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Emulsifier effects on fat crystallisation

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DOI:
10.1016/j.foostr.2014.11.002

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Document Version
Peer reviewed version

Citation for published version (Harvard):
Rizzo, G, Norton, J & Norton, I 2015, 'Emulsifier effects on fat crystallisation', *Food Structure*, vol. 4, pp. 27–33. https://doi.org/10.1016/j.foostr.2014.11.002

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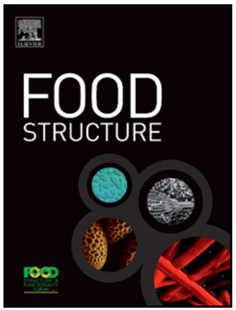

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PII:	S2213-3291(14)00031-8
DOI:	http://dx.doi.org/doi:10.1016/j.foostr.2014.11.002
Reference:	FOOSTR 24

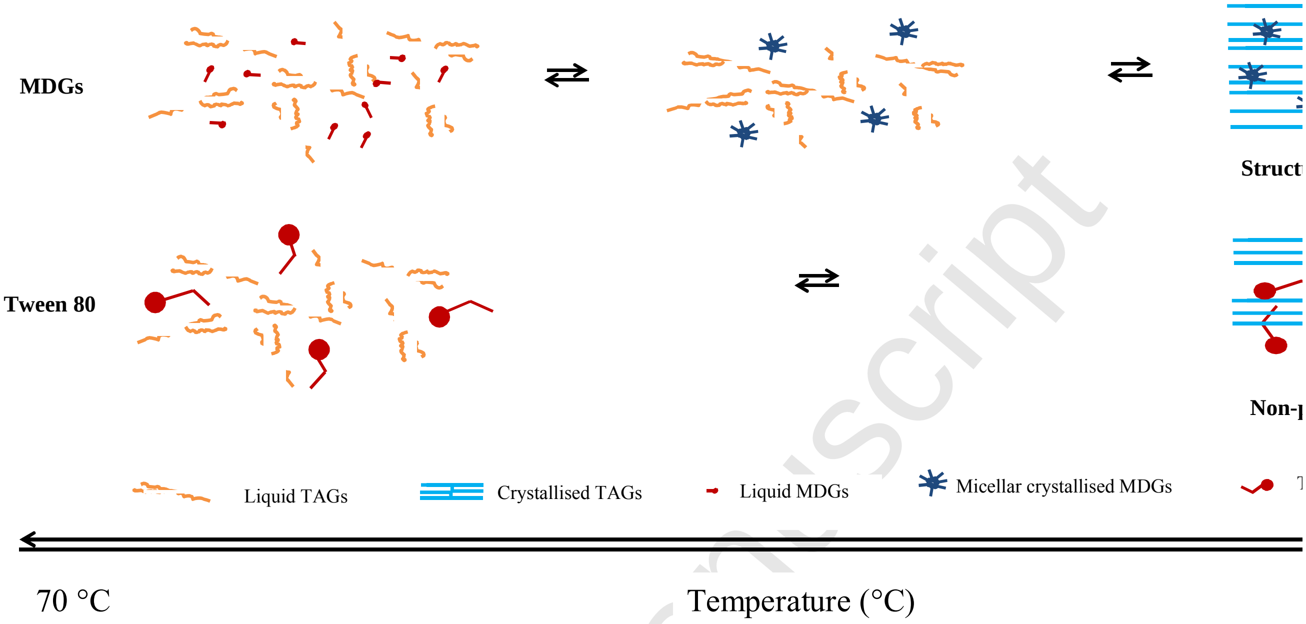
To appear in:

Received date:	1-5-2014
Revised date:	17-10-2014
Accepted date:	6-11-2014

Please cite this article as: G. RizzoJ.E. NortonI.T. Norton Emulsifier effects on fat crystallisation (2014), http://dx.doi.org/10.1016/j.foostr.2014.11.002

Highlights

- Effect of Tween 80 and mono di glycerides on the thermal behaviour of a fat blend containing solid and liquid components
- Mono di glycerides melt and crystallised independently from the bulk fat, but have a templating effect.
- Tween 80 act like a liquid impurity leading to the formation of less perfect crystals.


MDGs
Struct
Tween 80
Non-
Liquid TAGs
Crystallised TAGs
Liquid MDGs
Micellar crystallised MDGs
70 °C
Temperature (°C)

Emulsifier effects on fat crystallisation

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Abstract

The effect of the addition of two emulsifiers differing in their molecular structure (mono and di glycerides and Tween 80) on the thermal behaviour of a bulk fat containing both solid and liquid components (75% coconut oil and 25% of sunflower oil) was investigated using differential scanning calorimetry (DSC). Different ratios of emulsifier to bulk fat were considered (emulsifier / bulk fat of 0.02, 0.05, 0.08, 0.1, 0.3, 0.6 and 1). Both the emulsifiers had an effect on the melting and crystallisation of the bulk lipid. Mono and di glycerides (MDGs), although crystallising independently of the bulk fat (i.e. the observation of the presence of independent melting peaks and enthalpies that were not dependent on the ratio of MDGs to bulk fat), were thought to act as templates for the crystallisation of the bulk fat, having an effect on the shape of the melting and crystallisation peaks. Tween 80, due to its structural properties (unsaturated carbon chain and large hydrophilic head) was thought to act as an impurity leading to the formation of less perfect crystals and a loosely packed lattice, resulting in less energy required to melt. Due to the bulk fat and emulsifiers used this work has relevance to the ice cream industry, and could have implications for the physical properties of ice cream, particularly partial coalescence during manufacture, meltdown properties, texture and sensory perception during consumption.

