



Interactions between kappa-carrageenan and some surfactants in the bulk solution and at the surface of alumina



E. Grządka

Department of Chemistry, Maria Curie-Skłodowska University, M. Skłodowskiej, Curie 3 Sq., 20-031 Lublin, Poland

ARTICLE INFO

Article history:

Received 8 December 2014

Accepted 11 January 2015

Available online 21 January 2015

Keywords:

Carrageenan

Alumina

Surfactants

Interface

ABSTRACT

The interactions between surfactants (SDS, CTAB, TX-100 or their equimolar mixtures) and kappa-carrageenan (Carr) in the bulk solution and at the surface of alumina were determined using the surface tension and the spectrophotometric adsorption measurements. The obtained results show that Carr has the ability to create the multilayer complexes with CTAB, TX-100 and the equimolar mixtures of surfactants (CTAB/TX-100), but does not interact with SDS. The created complexes are electrostatic (with CTAB) or they are of different mechanisms such as the hydrogen bonding or the acid–base interactions (with TX-100). The electrokinetic measurements (the surface charge density and the zeta potential) allow to analyze the structure of the adsorption layer: polymer/surfactant/metal oxide. It turned out that the macromolecules of Carr are directly bonded to the surface whereas the surfactants are present in the upper parts of the electrical double layer.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Carrageenan (Carr) is a natural, anionic, polysaccharide produced by alkaline extraction of *Rhodophyceae* red seaweeds. The major constituents of this compound is a linear backbone of β -D-galactose and 3,6-anhydro- α -D-galactose partially sulfated. There are three main forms of this compound: lambda- λ (with three sulfate groups, non-gelling), iota- ι (with two sulfate groups, weak gelling) and kappa- κ (with one sulfate group, strong gelling) (Fig. 1). Carrageenans are broadly used as cost-effective stabilizers, thermoreversible gelling agents, binders, carriers, thickeners, texture modifiers, glazing agents, emulsifiers, and humectants in many branches of industry (Piculell, 2006; Prajapati, Maheriya, Jani, & Solanki 2014).

It is well known that surfactants can interact with polymers involving such processes as complexation, precipitation and gelation in the solution and the competitive or the cooperative adsorption at the surface of the solid. The interactions between polymers and surfactants can have different origins electrostatic, dipole–dipole and hydrophobic ones as well as hydrogen bonding. Among the factors influencing these interactions with respect to the surfactant are: the structure of the hydrophobic part and the head group and also the concentration (Bakshi & Kaur, 2003;

Thalberg, Lindman, & Karlstrom, 1991; Vinceković, Bujan, Šmit, & Filipović-Vinceković, 2005), with respect to the polymer are: its chemical character, charge density, hydrophobicity (Persson, Hugerth, Caram-Lelham, & Sundelof, 2000) as well as conformation and flexibility of polymer chain (Hansson, 2001; Jönsson, Lindman, Holmberg, & Kronberg, 1998). The solvent can also play an important role because it can regulate the degree of dissociation of ionisable groups (Caram-Lelham & Sundelöf, 1996).

As far as interactions between carrageenans and surfactants are concerned Yin and co-workers (Yin et al., 2014) studied the interactions between ι -carrageenan and some cationic surfactants. They found out that at a low surfactant concentration, the monomers adsorbed on the polymer chains through the electrostatic attraction, followed by the formation of induced micelles on the polymer chains through the hydrophobic interaction until the ι -carrageenan chains are saturated by surfactant molecules. The data obtained by Vinceković et al. (2011) at the lower limit of the semidilute region showed that in the absence of salt, the charge groups within the carrageenan chains repel each other and they are in an extended form and quite stiff. At this conformation, the intrachain soluble complexes between cationic surfactant and carrageenan are the prevailing form and their structure is mainly controlled by surfactant concentration. Rosas-Durazo et al. (2011) conducted studies on the gelling processes during cooling in the non-stoichiometric complex between κ -carrageenan and dodecyltrimethylammonium chloride in KCl. The mechanical properties of the hydrogels show a gradual reinforcement when the

E-mail address: egrzadka@wp.pl

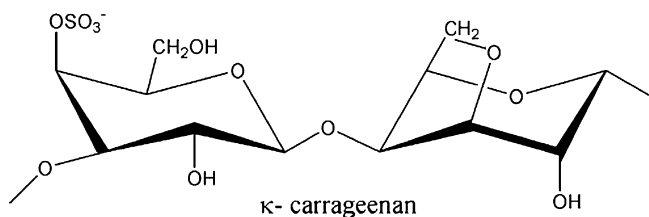


Fig. 1. Structure of kappa carrageenan.

amount of surfactant in the complex increases, indicative of a more densely cross-linked polymer network as a consequence of the cooperative nature of polyelectrolyte-surfactant interactions. Bao, Li, Gan, & Zhang, 2008 studied the polymer-surfactant interactions between three polysaccharides (methylcellulose, chitosan, and κ -carrageenan) and two ionic surfactants (SDS and CTAB) by isothermal titration calorimetry (ITC). A general rule to determine the interactions between polymer – surfactant is: ionic interaction > hydrophobic interaction > ion–dipole interaction.

As far as the interaction of carrageenan with the solid surface is concerned Fares and co-workers (Fares, Maayta, & Al-Mustafa, 2012) studied κ -carrageenan as a corrosion inhibitor of aluminum in the presence of pefloxacin mesylate (zwitterion mediator) for the adsorption of κ -carrageenan on the aluminum surface. They found an increase in the inhibition efficiency in the presence of the mediator, attributed to the formation of a well-ordered and coherent physical adsorption layer on the surface of aluminum. Daniel-da-Silva, Lóio, Lopes-da-Silva, Trindade, Goodfellow, and Gil (2008a) investigated the influence of magnetite nanoparticles on the rheological properties of the carrageenan gels. They showed that formation of the Fe₃O₄ nanoparticles in the presence of the κ -carrageenan promotes gelation and produces stronger gels. This scientific group (Daniel-da-Silva, Pinto, Lopes-da-Silva, Trindade, Goodfellow, & Gil, 2008b) measured also the rheological behavior of the silica/ κ -carrageenan nanocomposites as a function of silica particle size and load. They found out that the addition of silica nanoparticles impairs the gelation of κ -carrageenan.

