Journal of Colloid and Interface Science 460 (2015) 247–257

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

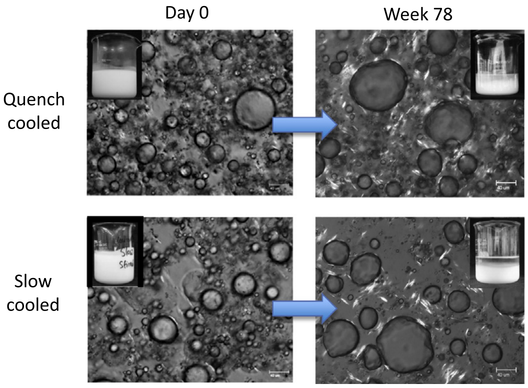
journal homepage: www.elsevier.com/locate/jcis

Long-term stability of crystal-stabilized water-in-oil emulsions

Supratim Ghosh [a,*], Mamata Pradhan [b], Tejas Patel [b], Samira Haj-shafiei [b], Dérick Rousseau [b,*]

[a] Department of Food and Bioproduct Sciences, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[b] Department of Chemistry and Biology, Ryerson University, Toronto, Ontario, Canada

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 June 2015
Revised 28 August 2015
Accepted 31 August 2015
Available online 1 September 2015

Keywords:
Emulsion stability
Pickering
Network
Wax crystallization
Interfacial crystallization
Coalescence
Sedimentation
Microstructure
Contact angle

ABSTRACT

The impact of cooling rate and mixing on the long-term kinetic stability of wax-stabilized water-in-oil emulsions was investigated. Four cooling/mixing protocols were investigated: cooling from 45 °C to either 25 °C or 4 °C with/without stirring and two cooling rates – slow (1 °C/min) and fast (5 °C/min). The sedimentation behaviour of the emulsions was significantly affected by cooling protocol. Stirring was critical to the stability of all emulsions, with statically-cooled (no stirring) emulsions suffering from extensive aqueous phase separation. Emulsions stirred while cooling showed sedimentation of a waxy emulsion layer leaving a clear oil layer at the top, with a smaller separation and droplet size distribution at 4 °C compared to 25 °C, indicating the importance of the amount of crystallized wax on emulsion stability. Light microscopy revealed that crystallized wax appeared both on the droplet surface and in the continuous phase, suggesting that stirring ensured dispersibility of the water droplets during cooling as the wax was crystallizing. Wax crystallization on the droplet surface provided stability against droplet coalescence while continuous phase wax crystals minimized inter-droplet collisions. The key novel aspect of this research is in the simplicity to tailor the spatial distribution of wax crystals, *i.e.*, either at the droplet surface or in the continuous phase via use of a surfactant and judicious stirring and/or cooling. Knowledge gained from this research can be applied to develop strategies for long-term storage stability of crystal-stabilized W/O emulsions.

1. Introduction

Emulsions in products such as cosmetics, pharmaceuticals and foods rely on the presence of crystallized species such as polymers, paraffins or triacylglycerols for long-term stability [1–6]. Water-in-

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* Corresponding authors at: Department of Food and Bioproduct Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7J 2X3, Canada (S. Ghosh). Department of Chemistry and Biology, Ryerson University, Toronto, Ontario M5B 2K3, Canada (D. Rousseau).

E-mail addresses: supratim.ghosh@usask.ca (S. Ghosh), rousseau@ryerson.ca (D. Rousseau).

http://dx.doi.org/10.1016/j.jcis.2015.08.074
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oil (W/O) emulsions used in such applications must satisfy different criteria including: (i) stability against physical breakdown (particularly once in the hands of the consumer), (ii) resistance to changes in environmental conditions (temperature, vibration/shaking) and (iii) lack of change in quality attributes (texture, *etc.*) over time. Key factors include the composition and volume fraction of the continuous and dispersed phases, the mean droplet size and distribution of the dispersed phase, the presence and concentration of stabilizing agents (surfactants, thickeners or crystals) and how the emulsion is processed and stored [7]. Finally, the interactions between the various components in an emulsion will also affect their stability [8].

Emulsion processing requires that the droplets be well-dispersed within the continuous phase, which is normally achieved via valve homogenization or high-shear mixing. In many thickened or solid-like emulsions, subsequent gelation or crystallization of the continuous phase helps to keep the dispersed droplets in place. Yet, little is known regarding how to tailor the spatial distribution of crystals in oil-continuous emulsions to assist in retarding physical breakdown. If crystals are adsorbed to the oil–water interface, they create a solid shell around individual dispersed droplets which prevents droplet–droplet coalescence [9,10]. Such surface-active species are usually surfactants that solidify directly at the interface or adsorb onto the droplet surface [3]. As they are surface-inactive, many crystalline species such as wax or triacylglycerols will form a continuous phase network that envelops the dispersed aqueous phase thereby limiting droplet–droplet collisions [8].

We have previously shown that the surfactant glycerol monooleate can promote the heterogeneous interfacial nucleation of hydrogenated canola oil (a surface-inactive fat) at the water droplet surface in W/O emulsions [11]. We also showed that the addition of a dispersed aqueous phase significantly altered the rheological properties of W/O emulsions [12], as has also been reported by others [5]. Visintin et al. characterized emulsion rheology, and showed that presence of a dispersed aqueous phase was a key contributor to emulsion elasticity [13]. Finally, Hodge and Rousseau showed that the addition of crystallized fat prior to, or after, homogenization (and subsequently quench-crystallized) enhanced the stability of surfactant-stabilized W/O emulsions, with the latter conferring greater stability [14,15].