Keywords: DSC, Emulsifiers, Thermal behaviour, crystallisation

1. Introduction

The effect of emulsifiers on fat crystallisation has been well documented (Wright *et al.,* 2000; Wright & Marangoni, 2002; Litwinenko *et al.,* 2004; Fredrick *et al.,* 2008; Basso *et al.*, 2008). Depending on the homogeneity between the emulsifier and the lipid in terms of chain length and degree of saturation, emulsifiers can retard or accelerate nucleation, crystal growth, and/or polymorphic transitions (Garti, 1988; Garti & Yano, 2001). In the ice cream industry, two emulsifiers are commonly used: Tween 80 (polysorbate 80) and mono and di glycerides (MDGs) (Hartel & Goff, 2013). These two emulsifiers are different in their structure: Tween 80 is more hydrophilic (due to the polyoxyethyleted sorbitol hydrophilic head) and has a bent carbon chain; MDGs have straight carbon chains and glycerol hydrophilic heads, making them more hydrophobic than Tween 80 (Hasenhuettl & Hartel, 2008).

It has been reported that polysorbates with saturated chains (such as Tween 40 or Tween 60) can act as seeds and promote fat crystallisation (reducing the free energy required for nucleation) and co-crystallise with the fat enhancing fat crystal growth. This effect is probably due to the similarity between the saturated carbon chains of the fat and the emulsifiers. In fact, Litwinenko and colleagues (2004) reported higher rate of crystal growth, smaller crystallites, and shorter nucleation induction time in samples containing Tween 60 in comparison with samples without emulsifier. Sorbitan esters are similar emulsifiers to polysorbates, but with lower hydrophilicity because of the lack of the polyoxyethylene groups attached to the sorbitol molecule (Hasenhuettl & Hartel, 2008). The effect that these emulsifiers have on the crystallisation has been studied for a fat blend containing palm oil (Garbolino *et al.*, 2005), showing that long chain emulsifiers with at least 16 carbon atoms (sorbitan monopalmitate and sorbitan monostearate) will allow for optimal chain-chain interactions and result in co-crystallisation of the emulsifier and the fat, whose major fatty acids are palmitic and oleic acid, whereas sorbitan monolaurate has a shorter carbon chain which prevents interaction between the fat and the emulsifier.

Fredrick and colleagues (2008) showed that unsaturated monoaylglicerols (MAGs) from sunflower oil did not have an effect on the nucleation of palm oil crystals, whereas saturated MAGs (derived from palm oil) promoted nucleation. These authors suggested that the homogeneity between the fatty acids of MAGs and palm oil and their degree of saturation were the principal causes of the acceleration of palm oil crystallisation. MAGs can associate as reverse micelles (Walstra and Vanberesteyn, 1975), which can decrease the energy barrier for the nucleation of triacylglycerols (TAGs). If the MAGs are from palm oil they can form micelles and crystallise because of their higher melting point compared to MAGs from sunflower oil. Subsequently, these MAGs micellar crystals may act as seeding material and are more effective than micellar structures alone at promoting earlier nucleation. Foubert *et al.* (2004) showed that the degree on saturation is an important factor in terms of the effect of the emulsifier on the fat. These authors investigated the influence of diacylglycerols (DAGs) and MAGs on the crystallisation of milk fat, showing that it was dependent on the acyl groups present in the additives. With stearic acyl chain the crystal growth rate was reduced, whereas an oleic acyl chain had no effect. The reason probably resides in the fact that stearic based MAGs and DAGs may be easily incorporated into the crystal lattice impeding further growth, whilst oleic based MAGs and DAGs are incorporated to a lesser extent due to their unsaturated carbon chain. The importance of the similarity between the fat and the emulsifier structure has also been highlighted by Smith *et al.* (1994) and Smith and Povey (1997) who discussed the effect of different additives on the crystallisation of a trilaurin model system. The crystal growth rate increased in the presence of monolaurin, while it was hardly affected by MAGs, whose chain length differs from lauric acid. This was probably due to the co-crystallisation of monolaurin with trilaurin, which was not possible for emulsifiers with a different carbon chain length due to structural diversity. More recently, Basso *et al.* (2008) showed that the addition of MAGs accelerated the crystallisation of palm oil by increasing the number of crystallisation seeds (heteronuclei).

To conclude, there is a well-documented effect of the emulsifiers on fat crystallisation. In particular, depending upon the affinity between the emulsifier and the fat (saturation and carbon chain length) emulsifiers can interact with the fat favouring or interfering with the fat crystallisation.

The aim of this study was to investigate the thermal behaviour of a fat blend of 75 % coconut oil and 25 % sunflower oil in presence of Tween 80 and MDGs. The intention for the work was to investigate both a bulk fat blend and emulsifiers that have relevance for the production of ice cream; as such this was considered a model system to understand the effect in an emulsified ice cream. This is a novel area of investigation for two reasons: 1. the thermal behaviour of this blend has not been investigated previously and the effect of the presence of liquid oil on the crystallisation of coconut oil is required as it can decrease its crystallisation and increase its melting temperature (Norton *et al.*, 2009); 2. the effect of these two emulsifiers on the thermal behaviour of this fat blend has also not been investigated previously, and the effect of chain length and hydrophobicity of the head is interesting and useful for the scientific community as it is likely to have an impact upon the microstructure of ice cream. Our hypothesis is that Tween 80 interferes with the fat crystallisation (due to the unsaturated carbon chain and large hydrophilic head), whereas MDGs co-crystallise with the fat (due to the structural homogeneity with the bulk fat), favouring its crystallisation.

