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Surfactant-polysaccharide complexes based on quaternized chitosan. Characterization and application to emulsion stability

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ABSTRACT

The interactions between a polyelectrolyte and an oppositely charged surfactant allows obtaining complexes with specific properties. Such complexes between a quaternized chitosan, obtained from the reaction between chitosan and quaternary ammonium epoxides, and sodium 1-decanesulfonate were studied. Physico-chemical characteristics were obtained from conductimetric experiments as well as surface tension studies. A strong associative electrostatic interaction between the polysaccharide and the surfactant was shown from conductimetric experiments and a degree of association equal to 0.74 was determined. The complex presents better interfacial properties than surfactant and polysaccharide alone. The critical aggregation concentration is much smaller than the critical micellar concentration of the surfactant alone in solution. Moreover the viscoelastic moduli of the interfacial layer was increased in presence of the complex by comparing with surfactant alone. All these considerations allow using the surfactant-polysaccharide complex as a better emulsion stabilizer than either surfactant or polysaccharide alone.

1. Introduction

The interaction of surfactants and water soluble polymers has been the subject of active research for several years. The effect of synthetic surfactants on natural proteins such as gelatin, serum albumin and hemoglobin was early investigated [1]. Initially, these studies were motivated by observations of biological phenomena involving surfactants and proteins [2], but since then intensive research and fundamental studies have been developed [3]. Polymer-surfactant mixtures are widely used in many applications, such as paper industry, foods, cosmetics, water-based formulations (paints, drilling muds, oil recovery), biomedical applications (loading and releasing of drugs, isolating and purifying DNA) and for tuning the stability and regulating the rheology of composites [4,5], due to their unexpected properties.

In relation with their wide-spread usage and complex physico-chemical properties, these systems were the focuses of numerous studies, aimed to determine the role of the surfactant-polymer interactions, both in the bulk and on the solution surface [6–8]. For instance, the presence of polymers in surfactant solutions significantly affects the structure and composition of the adsorption layers, their rheological properties, modifying the ability of polymer-surfactant solutions to foam. A great number of properties, including fluid rheology, wetting, emulsification and wettability, is affected by this association [9]. Among the different types of polymers used in such systems, polyelectrolytes are of particular interest because of the important role of polymer charges. Considering the specific case of mixtures containing a polyelectrolyte and an oppositely charged surfactant, their association is commonly accepted as the result of electrostatic attractions which are reinforced by cooperative aggregation of the bound surfactant molecules [10,11]. Soluble or insoluble aggregates may be obtained [12] and their properties may be tuned by many variables such as hydrophobicity, polymer backbone rigidity and charge density, surfactant chain length, the nature and the concentration of added salts [13,14]. These factors may affect the complex stoichiometry and, consequently, its solubility. Anionic surfactants can self-associate to form micelles under appropriate conditions, but also strongly associate polymer, wherein the presence of the latter generally causes the occurrence of micellization at lower surfactant concentrations.

In aqueous solution, the association between polymer and surfactant results in thermodynamically stable complex, with physicochemical properties different from those observed in pure surfactant solutions. Complexes between surfactants and polyelectrolytes have gained

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increasing attention, from academic and industries fields, because of their complex behavior and its potential applications in areas such as encapsulation and drug delivery, wastewater treatment and oil recovery [15,16]. Recent studies have also shown that polyelectrolyte/surfactant complexes have extremely high adsorption activity and, therefore, are able to stabilize emulsions and foams [17]. Thus, owing to the numerous and important applications of such systems and due to their complex physical chemical behavior, several studies are dedicated to investigate the complex formation involving different polymers and surfactants.

Using natural polymers, such as polysaccharides, allows to consider the environmental constraints related to industrial applications as well as specific interest due to their origin and chemistry. Indeed, polysaccharides are renewable, in contrast with petroleum-based polymers, they are usually biocompatible and biodegradable and, owing to the presence of functional groups, they can be chemically modified to develop functionalities and properties to be explored in specific applications. Cellulose and chitin are the most abundant polysaccharides, the latter occurring mainly in crustaceans, mollusks and insects as an important structural constituent of exoskeletons. The *N*-deacetylation of chitin results in chitosan, an aminopolysaccharide which occurs in the cell wall of some fungi and that is biodegradable, biocompatible and displays very low toxicity. Additionally, chitosan is a non-irritant film-forming polysaccharide exhibiting high mechanical properties and mucoadhesiviness [18,19]. Such properties give rise to an ample range of potential applications that are, however, severely limited by the solubility of chitosan, which is restricted to moderately acidic aqueous media. Thus, several studies have focused on the development of different chitosan derivatives exhibiting improved solubility in aqueous media [20]. Polyelectrolyte derivatives of chitosan, *i. e.* those derivatives resulting from the introduction of anionic or cationic substituents in the chitosan chains, such as *N,O*-carboxymethylchitosan and *N,N,N*-trimethylchitosan have been prepared to reach such an objective. Cationic derivatives of chitosan, briefly CatCh, have much higher water solubility than chitosan and chitosan salts, especially in neutral or basic media, and they were developed to be applied, among other domains, in the biomedical field [21] as, regardless of the pH, they exhibit antimicrobial properties [22,23]. Such cationic derivatives can be prepared either by reacting chitosan with alkylating agents such as alkyl halide [24] and dialkyl sulfate (dimethylsulfate or diethylsulfate) [25], as is the case of *N,N,N*-trimethylchitosan, or with epoxydes containing a quaternized nitrogen atom [26]. Although the reaction of chitosan with alkyl halides results in *O,N*-substituted derivatives, that one carried out with epoxydes in acidic medium is highly regioselective, with high predominance of *N*-substitution [27]. Moreover, the production of amphiphilic derivatives exhibiting different hydrophilic/hydrophobic balance can be obtained by reacting chitosan with epoxides composed by alkyl chains of different lengths (up to C12 – C14) [28]. Additionally, it is important to highlight that the presence of quaternized nitrogen atoms pertaining to the substituents groups confers permanent positive charges to the chitosan derivative chains, improving the polymer water solubility and enlarging its domain of applications.