This paper discusses the impact of cooling rate and stirring on the long-term properties of wax-stabilized W/O emulsions. The goal was to investigate how the presence of a dispersed aqueous phase impacted emulsion macroscopic phase separation, wax crystal morphology, solid wax content and droplet size distribution. In particular, we were interested in showing how it is possible to use minimal amounts of surfactant to generate W/O emulsions with long-term stability against physical breakdown. This was achieved through the use of a low concentration of wax in the continuous oil phase that was suitably crystallized. Importantly, we showed that the optimal stabilization of model W/O emulsions depends on the concerted role of interfacial and network wax crystallization, with the combination of stirring and rapid cooling from the melt conferring the highest kinetic stability.

The results from this study are relevant to processed products that exist as oil-continuous emulsions and may serve as a guide for the judicious formulation of emulsions where long-term kinetic stability is desired.

2. Materials and methods

2.1. Materials

All emulsions consisted of a 20 wt% aqueous phase and a 80 wt% oil phase containing 5 wt% paraffin wax, mineral oil and sufficient surfactant to aid in emulsification, yet not keep the emulsion stable for any length of time. The light mineral oil was obtained from Fisher Scientific (Nepean, ON, Canada). The stated maximum kinematic viscosity at 40 °C was 33.5 mPa s and its density (ρ) was 0.84 g/ml at 25 °C. A 3.5 wt% sodium chloride (Fisher Scientific, Nepean, ON, Canada) in de-ionized water (resistivity $\geqslant$18.0 MOhm cm) solution was used as the dispersed aqueous phase (ρ = 1.02 g/ml). The surfactant used was glycerol monooleate (GMO) (Dimodan MO 90®, Danisco, New Century, KS, USA). Dimodan MO 90 is a food-grade low-HLB (hydrophilic/lipophilic balance) emulsifier composed of >92% glycerol monooleate, with the rest consisting of small amounts of glycerol, glycerol dioleate and glycerol trioleate. A highly-refined paraffin wax (IGI-1242; m.p. 56.7–58.9 °C) was obtained from The International Group, Inc. (Toronto, ON, Canada). Its *n*-paraffin composition provided by the manufacturer is given in Fig. 1.

2.2. Emulsion preparation

A schematic of the emulsion preparation protocol is shown in Fig. 2. The oil phase contained 0.05 wt% GMO as emulsifier and 5 wt% paraffin wax. This level of emulsifier allowed for the formation of dispersed droplets, but did not prevent them from measurably coalescing within a few days in the absence of stabilizing wax. All emulsions were formulated to initially consist of dispersed aqueous droplets with a mean diameter of ~30 µm with a maximum size of ~300 µm, which permitted direct comparison between the different W/O emulsions. The aqueous phase contained 3.5 wt% NaCl, which was necessary to prevent undue formation of oil droplets in the water phase (hence double emulsion formation), which we ascribed to charge generation by the intense shearing action of the homogenizer [16]. Pre-mixing was performed by slow addition of the aqueous phase (9 ml/min) to the oil phase in a beaker at 45 °C *via* magnetic stirring at 500 rpm for 15 min. The pre-mix was quickly transferred to a valve homogenizer (APV-1000, APV, Albertslund, Denmark) preheated to 45 °C and homogenized at 500 psi for 4 cycles. Afterwards, ~100 ml samples were collected in 250 ml glass beakers (diameter: 6.5 cm and height: 9 cm) and cooled *via* one of the four methods denoted at 'quench-static', 'quench-stirred', 'slow-static' or 'slow-stirred'. For quench cooling, samples were transferred to a 0 °C waterbath whereas slow-cooled samples were placed in a temperature-controlled waterbath (Model 1157P, VWR International, Mississauga, ON) at 45 °C and cooled at a rate of 1 °C/min. Stirring during cooling was performed using a magnetic stirrer at 300 rpm. All samples were prepared in triplicate. Emulsion temperatures during the cooling regimes were measured along the centreline of the bea-

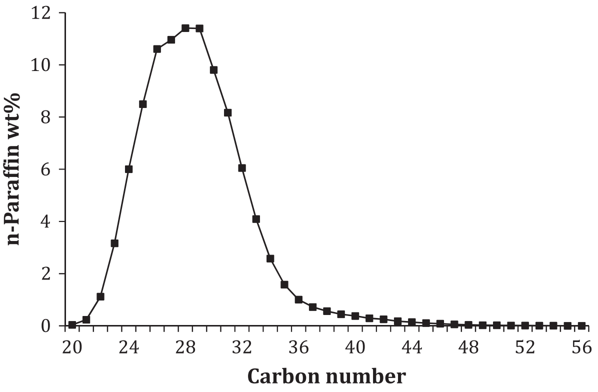

Fig. 1. n-Paraffin compositional analysis of the solid wax sample. Analysis is performed by high temperature gas chromatography yielding a n-paraffin distribution of the wax from C20 to C90.