



# Interactions and hybrid complex formation of anionic algal polysaccharides with a cationic glycine betaine-derived surfactant



Rudy Covis<sup>a,b</sup>, Thomas Vives<sup>a,b</sup>, Cédric Gaillard<sup>c,b</sup>, Maud Benoit<sup>d</sup>, Thierry Benvegnu<sup>a,b,\*</sup>

<sup>a</sup> Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

<sup>b</sup> Université Européenne de Bretagne (UEB), France

<sup>c</sup> U.R.1268 Biopolymères Interactions Assemblages INRA–BP 71, 627 Rue de la Géraudière, 44316 Nantes Cedex 3, France

<sup>d</sup> Centre d'étude et de Valorisation des Algues, Presqu'île de Pen Lan–BP3, 22610 Pleubian, France

## ARTICLE INFO

### Article history:

Received 1 September 2014

Received in revised form

15 December 2014

Accepted 2 January 2015

Available online 8 January 2015

### Keywords:

Algal polysaccharides

Cationic surfactant

Polymer–surfactant interactions

Polysaccharide/surfactant hybrid structures

Physicochemical characterizations

Food, cosmetics and detergency

applications

## ABSTRACT

The interaction between anionic algal polysaccharides (( $\kappa$ )-, ( $\iota$ )-, ( $\lambda$ )-carrageenans, alginate and ulvan) and a cationic glycine betaine (GB) amide surfactant possessing a C<sub>18:1</sub> alkyl chain has been studied using isothermal titration calorimetry (ITC), zeta-potential measurements, dynamic light scattering (DLS), transmission electron microscopy (TEM), atomic force microscopy (AFM), and surface tension measurements. It was observed that this cationic surfactant derived from renewable raw materials induced cooperative binding with the anionic polymers at critical aggregation concentration (CAC) and the CAC values are significantly lower than the corresponding critical micelle concentration (CMC) for the surfactant. The CMC of cationic GB surfactant was obtained at higher surfactant concentration in polysaccharide solution than in pure water. More interestingly, the presence of original polysaccharide/surfactant hybrid complexes formed above the CMC value was evidenced from ( $\kappa$ )-carrageenan by microscopy (TEM and AFM). Preliminary investigations of the structure of these complexes revealed the existence of surfactant nanoparticles surrounded with polysaccharide matrix, probably resulting from electrostatic attraction. In addition, ITC measurements clearly showed that the interactions of the  $\kappa$ -carrageenan was stronger than for other polysaccharides (( $\iota$ )-, ( $\lambda$ )-carrageenans, alginate and ulvan). These results may have important impact on the use of the GB amide surfactant in formulations based on algal polysaccharides for several applications such as in food, cosmetics, and detergency fields

© 2015 Elsevier Ltd. All rights reserved.

