Trends in Food Science & Technology 60 (2017) 23–30

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

Review

# Low temperature stability of surfactant systems

Emily Summerton [a,*], Georgina Zimbitas [a], Melanie Britton [b], Serafim Bakalis [a]

[a] School of Chemical Engineering, University of Birmingham, Edgbaston, B15 2TT, UK
[b] School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, UK

ARTICLE INFO

*Article history:*
Received 24 March 2016
Received in revised form
17 October 2016
Accepted 28 October 2016
Available online 7 November 2016

*Keywords:*
Surfactants
Low temperature
Crystallisation
Nucleation
Seeding
Ultrasound

ABSTRACT

*Background:* Both naturally occurring and synthetic **surfactants** are present in many food products including butter, margarine, mayonnaise and salad dressing. In addition, surfactants are essential components in detergent formulations used in the various cleaning processes of the food industry. These surfactant systems are supplied and transported on a global scale and, as such, must retain appearance upon exposure to **low temperature** conditions when there can be a risk of surfactant **crystallisation**.

*Scope and Approach:* This review summarizes the relationship of surfactants to the food industry with specific emphasis on surfactant crystallisation behaviour displayed at low temperatures. Stability test methods detecting these crystallisation failures can have long timescales. These time-consuming tests can result in increased cost and probability of samples failing after distribution. As a result, there is an interest in a method that reduces the **nucleation** time of crystallisation so as to detect the failures over a shorter time.

*Key findings and Conclusions:* There are various methods that could provide an opportunity to reduce nucleation time. These include heterogeneous **seeding** and the application of **ultrasound**. An advantage of the use of ultrasound is that it does not require for the addition of any foreign bodies into the system, especially applicable to sterile products. Ultrasound has received much interest in recent years in the food processing industry, with the majority of a sonocrystallisation work being completed on a small scale. However, there is the potential for this technique to be scaled up and applied to industry test methods.



## 1. Introduction to surfactants

### 1.1. Structure and function

Surfactants, also termed as surface-active agents, have a distinct molecular structure and can be classified as amphiphilic compounds since they possess both hydrophobic and hydrophilic properties (Rosen, 2004). The basic chemical structure is composed of a hydrophobic hydrocarbon chain attached to a hydrophilic head group (Farn, 2008). Depending on the strength and polarity of the functional head group, surfactants can be further sub-classified into four distinct categories; cationic, anionic, zwitterionic and non-ionic (Zhang, Wang, Liu, Chen & Liu, 2006). Examples of cationic surfactants include those based around ammonium and amine salts, both of which have positively charged head groups. Sulfonate and sulfate salts, such as sodium dodecyl sulfate (SDS), are examples of anionic surfactants. Zwitterionic surfactants contain both negative and positively charged head groups and non-ionic surfactants possess neutral head groups. Some amine oxide derivatives are examples of surfactants that possess both zwitterionic and non-ionic properties, depending on the pH of the system.

At low concentrations, surfactants exist mostly in their monomer form as a result of the entropy of mixing outweighing the forces of attraction between the molecules. Surfactant monomers tend to reside at the solution-air interface. These monomers will displace some surface water molecules subsequently reducing the intermolecular forces and lowering the surface tension (Holmberg, 2002).

Surfactants aggregate when the surfactant concentration exceeds a specific value termed the critical micelle concentration (CMC). The CMC depends on a variety of factors, with the most important being the nature of the surfactant(s) involved in the system. These aggregates form due to the hydrophobic effect (Maibaum, Dinner, & Chandler, 2004; Southall, Dill, & Haymet, 2002). Such a phenomenon results in a surfactant arrangement in

* Corresponding author.
*E-mail address:* els303@student.bham.ac.uk (E. Summerton).

http://dx.doi.org/10.1016/j.tifs.2016.10.020
0924-2244/© 2016 Published by Elsevier Ltd.

which the degree of unfavourable contact of the hydrophobic surfactant tail with polar water molecules is minimised (McClements, 2015). These aggregates can adopt a variety of molecular arrangements inclusive of micelles, vesicles, bilayers and reverse micelles, with micelles being the most common in food emulsions (Menger, Zana, & Lindman, 1998). A 2D image of a cross-section of a micelle is illustrated in Fig. 1. It is this micellar structure that enables surfactants to solubilise hydrophobic molecules, such as fats and oils which results in the capability of surfactants to provide cleaning and emulsifying properties (Rosen, 2004). Additionally, surfactants provide foaming properties as well as acting as wetting agents and solubilising agents (Attwood, 2012). Upon an increase in surfactant concentration, other aggregates can be formed in aqueous solution (Yan & Texter, 2006). A typical phase diagram as a function of weight percent of surfactant is shown in Fig. 2 (Brinker, Lu, Sellinger, & Fan, 1999). An increase in surfactant concentration favours the formation of liquid crystal phases (Rosevear, 1968). These liquid crystal mesophases can have various formations, namely hexagonal, cubic and lamellar phases, the latter of which is formed at the highest concentrations. The hexagonal phase is formed by hexagonal close packing of the rod-shaped cylindrical micelles and the cubic form originates from spherical micelles cubic close packing (Tiddy, 1980). However, the surfactant concentration within food emulsions is not usually high enough to enable the molecules to form a liquid crystal structure.

