Colloids and Surfaces B: Biointerfaces 154 (2017) 279–286

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

Protocols

Micellization in vegetable oils: A structural characterisation

Ophélie Fadel[a], Luc Girard[a], Donatien Gomes Rodrigues[a], Pierre Bauduin[a], Xavier Le Goff[a], Anne Rossignol-Castera[b], Annabelle L'Hermitte[b], Olivier Diat[a,*]

[a] Institut de Chimie Separative de Marcoule, UMR 5257 (CEA, CNRS, Université de Montpellier, ENSCM), BP17171, 30207 Bagnols sur Cèze, France
[b] OLEOS SA/Hallstar France, 50 rue du Rajol, Fréjorgues Est, 34130 Mauguio, France

ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form 10 March 2017
Accepted 11 March 2017
Available online 21 March 2017

Keyword:
Reverse micelle
Vegetable oil
Polyphenol antioxidant
SAXS

ABSTRACT

The solubilisation of polar and polyphenol antioxidant in vegetable oils was studied. It was shown that the use of a polyglyceryl-3-diisostearate (PG3DS), a bio-sourced emulsifier well known in cosmetics, increases the yield of solubilisation thanks to some aggregation properties analysed using x-ray scattering technique. We show indeed that PG3DS forms reverse aggregates with a critical concentration that depends on the oil polarity. PG3DS reverse aggregates are elongated with a polar core and cannot be really swollen by addition of water. This supramolecular organisation allows however an efficient solubilisation of polar antioxidants in vegetable oils.

1. Introduction

During the last two decades, reverse microemulsions have been largely investigated for pharmaceutical, cosmetic, nutraceutical and food purposes as promising vectors for hydrophilic, lipophilic and amphiphilic active molecules [1–6]. Microemulsions are relevant complex liquid systems for drug vectorization because of their high solubilisation capacity, long term stability and because of their large exchange surface that enhances drug bioavailability [7]. However, within the formulation of cosmetic, pharmaceutical or food microemulsions, some significant issues still exist; they are indeed often related first to the amount of water content that can be a source of bacteria development or generate hydrolysis of fragile polar encapsulated compounds. They are also related to the potential toxicity of amphiphilic components conventionally used for the system stabilisation [8,9]. Thus, the formulation of W/O microemulsions made from bio-sourced amphiphilic molecules and that can incorporate only limited amounts of water, remains challenging. This explains the growing interest in polar lipids as surfactant, cosurfactant and/or as solvents for the development of safe and efficient cosmetics, pharmaceutical and food formulations [10–18].

Micellization in oil rich systems using amphiphilic molecules with high Hydrophilic Lipophilic Balance characteristics (HLB) [19] is known for a long time. For instance sodium bis(2-ethylhexyl) sulfosuccinate (AOT) [20], an anionic surfactant with two branched aliphatic chains, can self-assemble to form inverted structures in pure oil or oil-rich/water systems [21–23]. When amphiphilic molecules have a compact and rigid polar head balanced by flexible aliphatic chains, the formation of reverse aggregates in organic solvent above a critical concentration depends on the presence of a few molecules of polar solvent [24–27]. Indeed, the water molecules structure the core of the aggregation by adding a H-bond contribution to the dipole-dipole interaction between the polar heads of the surfactants [28]. Moreover, compared to direct micelles in water, the micellar aggregation number is much smaller, seldom exceeding 10–15, in low polarity solvents [26,29]. Then, when water is added to surfactant/oil binary systems, reverse micelles can swell with some limit in size. They can also change their shapes depending on the interactions between the polar heads and between the aliphatic chains and the apolar solvent. In terms of water molecules per surfactant, there is a ratio above which the molecules are not anymore bounded to the polar heads of the amphiphilic molecules but begin to form a bulk like core of polar molecules [30]. Beyond this water concentration such a micellar system can be called swollen reverse micelles or water in oil (W/O) microemulsion and that we can consider that some water molecules are solubilized in an oily system.

Several physical chemistry approaches exist to quantify the water solubilisation capacity of amphiphilic systems in oil-rich media; the construction of phase diagrams is one of them [31–34]. Solubilisation parameters such as the area of the total monophasic microemulsion region (A_T) [35], or the maximum of water solu-

* Corresponding author.
E-mail address: olivier.diat@cea.fr (O. Diat).

http://dx.doi.org/10.1016/j.colsurfb.2017.03.025
0927-7765/

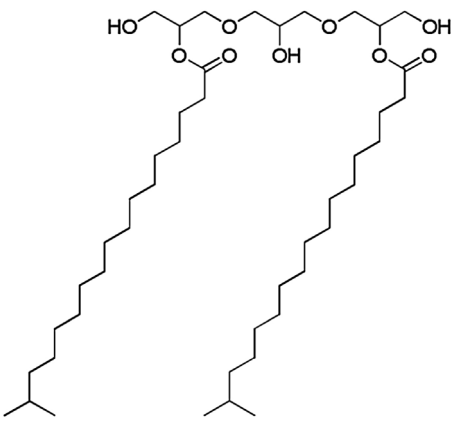

Fig. 1. Polyglyceryl-3-diisostearate (PG3DS) chemical structure.

