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Design of oleofoams from citric acid esters of mono−/diglycerides

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ABSTRACT

Citric acid esters of mono- and diglycerides (CITREM E472c) are widely used as emulsifiers in the food industry. They result from the esterification of citric acid with mono- and diglycerides of fatty acids. CITREM was recently shown to produce stable aqueous foams but its potential in oil foam production remains unexplored. Due to its unique chemical structure, featuring free hydroxyl groups, along with its solubility in vegetable oils, CITREM is a highly promising candidate for this application. This study aimed to investigate the possibility of using CITREM as a surfactant to produce vegetable oil foams. We first determined the solubility of CITREM in sunflower oil to identify the solubility limit and the crystal formation temperature. We determined the critical aggregation concentration (CAC) of CITREM through Small Angle X-ray scattering (SAXS). The foamability was examined above the melting point at different surfactant concentrations. The impact of crystal formation on the foam stability was also examined at various storage temperatures. To determine the mechanisms leading to foam formation and stabilization, a multiscale approach was used by combining macroscopic observations of the foam, with optical microscopy and SAXS. We showed that oil foams were produced only above the CAC. We demonstrated that CITREM surfactants stabilize oil foams in the same manner as sucrose ester and sorbitan ester surfactants confirming that the key factor in forming vegetable oil foams with surfactants is the use of a lipophilic surfactant containing free hydroxyl groups, which can form hydrogen bonds with the triglycerides in the oil.

1. Introduction

Citric acid esters of mono- and diglycerides (commonly known as citroglycerides or CITREM E472c) are versatile emulsifiers used in various food applications due to their multifunctional properties (Amara et al., 2014). CITREM represents a unique category of surfactants in which the tri-carboxylic acid citric acid is reacted with mono−/diglycerides of fatty acids to form esters, enabling their diverse functionality. The typical chain length of the mono−/diglycerides are palmitic acid, stearic acid, oleic acid or linoleic acid. CITREM is widely used as a dispersing agent in food products, such as margarine, shortenings, chocolate, dried yeast, and powdered foods. It is particularly important in the formulation of infant foods, including powdered and liquid energy-dense formulas, and products for special medical purposes (Amara et al., 2014; Argudo, Zhou, & Rousseau, 2022). In the production of margarine, CITREM improves frying properties by forming a water-in-oil emulsion, while in chocolate production, it contributes to viscosity control and serves as an alternative to conventional emulsifiers such as soybean lecithin and polyglycerol polyricinoleate (Argudo et al., 2022; Kadiya, Sharma, & Ghosh, 2022; Nilsson et al., 2012). In addition to its emulsifying function, CITREM acts as a sequestering agent that binds heavy metals. This property further extends its utility in maintaining the stability and quality of food products (Amara et al., 2014; Mustan et al., 2022; Podchong & Rousseau, 2025).

CITREM is recognized as a food substance with very low toxicity, posing no risk to human health. It has no specified acceptable daily

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intake (ADI) or Food Chemical Codex specifications, while it is classified as "generally recognized as safe" (GRAS) by the FDA (reference number 977093–28-9). Its broad functionality and safety profile solidify CITREM's position as an essential component in modern food technology. In addition to these established applications, new properties and uses are currently emerging in the literature. For instance, CITREM has recently been employed to modulate and enhance the performance of ethyl cellulose oleogels (Ji & Gravelle, 2025). CITREM has been shown to form very stable aqueous foams due to the formation of solid adsorption layers and the presence of multilamellar vesicles in the liquid channels of the foam, which could expand its field of application (Mustan et al., 2022). However, the possibility of oil foam formation with CITREM has not been explored before. Currently, oil foams are being actively studied to develop innovative systems for their production and stabilization (Binks & Vishal, 2021; Fameau & Saint-Jalmes, 2017). This research is particularly important for the food industry, aiming to find alternatives to products rich in saturated fats while maintaining a texture and sensory experience that consumers appreciate (Heymans, Tavernier, Dewettinck, & Van der Meeren, 2017). Given its unique chemical structure with free hydroxyl groups and solubility in vegetable oils, CITREM appears to be a promising candidate for this application, based on contemporary findings on oil foams with lipophilic surfactants. The group of Prof. Binks demonstrated recently that hydroxyl-rich, lipophilic surfactants, such as sorbitan ester and sucrose ester surfactants, enable the production of oil foams in vegetable oils without the need for crystalline particles to stabilize the air bubbles (Liu & Binks, 2021, 2022). The stabilization mechanism of these oil foams is believed to involve the formation of complexes between the surfactants and the triglyceride molecules in the vegetable oils through hydrogen bonding, both in the bulk and at the air-oil interface. Crystalline particles of these surfactants are required only when producing ultra-stable foams capable of withstanding varying temperatures from – 20 °C to around 40–50 °C, as it has been shown for other oil foam systems based on crystalline particles from mono- and di-glycerides, fatty alcohols, fatty acids, waxes, *etc.* (Binks, Garvey, & Vieira, 2016; Brun, Delample, Harte, Lecomte, & Leal-Calderon, 2015; Callau, Sow-Kébé, Jenkins, & Fameau, 2020; Chisholm et al., 2016; Fameau & Saint-Jalmes, 2017; Gehin-Delval et al., 2019; Gunes et al., 2016; Gunes et al., 2017; Qiu, Lei, Lee, Zhang, & Wang, 2021; Shrestha, Shrestha, Sharma, & Aramaki, 2008). In this case, the air bubbles are stabilized by a thick shell of crystalline particles, thus reducing coarsening and coalescence of bubbles, while the continuous phase is an oleogel containing an excess of crystals, which effectively reduces the oil drainage (Fameau & Binks, 2021).

Within the scope of finding additional surfactants suitable for oil foam production, this study aims to investigate the foaming properties of CITREM surfactant in different vegetable oils and at various temperatures. We first established the phase diagram of CITREM in sunflower oil by determining the solubility limit, and the temperature at which crystals of CITREM were formed by Differential Scanning Calorimetry (DSC). Small Angle X-ray Scattering was used to determine the critical aggregation concentration (CAC) and the shape of the reverse micelles of CITREM in sunflower oil. Subsequently, oil foams were produced in the one phase molecular region where only surfactants were present (*i.e.*, above the melting point of the crystals) to investigate the influence of surfactant concentration on the foaming behaviour as solvated molecules. The stability of the resulting foams was further characterized over time. The effect of cooling below the solubility limit and the crystals formation on foam stability was then investigated. Foams prepared in the one-phase region were subsequently cooled and stored at different temperatures to induce crystallization: room temperature (20 °C ± 2 °C), refrigeration (7 °C ± 0.5 °C), and freezing conditions (−20 °C ± 1 °C). The mechanisms responsible for foam formation and stabilization, both with and without the presence of crystals, were investigated using a multiscale approach. This included macroscopic observations of the foam to determine foamability and foam stability with time as a function of surfactant concentration, and optical microscopy techniques to determine bubble size. SAXS measurements were carried out to characterize surfactant self-assembly and CAC in the bulk. Finally, the foaming potential of CITREM in combination with various vegetable oils was described.

