Colloids and Surfaces A xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A

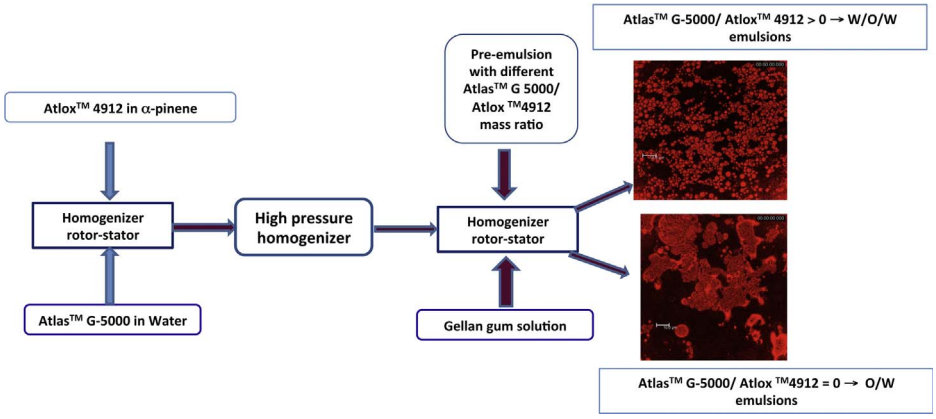
journal homepage: www.elsevier.com/locate/colsurfa

Rheology, microstructural characterization and physical stability of W/α-PINENE/W emulsions formulated with copolymers

Mª Carmen García[a,*], Phil Cox[b], Luis Trujillo-Cayado[a], José Muñoz[a], Mª Carmen Alfaro[a]

[a] Universidad de Sevilla, Departamento de Ingeniería Química, C/Profesor García González 1, Facultad de Química, 41012 Sevilla, Spain
[b] University of Wolverhampton, School of Chemical Engineering, Wulfruna Street, Wolverhampton WV1 1LY, United Kingdom

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Multiple emulsion
Physical stability
Green solvent
Amphiphilic block copolymer
High pressure homogenizer

ABSTRACT

In this work the microstructure and the physical stability of emulsions containing α-pinene and gellan gum were studied as a function of Atlas™ G-5000/Atlox™ 4912 copolymer mass ratio, R, used as emulsifier. In order to reach this objective, electrolytic conductivity measurements, laser diffraction, confocal laser scanning microscopy (CLSM) and rheology were used. Electrolytic conductivity tests along with CLSM supported the formation of W/α-pinene/W multiple emulsions in all systems containing the most hydrophilic copolymer. Parameter R did not significantly influence either the mean diameters or the span when both copolymers were used. However the lack of Atlas G-5000, not only did it provoke an important increase of mean diameter of droplets, but it also caused the formation of a simple O/W emulsion instead of a multiple emulsion. All emulsions showed shear thinning flow behaviour. The mechanical spectra of multiple emulsions with R ≥ 2 were similar to each other and independent of aging time. A reduction of R led to a decrease in G′ and G″ values and aging time yielded increasing G′ values probably due to the occurrence of incipient creaming. Conversely, the emulsion without Atlas™ G-5000 showed a drop of viscoelastic moduli with aging time due to a coalescence process. These multiple emulsions may find applications in agrochemistry since some active ingredients may be encapsulated in the inner phase, enabling the delivery of hazardous ingredients in a safer way, along with the use of α-pinene which is an easily biodegradable green solvent.

* Corresponding author.
E-mail address: mcgarcia@us.es (M.C. García).

http://dx.doi.org/10.1016/j.colsurfa.2017.07.029
Received 30 September 2016; Received in revised form 26 June 2017; Accepted 8 July 2017

1. Introduction

Multiple emulsions can be defined as “emulsions of emulsions”, which consist of dispersed droplets (globules) that contain smaller droplets of different phases. Frequently, they are classified depending on the number (1) or on the nature (2) of internal droplets present in the emulsion globules: (1) into three groups [1,2]: (a) type A, where the multiple emulsion globule contain one large internal droplet, (b) type B, where there are several small internal droplets in the globules of multiple emulsion and (c) type C, where the globules of the multiple emulsion contain a large number of internal droplets (2) into two groups [3]: water/in oil/in water (W/O/W), and oil/in water/in oil (O/W/O).

The potential applications of multiple emulsions are numerous, especially in areas such as drug delivery systems, cosmetics [4,5], foods [6] or agrochemicals [7,8]. In the latter field, the W/O/W multiple emulsions are a good option to satisfy the trend to develop new formulations of pesticides, which must be cleaner and safer for users. This fact is due to the possibility to encapsulate active materials into the inner drops, which can be released under certain environmental conditions.

Recently, in order to develop more ecofriendly and safer formulations, the replacement of traditional organic solvents (oil phase) by biodegradable solvents is increasingly promoted. In order to accomplish this goal, several authors have studied the applications of solvents obtained from renewable sources such as essential oils, which may be used as organic phase in simple and multiple emulsions [8–13]. An interesting essential oil for the formulation of agrochemical emulsions is α-pinene, a terpenic solvent usually obtained from the pine bark or by distillation, which provides some activity as bio-based pesticide [9,10,14].