### 1.2. Industry importance

Due to their chemical nature, surfactants are extensively used in a variety of industries on a global scale. These industries include those of food, personal care, textiles, plastic and cleaning (Azarmi, 2015; Farn, 2008; Rosen, 2004; Salager, 2002) with further examples illustrated in Fig. 3.

Due to the extensive use of surfactants within industries, the global surfactant market is increasing in market size especially in light of the introduction of synthetic surfactants in recent years. The compound annual growth rate for the period from 2015 to 2020 is forecasted as 5.3% with an estimated end value of $42,120.4 million in the year 2020 (Surfactants market by product type, by substrate type, by application - Trends & Forecast to 2020, 2015). The different categories of surfactants, namely anionic, cationic, non-ionic and amphoteric, are used to varying extents within the industry, with anionic surfactants accounting for the majority segment. This is attributed to the ubiquitous nature of this type of surfactant within the detergent and laundry industry.

Many products in the food industry contain surfactants as a result of their emulsifying properties (Sharma, 2014). Emulsions consist of at least one immiscible liquid dispersed as droplets throughout a continuous phase with examples including mayonnaise, milk, butter, margarine and salad dressing (Guzey &

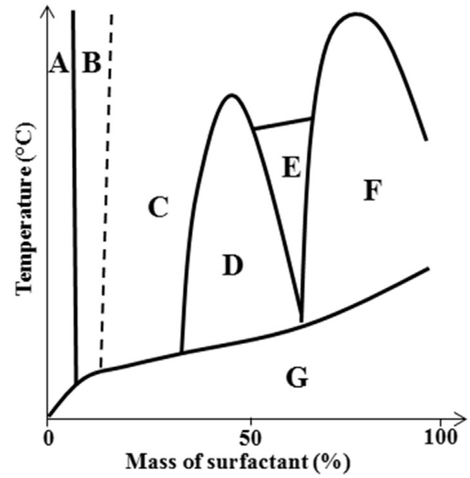


**Fig. 2.** Typical phase diagram for an aqueous surfactant systems displaying the various phases above the CMC; A = Ideal solution, B and C = Micellar solutions, D = Hexagonal phase E = Cubic phase F = Lamellar phase, G = Crystals in the mixture; Adapted from Ref. (Brinker et al., 1999).

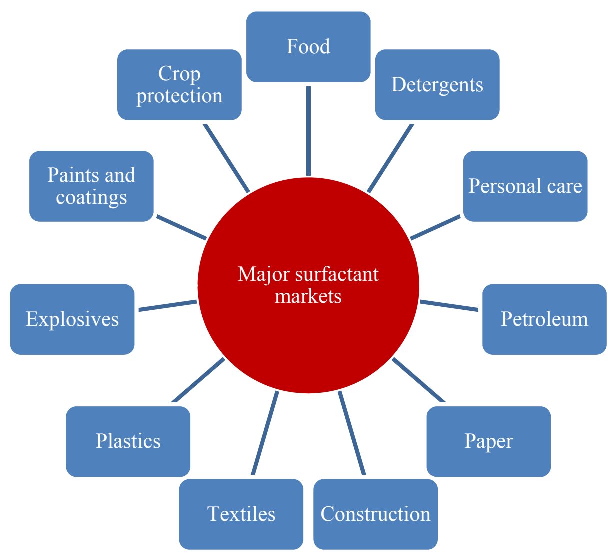


**Fig. 3.** Plot showing examples of industries requiring the use of surfactants.

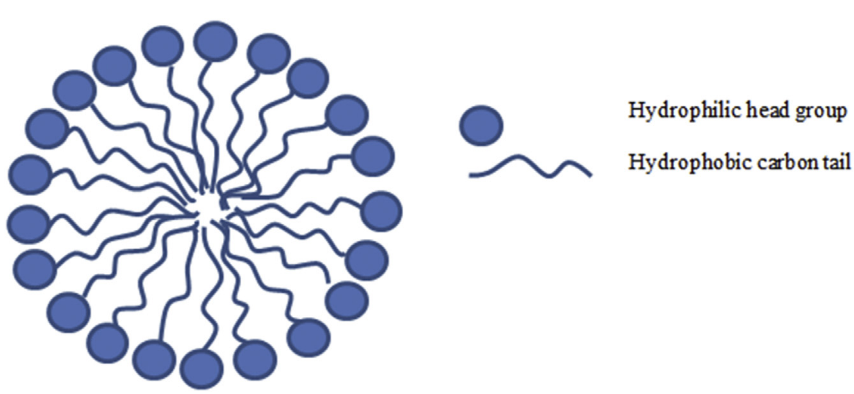


**Fig. 1.** Two-dimensional graphical representation of a micelle.