2. Materials and methods

2.1. Materials

The CITREM surfactant was obtained from BASF (product name: Lamegin®ZE 609 powder). CITREM is a citric acid ester of mono- and diglycerides derived from edible fatty acids and are commonly used as a food-grade emulsifier E 472c. The CITREM powder has a melting point between 55 and 63 °C. The molecular structure of CITREM, shown in Fig. S1, Supporting Information, consists of a citric acid backbone esterified with mono- and diglycerides of long-chain fatty acids with typical main chain lengths of 1–3 % myristic, 35–60 % palmitic, 35–60 % stearic. CITREM was used as received. Various types of oils were used in this study. Extra virgin olive oil and sunflower oil were purchased from the local store (Cora brand), and virgin sesame oil and linseed oil were from the Bio Cauvin brand. All vegetable oils were used as received.

2.2. Solubility determination of CITREM in oil

A given amount of CITREM and vegetable oil were placed in a glass vial with a screw cap, which was then placed in a water bath with a temperature-controlled plate. The temperature of the sample was monitored with a Testo 175 T2 thermometer (Testo SE & Co. KGaA, Germany) (± 0.1 °C). The surfactant-oil mixture was initially heated to 90 ± 1 °C for 10 min, under magnetic stirring at 150 rpm, until CITREM was fully melted in the oil phase, giving rise to a clear and homogeneous solution. The mixture was then cooled down to room temperature leading to turbid samples due to crystals formation. After being kept at room temperature for 24 h, the sample was carefully heated with a 2 °C stepwise increment under magnetic stirring, until the solution was clear and homogeneous again. The sample was visually observed and photographed at different temperatures and concentrations to determine the temperature at which the mixture became clear when heated corresponding to the end of crystals melting. The experiments were repeated three times for each concentration.

2.3. Differential scanning calorimetry

The crystallization and melting behaviour of CITREM in sunflower oil was analyzed using the DSC2 differential scanning calorimeter (DSC), from Mettler-Toledo, USA. The instrument was calibrated with an empty pan, and nitrogen served as the purge gas. Samples were weighed in standard 40 μL aluminum pans (around 6 mg) using an analytical balance and then sealed at room temperature, without the presence of holes. A sealed pan containing oil was used as the reference. Three temperature cycles from 5 °C to 60 °C were performed, at a scanning rate of 2.5 °C/min. Using the integrated software, the melting and freezing temperatures were determined from the endothermic and exothermic peaks, respectively.

2.4. Optical microscopy

The crystals and the morphology of the air bubbles within the foams were analyzed using a ZEISS Axioscope 5 optical microscope, with an Axiocam 208 camera (Zeiss, Germany) and a temperature-controlled plate (Linkam, model LTS120) connected to a water circulation pump. The foam samples were transferred to the center of a glass slide by using a spatula and then gently covered with a thin glass coverslip. Images of individual bubbles were captured to observe structural characteristics, including bubbles size and distribution. The dimensions of about 200

bubbles from at least ten images were quantified using ImageJ software (1.47 V).

2.5. SAXS measurements

Small-angle X-ray scattering (SAXS) experiments were performed with a XEUSS 2.0 device (Xenocs, France). The instrument uses a micro-focused Cu-Kα source with a wavelength of 1.54 Å and a Pilatus3 detector (Dectris, Switzerland). The samples were loaded into thin quartz capillaries (optical path 1.5 mm, WJM-Glas/Müller, Germany) and placed on a temperature-controlled sample-changer connected to a Lauda bath. The samples temperature was equilibrated during minimum 3 h in the sample-changer before starting the measurement. The experiments were performed at one sample-to-detector distance: 1000 mm with a collimated beam size of 0.8 mm × 0.8 mm, to access a scattering wave vector q-range of 0.01 $Å^{-1}$ to 0.6 $Å^{-1}$.

The scattered intensities are expressed as a function of the magnitude of scattering vector: $Q = 4\pi\sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident radiation. The intensity scattered by surfactant supramolecular assembly in solution can be described as the product of structure factor S(Q), which is characteristic of the correlations between the supramolecular assemblies, with a form factor P (Q), which describes the shape of the self-assembly. At 60 °C, at large Q, the scattering curves scatters like Q^{-4} that is characteristic of a Porod behaviour corresponding to the surface scattering of 3-D objects. The form factor of a completely filled spherical object of radius R like reverse micelles is given by:

$$P_{sphere}(Q) = 9\left[(\sin(QR) - QR\cos(QR))\Big/(QR)^3\right] \quad (1)$$

S(Q) can be neglected (=1) at low concentration of surfactants and for centrosymmetrical objects like spheres at large Q. The data were analyzed using the fitting software SASview.

2.6. Foam preparation and characterization methods

The foamability of CITREM in vegetable oil was determined at different concentrations from 1 to 10 wt%. In a glass vial (5.7 cm height and 3.4 cm diameter), 10 g of CITREM-vegetable oil mixture was initially kept at 60 °C (above the solubility limit in the one-phase soluble region of CITREM) under magnetic stirring for 20 min, at 300 rpm. Foams were then produced by whipping the mixture at 60 °C for three minutes using a handheld commercial milk frother (Bonsenkitchen brand). The overrun value is defined as:

$$overrun\,(\%) = \frac{V_t - V_0}{V_0} \times 100 \quad (2)$$

where, V_0 is the initial volume of the mixture, and Vt is the total volume after foaming. After formation, the fresh foams were stored at four different temperatures: in a freezer at −20 °C ± 1 °C, in a refrigerator at 7 °C ± 1 °C, at room temperature (20 ± 2 °C), and in an oven set to 60 °C ± 1 °C. The stability of the foams was monitored over time by measuring the evolution of the foam volume, the volume of drained oil, and the average bubble size, as a function of storage time. Photographs of each foam were taken at regular intervals. All photographs captured were analyzed using the ImageJ software (1.47 V).