The results are likely to have many applications in the ice cream industry. This fat blend is an economic substitute to milk fat as it mimics milk fat it in terms of partial coalescence, meltdown behaviour and flavour.

2. Material and methods

2.1 Materials

Sunflower oil was purchased from a retailer (Sainsbury’s, UK); coconut oil was purchased at Akoma International (UK) LTD. MDGs (product number: 149563) were purchased at Danisco (UK) LTD and Tween 80 (product number: 9005-65-6) was purchased at Croda (EU) LTD. MDGs were palm based (saturated sixteen-carbon chain) and mono glycerides represent more than 60%. Most abundant fatty acid in coconut oil and sunflower oil were lauric acid (saturated twelve-carbon chain) and linoleic acid (unsaturated eighteen-carbon chain) respectively.”

2.2 Preparation of the fat-emulsifier blends

The fat blend used was a blend of coconut oil 75% and sunflower oil 25% (bulk fat). Emulsifiers, Tween 80 and MDGs were dispersed at different ratios (emulsifier / bulk fat of 0.02, 0.05, 0.08, 0.1, 0.3, 0.6 and 1) in the melted bulk fat and stirred with a magnetic stirrer at 80 °C for approximately 20 minutes, until a homogeneous sample was obtained.

2.3 Differential Scanning Calorimetry

The effect of the emulsifiers on the thermal behaviour of the bulk fat used was determined using differential scanning calorimetry (DSC), a Perkin Elmer DSC Series 7 (UK), with thermal analysis software (Pyris). Nitrogen was used as a purge gas, at a flow rate of 30 ml/min. The thermal behaviour of MDGs was also measured. The samples (8-10 µg) were loaded into Perkin Elmer 40 µl capacity aluminium pans, and sealed with aluminium covers; an empty pan was used as a reference. The following thermal program was used: holding isothermally at 70 °C for 10 min, cooling from 70 °C to -30 °C at 10 °C/min and then heating from -30 °C to 70 °C at 10 °C/min. The ΔH (J/g) was calculated using the thermal analysis software (Pyris). The DSC scans shown in all figures have been normalised according to total mass and mass of crystalline material (i.e. amount of coconut oil and MDGs). In order to determine if the ΔH (J/g) of crystallisation and melting of MDGs were independent from those of the bulk fat, predicted (theoretical ΔH according to the mass of crystallising material) and experimental enthalpies for samples containing different MDGs to bulk fat ratios were determined.

3. Results

3.1 Thermal behaviour of the bulk fat in presence of MDGs

In this section the effect of the addition of MDGs on thermal behaviour of the bulk fat (specifically the shape of the melting and crystallisation peaks, peak temperature and enthalpy) will be discussed.

As can be observed, on cooling the bulk fat crystallised in two peaks, the first at ~-5.5 °C and the second at ~-16.5 °C (see **1** and **2** in Fig. 1) and on heating it began to melt at ~6 °C, with the main peak at ~19 °C (see Fig. 2). Very similar results were obtained by Tan and Che Man (2002) who studied the thermal behaviour of coconut oil with DSC using the same scan rate. Our melting and crystallisation peaks are slightly lower due to the effect that the liquid oil has on the crystallisation of solid fat, a phenomenon that is well known (Norton *et al.,* 2009). We can assume that the two crystallisation peaks and the presence of a shoulder in the melting curve is due to the presence of two different TAGs, a higher and a lower melting fraction, where the higher fraction exhibits slower melting and more rapid crystallisation (Tan & Che Man, 2002). The MDGs melted between ~50 °C and ~60 °C and crystallised between ~40 °C and ~53 °C (see Fig. 1 and 2), thus at higher temperatures than the bulk fat.

The thermal behaviour of the bulk fat changed with the addition of different quantities of MDGs. In the crystallisation curves (see Fig. 1) the two exothermal peaks of the bulk fat were replaced by a single peak at around ~0-5°C. Moreover, with the addition of greater quantities of MDGs a second peak appears on both melting and crystallisation, one in the position of the bulk fat peak (see '**A'** in Fig. 1 and 2), and the other at a higher temperature representative of the MDGs (~35-50 °C for the crystallisation and ~40-57 °C for the melting thermograms; see '**B'** in Fig. 1 and 2). The melting and crystallisation peaks in position 'B' (see Fig. 3B) shifted to higher temperature with the addition of MDGs (logarithmic $R^2 = 0.97$ and 0.93 for melting and crystallisation, respectively). However, the peak temperatures were always lower than the MDGs alone, probably due to the effect that the sunflower oil exerted on it.

Given the presence of the peaks in position **B** it was assumed that there was independent melting and crystallisation of the bulk fat and the MDGs. In order to have a clearer understanding of the behaviour observed, experimental enthalpies of peaks in position **B** were calculated and compared to predicted enthalpies calculated assuming that this peak was as a result of melting or crystallisation of the MDGs alone.

