Advances in Colloid and Interface Science 203 (2014) 1–10

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

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

Fat crystallisation at oil–water interfaces

M. Douaire [1], V. di Bari, J.E. Norton, A. Sullo, P. Lillford, I.T. Norton

Chemical Engineering, the University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Available online 30 October 2013

Keywords:
Emulsion
Fat crystal
Interfacial crystallisation
Heterogeneous nucleation
Templating

ABSTRACT

This review focuses on recent advances in the understanding of lipid crystallisation at or in the vicinity of an interface in emulsified systems and the consequences regarding stability, structure and thermal behaviour. Amphiphilic molecules such as emulsifiers are preferably adsorbed at the interface. Such molecules are known for their ability to interact with triglycerides under certain conditions. In the same manner that inorganic crystals grown on an organic matrix see their nucleation, morphology and structure controlled by the underlying matrix, recent studies report a templating effect linked to the presence of emulsifiers at the oil/water interface. Emulsifiers affect fat crystallisation and fat crystal behaviour in numerous ways, acting as impurities seeding nucleation and, in some cases, retarding or enhancing polymorphic transitions towards more stable forms. This understanding is of crucial importance for the design of stable structures within emulsions, regardless of whether the system is oil or water continuous. In this paper, crystallisation mechanisms are briefly described, as well as recent technical advances that allow the study of crystallisation and crystal forms. Indeed, the study of the interface and of its effect on lipid crystallisation in emulsions has been limited for a long time by the lack of in-situ investigative techniques. This review also highlights reported interfacial effects in food and pharmaceutical emulsion systems. These effects are strongly linked to the presence of emulsifiers at the interface and their effects on crystallisation kinetics, and crystal morphology and stability.

Contents

1. Introduction

Thermodynamic aspects of thermal phase transition and the kinetics of crystallisation in lipids are affected by several factors, including their physical state, i.e. the bulk versus emulsified state. Intuitively, some differences in thermal phase transition of lipids are expected to occur in cases where they exist as part of physically heterogeneous systems, such as emulsions. Several parameters can affect interfacial crystallisation and/or crystallisation in emulsions:

- Type of emulsion (oil continuous or water continuous);
- Type of nucleation process (surface – heterogeneous nucleation, or volume – homogeneous dependent nucleation);

E-mail address: m.douaire@bham.ac.uk (M. Douaire).
[1] Tel.: +44 121 414 5284.

0001-8686/$ – see front matter
http://dx.doi.org/10.1016/j.cis.2013.10.022

- Composition of the lipid phase and molecular interaction with the additive or emulsifier present;
- Molecular packing geometry and mobility of surfactant at the interface.

It has been long observed that oil contained within a droplet requires more supercooling than the equivalent bulk fat, the most accepted explanation being that these droplets are statistically free of impurities, therefore preventing heterogeneous nucleation. More recently, a difference in crystallisation and/or melting behaviour of oil continuous systems has been highlighted. For example, Alexa and co-workers [1] noticed that the melting temperature of water in oil (W/O) spreads decreases as the κ-carrageenan concentration within the internal aqueous phase increases. It has been suggested that this is due to the destabilisation effect of the κ-carrageenan on the emulsion, which leads to the lower melting point observed. The following paragraphs aim to describe the mechanisms involved in interfacial crystallisation, and the consequences regarding the physical behaviour of emulsion systems.

Recent studies have shown that the oil–water interface plays a crucial role in the crystallisation of emulsions, which is of high importance in the design of food emulsion structures, especially as emulsions systems are increasingly designed as tools for controlled delivery [2]. Regardless of the type of emulsion considered (i.e. oil in water (O/W), water in oil (W/O), or double emulsions systems), crystallisation at the interface has a great effect as it will determine the stability of the structure formed. Numerous studies have been carried out in order to explain the mechanisms leading to either improved stability or de-emulsification. These studies aim to either describe the phenomenon or to understand the mechanisms of interfacial nucleation and crystallisation. Interfacial crystallisation of triglycerides (TAG) will, in most cases, happen in the presence of an emulsifier (either protein, monoglyceride, polyglycerol polyricinoleate (PGPR), lecithin, sucrose ester), with each type of emulsifier exhibiting a different effect on the crystallisation behaviour. It is fundamental to understand the mechanisms of heterogeneous nucleation at interfaces, which may be through hydrophobic interactions and templating. In the following sections, we will try to summarise these observed effects in both 'bulk' conditions and within an emulsified system, bearing in mind that nucleation (heterogeneous nucleation via either templating effects or prior crystallisation of the emulsifier present at the interface), growth rate (crystallisation kinetics) and crystal morphology are affected by the presence of additives, droplet–droplet interaction (protruding crystals) and interfacial membrane structure. While fat crystallisation in dispersed oil droplets has been extensively reviewed [2–5], here we will highlight recent advances in the understanding of interfacial effects on fat crystallisation in W/O and O/W emulsion systems. The observed effects of the interface will be discussed, leading to concluding remarks on the overall impact of interfacial films on the crystallisation phenomenon in food and pharmaceutical applications.