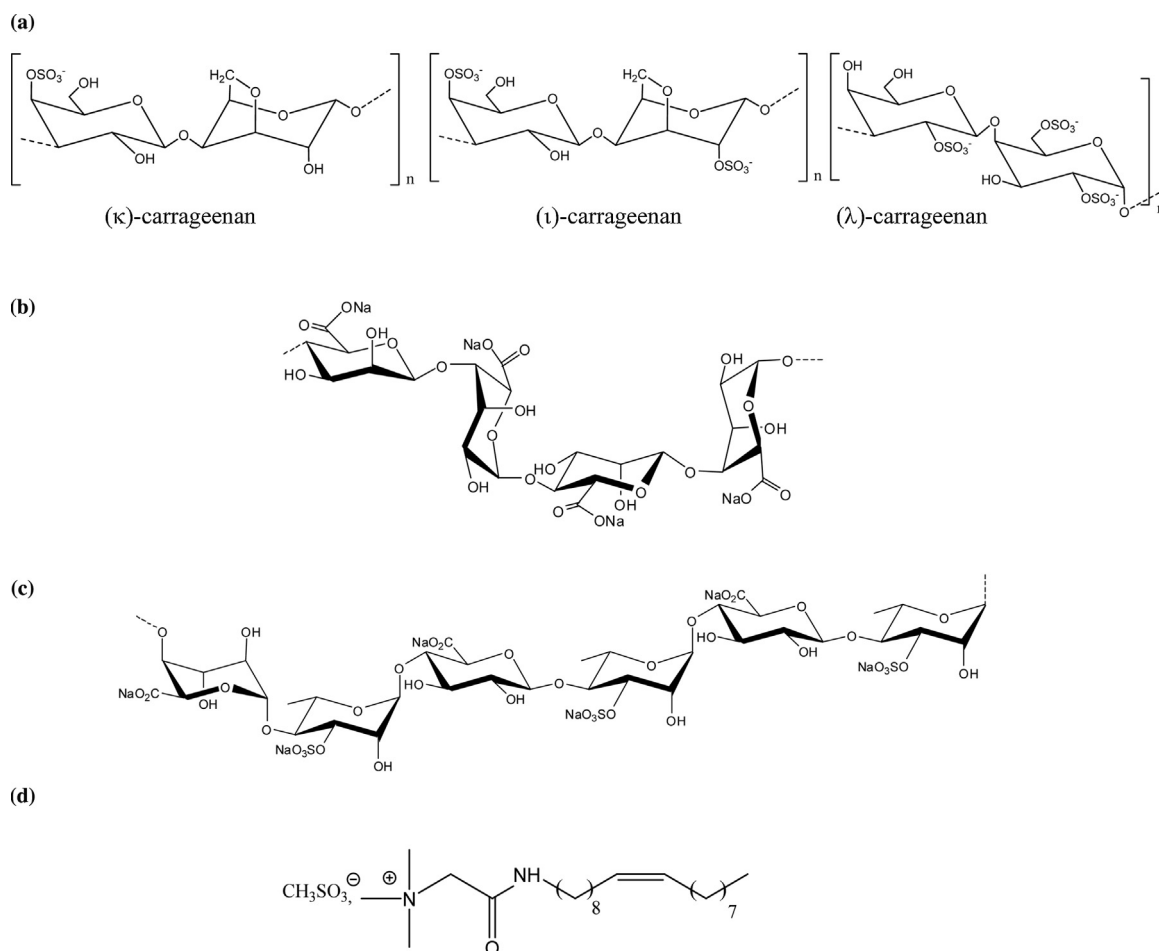
## 1. Introduction

Algal polysaccharides represent a wide family of biopolymers that are derived from red seaweeds such as carrageenans, brown seaweeds such as alginates, and green seaweeds such as ulvans. These hydrocolloids have been widely used in industry (especially alginates and carrageenans) because of their rheological properties (gelling and thickening agents) and their biological activities (anticoagulant, antiviral, and immune-inflammatory) that are highly valuable in food, cosmetic and pharmaceutical applications (Kraan, 2012). Carrageenans are linear sulfated polysaccharides composed of repeating disaccharide units with alternating 3-linked  $\beta$ -D-galactopyranose and 4-linked  $\alpha$ -galactopyranose or

3,6-anhydro- $\alpha$ -galactopyranose (Fig. 1a). There are three main varieties of carrageenan, which differ mainly in their degree of sulfation. Kappa ( $\kappa$ )-carrageenan is composed of alternating 3-linked  $\beta$ -D-galactose 4-sulfate and 4-linked 6-anhydro- $\alpha$ -galactopyranose with one elementary charge per disaccharide repeating unit. Iota ( $\iota$ )-carrageenan has two sulfate groups per disaccharide repeating unit. Lambda ( $\lambda$ )-carrageenan has three sulfate groups per disaccharide unit, but they do not include any 3,6-anhydride bridge contrary to the first two carrageenans (Campo, Fabio, Braz da Silva, & Carvalho, 2009). ( $\kappa$ )-carrageenan and ( $\iota$ )-carrageenan form gels, whereas no gel formation has been observed for the most highly charged ( $\lambda$ )-carrageenan. Alginates are anionic polysaccharides that contain linear blocks of covalently (1-4)-linked  $\beta$ -D-mannuronate (M) with the C5 epimer  $\alpha$ -L-guluronate (G) (Benvegnu & Sassi, 2010). Within the structure of alginate, the M and G monomers are sequentially assembled in either homopolymeric repeating (MMM or GGG) blocks or heteropolymeric alternating (MGMG) blocks (Fig. 1b). It has been shown that the physical properties of alginates depend on the relative

\* Corresponding author at: Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.  
Tel.: +33 0 2 23238060.