Besides the typical destabilization mechanisms affecting simple emulsions, there are further mechanisms of instability in W/O/W multiple emulsions. Multiple drops may coalesce with other oil droplets (simple or multiple) or they could lose their internal droplets. The occurrence of an osmotic gradient leads to either swelling or shrinkage of the internal droplets depending on the direction of this gradient. Another possible breakdown mechanism may be coalescence of the internal aqueous droplets within the oil phase. A combination of these mechanisms may frequently take place such that the actual breakdown mechanisms remain usually unclear [3]. There is another type of destabilization mechanism which takes place by the coalescence of internal drops with the external phase. The appearance of this mechanism usually is caused by the presence of a hydrophilic surfactant in the outer aqueous phase [15–17]. In fact, this destabilization mechanism is responsible for encapsulation efficiency values lower than 1. The encapsulation efficiency is the ratio of water actually encapsulated in the multiple emulsion to the water content of the primary W/O emulsion [18].

However a major problem associated with W/O/W emulsions is creaming, which is probably due to the large size of the multiple drops. Creaming may be reduced by using a thickening agent in the external aqueous phase. In this work a commercial biopolymer obtained by fermentation, gellan gum, has been used.

In order to obtain stable multiple emulsions, two surfactants are needed, one of them of low HLB, to stabilize the w/o interface (lipophilic) and the other of high HLB, to stabilize the o/w interface (hydrophilic). This paper will explore the use of a combination of polymeric surfactants as emulsifiers. Namely, we report the performance as emulsifiers of an AB hydrophilic nonionic polyalkylene oxide (EO-PO) block copolymer, Atlas™ G-5000 (HLB: 16.9), and ABA hydrophobic block copolymer, Atlox™ 4912 (HLB: 5-6), obtained by esterification of poly (12-hydroxystearic acid), PHSA (A) with poly alkylene glycols (B). In a previous work, this combination of polymeric surfactants was used to prepare in a single step multiple emulsions containing 2-ethylhexyl lactate as dispersed phase [17,18].

W/O/W double emulsions can be prepared via a phase inversion method [19], one-stage emulsification method [17], or two-stage emulsification method. Firstly, the inner W/O emulsion is obtained by traditional shear-rate homogenizer devices. Secondly, a multiple emulsion is produced dispersing this W/O emulsion in an aqueous solution [3,20–22].

The objectives of the present work were to study the physical stability, rheological and microstructural behaviour of W/O/W emulsions formulated with a “green” solvent (α-pinene) as dispersed phase and gellan gum as thickener, as a function of the mass ratio of two amphiphilic copolymers (Atlas™ G-5000 and Atlox™ 4912) used as emulsifiers.

2. Materials & methods

2.1. Materials

Commercial low-acyl gellan gum, Kelcogel F type was used as supplied by CP Kelco Company (San Diego, USA) The final concentration of polysaccharide in the emulsion was 0.4 wt%. 0.1 wt% sodium azide was added to the final formulation to prevent the growth of microorganisms.

The organic solvent used was rectified α-pinene Leavo 95, an extremely non-polar solvent, which was supplied by Destilaciones Bordas-Chinchurreta S.A. (Sevilla, Spain). Its density (20° C) is 898 kg/m^3, its refractive index is 1.464 and its boiling point is around 67.5 °C.

Atlas™ G-5000 (hydrophilic AB block copolymer, HLB: 16.9) and Atlox™ 4912 (hydrophobic ABA block copolymer, HLB:5.5) surfactants were supplied by Croda Iberica S.A. (Barcelona, Spain).

In addition, the Dow Corning^R MD 10 defoaming agent supplied by Dow Corning was used.

2.2. Methods

Each multiple emulsion studied was denominated as E(2)30/X/Y where 30 indicates 30 wt% of α-pinene, X is wt% of Atlas™ G-5000 and Y is wt% of Atlox™ 4912. The total concentration of copolymers was 3.0 wt%, although the ratio Atlas™ G-5000 to Atlox™ 4912 was varied.

The gellan gum solution was prepared using a protocol described in previous paper of this group [9] and the emulsions were prepared as follows.

1 The components of the aqueous phase (Atlas™ G-5000 copolymer, defoaming agent and water) were mixed using a magnetic stirrer (Hotplate stirrer [SB162-3], Stuart) in order to achieve an homogeneous phase. Likewise, the components of the oil phase (Atlox™ 4912 and α-pinene) were also mixed by means of the magnetic stirrer.
2 Subsequently, the oil phase was slowly added to the aqueous phase to prepare the emulsion with rotor-stator device (Silverson L4RT homogenizer equipped with an emulsor screen) at 10600 r.p.m. for 150 s.
3 The pre-emulsion obtained was passed through a high-pressure valve homogenizer (FT9 Homogeniser, Armfield) three times at 6.9·103 kPa. The pre-emulsions were prepared in batches of 200 g
4 Finally, this emulsion was mixed with an equal amount of 0.8 wt% gellan gum aqueous dispersion. For this purpose, the Silverson L4RT was used at 10600 r.p.m. for 60 s.

The methods used to characterize the emulsions studied are described below.

2.2.1. Confocal laser scanning microscopy

Emulsions were analysed by means of a Leica SPE confocal laser scanning microscope (CLSM). Red Nile dye was used to stain the oil phase and Blue Nile dye was utilized for aqueous phase. The samples