bilisation [4] were used to show, for instance, that an increase in the solubilisation capacity of microemulsion containing short chain alcohol is correlated to an interfacial fluidification. When the phase diagram does not exist or is not complete, the surfactant aggregation phenomenon can be studied. We investigate here the micellization of polyglyceryl-3-diisostearate (PG3DS), a well-known and bio-sourced emulsifier used in cosmetics. The main reason for this study is related to its solubilisation capacity for polar antioxidant within triglycerides systems [36]. This capacity was analysed using the electron paramagnetic resonance (EPR) technique. Medium chain triglycerides (MCT), sunflower vegetable oil and jojoba wax are three oils chosen to investigate the influence of the solvent polarity on the PG3DS micellization property. The supramolecular aggregation in a solvent can be studied by various methods such as conductimetry, nuclear magnetic resonance, viscosimetry, vapor pressure osmometry, spectrometry and scattering techniques. The later ones remain the most suitable option to analyse their shape. Here, small and wide angle X-ray scattering (SWAXS) technique was carried out to analyse the PG3DS aggregation in vegetable oils as a function of their polarity degree and the water content. It is indeed a very suitable technique to probe supramolecular aggregation and was already used to study reverse aggregation in vegetable oil [15,18,33,37–44]. Finally, we have shown that there is a link between aggregation and the polar antioxidant solubilisation capacity of the PG3DS.

2. Materials and methods

2.1. Sample preparation

The Jojoba wax from Aroma Herbiotech, the partially refined sunflower oil from Cauvin as well as the medium chain triglyceride (MCT) oil (LABRAFAC CC) from Gattefossé are oily vegetable systems and have been used as received.

The amphiphilic compound, Polyglyceryl-3 Diisostearate (PG3DS) represented in Fig. 1 (CAS 66082-42-6/85666-92-8) is also a product of Gattefossé with a molar mass of 773,2 g/mol and a density of 0,935. Decane solvent was purchased from Alfa Aesar 99% and used without further purification. Ultrapure water (Milli-Q Labo, Millipore) was used in all samples preparations.

Galvinoxyl used as free-radical scavenger in the EPR experiments was supplied by Sigma-Aldrich and was used as received. The Effialine® from Purextract was used as a model mixture of antioxidant molecules. It contains antioxidant molecules from olive tree leaf and its composition is roughly 50–70% of oleuropeine, 1–5% hydroxytyrosol, 5–10% oleuroside and 5–15% luteolin glucoside. This mixture is a yellow-brown powder partially soluble in water.

For the study of the aggregation in oil, different samples (series 1) were prepared at room temperature varying the PG3DS concentration in jojoba oil, sunflower oil, MCT and decane/MCT mixtures.

The choice of these different oil mixtures allows a variation of the oil polarity which is a concept not so often used in physical chemistry. Indeed, oils are not only hydrocarbon compounds from petrochemical industry but also esters, fatty alcohols, triglycerides more often encountered in vegetable or animal sources and used in medicine, cosmetic or nutraceutical domains. The main difference between mineral and natural oil is the presence of heteroatoms that differ in electronegativity and form groups with polar characteristics. Then, depending on the hydrocarbon chain lengths, branching and number of unsaturation, the oil can be already structured at the molecular scale with a correlation distance between the polar groups [45]. Thus, the aggregation phenomena of amphiphilic molecules can be strongly affected by the chemical nature of the oil [26,46]. One way to classify such a property is to simply determine the volume ratio between the polar group and the molecule, the "polar" ratio of an alkane chain being zero by definition since it contains no heteroatoms. These ratios are gathered in Table 1 for various oils or oil mixtures that we used in our study by estimating the molar volume of the molecules and of their subparts using the R.F. Fedors tables [47]. We calculated 0.026 for jojoba oil and 0.103 for MCT. The polarity of the refined sunflower oil is more complicated to estimate precisely due to i) the presence of unsaturation along the alkyl chains that can modulate the apolar volume, ii) the distribution of molecules with various lengths in this natural oil and iii) the possible presence of polar molecules such as fatty acids and phospholipids that are not totally extracted during the refining process. However, because most of the fatty acid groups of these triglyceride molecules contain 18 carbons whatever the number of unsaturation, its polarity parameter can be evaluated to be between those of pure MCT and jojoba oils, the more polar and more apolar oil respectively in this study. There are of course other ways with more or less advanced studies to characterize the oil polarity or "hydrophilicity" of a molecule. This property can be classified for example either via the solubilisation of a benchmark surfactant or via the determination of the phase inversion temperature (PIT) [39,48–50] or the equivalent alkane carbon number using the surface tension measurement [51]. The scaling of the oils used here is basic and arbitrary but can be used for comparing oil polarity for this study.

The residual water content of the oil samples was determined by the Karl-Fischer titration when it was possible. A second series of samples (series 2) was prepared by adding water to the previous compositions until the saturation. Beyond this saturation a degumming effect appears (not discussed here). These samples were also analysed by Karl Fisher titration and by SWAXS. A third and last series was prepared by adding Effialine till its maximum of solubilisation into MCT and jojoba oil with and without PG3DS and with and without water also at the saturation level.

2.2. Coulometric KF titration

It was performed by using a Metrohm 831 KF Coulometer instrument with an anhydrous cell and a generator electrode with diaphragm. HYDRANAL® -Coulomat AG-H was used as the anolyte solution.

2.3. Small and wide angle X-Ray scattering (SWAXS)

SWAXS measurements using Mo-radiation ($\lambda = 0.71$ Å), were performed on a Xenocs bench. The collimated beam via a focusing multilayer mirror and a set of two pairs of scatterless slits is scattered by the oily samples in glass capillaries used as x-ray transparent containers (2 mm in diameter) and was recorded using a