Colloids and Surfaces A 529 (2017) 137–145

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

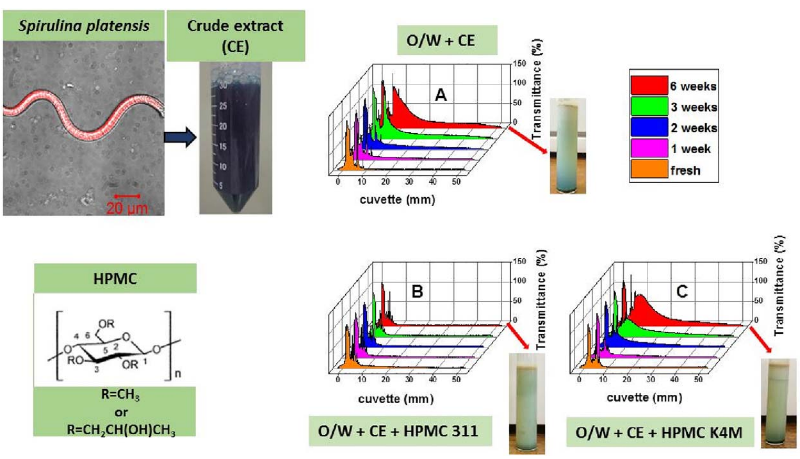
Research Paper

The role of hydroxypropyl methylcellulose structural parameters on the stability of emulsions containing Spirulina biomass

Robson T. Shimada, Matheus S. Fonseca, Denise F.S. Petri*

Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, SP, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydroxypropyl methylcellulose
Spirulina
Emulsion stability
Sunflower oil

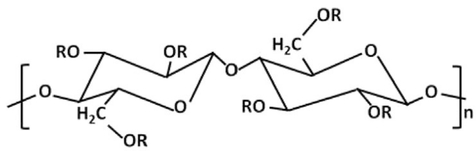
ABSTRACT

Hydroxypropylmethyl cellulose (HPMC) samples with varying degrees of substitution of methoxy groups (DS), mass molar substitutions of hydroxypropoxy groups (MS) and molecular weights were used in combination with *Arthrospira platensis*, a nutritious microalgae, as oil in water emulsion stabilizers. The HPMC samples presented DS ranging from 1.37 to 2.00, MS ranging from 0.23 to 0.85 and average molecular weights (M_w) of 2.5×10^5 g/mol and 6.7×10^5 g/mol. Crude extracts of Spirulina were prepared in buffers at pH 6 (CE6) and pH 8 (CE8) by sonication and part of the extracts was centrifuged (CCE6 or CCE8). All extracts contained protein (50%), lipids and phycocyanin and presented mean ζ-potential ranging from −(16 ± 2) mV to −(20 ± 2) mV, mean diameter ranging from (108 ± 52) nm to (306 ± 68) nm and interfacial activity. The HPMC with the highest values of DS, MS and molecular weight led to the lowest O/W interfacial tension. The combination of CE6 (at 10 g/L) and four different types of hydroxypropyl methylcellulose (HPMC) at concentration range from 0.3 to 1.0 wt% increased substantially the emulsion stability, although the ζ-potential values decreased one order of magnitude. Particularly, the HPMC (at 1.0 wt%) with the highest values of DS, MS and molecular weight led to the most stable emulsions, due to (i) chains segments arrangements at the interface, (ii) favorable interactions between microalgae proteins and lipids and HPMC chains segments at the O/W interface and (iii) the increase of the emulsion continuous phase viscosity.

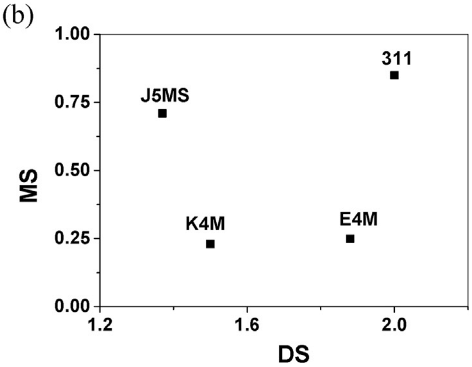
* Corresponding author.
E-mail addresses: dfsp@usp.br, dfsp@iq.usp.br (D.F.S. Petri).

http://dx.doi.org/10.1016/j.colsurfa.2017.06.001
Received 17 April 2017; Received in revised form 31 May 2017; Accepted 2 June 2017
Available online 03 June 2017

(a)



(b)



Scheme 1. (a) Representation of HPMC chemical structure, with R = −H, $-CH_3$ or $-CH_2$-CHOH-CH_3. DS and MS refer to degree of substitution of cellulose hydroxyl groups by methyl groups and molar substitution of cellulose hydroxyl groups by hydroxypropoxyl groups, respectively. (b) Graphical representation of DS and MS for the HPMC samples indicated in Table 1.