E-mail address: [thierry.benvegnu@ensc-rennes.fr](mailto:thierry.benvegnu@ensc-rennes.fr) (T. Benvegnu).



**Fig. 1.** Chemical structure of carrageenans (a); alginate (b); ulvan (c); and glycine betaine (GB) amide surfactant **1** (d).

proportion of these three types of blocks (Haug, Larsen, & Smidsrod, 1967; Smidsrod & Haug, 1972a; Smidsrod, Haug, & Whittington, 1972b). For example, the ability to form gels from alginate, by addition of calcium ions, involves the G blocks so the higher the proportion of these, the greater the gel strength (Draget & Taylor, 2011). Ulvans are complex polysaccharides composed of sulfate, rhamnose, xylose, iduronic and glucuronic acids as main constituents (Fig. 1c) (Lahaye & Robic, 2007). They possess structural properties close to glycosaminoglycans such as hyaluronan and chondroitin sulfate due to its content of glucuronic acid and sulfate constituents (Chiellini & Morelli, 2010; Dash et al., 2014). Ulvans form gels in the presence of boric acid, calcium ions and at a pH between 7.5 and 8.0 (Haug, 1976).

Amphiphilic versions of these polysaccharides could represent an attractive strategy to improve their properties and functions. They can be achieved either by chemical modification of the macromolecular backbone (Yang, Zhou, & He, 2013), or by interactions between the anionic biopolymer and surfactants of opposite charge. Many practical systems for industrial applications contain mixtures of polymers and surfactants, widely used in foods, cosmetics, detergents, personal-care products and mineral processing (Goddard & Ananthapadmanabhan, 1993; Ivanov, Kamenova, Georgieva, Kamenska, & Georgiev, 2006). The association of surfactants with polysaccharide chains can give rise in aqueous media to soluble or insoluble complexes/aggregates with various properties depending on several parameters, such as electrostatic, hydrophobic, dipolar, and hydrogen bonding interactions and steric hindrance effects. Changes in the structure of the polymer and/or the surfactant, the charge density

of the polyanion and the relative ratio between the oppositely charged polymer–surfactant pair may also affect the structure and the physicochemical properties of these mixed systems. Polymer/molecule or polymer/macromolecule complexes resulting from electrostatic interactions were recently developed to exhibit attractive rheological properties or to form nanoparticle (NP) systems for drug delivery (Wu et al., 2007, 2014). In particular, new hybrid polymer/protein complex NPs were prepared by utilizing the electrostatic interaction between proteins and NPS made from diblock copolymer of poly(lactide-co-glycolic acid) (PLGA) and L-arginine-based polycation (PC). This study highlighted a novel strategy for the robust delivery of proteins and other relevant molecules.

Generally, when surfactants are introduced into a solution containing oppositely charged polysaccharide, electrostatic interactions occur until complete neutralization of the polyanionic biopolymer. Surfactants in the presence of oppositely charged polysaccharides start forming aggregates with the polysaccharides at the so-called critical association concentration, CAC, involving both strong electrostatic binding and aggregation of alkyl chains of the bound surfactant ions (Wang, Li, Li, & Niu, 2014; Holmberg, Jönson, Kronberg, & Lindman, 2003; Kogej & Kerjanc, 2001). CAC is usually far below the critical micelle concentration, CMC, of a particular surfactant.

Over the last decade, mixed systems composed of cationic surfactants and anionic polysaccharides were investigated increasingly. In particular, the interaction of lauric arginate (LAE), a food-grade cationic surfactant with a high antimicrobial activity, with various biopolymers was analyzed to evaluate the effect

Download English Version:

<https://daneshyari.com/en/article/1383284>

Download Persian Version:

<https://daneshyari.com/article/1383284>

[Daneshyari.com](https://daneshyari.com)