3. Results and discussion

3.1. Crystallization and thermal properties of CITREM in sunflower oil

We first investigated the crystallization and melting behaviour of CITREM in sunflower oil as a function of temperature. The CITREM surfactant (0.5 to 10 wt%) was dissolved in sunflower oil at 90 °C and then cooled to room temperature. During cooling, all samples, regardless of concentration, became cloudy due to the formation of crystal (Fig. 1.a). After a resting time of 24 h at room temperature, the samples with CITREM concentrations below 7 wt% remained liquid. In contrast, samples with concentrations above 7 wt% formed oleogels that did not flow when the glass vials were inverted (Fig. S2, Supporting Information). Subsequently, all samples were gradually heated at a rate of 2 °C/min to determine the so-called solubility limit between a dispersion of surfactant crystals in oil containing dissolved surfactant and a molecular solution of surfactant in oil at higher temperatures (Fig. 1.a). Upon heating, the viscosity and turbidity of the samples gradually reduced as the crystals melted and turned into clear oil solutions. We defined the solubility limit as the temperature at which the cloudiness completely disappeared to the naked eye (Fig. 1.a). The insets in Fig. 1.a show photographs of a sunflower oil solution at 58 °C illustrating the appearance of the molecular solution, and of an oleogel at 20 °C, showing the turbidity of the gel containing 10 wt% CITREM. The turbidity was due to the presence of crystalline particles in sunflower oil as illustrated in Fig. 1.b-c. At 0.5 wt% CITREM, spherical crystals could be observed, under the microscope, with a single-crystal size around 10–20 μm (Fig. 1.b). At 10 wt% CITREM, a dense network of birefringent crystals was randomly distributed inside the oil liquid phase (Fig. 1.c). We observed that the solubility limit increased with the concentration of CITREM. For an ideal solution, it is known that the variation of solubility of a chemical substance into a given solvent as a function of the

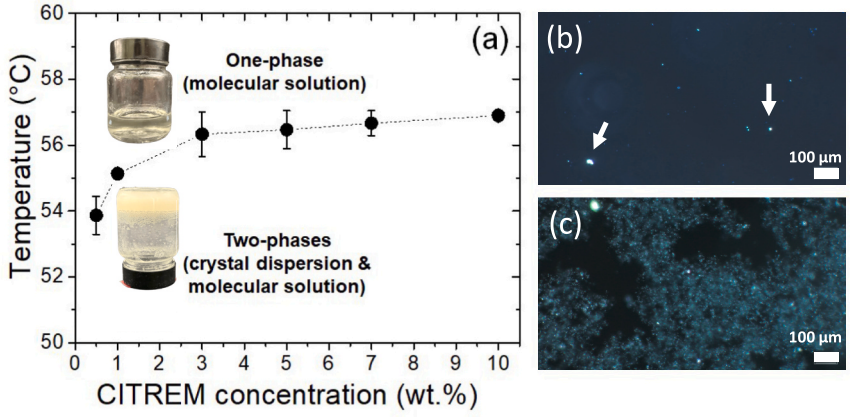

Fig. 1. (a) Solubility diagram of CITREM in sunflower oil based on visual observations upon warming at a rate of 2.5 °C/min. Inset: photographs of the vials containing 10 wt% CITREM in sunflower oil at 20 °C in the two-phase region (crystals inside the liquid oil) and at 58 °C in the one-phase region. (b-c) Polarized light microscopy images of CITREM in sunflower oil at 20 °C: (b) at 0.5 wt% with the arrows pointing at some of the crystals, and (c) at 10 wt%.

temperature is given by:

$$\ln x = \frac{\Delta fusH}{R}\left(\frac{1}{Tf} - \frac{1}{T}\right) \quad (3)$$

where x is the mole fraction of solute (CITREM) in the saturated solution (sunflower oil) at absolute temperature T, R is the gas constant, Δ_{fusH} is the enthalpy of fusion and T_f is the temperature of fusion. That is why an increase of CITREM concentration lead to an increase in solubility limit.

Differential scanning calorimetry was also used to investigate the thermal properties of CITREM in the sunflower oil as a function of concentration (Fig. S3, Supporting Information). No peak was observed below 1 wt% CITREM, even at a slow heating rate of 2.5 °C /min, due to the low enthalpy transition at those concentrations. At 1 wt%, a peak was observed at 9.4 °C. With increasing CITREM concentration, two peaks were observed on the thermograms during both heating and cooling cycles indicating the presence of different crystal polymorphs (Fig. S3a-b, Supporting Information). Both peak temperatures of melting and crystallization increased with CITREM concentration showing that the thermal stability of the oleogels was improved upon increased surfactant concentration, as it has already been observed in various oleogel systems (Fig. S4, Supporting Information) (Blake & Marangoni, 2015; Callau, Sow-Kébé, Nicolas-Morgantini, & Fameau, 2020; Co & Marangoni, 2012; A.-L. Fameau et al., 2015; Pernetti, van Malssen, Flöter, & Bot, 2007).

3.2. Self-assembly of CITREM in sunflower oil

The small angle X-ray scattering technique was performed to analyse the supramolecular aggregation of CITREM in sunflower oil at various concentrations, and at two temperatures (20 °C and 60 °C). SAXS has already been used to study reverse aggregation in vegetable oil and determine the CAC (Fadel et al., 2017). We first recorded the SAXS spectra at 20 °C, in the two-phase region. At Q between 0.15 and 0.5 $Å^{-1}$ a broad peak was observed for pure sunflower oil (Fig. 2), which arises from the interaction between oxygen-rich groups, such as ester moieties. This peak is typically correlated with the average length of the aliphatic chains, while it can also be associated with the clustering of these groups. We observed this peak in all samples containing CITREM. The Q-position of this peak was slightly shifted due to the introduction of the CITREM oil-soluble molecule and the interactions between CITREM and sunflower oil in the bulk. At 20 °C, Bragg peaks were observed for all the samples. For CITREM concentration of 0.5 and 1 wt%, only one peak was present, corresponding to the first harmonic, located at 0.103 and 0.107 $Å^{-1}$, respectively. These peaks correspond to a d-spacing of about 61 Å and 58.7 Å, respectively, and show that CITREM crystallizes in a double layer structure (Fig. 2a). For CITREM concentration at 3 wt%, two peaks at 0.101 and 0.125 $Å^{-1}$ were observed. The peak at 0.101 $Å^{-1}$ corresponds to the CITREM crystallized in a double-layer structure as described for the lower concentration (Fig. 2a). The second peak at 0.125 $Å^{-1}$ showed the presence of other CITREM crystals. Since the CITREM used in this study was composed mainly of three different alkyl chain lengths (*i.e.*, myristic, palmitic, and stearic), we suppose that this peak corresponds to the crystals formed by the different chain lengths, thus leading to the coexistence of different crystalline structures. This is confirmed with the results obtained at a concentration of 5 wt% CITREM, for which three peaks were present at 0.09, 0.104 and 0.125 $Å^{-1}$. The peak at 0.104 $Å^{-1}$ corresponded to the same crystalline structure observed at lower concentrations, with a d-spacing of approximately 60.4 Å, which corresponds to CITREM crystallized in a double layer structure (Fig. 2a). However, the two other peaks correspond to a d-spacing of around 69.8 and 50.2 Å, respectively. We suppose that these two additional d-spacing correspond to the presence of double layer structure of CITREM with longer chain lengths (*i.e.*, myristic, palmitic, and stearic). Most probably, the d-spacing of 50.2 Å corresponds to CITREM with myristic chain, and the 69.8 Å corresponds to CITREM with stearic chain. Indeed, by increasing the concentration of CITREM, the amount of CITREM with minority chain lengths gradually increased, reaching a sufficient concentration to form crystals that SAXS can detect. For a CITREM concentration of 7 and 10 wt%, three peaks were observed, located at around 0.085, 0.097 and 0.115 $Å^{-1}$. The peak at 0.097 $Å^{-1}$ corresponds to the same crystalline structure observed at lower concentration with a d-spacing of around 64.7 Å, correlating to the CITREM crystallized in a double layer structure (Fig. 2a). For the two other peaks, their position was close to the one already observed at lower concentrations showing some CITREM molecules with different chain lengths were also organized in a double-layer structure. Thus, for 0.5 and 1 wt% of CITREM in sunflower oil, only one crystalline structure was detected by SAXS, but at higher concentrations there was the coexistence of three different crystal structures, most probably linked to the presence of CITREM molecules with different chain lengths. This hypothesis is also supported by the presence of two broad peaks on the DSC curves, indicating the existence of multiple crystalline structures (Fig. S3, Supporting Information).