As the experimentally measured enthalpies were very similar to the predicted ΔH's (see Fig. 4) it was concluded that MDGs melt and crystallise independently from the bulk fat, with the peak in position 'B' being a result of the melting or crystallisation of the MDGs only. Nevertheless, on the addition of MDGs there was still an effect on the melting and crystallisation of the bulk fat as the shape of the curves in position 'A' changed (see Fig. 1 and 2), even if the melting peak maximum (see Fig. 3A) and the enthalpies (see Fig. 5) did not change significantly (linear R^2 = 0.57 and 0.3 for melting and crystallisation peak maximums and linear R^2 = 0.08 and 0.01 for melting and crystallisation ΔH, respectively, indicating poor correlations between the ratio of MDGs to bulk fat for both peak maximum and ΔH).

These results suggest the presence of two phenomena: an independent melting and crystallisation of MDGs and the bulk fat and a templating effect exerted by MDGs. MDGs crystallise first in the form of reverse micelles (Fredrick *et al.*, 2008) which act as templates for the crystallisation of the bulk fat, resulting in more rapid growth of the bulk fat crystals. A schematic representing this effect is shown in Figure 6A. This hypothesis is supported by the earlier crystallisation of the bulk fat in the presence of MDGs than without this emulsifier (see Fig. 1). As already mentioned, without MDGs two crystallisation peaks are observed for the bulk fat due to the presence of two TAGs fractions. In presence of MDGs we observe one peak because when the bulk fat crystallises the MDGs micellar crystals are included in the lattice. This is in accordance with findings reported in the literature (Basso *et al.*, 2008, Foubert *et al.*, 2004). Nevertheless, our results also show an independent melting and crystallisation of bulk fat and MDGs that has not been showed previously, and represent a novel area for future investigations.

MDGs are currently used in the ice cream production. In addition to providing understanding of the effect of this emulsifier on the thermal behaviour of the bulk fat, is useful in the context of ice cream production: with the addition on MDGs the fat crystallisation occurs earlier, so the fat will be completely crystallised by the end of the commercial freezing process (~5 °C to -8 °C). Earlier crystallisation enhances the destabilisation phenomenon. It is likely that the fat droplets would have then large protruding crystals, which would easily interact with other crystals giving rise to the partial coalescence of the droplets. Partial coalescence is in turn important because it contributes to some of the characteristics of the final product, such as the speed of melting, the degree of shape retention during melting and smoothness during consumption (Hartel & Goff, 2013). The effect of MDGs on the thermal behaviour and structure of ice cream would be an interesting area for future research.

3.2 Thermal behaviour of the bulk fat in presence of Tween 80

In this section the effect of the addition of Tween 80 on thermal behaviour of the bulk fat (specifically the shape of the melting and crystallisation peaks, peak temperature and enthalpy) will be discussed.
Figures 7 and 8 show the thermal behaviour of the bulk fat with the addition of increasing amounts of Tween 80. As can be seen the general shape of the curves (i.e. two peaks) does not change with the addition of Tween 80. However, increasing the ratio of Tween 80 to bulk fat, the exothermic and endothermic energy of melting and crystallisation does differ. As can be seen in Figure 9 increasing the amount of Tween 80 decreased the amount of energy required to melt the fat (linear $R^2 = 0.83$ indicating a strong relationship between Tween to bulk fat ratio and ΔH) and increased the amount of energy released during crystallisation (linear $R^2 = 0.74$ indicating a strong relationship between Tween to bulk fat ratio and ΔH).

The effect of Tween 80 on the bulk fat is different from that observed for the samples containing MDGs. It is hypothesised that Tween 80 acts as a liquid impurity that is incorporated into the lattice during crystallisation. As a consequence it leads to the formation of less perfect crystals. The imperfection of these crystals explains the decrease in the ΔH of the exothermic and endothermic peaks: the energy required and released is lower in lattices with more loosely packed crystals. Tween 80 has a large hydrophilic head (due to the polyoxyethyleted sorbitol) and a kinked carbon chain (because it is unsaturated), and both these features interfere with the crystallisation of bulk fat. In the literature, unlike MDGs, there are few studies considering the effect of Tween 80 on fat crystallisation, but it is known that Tween 80 can delay fat crystallisation (Dickinson & McClements, 1996). Whilst this work does not indicate a delay in the crystallisation, it does suggest interference of this emulsifier with crystal packing. A schematic representation of the effect of Tween 80 on lipid crystallisation is shown in Figure 6B. These results, in addition to those obtained for MDGs are useful not only to understand the effect of the emulsifier on the thermal behaviour of the bulk fat, but also provide information relevant to ice cream production. As Tween 80 results in the formation of less perfect crystals it is likely to decrease fat destabilisation: the crystals protruding from the fat globules will be less structured and this could lower their interaction with other fat crystals, and could decrease the partial coalescence phenomenon, having a negative influence on the final product.

5. Conclusion

Both the emulsifiers investigated have an effect on the melting and crystallisation of the bulk fat. MDGs melt and crystallise independently from the bulk fat, but have an effect on its thermal behaviour, acting as templates for the crystallisation of the bulk fat. Tween 80 acts as an impurity, leading to the formation of less perfect crystals in the bulk fat. As this work has relevance due to the use of both the bulk fat blend and the emulsifiers in the production of ice cream, future work should consider the effect of these emulsifiers on the thermal behaviour of an emulsified system, to determine the effect of additional ingredients (such as water and sugar) and consider interfacial effects. Further investigations should take into account their effect on the final ice cream product, in terms of fat destabilisation, meltdown properties, texture and sensory perception.

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Fig. 1 Thermal behaviour of MDGs, bulk fat, and different ratios MDGs to bulk fat during cooling from 70 °C to -30 °C at a scan rate of 10 °C/min.

