Journal of Colloid and Interface Science 509 (2018) 178–188

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

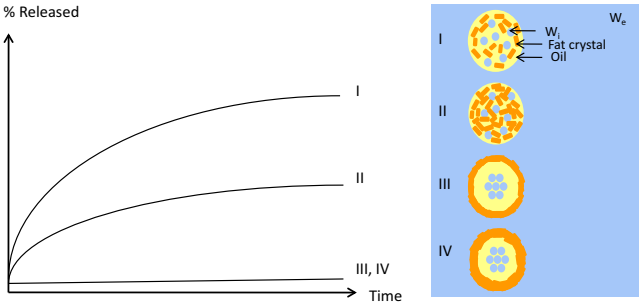
Regular Article

Different magnesium release profiles from W/O/W emulsions based on crystallized oils

Sameh Herzi [a,b], Wafa Essafi [c,*]

[a] Institut National de Recherche et d'Analyse Physico-Chimique, Pôle Technologique de Sidi Thabet, 2020 Sidi Thabet, Tunisia
[b] Institut National Agronomique de Tunisie, 43 Avenue Charles Nicolle 1082 Tunis-Mahrajène, Tunisia
[c] Laboratoire Matériaux, Traitement et Analyse, Institut National de Recherche et d'Analyse Physico-Chimique, Pôle Technologique de Sidi Thabet, 2020 Sidi Thabet, Tunisia

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 May 2017
Revised 16 August 2017
Accepted 28 August 2017
Available online 31 August 2017

Keywords:
W/O/W double emulsion
Crystallizable oil
Fat crystals distribution
Encapsulation
Release kinetics
Permeation/diffusion
Polyglycerol polyricinoleate
Sodium caseinate

ABSTRACT

Water-in-oil-in-water (W/O/W) double emulsions based on crystallized oils were prepared and the release kinetics of magnesium ions from the internal to the external aqueous phase was investigated at T = 4 °C, for different crystallized lipophilic matrices. All the emulsions were formulated using the same surface-active species, namely polyglycerol polyricinoleate (oil-soluble) and sodium caseinate (water-soluble). The external aqueous phase was a lactose or glucose solution at approximately the same osmotic pressure as that of the inner droplets, in order to avoid osmotic water transfer phenomena. We investigated two types of crystallized lipophilic systems: one based on blends of cocoa butter and miglyol oil, exploring a solid fat content from 0 to 90% and the other system based on milk fat fractions for which the solid fat content varies between 54 and 86%. For double emulsions based on cocoa butter/miglyol oil, the rate of magnesium release was gradually lowered by increasing the % of fat crystals i.e. cocoa butter, in agreement with a diffusion/permeation mechanism. However for double emulsions based on milk fat fractions, the rate of magnesium release was independent of the % of fat crystals and remains the one at t = 0. This difference in diffusion patterns, although the solid content is of the same order, suggests a different distribution of fat crystals within the double globules: a continuous fat network acting as a physical barrier for the diffusion of magnesium for double emulsions based on cocoa butter/miglyol oil and double globule/water interfacial distribution for milk fat fractions based double emulsions, through the formation of a crystalline shell allowing an effective protection of the double globules against diffusion of magnesium to the external aqueous phase.

* Corresponding author.
E-mail addresses: wafa.essafi@wanadoo.fr, essafi.wafa@inrap.rnrt.tn (W. Essafi).

http://dx.doi.org/10.1016/j.jcis.2017.08.089
0021-9797/

1. Introduction

Water-in-oil-in-water multiple emulsions (ME's) are multiple compartment structure systems consisting of small aqueous droplets embedded within larger oil globules, which themselves are dispersed within an external aqueous phase [1–3]. Hydrophilic actives (drugs, nutrients, reactants, etc.) can be loaded within the inner droplets and their encapsulation makes it possible to implement strategies such as isolation/protection from incompatible environments, and/or to retain their activity until required, for taste masking, for the reduction of fat content, for sustained delivery, etc. [3–7], that can be applied in various domains such as pharmaceutics, cosmetics and food.

Double emulsions are generally produced following a two-step sequential emulsification and the most common problem associated with double emulsions is their thermodynamic instability. The existence of two oppositely curved interfaces within the same structure requires two different emulsifiers of opposite solubility (water soluble and oil soluble). Being metastable, such materials undergo a destabilization progress that provokes structural changes and progressive leakage of the encapsulated species. The ageing of double emulsions may involve both coalescence and diffusion phenomena. Coalescence consists in the rupture of thin liquid films and may occur at several levels [8–10]: between the inner droplets, between the oil globules, and between the inner droplets and the oil globule. This latter case leads to the delivery of the whole inner droplet content into the external aqueous phase. Hydrophilic species can also migrate from the internal phase to the external one and vice versa without film rupturing i.e. by diffusion/permeation through the lipophilic phase. In that case, the transport is generally driven by concentration gradients of the molecules dissolved in the two aqueous compartments (electrolytes, low-molecular weight neutral molecules, emulsifiers) and by Laplace pressure and leads to equilibration of the chemical potentials.