Then, we measured the self-assembly of CITREM in the one-phase region at 60 °C. For all the scattering curves, we observed at Q between 0.15 and 0.5 $Å^{-1}$ the broad peak coming from the sunflower oil. At low concentrations of CITREM, such as at 0.5 and 1 wt%, the scattering spectra remain very similar to the neat sunflower oil. However, at 3 wt%, the scattered intensity at the lowest Q-values increased. By increasing the concentration from 3 wt% to 10 wt%, we observed an increase of the intensity at low Q. For 5 and 7 wt%, a small peak was observed probably coming from some non-melted CITREM crystals. We plotted the intensity at the lowest Q-value and subtracted the solvent contribution to determine the CAC as described by Fadel et al. (Fig. 3) (Fadel et al., 2017). As shown in Fig. 3, the CAC was estimated at about

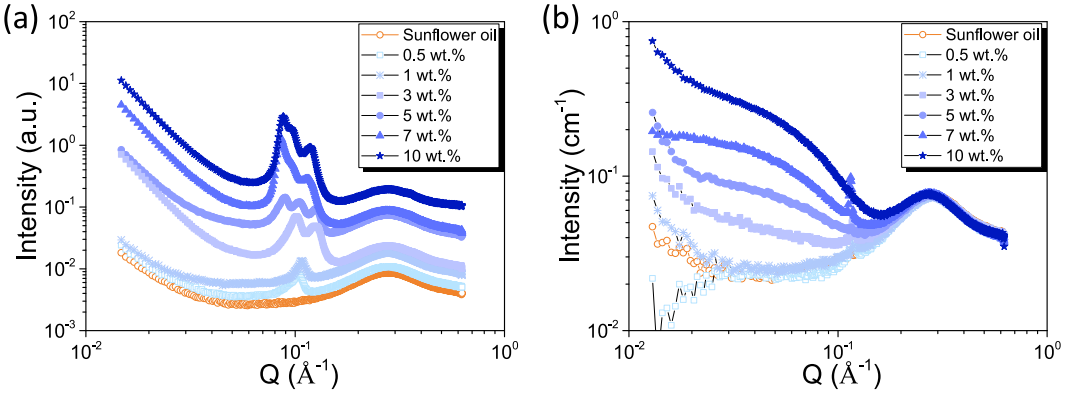

Fig. 2. SAXS spectra for CITREM in sunflower oil as a function of CITREM concentration from 0 to 10 wt%: (a) at 20 °C in the two-phase region. The scattering curves were shifted in intensity for clarity, and (b) at 60 °C in the one-phase region.

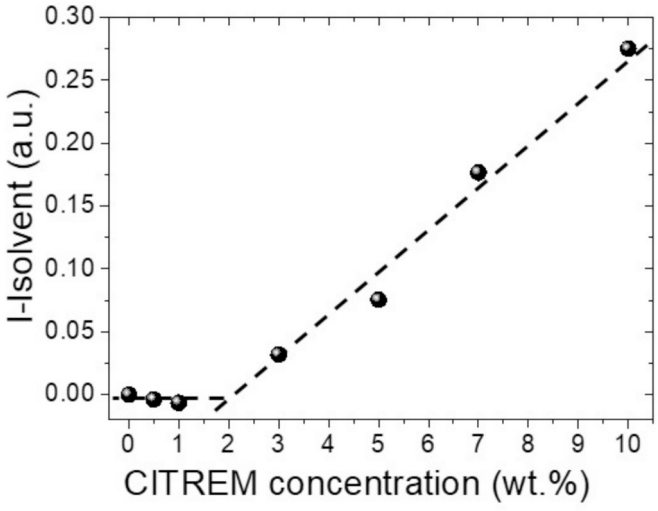

Fig. 3. Scattering intensity of the sample after subtraction of that for neat sunflower oil at $Q = 0.048$ Å^{-1} in arbitrary units as a function of CITREM concentration. The CAC estimation comes from the intersection between the dotted line and the horizontal line. Above the CAC, the concentration of supramolecular CITREM structure increases.

2 wt%.

Given that CITREM aggregates in sunflower oil and is typically used as an emulsifier, it is reasonable to suppose that CITREM could form reverse micelles as already described from similar surfactants in vegetable oils (Fadel et al., 2017; Penttila et al., 2019; Shrestha et al., 2006). To determine the supramolecular assembly structure above the CAC, we fitted the scattering spectra in the middle Q range for CITREM concentrations at 7 and 10 wt% with a form factor of a sphere (see Materials and Methods section) corresponding to reverse micelles (Fig. S5, Supporting Information) (Fadel et al., 2017). From the fitting, we deduced a polar core radius of the reverse micelles composed by the polar head and a few water molecules of the order of 32.9 and 35 Å for 7 wt. and 10 wt %, respectively. Thus, above 2 wt% in the one-phase region, CITREM molecules self-assemble into reverse micelles.