Fig. 2 Thermal behaviour of MDGs, bulk fat, and different ratios MDGs to bulk fat during heating from -30 °C to 70 °C at a scan rate of 10 °C/min.

Fig. 3 Crystallisation and melting peak maximums in position **A** (A) and **B** (B) (see Fig. 1 and 2) as a function of MDGs to bulk fat ratio during cooling from 70 °C to -30 °C and heating from -30 °C to 70 °C at a scan rate of 10 °C/min. Error bars represent one standard deviation of the mean of six measurements.

Fig. 4 Predicted and experimental ΔH's of the melting and crystallisation peaks in position **B** (see Fig. 1 and 2) as a function of MDGs to bulk fat ratio during cooling from 70 °C to -30 °C and heating from -30 °C to 70 °C at a scan rate of 10 °C/min. Error bars show the standard deviation of six measurements.

Fig. 5 ΔH (J/g of total crystalline material) of the crystallisation peaks in position A (Fig. 1) and melting peaks in position A (Fig. 2) as a function of MDGs to bulk fat ratio during cooling from 70 °C to -30 °C and heating from -30 °C to 70 °C at a scan rate of 10 °C/min. Error bars show the standard deviation of six measurements.

Fig. 6 Schematic representation depicting the interaction between the emulsifiers and the lipid during crystallisation on cooling from 70 °C to -30 °C (A: MDGs, B: Tween 80).

Fig. 7 Thermal behaviour of bulk fat and different ratios Tween 80 to bulk fat during cooling from 70 °C to -30 °C at a scan rate of 10 °C/min.

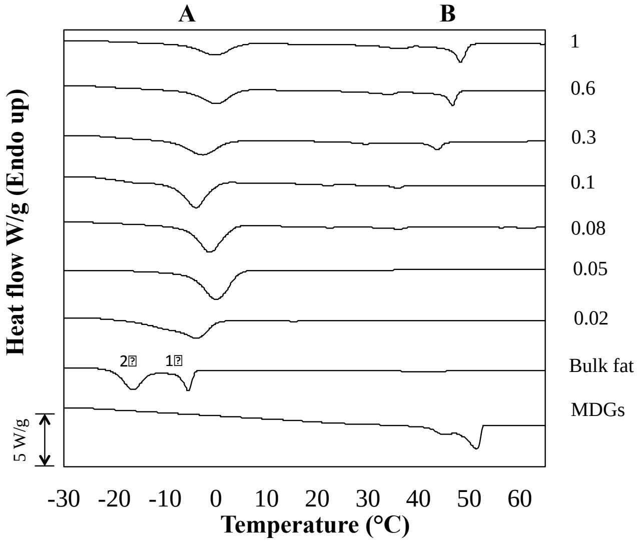
Fig. 8 Thermal behaviour of bulk fat and different ratios Tween 80 to bulk fat during heating from -30 °C to 70 °C at a scan rate of 10 °C/min

Fig. 9 ΔH (J/g of crystalline material) of melting and crystallisation peaks (see Fig. 7 and 8) as a function of increasing ratio of Tween 80 to bulk fat during cooling from 70 °C to -30 °C and heating from -30 °C to 70 °C at a scan rate of 10 °C/min. Error bars show the standard deviation of six measurements.

Industrial Relevance

The fat blend studied in this work is a possible economic substitute for milk fat in the production of ice cream as it mimics milk fat in terms of partial coalescence, meltdown behaviour and flavour. As a consequence it is likely to be extensively used for this aim in the future. Studying the effect of different emulsifiers (varying in molecular structure) on the thermal behaviour (crystallisation and melting) of this fat blend provides understanding relevant to the physical characteristics of ice cream. The emulsifiers studied lead to the formation of different fat crystal structures (i.e. differences in peak shape and enthalpy), which are likely to influence the destabilisation phenomenon (i.e. partial coalescence) and thus the properties of the final product.

