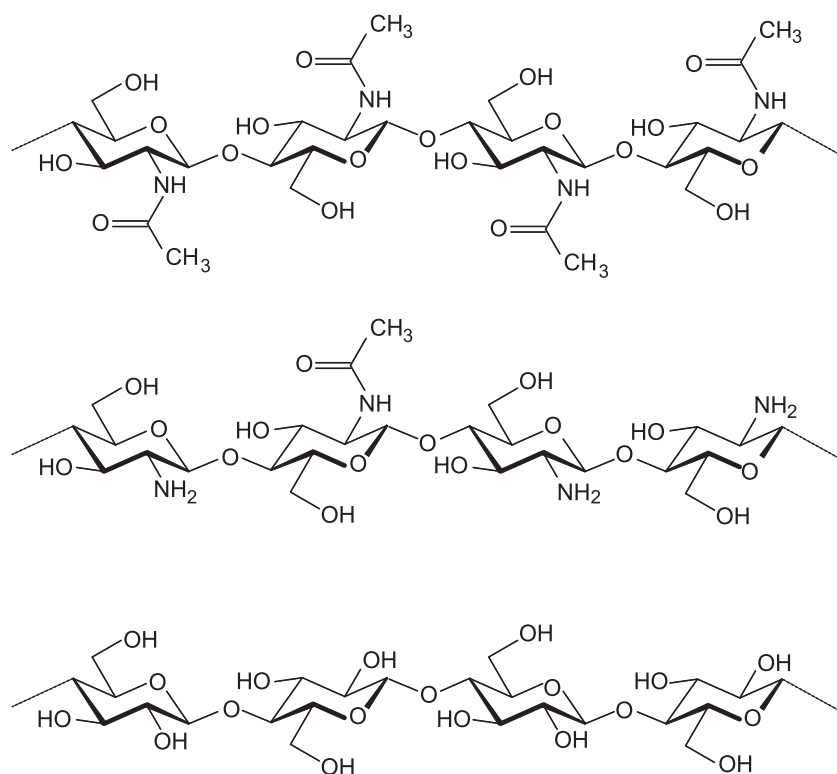


Fig. 1. Chemical structure of, from top to bottom, chitin, chitosan and cellulose.

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