3.3. Foaming properties of CITREM in sunflower oil at high temperature

The foaming properties of CITREM in sunflower oil were studied at different concentrations at a fixed temperature of 60 °C (Fig. 4). This temperature was chosen because it was above the solubility limit, in the one-phase region for all mixtures, ensuring the absence of crystals, and the presence of solely CITREM as reverse micelles. These conditions allowed the evaluation of the foaming performance of CITREM as a surfactant molecule without any intervention from crystals, providing a better understanding of the effect of surfactant concentration on foam formation and stability. At 60 °C, the minimum CITREM concentration required to obtain oil foams was 3 wt% which is above the CAC as determined by SAXS. At 0.5 wt%, no foam was observed and at 1 wt% only a few bubbles were stabilized, as shown in Fig. 4.a. At 2 wt%, just a very thin foam layer was obtained with big bubbles. This concentration range for producing oil foams is similar to the one required when using

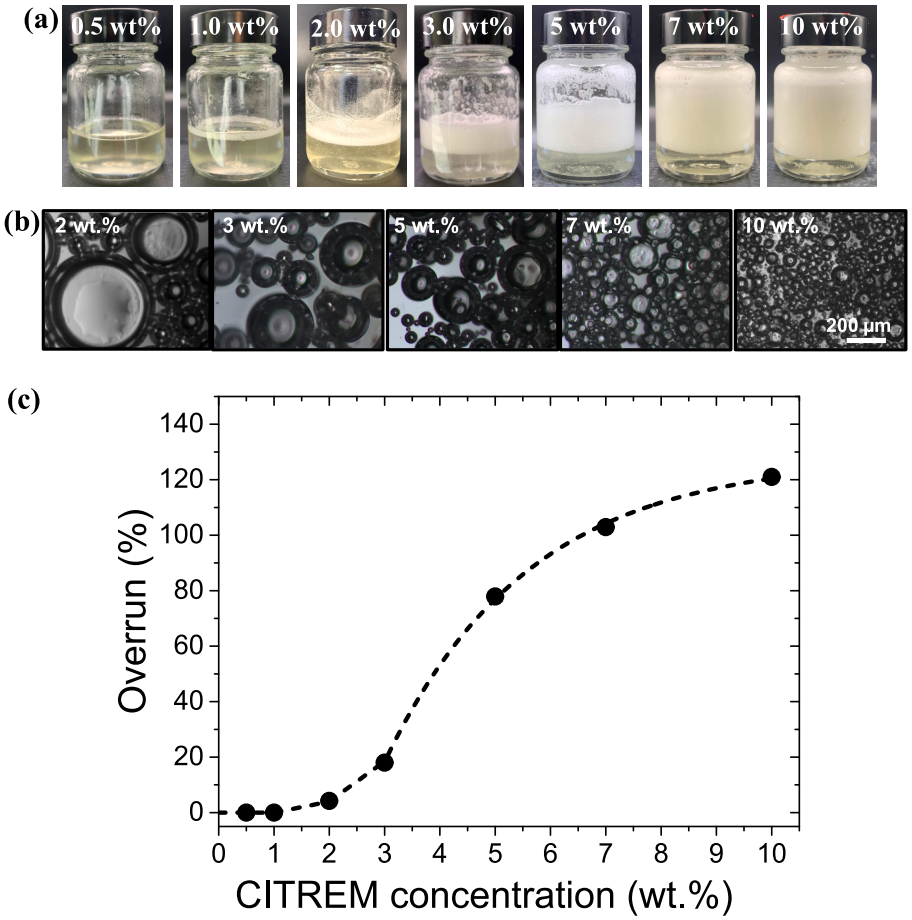

Fig. 4. Sunflower oil foams prepared at 60 °C at different CITREM concentration given. (a) Photos of samples immediately after 3 min of whipping. (b) microscope images, and (c) evolution of the overrun obtained at 60 °C as a function of CITREM concentration. The standard deviation is smaller than the size of the symbol displayed on the curve.

sucrose esters as surfactants (1–3 wt%) and significantly lower than the concentration needed for sorbitan esters (*e.g.*, ≥ 6 wt% for Span 60), to generate oil foams (Kaade et al., 2024; Kaade, Drouet, Dousset, Daniellou, & Huc-Mathis, 2025; Liu & Binks, 2021, 2022). These results demonstrate that the CITREM surfactant was highly efficient, even at relatively low concentrations, in producing oil foams and stabilizing air bubbles. Herein, we need to use a CITREM concentration above the CAC to produce oil foams, whereas for aqueous systems, already below the CMC aqueous foams can be produced. Optical microscope images of the foams are shown in Fig. 4.b, where spherical bubbles with smooth surfaces are visible, indicating the absence of crystals and confirming the surfactant stabilization of these oil foams. The diameter of the bubbles was around 108 μm, 102 μm, 82 μm and 66 μm for 3 wt%, 5 wt%, 7 wt% and 10 wt%, respectively. Thus, there was an almost linear decrease in the bubble's diameter with an increase of CITREM concentration, as more surfactant molecules were available for bubble stabilization. Increasing the CITREM surfactant concentration from 3 to 10 wt% led to an increase in the overrun from 18 % to 121 % respectively (Fig. 4.c). Based on previous studies of oil foams utilizing surfactants rich in hydroxyl groups, such as sucrose esters and sorbitan esters, we suppose that the carbonyl groups of the triglycerides in sunflower oil molecules form hydrogen bonds with the hydroxyl groups of the CITREM surfactant. CITREM is an H-bond donor while the triglycerides of the sunflower oil are H-bond acceptor. These molecular complexes likely adsorb at the air–oil interface, leading to efficient foam formation when whipped at 60 °C in the one-phase region. This foaming behaviour is in accordance with the one obtained for sorbitan esters and sucrose esters surfactants in oil confirming the specificity of these hydroxyl group rich surfactant for producing oil foams in contrary to many other systems such as fatty acids, fatty alcohols, monoglycerides, *etc.,* where foam production is only possible when crystals are present in the oil (Fameau & Binks, 2021; Liu & Binks, 2021, 2022).

Then, we followed the foam stability with time at 60 °C for foams produced with CITREM surfactant from 3 to 10 wt% in sunflower oil

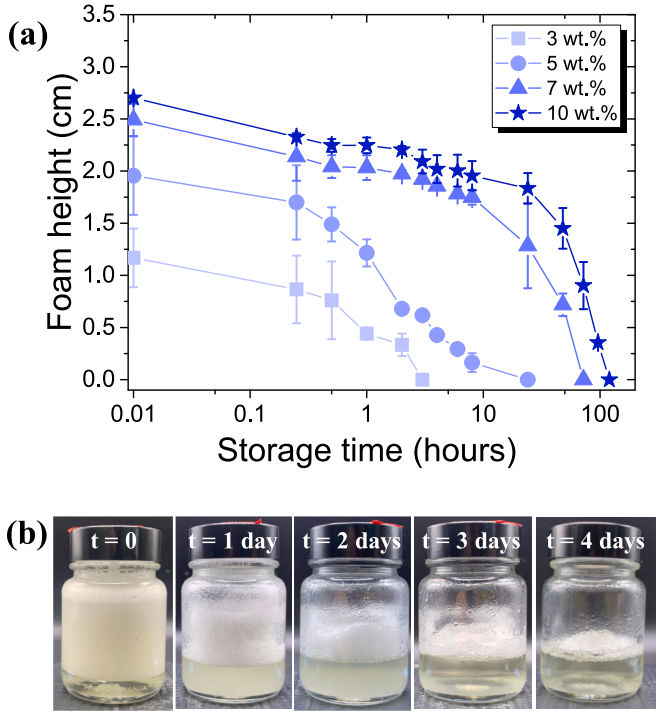

Fig. 5. (a) Evolution of the foam height as a function of storage time in hours for oil foams produced and stored at 60 °C at different CITREM concentrations. (b) Photographs of oil foam obtained with CITREM surfactant at 10 wt% in sunflower oil produced and stored at 60 °C.