Figure 1


A
B
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0.6
0.3
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0.05
0.02
Bulk fat
MDGs
2
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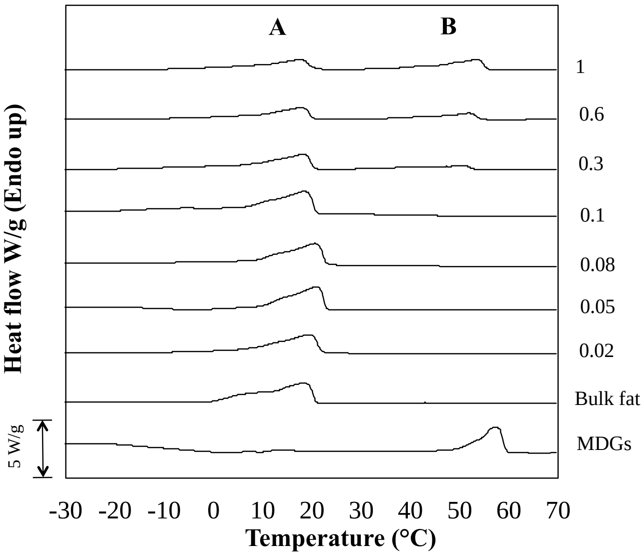
Temperature (°C)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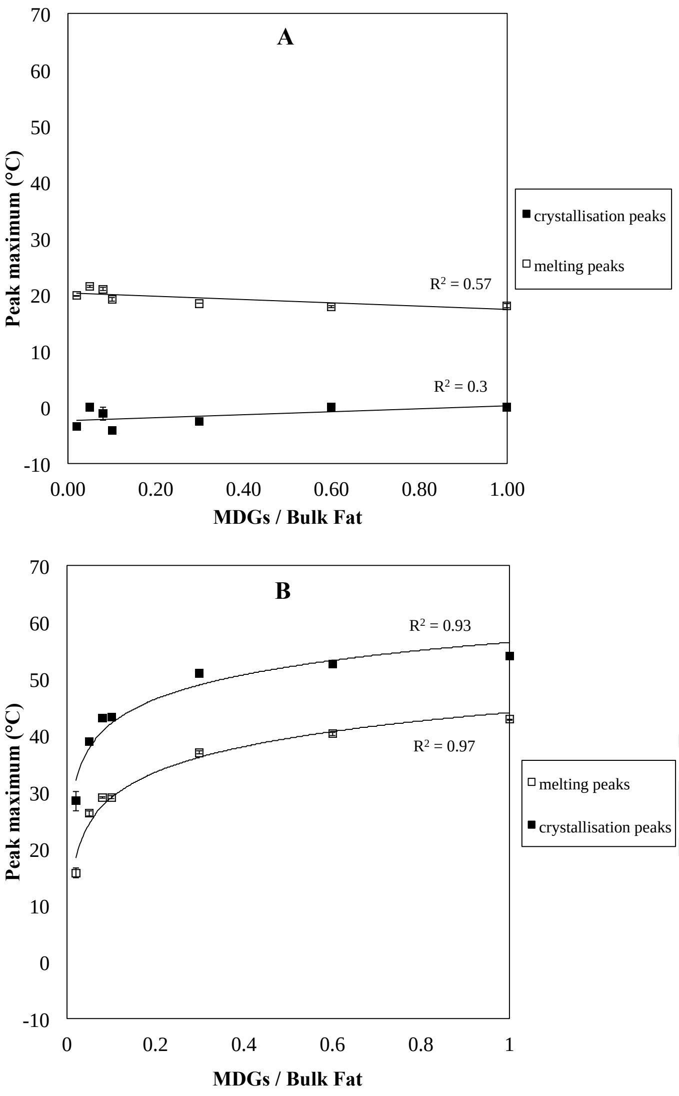
Temperature (°C)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Peak maximum (°C)
■ crystallisation peaks
□ melting peaks
R² = 0.57
R² = 0.3
0.00
0.20
0.40
0.60
0.80
1.00
MDGs / Bulk Fat
B
70
60
50
40
30
20
10
0
-10
Peak maximum (°C)
R² = 0.93
R² = 0.97
□ melting peaks
■ crystallisation peaks
0
0.2
0.4
0.6
0.8
1
MDGs / Bulk Fat

Figure 4

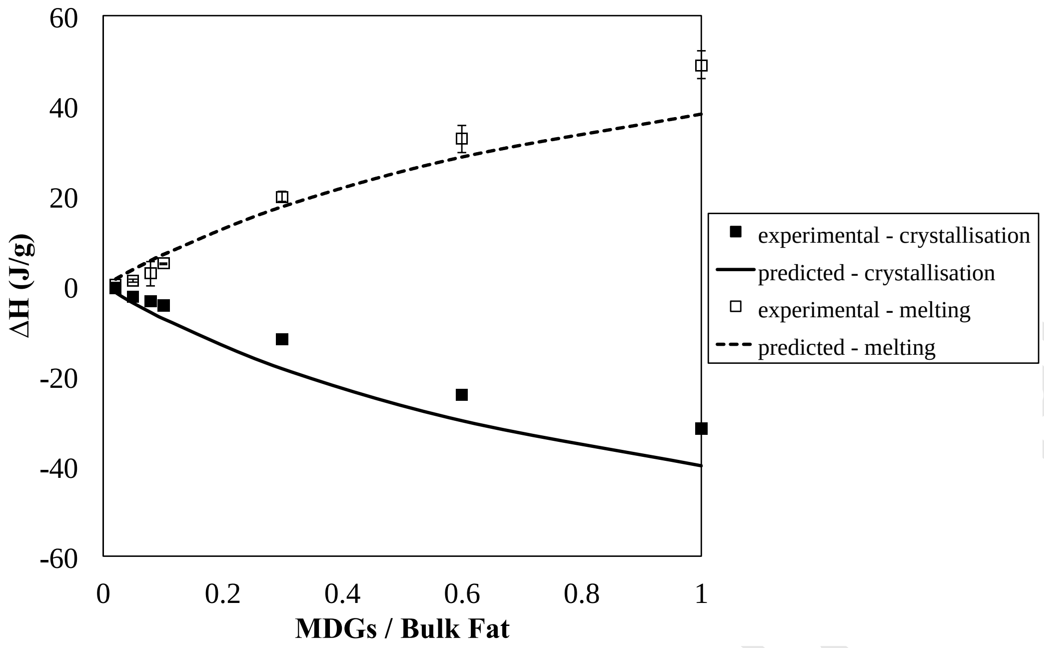

60
40
20
0
-20
-40
-60
ΔH (J/g)
0
0.2
0.4
0.6
0.8
1
MDGs / Bulk Fat
experimental - crystallisation
predicted - crystallisation
experimental - melting
predicted - melting

