



# Structural features and water sorption isotherms of carrageenans: A prediction model for hybrid carrageenans



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## ABSTRACT

**Experimental:** water adsorption and desorption isotherms of kappa/iota-hybrid carrageenan (KIC) extracted from *Mastocarpus stellatus* red seaweed as well as commercial kappa-carrageenan (KC) and iota-carrageenan (IC) were obtained at several temperatures (5, 25, 45, 65 °C). Spectroscopic and X-ray diffraction techniques allowed identifying the fundamental composition of above biopolymers. Crystallinity values (%) followed the order IC ( $25.4 \pm 0.6$ ) > KIC ( $9.3 \pm 0.4$ ) > KC ( $4.8 \pm 0.2$ ), which nicely matched with the hygroscopic properties of the tested biopolymers (KC > KIC > IC) at each temperature. Sulphate content and sulphation degree of KIC were also intermediate. The experimental sorption data were successfully fitted using the two-parameter Caurie model, selected following a statistical analysis. A prediction model to estimate the KIC water sorption isotherms based on its individual disaccharides units content (% mol) (kappa- ( $73 \pm 4$ ) and iota- ( $27 \pm 4$ )) and including the temperature effect was successfully developed.

## 1. Introduction

The hygroscopic nature of the biopolymers is a relevant aspect on moisture, texture or quality of foodstuffs, since the biopolymers tend to develop physical and chemical changes strongly dependent on their temperature/moisture history (Rosell, Collar, & Haros, 2007). Nowadays, the use of alternative biopolymers as gelling, thickening or stabilising agents rises in several food (Larotonda, Torres, Gonçalves, Sereno, & Hilliou, 2015) and non-food (Jonathan & Karim, 2016) applications to achieve determined thermo-rheological properties of final products. Namely, the food industry requests biopolymers as solid powders that are incorporated to various solid or liquid materials during processing (Imeson, 2010). The understanding of water sorption characteristics among biopolymers and atmosphere is essential for the suitable process conditions selection owing to physicochemical characteristics, microbial safety or other features dependents on water activity (Bahloul, Boudhrioua, & Kechaou, 2008; Chenlo, Moreira, Prieto, & Torres, 2011).

The experimental water sorption isotherms can be obtained by the determination, usually at atmospheric pressure, of the equilibrium moisture content and the water activity at fixed temperature. These isotherms can be gotten either for water adsorption or desorption procedures by increasing or decreasing the sample water activity. Both processes are not completely reversible (Bonilla, Azuara, Beristain, & Vernon-Carter, 2010). Water sorption isotherms are notably

influenced by the biopolymer structure or state (i.e. crystal, an ordered molecular lattice, or amorphous, lacking in molecular order). In simple terms, amorphous non crystalline materials are more hygroscopic since can hydrogen-bond water internally, non just on the surface which is the only way water can interact with a perfect crystal (Labuza, Knnane, & Chen, 1985). In the bibliography, it can be found numerous empirical and semi-empirical models that allow establishing mathematical correlations between the equilibrium moisture content and the water activity and are commonly evaluated by the fitting of the experimental data sets; see as e.g. a recent comprehensive review (Willems, 2015). Another option is estimate the water activity, at each temperature and moisture content, from fundamental laws and empirical relationships using estimation algorithms based on materials chemical composition (Moreira, Chenlo, & Torres, 2009), which would be of great interest, since the current literature displays relevant discrepancies between different experimental water sorption isotherms for certain products as well as reduce time in the experimental determination.

Carrageenans are sulphated galactans isolated from red seaweeds (*Gigartinales*, *Rhodophyta*), which have been ever more employed in industrial applications as gelling, thickening, texturing or stabilising agents. The main commercial carrageenans are usually divided into kappa- and iota- carrageenans. Kappa-carrageenan strands are less oriented and less crystalline than the salts of iota-carrageenan with glass transition temperatures between 160.8 and 89.5 °C (10% and 50%,

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respectively) (Mahmood, Rahman, & Yee, 2014). Commonly, carrageenophyte seaweeds do not produce these pure carrageenans, but rather a range of hybrid structures (Pereira, Amado, Critchley, van de Velde, & Ribeiro-Claro, 2009). A specific type of hybrid carrageenans is kappa/iota-hybrid carrageenans (KIC). Particularly, those KIC extracted from underexploited algal resources as *Mastocarpus stellatus* red seaweeds would contribute to meet the growing demand for biopolymers with specific physicochemical and mechanical features to be used in food, biomedical or pharmaceutical applications (van de Velde, 2008; Yan et al., 2012).