(Fig. 5 and Fig. S6, in Supporting Information). We observed that at the lowest CITREM concentration (3 wt%), no more foam was observed after 3 h, while at the highest concentration (10 wt%) some foam remained for almost 4 days at 60 °C (Fig. 5 a-b). All foams collapsed completely after longer time. The foam stability was similar to the one obtained for example with Span 60 showing that oil foams stabilized by surfactant are relatively stable with time even at high temperatures. It is important to highlight that in the two-phase region where crystals were present, almost no foam was produced even at 10 wt%, showing that CITREM as surfactant was efficient to stabilize foam but not under crystalline form (Fig. S7, Supporting Information).

3.4. Foam stability below the solubility temperature

We then produced oil foams at 60 °C in the one phase region and put them immediately at three different storage temperatures in the two-phase region below the solubility limit. We monitored the stability of the oil foams with time at 20 °C, 7 °C, and - 20 °C. We followed the evolution of the foam height over time at various CITREM concentrations, as well as the changes in the appearance of the bubbles throughout the storage period. At all storage temperatures and concentrations, non-spherical bubbles coated by birefringent surfactant crystals were observed after one hour of storage (Fig. 6 and S8, Supporting Information). The crystals formation occurred quickly within the first hour of storage. In all foams, the presence of crystalline particles was observed, not only at the surface of the bubbles but also, in the continuous phase between the air bubbles. The average size of the air bubbles decreased with increasing CITREM concentration. For example, the bubble diameter in oil foams stored at room temperature decreased from approximately 100–150 μm at 3 wt% to around 25–50 μm at 10 wt%, as more CITREM crystals were available for bubbles and foam stabilization (Fig. S8, Supporting Information).

We followed the evolution in foam height as a function of time for various CITREM concentrations at the three storage temperatures (Fig. 7). At room temperature, we observed a slight decrease in foam height after 3500 h for the oil foams containing 10 wt% of CITREM, whereas after 600 h no more foam was present for a CITREM concentration at 3 wt% (Fig. 7a and S9, Supporting Information). When the storage temperature was reduced to 7 °C, a slight decrease in foam height for oil foams based on CITREM at the lowest concentration (3 wt %) began after 600 h. A slight decrease in foam height was observed from 1500 h for the oil foams based on 5 wt% CITREM. For oil foams based on higher concentrations of CITREM (7 and 10 wt%), the oil foam height was stable during more than 3000 h (Fig. 7b and S10, Supporting Information). The same trend was observed at even lower temperature (− 20 °C) when the foams were kept in the freezer (Fig. 7c and S11, Supporting Information). It is important to notice that since the oil foams were produced at high temperature where no crystals were present (*i.e.*, only reverse micelles), drainage took place in all samples. The oil drainage was stopped only when enough crystals were formed under cooling since the crystal's formation led to an increase of bulk viscosity between the air bubbles (Fig. 7, bottom). Thus, by increasing the surfactant concentration and decreasing the storage temperatures, it was possible to obtain very stable oil foams during more than 150 days. Moreover, for CITREM at 10 wt%, no evolution of bubble size and no change in appearance was observed after 24 h, and even after more than 4 months at all temperatures studied, demonstrating the very high stability of the air bubbles coated by the crystalline particles (Fig. 6).

The higher surfactant concentrations led to an increase in the amount of crystals both on the surface of the bubbles and in the bulk oil between the bubbles. Interfacial and bulk crystallization increased both the rigidity of interfaces and increased the bulk viscosity forming an oleogel slowing down the three main mechanisms of foam destabilization: drainage, coalescence and coarsening (Anne-Laure Fameau & Binks, 2021; Metilli et al., 2021; Mishra, Bergfreund, Bertsch, Fischer, & Windhab, 2020; Rio, Drenckhan, Salonen, & Langevin, 2014; Saha,

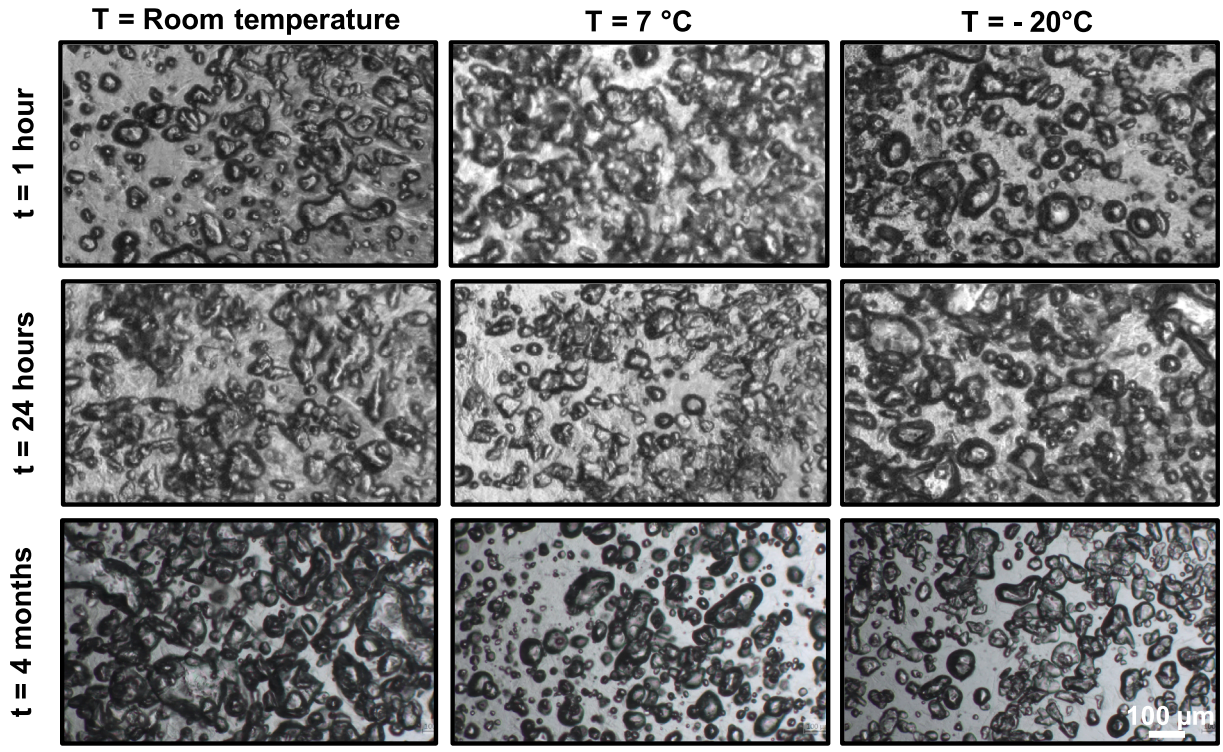

Fig. 6. Optical images of oil foams obtained with CITREM at 10 wt% in sunflower oil prepared at 60 °C and stored at different temperatures (room temperature, 7 °C and - 20 °C) after 1 h, 24 h and 4 months of storage. The scale bar is the same for all images.