2. Crystallisation, a general phenomenon

In order to understand crystallisation within emulsions (both in the bulk and at the interface), it is important to briefly cover the key features of crystallisation in bulk fats, including polymorphism, nucleation and growth, crystallisation in mixed systems, and the effect of temperature and shear. In food systems, fat crystal number, size (both the mean size and the distribution) and polymorph all affect the physical and textural properties, and subsequent sensory properties (e.g. appearance, mouthfeel or flavour release), of the final product.

2.1. Crystallisation of triacylglycerols (TAGs)

Fats and oils are complex mixtures of triacylglycerols (TAGs) (which typically make up approximately 98% of the mixture), and more polar lipids like diacylglycerols (DAGs), monoacylglycerols (MAGs), free fatty acids (FFAs), phospholipids, glycolipids, sterols, and other minor components [6] TAGs are composed of three fatty acyls/acids (R_1, R_2 and R_3; for example, oleic, linoleic, lauric, palmitic or stearic) arranged on a glycerol molecule, with TAG species varying in fatty acid chain length (i.e. carbon number, typically between 12 and 24), degree of saturation of the fatty acids (i.e. number and position of double bonds) and arrangement on the glycerol backbone (i.e. positions *sn*-1, *sn*-2 and *sn*-3 [7–10]).

Crystallisation is a first-order transition: the process of formation of solid crystals from the liquid state (i.e. melt). When TAGs nucleate the molecules orient in a 'chair' (where the fatty acids in *sn*-1 and *sn*-2 become the legs, and *sn*-3 becomes the back of the chair) or an asymmetric 'tuning fork' configuration (where the fatty acid chains in positions *sn*-1 and *sn*-3 point in one direction, and the fatty acid in *sn*-2 points in the opposite direction) [11]. During TAG crystallisation, TAG molecules stack in pairs that self-assemble into lamellae, which in turn stack into crystalline nanoplatelets, that aggregate to form clusters (primary crystal particles), that then pack in an arbitrary manner to form flocs, until a three-dimensional network is created [8,11–13].

2.2. Polymorphism

The TAG molecule can crystallise into different crystalline forms in the crystal lattice (i.e. conformation and arrangement), depending on processing conditions (e.g. cooling rate and shear), a phenomenon termed polymorphism. As such, rapid cooling of liquid fat results in the formation of a diffuse crystalline phase (low-energy polymorph), whereas slower cooling means that the molecules have time to organise into lamellae to form consistent, three-dimensional crystals. Polymorphic behaviour, such as melting point, is affected by the chain length of the fatty acids within the TAG [7,10].

Often the polymorphic forms of fats are classified into three categories, α, β′, and β, in increasing order of stability (due to the density of hydrocarbon chain packing), melting point and latent heat of fusion. The packing of the hydrocarbon chains is different for the different polymorphs. This can be explained in a simplistic way, whereby α has a disorganised, least dense hexagonal (H) subcell structure, β′ an intermediate packed orthorhombic perpendicular ($O_\perp$) configuration, and β a tightly packed triclinic parallel ($T_{//}$) subcell structure [14]. The main polymorphic forms are illustrated in Fig. 1 [15]. The polymorphic form of fat can be measured using X-ray diffraction patterns (short spacings), and inferred using differential scanning calorimetry.

Lipids exhibit monotropic polymorphism (i.e. they can exist in multiple forms, but only one form is stable at all temperatures and pressures, though different polymorphs can coexist). Unstable forms are the first to crystallise in a subcooled fat. Subsequent transformation of unstable polymorphs into more stable forms occurs over time until, eventually, the most stable polymorph for a given lipid is reached. The difference in Gibb's free energy (G) between polymorphs is the driving force for this transformation, which is defined as:

$$G = H - TS$$

where H is enthalpy, S is entropy, and T is temperature [10,14]. Values of Gibbs free energy are highest in α, intermediate in β′ and lowest in β. Fatty acid chain length affects the rate of transformation, with faster transformation for TAGs with short-chain fatty acids. This transformation is also shear and temperature dependent, which can be utilised to produce particular, desirable, polymorphs (for example, tempering of cocoa butter/chocolate). Interpolymorphic transitions are unidirectional (i.e. β cannot transform to β′ and β cannot transform to α), without returning to system to the melt [10].

2.3. Nucleation and growth

Crystallisation is a two stage process, involving the formation of nuclei followed by crystal growth. Crystallisation occurs providing that the phase is supersaturated (i.e. the concentration of dissolved species is