KIC are natural polyelectrolyte copolymers consistent in blocks of kappa-carrageenan (alternating sequences of 3-linked  $\beta$ -D-galactopyranose bearing a sulphate group on the fourth carbon of the sugar ring (G4S) and 4-linked  $\alpha$ -D-anhydrogalactopyranose (DA)) and blocks of iota-carrageenan (alternating sequences of G4S and 4-linked  $\alpha$ -D-anhydrogalactopyranose with a sulphate group on the second carbon of the anhydro ring (DA2S)) (Azevedo, Torres, Sousa-Pinto, & Hilliou, 2015). The kappa-/iota- ratio, the length of the block or the relative content of more sulphated carrageenan units notably depend on family and life stage of the seaweeds (Bixler & Porse, 2011). It is well-known that the carrageenans quality can be influenced by numerous aspects such as the season of harvest (Azevedo et al., 2015), the seaweed maturity state (Hilliou et al., 2012) or the post-harvest storage (van de Velde, 2008). In this context, the knowledge of the carrageenans sorption behaviour is a critically relevant step in the industrial processing to select more appropriately the drying and storage conditions. This knowledge is also relevant to reduce the impact of an inappropriate equipment use which could change the quality of the raw material and increase the operation costs (Williams, 2007).

In the past decade, some studies have been made concerning the sorption properties of different galactomanans such as guar gum (Vishwakarma, Shivhare, & Nanda, 2011), locust bean gum (Wang & Somasundaran, 2007) or carrageenan gum films (Larotonda et al., 2015) and other hydrocolloids such as carboxymethyl cellulose, tragacanth or xanthan (Torres, Moreira, Chenlo, & Vázquez, 2012). Nevertheless, scarce information restricted to specific temperatures is available in the bibliography on water sorption characteristics of selected biopolymers. In this context, the main objective of this work is to get the experimental water adsorption and desorption isotherms of different types of carrageenans (kappa-, iota- and kappa/iota-hybrid carrageenan), over a wide range of water activities and temperatures of interest. The particular objectives include: (i) the determination of some chemical characteristics of the tested biopolymers relevant on the hygroscopic behaviour; (ii) the experimental water sorption data fitting using Caurie model and (iii) the prediction of the kappa/iota-hybrid carrageenan water sorption isotherms from the individual water sorption isotherms of kappa- and iota- carrageenans.

## 2. Materials and methods

### 2.1. Raw materials

Fresh *Mastocarpus stellatus* seaweeds (moisture content of  $67.9 \pm 2.5\%$ , wet basis, AOAC, 2000) were gently provided by Conservas Mar de Ardora Company (Ortigueira, A Coruña, Spain). The tested hydrocolloids were kappa/iota-hybrid carrageenan (KIC) extracted from above seaweeds, and commercial kappa-carrageenan (KC) (Sigma-Aldrich, St. Louis, MO) and iota- carrageenan (IC) (Sigma-Aldrich, St. Louis, MO) with weight-average molar masses ( $M_w$ ) of  $2.20 \cdot 10^6$ ,  $2.31 \cdot 10^6$  and  $1.32 \cdot 10^6$  g/mol, respectively, determined by gel permeation chromatography as previously detailed (Torres, Hallmark, & Wilson, 2014).