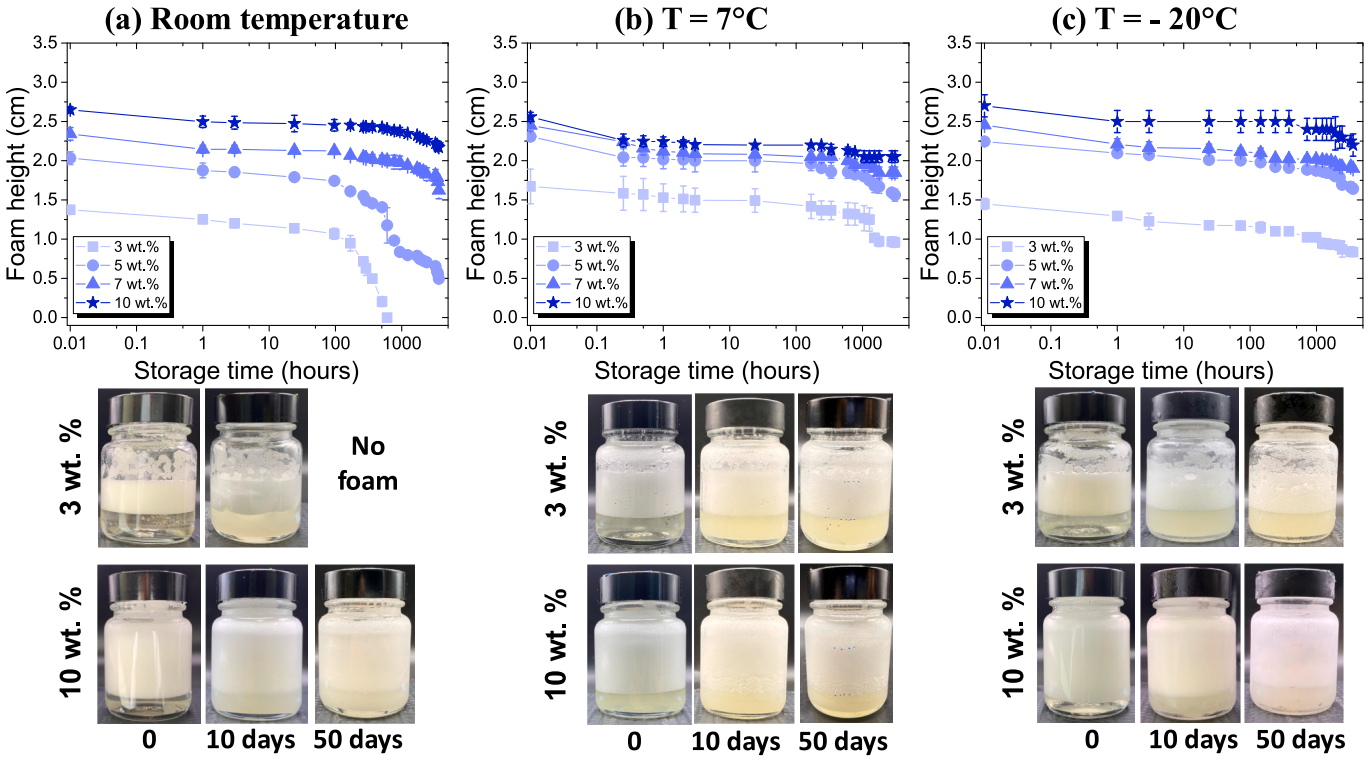

Fig. 7. Evolution of the foam height as a function of storage time in hours for sunflower oil foams produced at 60 °C and stored at different temperatures and at different CITREM concentrations: (a) room temperature (20 °C ± 2 °C), (b) 7 °C ± 0.5 °C, and (c) – 20 °C ± 1 °C. Below graphs: photos of oil foam obtained with CITREM surfactant at 3 and 10 wt% in sunflower oil produced and stored at the corresponding temperatures taken immediately after foam formation, 10 days and 50 days of storage.

Saint-Michel, Leynes, Binks, & Garbin, 2020). That is why all oil foams, regardless of the CITREM concentrations, were more stable in the two-phase region in which crystals formation took place, than at 60 °C where only CITREM molecular surfactants existed for the foam stabilization. Our results show that ultra-stable oil foams can be obtained at high surfactant concentrations by producing first the oil foam in the one-phase region where reverse micelles were present and then rapidly cooling to a low storage temperature to induce surfactant crystallization. We confirmed the protocol already observed on oil foams produced with sorbitan and sucrose ester surfactants (Kaade et al., 2024; Liu & Binks, 2021, 2022).

3.5. Foaming properties of CITREM in various edible oils

To generalize, we investigated the foamability and foam stability of CITREM at 10 wt%, in three additional vegetable oils: olive oil, sesame oil, and linseed oil. These oils are all rich in long-chain unsaturated fatty acids and remain liquid at ambient temperatures. The mixtures of CITREM and vegetable oils were prepared according to the same protocol as before and then stored at different temperatures. Initially, we measured the overrun just after foaming at 60 °C, and observed no difference between the different oils or the one previously obtained with sunflower oil, showing no effect of the oil nature for 10 wt% CITREM. However, the evolution of foam height with time at 60 °C showed small differences between the oils (Fig. 8a). Oil foams based on linseed oils were destabilized slightly before sesame oil foams. The oil foams based on olive oils were slightly more stable than the two other oil foams at 60 °C. However, all the oil foams completely collapsed after 4 days, as in the case of sunflower oil foams described previously (Fig. S12, Supporting Information). The same trend was observed when the oil foams were prepared at 60 °C and stored at room temperature (Fig. 8b). The decrease of the oil foam height was slightly more pronounced for linseed oil. However, a similar trend was observed for sesame oil and olive oil. All the oil foams were stable for more than 150 days (Fig. S13, Supporting Information). When the oil foams were stored at 7 °C and – 20 °C, all the oil foams were ultra-stable for more than 150 days with no difference between the oils used to produce the foams (Fig. 8c-d, and S14–15, Supporting Information). For all the oils, crystals were present to stabilize the foams both in bulk and at bubbles surface (Fig. S16, Supporting Information). Based on these results, we confirmed that the nature of the vegetable oil had no effect on the oil foam stability when surfactant crystals are absent, as already described by Binks et al. (Liu & Binks, 2021, 2022) However, in our study there was no effect on the overrun, probably linked to the high concentration of surfactants used. Furthermore, only very small differences were observed between the oils studied when the CITREM surfactant was crystallized in contrary to other studies on oil foams stabilized by surfactant crystals (Callau, Jenkins, Sow-Kébé, Levivier, & Fameau, 2021; Liu & Binks, 2021, 2022). A deeper understanding of the nature of oils and their effects on oil foam stabilization is essential for future research.

