



Preparation, surface activity and colloidal properties of the ionic complex of chitosan with hexadecyl-oligo-oxyethylene hemisuccinate

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ABSTRACT

Chitosan polyelectrolyte complex with high surface activity has been prepared by salt complexation of chitosan with hexadecyl-oligo-oxyethylene hemisuccinate (HOS), an anionic surfactant. Physicochemical properties of chitosan–HOS complex can be explained by unusual structure of HOS which has the polyoxyethylene chain located between the polar carboxyl head group and the hydrophobic alkyl tail. Aqueous solutions of chitosan–HOS complex are structured systems with pronounced thixotropic properties. The effect of content of hydrophobic exchanged groups on the solution properties of chitosan–HOS complex and various factors controlling the stability of oil-in-water emulsions in the presence of chitosan–HOS complex are studied. The synergistic effect of the enhanced emulsifying ability of chitosan–HOS complexes is shown. The study discloses a possibility to produce an effective bio-compatible emulsifier based on chitosan–HOS complex.

1. Introduction

Natural polymers are now finding increasing applications as emulsifiers, stabilizers, thickeners, food films and biological additives in food industry. Much research attention has been recently devoted to the development of effective methods of modification of polysaccharides with the aim to provide them new functional properties (Aider, 2010; Prashanth & Tharanathan, 2007).

Chitosan (Ch) and its derivatives do not accumulate in the body and in the environment, exhibit antibacterial activity and therefore have a proven potential in food and medicine industry as natural polymers for stabilization of emulsions (Dowling et al., 2011; Sashiwa & Aiba, 2004) and as functional food ingredients (Shahidi, Arachchi, & Jeon, 1999).

Chitosan is a cationic linear polysaccharide composed of randomly distributed β -(1–4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is produced by deacetylation of chitin separated from shells of crustaceans (crabs, shrimps).

Despite the advantages of chitosan, its application is limited by its low solubility at neutral pH. On the other side, chitosan shows weak surfactant properties owing to the presence of non-ionogenic N-acetyl groups. It is envisaged that improving the surface activity of chitosan

will enhance its solubility and thus open new perspectives for the chitosan applications. The presence of two hydroxyl groups and one amino group per chitosan unit suggests wide possibilities for chemical modification, including incorporation of covalently-bound hydrophobic groups. The most widespread methods of preparing of hydrophobically modified chitosan are based on the alkylation or acylation of amino- and hydroxyl group (Philippova & Korchagina, 2012). Another approach towards improved surface activity of chitosan is based on non-covalent electrostatic association of anionic surfactants with chitosan under the ionization conditions of the polysaccharide resulting in formation of chitosan polyelectrolyte complexes (PEC). The glucosamine unit of chitosan at pH below 6.5 (pK_a of chitosan) forms a protonated glucosammonium cation which combines with anions to produce salt complexes (Babak, 2001; Mun, Decker, & McClements, 2005; Schulz, Rodriguez, Del Blanco, Pistonesi, & Agulló, 1998).

Several groups have reported the formation of chitosan PECs with very high surface activity (Babak et al., 2000; Calero, Muñoz, Cox, Heuer, & Guerrero, 2013; Desbrières & Babak, 2010; Dowling et al., 2011; Venkataraman et al., 2013). For example, in one mentioned work (Desbrières & Babak, 2010) the surface tension measurements were carried out using a Tracker air bubble tensiometer at stable temperature

Abbreviations: Ch, chitosan; HOS, hexadecyl-oligo-oxyethylene hemisuccinate; PEC, polyelectrolyte complex; Ch-HOS, chitosan–hexadecyl-oligo-oxyethylene hemisuccinate polyelectrolyte complex; LCST, lower critical solution temperature; MW, molecular weight

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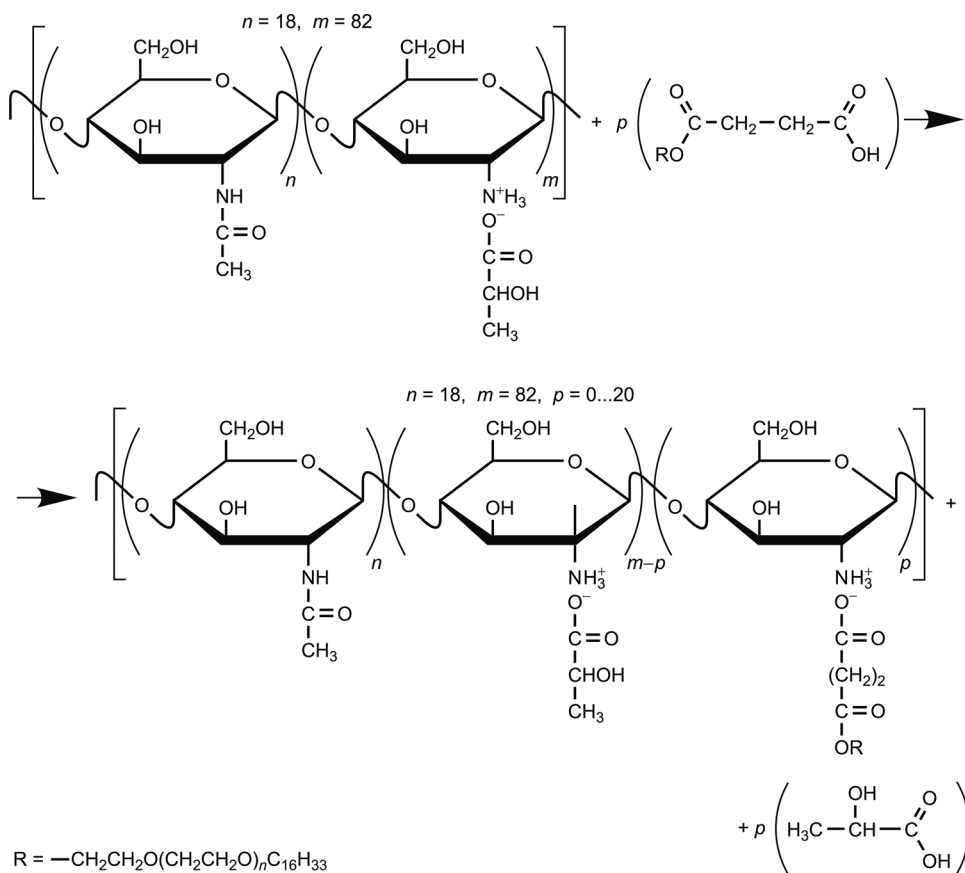