Figure 5

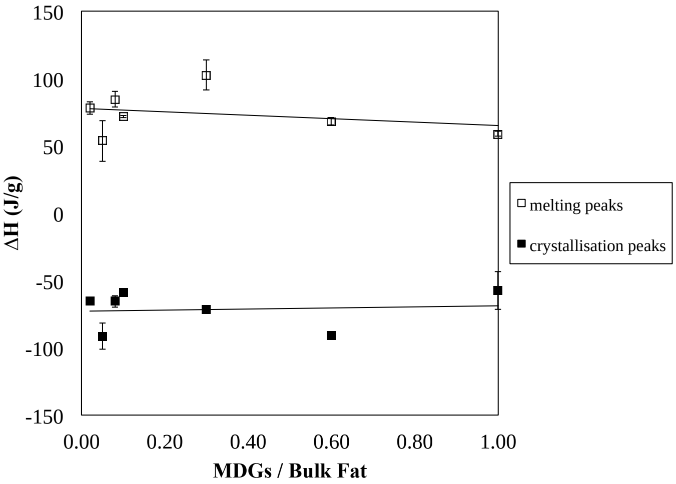
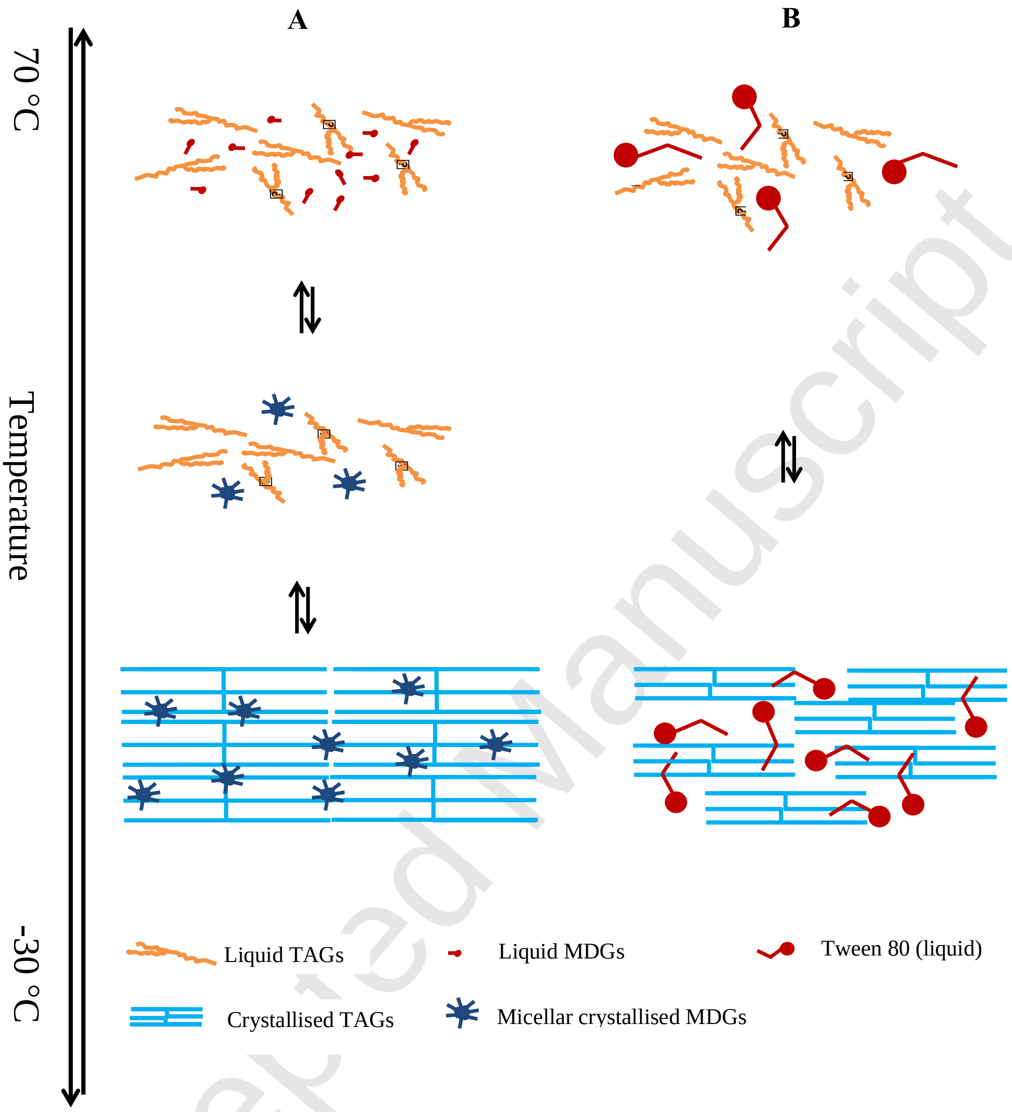