Due to the fact that the scientific literature does not present the data concerning the interactions between carrageenan and surfactants at the surface of the metal oxide, the goal of this work was to investigate the influence of some surface active agents (anionic, cationic, non-ionic) or their mixtures on the adsorption and elektrokinetic properties of the carrageenan/alumina system. The methods used let to analyzed (i) the interaction between Carr and surfactants in the bulk solution (surface tension), (ii) the interactions of Carr and surfactants with alumina (adsorption measurements) (iii) the structure of the adsorption layer (surface charge and zeta potential).

2. Experimental

2.1. Materials

Alumina (Al₂O₃) produced by Merck was used as the adsorbent. The specific surface area of this oxide was found to be 107 m² g⁻¹ (BET method). The adsorbent was washed with doubly-distilled water until the conductivity of the supernatant was lower than 2 μ S cm⁻¹. Anionic polysaccharide κ -carrageenan from Sigma-Aldrich was used as the adsorbate. The solubility of κ -carrageenan in water was found to be 5 mg/cm³, whereas viscosity of 0.3% solution in water (25 °C) was in the range 5–25 mPa s (supplier information). The surfactants: cationic hexadecyltrimethylammonium bromide (CTAB), anionic sodium dodecyl sulphate (SDS), non-ionic polyethylene glycol *tert*-octylphenyl ether (TX-100), as

well as the background electrolyte – NaCl were purchased from Fluka.

In order to avoid the influence of the temperature on the amount of polymer adsorption all measurements were conducted at the same temperature 25 °C (Wiśniewska, 2007, 2010).

2.2. Methods

2.2.1. Characterisation of polymer

The average molecular weight (M_w) of κ -carrageenan was estimated by gel permeation chromatography (GPC) using two detectors: the refractive index detector and the multiangle laser scattering detector miniDAWN Treos both from Wyatt Technologies. The column was from Shodex contained OHPak SB-806M-HQ. GPC was performed in water with 3 mM sodium azide at 30 °C with a flow rate of 1 cm³/min. The sample solutions were filtered through membrane filters with the nominal pore sizes of 0.2 μ m just before the measurements. The results were evaluated using the ASTRA 6 software from Wyatt Technologies. The M_w of κ -carrageenan was found to be 1.049 \times 10⁵ Da. The refractive index increment (dn/dc) taken in the calculations of κ -carrageenan was 0.1262 cm³/g. All polymer stock solutions were prepared by fast addition of 0.045 g of κ -carrageenan into 45 mL of vigorously stirred water and further stirring for 30 min. The obtained stock solution was used within one week in order to avoid retrogradation.

2.2.2. Adsorption measurements

0.2 g of Al₂O₃ was added to 10 cm³ of solution containing the polymer (Carr) (concentration range from 20 ppm to 300 ppm), the background electrolyte (NaCl) (10⁻² mol dm⁻³, doubly-distilled water and the surfactant (SDS, CTAB, TX-100) (concentration 10⁻⁴ mol dm⁻³) or the equimolar surfactants mixture (SDS/TX-100, CTAB/TX-100) of the same concentration. The pH of the solutions was adjusted to 7 using HCl and NaOH solutions and checked during the experiment with a Beckman ϕ 360 pH meter. Next, seven different initial concentrations (from 20 ppm to 300 ppm) of carrageenan were used. The obtained suspensions were shaken for 18 h in the water bath (OLS 2000, Grant). This time was estimated from kinetics measurement as time needed to achieve the adsorption-desorption equilibrium in all measured systems. To determine polymer adsorption, the colorimetric method described by Dubois, Gilles, Hamilton, Rebers, and Smith (1956) was used. 0.05 cm³ of 80% phenol and 5 cm³ of 98% sulphuric acid were added to 2 cm³ of supernatant obtained after centrifugation with a speed of 14,000 rpm using a high speed centrifuge (310b Mechanika Preczyzyna). Time of centrifugation was equal to 15 min. The absorbance of the complex was measured at 490 nm after 30 min of colour development from the start of the reaction with a UV-vis spectrophotometer (Cary 100, Varian Instruments). All measurements were done four times and the average values are reported. The measurement error in the analyses was from 5 to 9%.

SDS concentration was analyzed by a variation of Zeng method (Zeng & Osseo-Asare, 2004). One decimetre cube of indicator solution was prepared by dissolving 0.16 g of dimidium bromide and 0.04 g of patent blue in doubly-distilled water in the presence of 40 cm³ of 1.25 mol dm⁻³ sulfuric acid. Next, in a separation funnel, 0.5 cm³ of sample solution was mixed with 39.5 cm³ pure water, followed by the addition of 10 cm³ of indicator solution and 20 cm³ of chloroform. The obtained mixture was vigorously shaken for 1 min and allowed for phase separation. The spectrophotometric measurement of chloroform solution at 526 nm was performed, using pure chloroform as a reference. The SDS concentration in the pure solutions was calculated from a calibration curve. All measurements were done as triplicates and the average values are reported. The measurement error in the analyses was from 3 to 8%.

Download English Version:

<https://daneshyari.com/en/article/7788966>

Download Persian Version:

<https://daneshyari.com/article/7788966>

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