1. Introduction

The search for sustainable emulsifiers for new formulations is based on the need of creating functional products with low environmental impact [1]. Hydrocolloids, proteins and phospholipids from renewable sources are interesting alternatives for synthetic emulsifiers [2]. There is a plethora of natural hydrocolloids that work as emulsion stabilizers, as for instance, guar gum, xanthan, pectin [3]. Cellulose ethers are often used as stabilizers of O/W emulsions [4,5]. Hydroxypropyl methylcellulose (HPMC), a family of cellulose ethers, is widely applied as food emulsion stabilizer because it acts adsorbing on the particles surface [5] and increases the viscosity of continuous medium, thus preventing phase separation. Moreover, the hydrophilicity and hydrophobicity of HPMC chains can be tuned by the degree of substitution of methoxy groups (DS) and the mass molar substitution of hydroxypropoxy groups (MS) because high DS increases HPMC hydrophobicity, whereas high MS favors HPMC hydrophilicity [6,7].

Many studies reported about the ability of HPMC chains to act as stabilizers for O/W emulsions. For instance, Camino and Pilosof investigated the effect of molecular weight of HPMC (USP 2910) samples with high DS value (1.93) on the O/W emulsion stability at pH 3 and pH 6 [8]. They found out that at pH 3 the HPMC chains tend to aggregate due to hydrophobic interaction, leading t o O/W interfacial films with low stability, in comparison to those in emulsions prepared at pH 6. HPMC chains with low molecular weight (MW ~ 2000 g/mol) provided emulsions with narrower droplet size distribution and smaller droplets than the longer chains did (MW > 6000 g/mol), corroborating with reported data by Schulz and Daniels [9]. On the other hand, the short chains led to emulsions with low viscosity, causing creaming and flocculation as the emulsions aged, suggesting that the combination of short and long chains provide the best conditions for the emulsions stability [8]. Wollenweber and coworkers compared the behavior of three different types of HPMC (USP 2208, 2906 and 2910) at the O/W interface. HPMC USP 2208 and USP2906 both with the lowest MS values among the samples led to the highest stability of the droplet size upon temperature cycle test for 6 months [10].

Complexes of proteins and hydrocolloids might be formed by electrostatic and van der Waals interactions [11] or by chemical reactions (Maillard reactions) [12] and tend to reduce the interfacial tension O/W more efficiently than the proteins or hydrocolloids separately. The main reason for this is that the hydrocolloid/protein complexes are larger than each of them is, thus the amount necessary to saturate the interface is smaller [3]. The combination of HPMC short chains and whey protein displayed synergist interfacial effects [13]. Complexation between HPMC and β-lactoglobulin was not observed at pH 6, but at pH 3 associative interactions between both led to more elastic interfacial films [14].

Arthrospira platensis or Spirulina is a microalgae belonging to the cyanobacteria (blue-green alga) group, which has a very high nutritional value [15]. Its composition contains proteins (55%–70%), monosaccharides and polysaccharides (15%–25%), lipids (18%), vitamins, minerals, pigments like carotenes, chlorophyll a, and phycocyanin [16]. The group of phycobiliproteins is the major component of Spirulina and can be applied as food colorants and antioxidants, due to the presence of phycocyanins [17–19].

The combination of Spirulina extracts with HPMC was applied for increasing the nutritional properties of gluten free bread [20,21] or for the development of a colored ophthalmic product [22]. Although the role of HPMC as O/W emulsifier has been well explored, to the best of our knowledge there is no report about the relevance of HPMC structural parameters (DS, MS and molecular weight) in combination with microalgae for the stability of O/W emulsions. The present study focused on the stability of sunflower oil in water emulsions containing Spirulina extracts and four different types of HPMC at pH 6 and pH 8. We hypothesize that the structural parameters of HPMC samples play an important role on the stability of O/W emulsions containing Spirulina extracts because they might affect the O/W interfacial behavior and continuous medium viscosity. In order to test the hypothesis, we chose a set of four HPMC samples disclosing DS values from 1.37 to 2.00, MS values from 0.23 to 0.85 and molecular weights typically 2.5×10^5 g/mol and 6.7×10^5 g/mol, which were combined with Spirulina extracts, to compose O/W emulsions.

2. Material and methods

2.1. Materials

Spirulina biomass was kindly provided by Fazenda Tamanduá, Brazil, as dried powder. The protein content in the Spirulina biomass was estimated by the nitrogen content determination, which was done by elemental analysis in a Perkin Elmer–CHN 2400 equipment (Perkin Elmer, USA). The multiplication of the N content of (7.92 ± 0.09) % by 6.25 [23] yielded the protein content of (50 ± 1) wt% in the Spirulina biomass, corroborating with literature report [24].

The Dow Chemical Brazil Co. kindly provided the commercial HPMC samples; Scheme 1a represents their structure. Table 1 presents their USP codes and characteristics. Scheme 1b shows graphically the DS and MS values, which refer to the degree of substitution of cellulose hydroxyl groups by methyl groups and to the molar substitution of cellulose hydroxyl groups by hydroxypropoxyl groups, respectively, corresponding to each HPMC type.

O/W (10% v/v) emulsions were prepared with commercial edible sunflower oil (Bunge, Brazil). Na_2HPO_4 and NaH_2PO_4 (LabSynth, Brazil) were used for the preparation of buffers at pH 6.0 and pH 8.0.

2.2. Spirulina biomass treatment

Dried Spirulina biomass was macerated with mortar and pestle during 10 min in order to grind the powder. Then it was added to phosphate buffer 0.050 mol/L pH 6.0 or pH 8.0, so that the final concentration was 20 g/L. The dispersions were sonicated during different periods (Hielscher Ultrasound UP100H/UP50H, operating frequency of