Different strategies were adopted to enhance the long-term stability of liquid double emulsions and their encapsulation efficiency for hydrophilic species, such as the use of a large molecular size surfactants that "anchor" to the respective interface (the energy required to remove large molecules from an interface is high) and makes them less likely to diffuse between interfaces [11,12], or by thickening either the oil phase, or the internal aqueous phase [3,13–15] or the interface separating them by using charged complexes of protein-polysaccharide [16]. Another alternative was to stabilize double emulsions by fat crystals surfactants in regards to W/O emulsion, in order to prevent transfer between internal aqueous droplets or between internal aqueous droplets and double globule [17,18].

Furthermore, the use of crystallizable oil to formulate double emulsions has interesting properties for long term storage in comparison to liquid double emulsions which are subjected to rapid destruction by coalescence and diffusion phenomena. Indeed, the solid state of the matrix prevents the displacement of the internal droplets, their adsorption at the globule interface and eventually their coalescence. Moreover, the low permeability of the solid oil membrane allows the slowing down of diffusion phenomena of the encapsulated species.

Very few studies however have focused on the use of crystallizable oil in emulsions. In case of W/O emulsions containing a partially crystalline continuous phase [19,20], two mechanisms provide kinetic stability:

- Pickering stabilization: bulk formed fat crystals move to the interface, producing a layer of particulate matter encasing water droplets;
- Network stabilization: the development of a continuous fat network acts as a physical barrier limiting the mobility of dispersed water droplets.

Often the two mechanisms occur simultaneously, thus providing synergistic stability to emulsified systems. Although efforts have been made in elucidating the role played by each of them, there is still a lack of complete understanding.

In case of double emulsions based on crystallizable oil [21]; very few studies have investigated this system and stressed that the permeability and the local energy barrier for diffusion through solidified oil is largely reduced in comparison to liquid state at iso-osmotic conditions, but the authors specially focused on release through solid double emulsions under stress [21]. No further work was carried out exploring this option concerning the stability of solid double emulsions at iso-osmotic conditions.

In the present study, we have investigated a one month period stability of food-grade double emulsions based on edible crystallizable oils, encapsulating magnesium chloride, as a function of the nature and the proportion of solid fat crystals in the lipophilic matrix. We have demonstrated that in case of forming liquid core-solid shell globules, the release is stopped and it is independent of the % of fat crystals, unlike the case where the fat crystals form a continuous network dispersed in the lipophilic phase giving rise to a release that decreases continuously with the fat crystal content. Thus, we expect gaining knowledge and guidance about the main parameters controlling ion transport phenomena in crystallizable double emulsions.

2. Experimental section

2.1. Materials

The oil phases used for the formulation of W/O/W emulsions were miglyol (mixture of triglycerides with hydrophobic chains C8/C10 in the mass ratio 55/45, density at 20 °C = 0.95 g cm^{-3}) from Stéarinerie Dubois Fils (France), Anhydrous Milkfat (AMF), Oleic fraction and stearic fraction from Flechard (France) and cocoa butter (CB) from Barry Callebaut (France). The lipophilic surface-active species, polyglycerol polyricinoleate (PGPR) (esters of polyglycerol and polyricinoleate fatty acids, $M_w \approx 1800$ g mol^{-1}), was purchased from Palsgraad (France) and the hydrophilic one, sodium caseinate (SC) ($M_w \approx 20{,}000$ g mol^{-1}) was obtained from Lactoprot (Germany). Magnesium chloride hexahydrate ($MgCl_2$,-$\cdot 6H_2O$, 99%) was from Acros Organics (Belgium), sodium azide (SA, NaN_3) was from Merck (Germany), glucose, lactose, and xanthan were from Sigma-Aldrich (Germany). All species were used as received. The water used in the experiments was deionized with a resistivity close to 18 MΩ cm at 20 °C.

2.2. W/O/W emulsion formulation and preparation

The emulsification is always done in two steps, as described in Ref. [22]. Depending on the physical state of the used oil (liquid or solid at room temperature), emulsions were prepared at room temperature, at 37 °C or at 60 °C.

2.2.1. Emulsions based on cocoa butter/miglyol oil

In the first step, the primary W/O emulsions (emulsions 1–7) were prepared by introducing 80 wt% of a 0.1 M $MgCl_2$, $6H_2O$ aqueous solution into 20% of lipophilic phase (30% PGPR + 70% miglyol oil), at room temperature. The emulsification was carried out using an homogeneiser (RZR 2102 control Z Heidolph, Schwabach, Germany) with a stainless propeller rotating between 1000 and 1200 rpm, according to the emulsion formulation. The final droplet size resulting from the application of a shear depends on the