Fig. 1. The preparation of chitosan–hexadecyl-oligo-oxyethylene hemisuccinate polyelectrolyte complex.

($25.0 \pm 0.2^\circ\text{C}$). The dynamic tensiometry allows determining adsorption kinetics and equilibrium surface tension at different surfactant concentrations.

Although the surface activity of chitosan complexes with sodium dodecyl sulfate anions is two orders of magnitude higher than that of the surfactant itself (Babak, Lukina, Vikhoreva, Desbrières, & Rinaudo, 1999), they are not promising in food applications due to high water sorption and poor film formation properties of these complexes. Certain fatty acids such as oleic, linoleic, stearic, palmitic, and linolenic have been reported to interact with protonated amino groups at low pH giving rise to polyelectrolyte complexes with improved emulsifying ability of chitosan (Meler, Pluta, Ulański, & Krotkiewski, 2003; Nilsen-Nygaard, Strand, Vårum, Draget, & Nordgård, 2015).

In spite of a large number of papers on the hydrophobic derivatives of chitosan (Guzey & McClements, 2006; Rodríguez, Albertengo, & Agulló, 2002) the study of chitosan complexes with anionic surfactants in the preparation of effective food emulsifiers, stabilizers and thickeners is a promising research area. In our study we used a surface active monoester of succinic acid, namely hexadecyl-oligo-oxyethylene hemisuccinate (HOS) in the preparation of chitosan-based PEC.

The choice of HOS can be explained by its surfactant properties that promote its use as an effective food emulsifier. An unusual structure of HOS which includes the poly-(ethylene oxide) fragment ($-(\text{CH}_2\text{CH}_2\text{O})_n-$) between the hydrophilic head group $-\text{COOH}$, and the hydrophobic tail $-\text{C}_{16}\text{H}_{33}$ leads to the complex formation in which not only carboxylic group but also alkyl-oligo-(ethylene oxide) chain can interact with chitosan. Moreover, the hydrophobic interactions between carbon chain of HOS and nonpolar alkyl groups ($-\text{CH}_3$) of chitosan also may exist in this system. Such mechanism of salt complexation may provide the enhance of hydrophobicity of a chitosan-based PEC.

The goal of the present paper was to test a new anionic surfactant, a surface active monoester of succinic acid, with regard to its ability to

form surface active polyelectrolyte complexes with chitosan, which may open novel opportunities of their application.

2. Materials and methods

2.1. Materials

We used *chitosan* of two types, first one with MW = 83 kDa and second one with MW = 240 kDa. They were obtained from BioProgress Technology Ltd (Russia). The degree of deacetylation in both types was specified by manufacturer as $\sim 82\%$ (determined by H NMR).

The *lactic acid* used in this work was obtained from PURAC Biochem (the Netherlands) in the form of aqueous solution (80%).

Hexadecyl-oligo-oxyethylene hemisuccinate (also known as *cetyl-oligo-oxyethylene hemisuccinate*) used in the present work is a mixture of several substances with average MW ~ 1000 Da which share the common formula $\text{C}_{16}\text{H}_{33}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{OCOCH}_2\text{CH}_2\text{COOH}$ ($n = 18, 19$, or 20). It was obtained from AO TOC (Russia).

2.2. Methods

2.2.1. Preparation of chitosan polyelectrolyte complex

The chitosan PEC was prepared by ion exchange reaction between a surface active monoester of succinic acid in acidic form (HOS) and chitosan lactate. For the rest of the article, the resulting polyelectrolyte complex system will be called chitosan-HOS PEC, or, for sake of brevity, simply Ch-HOS.

Firstly, the 5 wt% aqueous solution of chitosan lactate was prepared as follows. 18 mL of 5 wt% solution of lactic acid were placed in a 100 mL three-neck flask with a magnetic stirrer and a thermometer, and distilled water was added up to 50 mL of total volume, resulting in solution of lactic acid with pH = 3.5. The solution was stirred at 50–60 °C and 1.62 g of chitosan powder was added in small portions for

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