4. Conclusion

This study demonstrates for the first time that CITREM (E472c), an emulsifier commonly used in food, can effectively produce and stabilize oil foams in various vegetable oils. Through a combination of macroscopic observations, optical microscopy, DSC and SAXS analyses, we identified key mechanisms driving foam formation and stability. We demonstrate that CITREM forms reverse micelles in oil above its melting transition in the one-phase region of the phase diagram, which enables the production of foams at elevated temperatures. Foam production was achieved solely using CITREM surfactants, without the need for crystalline particles, unlike other oleofoam systems that rely on oleogels and crystalline particles for bubbles stabilization and foam formation (Anne-Laure Fameau & Binks, 2021). Oil foams were only obtained for CITREM concentration above the CAC estimated by SAXS measurements to be around 2 wt%. If the surfactant does not start to aggregate in bulk, it is impossible to stabilize air bubbles. When CITREM was under its

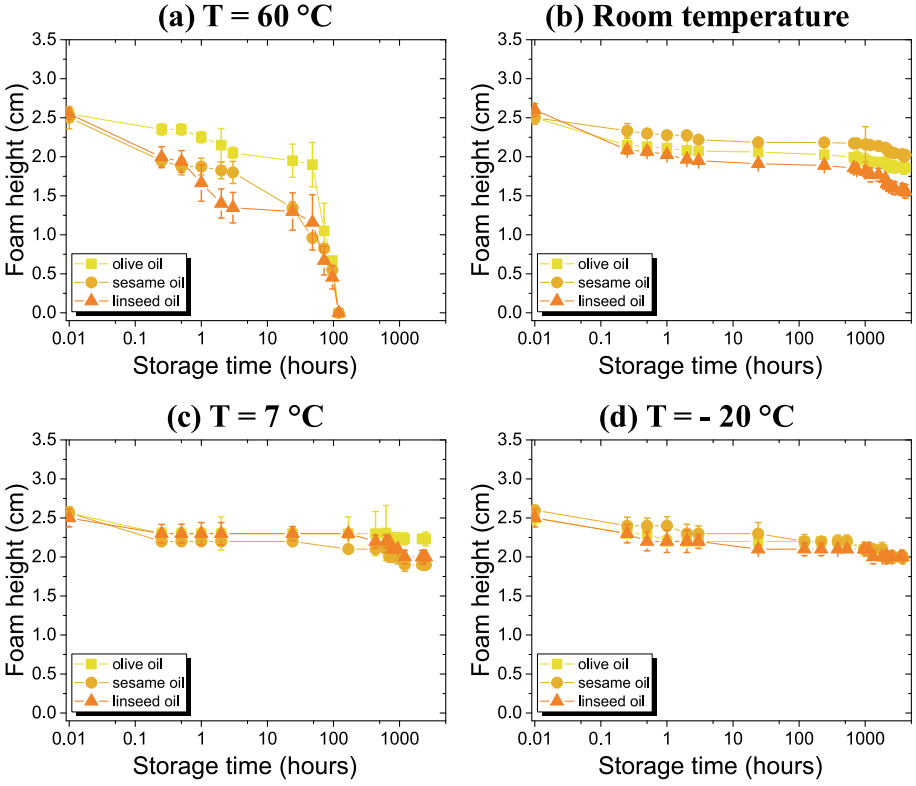

Fig. 8. Evolution of the foam height as a function of storage time in hours for oil foams prepared at 60 °C produced with 10 wt% of CITREM for olive oil, sesame oil and linseed oil at 60 °C and stored at different temperatures: (a) 60 °C ± 1 °C, (b) room temperature (20 °C ± 2 °C), (c) 7 °C ± 0.5 °C, and (d) – 20 °C ± 1 °C.

molecular form, at 60 °C, it was only possible to stabilize oil foams for a few days. However, by decreasing the temperature of the oil foams just after foam production, CITREM crystallization was induced inside the foam leading to the formation of crystals stabilizing both the air bubbles and bulk oil. Using SAXS, we observed different crystalline structures due to the presence of different fatty acids chain lengths comprising the commercial surfactant used in this study. Thus, upon cooling, the formation of crystalline particles further enhances foam stability, leading to long-term, persistent oil foams with high surfactant concentrations during more than 150 days at different temperatures of storage ranging from room temperature to - 20 °C.

Our results confirm that hydroxyl-rich lipophilic surfactants, such as CITREM, can stabilize oil foams similarly to sucrose and sorbitan esters (Anne-Laure Fameau & Binks, 2021). This study also raises new research questions, particularly regarding the influence of vegetable oil composition on foam stability and the precise organization of the surfactant layer at the air-oil interface, both of which require further studies. These oil foams based on CITREM surfactant have possible applications in cosmetics and foods, since the food industry is actively seeking alternatives to reduce saturated fat contents in food products and oil foams are a promising alternative (Marangoni, Van Duynhoven, Acevedo, Nicholson, & Patel, 2020; Rogers, Wright, & Marangoni, 2009). However, before going further the oxidative stability of these oil foams as possible food products also need to be studied as already determined for other oil foam systems (Ribourg-Birault et al., 2024).

CRediT authorship contribution statement

Carolina Ugarte-Pereyra: Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Smaragda-Maria Argyri:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation. **Romain Bordes:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Sébastien Vincent-Bonnieu:** Writing – review & editing, Validation, Supervision, Resources, Project administration. **Julie Beaucé:** Writing – review & editing, Methodology, Investigation. **Bernard P. Binks:** Writing – review & editing, Validation, Supervision, Methodology, Investigation. **Clémence Le Coeur:** Writing – review & editing, Validation, Investigation, Formal analysis. **Anne-Laure Fameau:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The SI contains the chemical structure of CITREM, additional oil foams pictures, DSC results, optical microscopy images of bubbles and SAXS curves. Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2025.117119.

Data availability

Data will be made available on request.

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