### 2.2. Biopolymer extraction

*Mastocarpus stellatus* seaweeds were cautiously washed with fresh

water and selected by their colour (reddish) and size ( $\sim 20$  cm) before being processed in order to get the KIC gum employed as raw material as previously described in detail (Torres, Chenlo, & Moreira, 2017). Concisely, the seaweeds were dried (temperature of  $35^\circ\text{C}$ , initial load density of  $1.5 \pm 0.1$  kg/m<sup>2</sup>, air velocity of 2 m/s and relative humidity of 30%) in a pilot-scale tray dryer (Angelatoni Challenge 250, Italy). Then, dried seaweeds were milled (weight-average particle size,  $D_w$  ( $\mu\text{m}$ )  $77.5 \pm 0.4$ ) using an ultra-centrifugal mill with an internal sieve of 200  $\mu\text{m}$  (ZM200 Retsch GmbH, Germany) and equilibrated at room temperature with an atmosphere generated by a saturated solution of  $\text{Mg}(\text{NO}_3)_2$  (water activity,  $a_w \sim 0.55$ ). Subsequently, equilibrated seaweed powders were stored at  $4^\circ\text{C}$  in vacuum sealed bags until its utilization to ensure adequate post-harvest preservation until KIC extraction.

The KIC extraction was carried out at least in triplicate using a set of optimized parameters get in an earlier work (Azevedo et al., 2015). Briefly, dried seaweed powders (1.5 g) were soaked in 100 mL of distilled water ( $90^\circ\text{C}$  for 2 h). Then, suspensions were cooled to  $55^\circ\text{C}$  and treated for 1 h with stirring with  $\alpha$ -amylase (1 mg/g algal material; amyloglucosidase from *Aspergillus niger*, Fluka Biochemika) in order to digest any floridean starch existent. Afterwards, samples were heated to  $80^\circ\text{C}$  to simplify the centrifugation (3000 rpm for 10 min). Supernatants were precipitated in 2.5 vols of ethanol (96%) and precipitates were filtered through cotton clothes, washed twice with ethanol and oven dried ( $50^\circ\text{C}$  for 24 h).

### 2.3. Spectroscopic measurements

The kappa/iota fractions and purity of the samples were determined using Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) and Nuclear Magnetic Resonance (NMR) analysis. FTIR-ATR spectra of sample materials (i.e. KIC, KC and IC) were recorded on a Varian 670-IR spectrometer at room temperature in the range between 500 and  $1500\text{ cm}^{-1}$ , following the procedure described in detail elsewhere (Pereira et al., 2009), for the qualitative characterization of the tested hydrocolloids.  $^1\text{H}$  NMR spectroscopy of the above materials was conducted on a Varian Unity plus 300 spectrometer operating at 300.13 MHz for the quantitative determination of the carrageenan fractions. The molar fractions of the carrageenan repeating units ( $\kappa$  and  $\iota$ ) are calculated as the integrated intensity of the corresponding  $^1\text{H}$  NMR peak (5.09 and 5.5 ppm, respectively) over the sum of the integrated intensities of all assigned carrageenan anomeric protons (Azevedo et al., 2015). The degree of sulphation (i.e. the relation of sulphate to total carbohydrate) was also estimated from infrared spectroscopy according to Rochas, Lahaye, and Yaphe (1986). Note here that the sulphate content was estimated by the widely used barium chloride precipitation method (Jackson and McCandless, 1978), after sulphate hydrolysis by 1N HCl at  $100^\circ\text{C}$  for 4 h as reported elsewhere (Villanueva, Mendoza, Rodriguez, Romero, & Montaña, 2004).

### 2.4. X-ray diffraction measurements

The crystalline structure analysis of KIC, KC and IC was conducted at room temperature on a Philips diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda$ : 0.154 nm) operating at 40 KV and 20 mA. The samples were scanned through the  $2\theta$  (diffraction angle) from  $2$  to  $50^\circ$  at a scanning rate of  $8^\circ/\text{min}$ . Note here that samples used for crystallinity measurements were those equilibrated at intermediate water activities ( $a_w \sim 0.55$ ,  $\text{Mg}(\text{NO}_3)_2$ ). The relative crystallinity degree was calculated following the method reported elsewhere (Correia, Cruz-Lopes, & Beirão-da-Costa, 2012), which takes into account the amorphous and crystallized area on the X-ray diffractogram. The measurements were made at least in duplicate.

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