Several techniques are used to investigate the nature of the interactions involving oppositely charged polyelectrolyte and surfactant, such as turbidimetry, surfactant selective electrode [29], isothermal titration calorimetry [30], conductometry [31], surface tension and interfacial rheology [32], diffusometry [33], NMR relaxometry [31,34] or dielectric spectroscopy [35].

Moreover, recently the pharmaceutical and cosmetic industries have made increasing efforts and investments for the development of new formulations of emulsions that are safer and use biocompatible constituents, stimulating the development of research with potentially applicable biopolymers in these areas. Indeed, many applications in food, cosmetics and pharmaceutical industries call for the development of safe emulsions displaying long term stability. Although surfactants confer longer shelf-life to emulsions, they may present risks to the environment and human health, while the use of surfactant-polyelectrolyte complexes (SPEC) may represent a viable alternative as they strongly affect the surface properties of emulsions [36,37]. Indeed, understanding how surfactant-polymer complexes (SPEC) alter fundamental interfacial and flow characteristics of multicomponent complex fluids as well as their surface properties has significant practical motivation.

Thus, the aim of this work was to study a new polyelectrolyte/surfactant complex based in a cationic chitosan derivative containing quaternized nitrogen atoms, namely *N*-(2-hydroxy)propyl-3-methylammonium chitosan (CatCh), and sodium 1-decanesulfonate (TA), its interfacial activity and ability to promote the stabilization of oil/water emulsions, aiming to evaluate its potential in pharmaceutical and cosmetic formulations.

2. Experimental

2.1. Materials

The surfactant, sodium 1-decanesulfonate (TA), was purchased from Sigma-Aldrich (Germany) and applied without further purification after mass spectroscopy analysis. Its Krafft temperature was 23 °C [38]. Its hydrohpile-lipophile balance (HLB) was calculated to 22.5 from HLB increments determined by Ho [39]. Due to its low Krafft temperature, conductivity and tensiometry experiments were performed at 30 °C to improve the surfactant solubility. Glycidyltrimethylammonium chloride (GTMAC), an analytical grade reagent used as received, employed in the reaction of quaternization of chitosan, was from Sigma/Aldrich (Germany).

Chitosan, extracted from fly larvae, was purchased from Cheng Yue Planting Co. Ltd. (Chang, China). Its viscosity-average molar mass was 74,000 $g.mol^{-1}$, using the Mark-Houwink-Sakurada equation in 0.3 M AcOH/ 0.2 M AcONa [40] and the degree of acetylation (DA) was 5% from ^1H NMR spectrum [41].

Considering the DA of this sample, the monomer molar (entitled monomol) mass to be considered to calculate the ionic ratio will be equal to 163.1 g (and corresponds to 0.95 mol of amino group or cationic charge when totally ionized).

2.2. Characterization of samples and surfactant-polysaccharide complexes

The NMR spectra were acquired on a Bruker Avance 400 spectrometer at 85 °C using D_2O/HCl (1%v/v) as solvent.

The viscosity of solutions of quaternized chitosan derivative (*N*-(2-hydroxy)propyl-3-methylammonium) chitosan, CatCh) in aqueous solution (0.3 $mol.L^{-1}$ acetic acid/0.2 $mol.L^{-1}$ sodium acetate, pH of 4.5) was analyzed using an AMVn Automated Micro Viscometer (Anton Paar, Graz, Austria) under precise temperature control (25.0 ± 0.1 °C).

A CDM230 conductimeter from MeterLab™ (France) was used to measure the conductivity of solutions at 30.0 ± 0.1 °C, higher than the surfactant Krafft temperature. The experiments were performed in a double-wall thermostated cell. Conductometric titration was used to determine the value of the critical micelle concentration (CMC) of sodium 1-decanesulfonate as well as the effect of the concentration of the surfactant on the critical aggregation concentration (CAC) of *N*-(2-hydroxy)propyl-3-methylammonium chitosan (CatCh). For the first study, a stock solution of sodium 1-decanesulfonate ($C = 0.3\ mol.L^{-1}$) in water was prepared. Aliquots of 0.2 ml of the surfactant stock solution were successively added to 25 ml of deionized water at 30 °C and the value of the solution conductivity was taken after each addition upon the stabilization of the signal. Concerning the study of sodium 1-decanesulfonate-CatCh complexes, aliquots of 0.2 ml of a stock solution of the surfactant were consecutively added to 25 ml of an aqueous solution of CatCh ($Cp = 1 \times 10^{-3}\ monomol.L^{-1}$ or $3 \times 10^{-3}\ monomol.L^{-1}$). Generally, around 30 additions were performed during each conductimetry experiment and this experiment was duplicated.