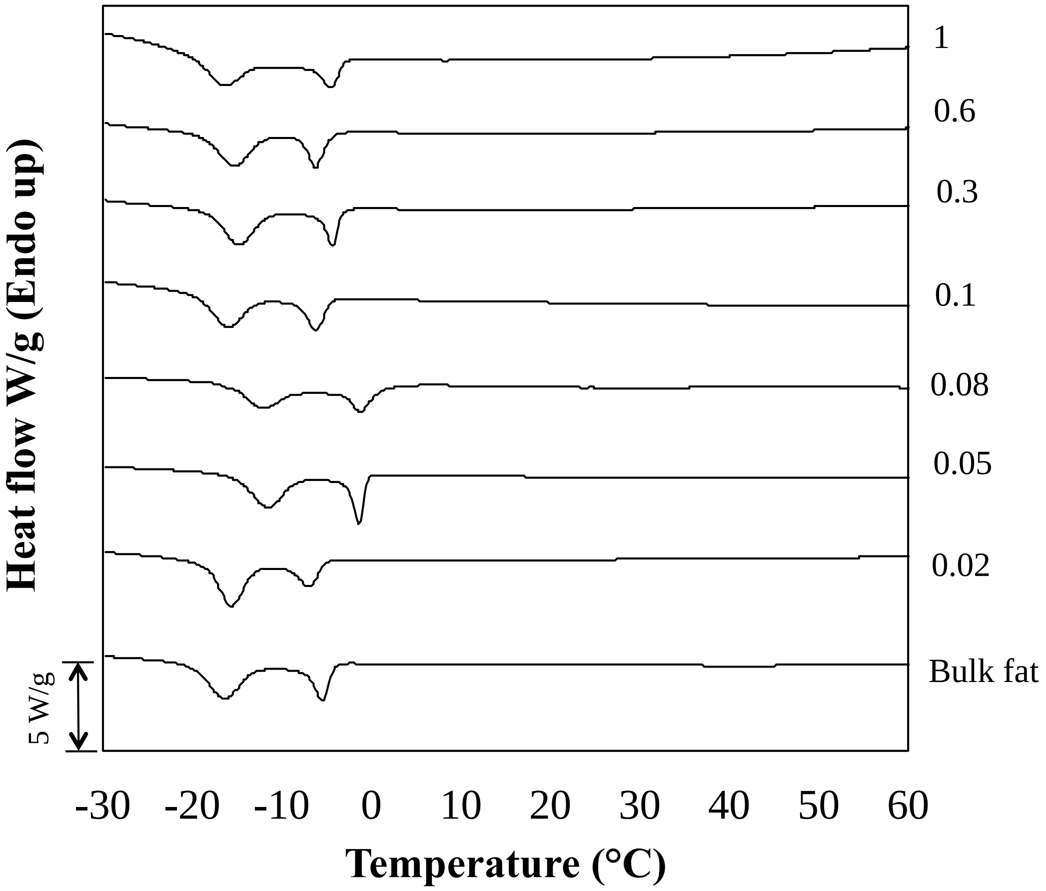
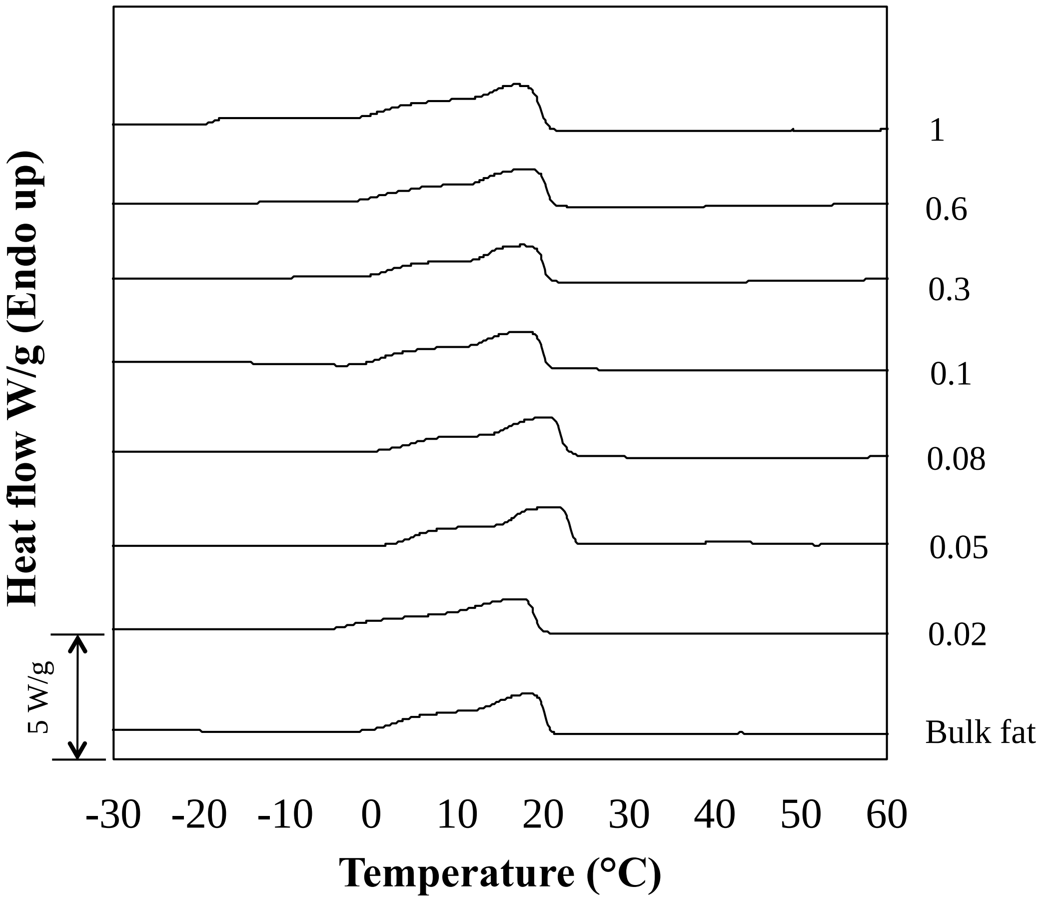
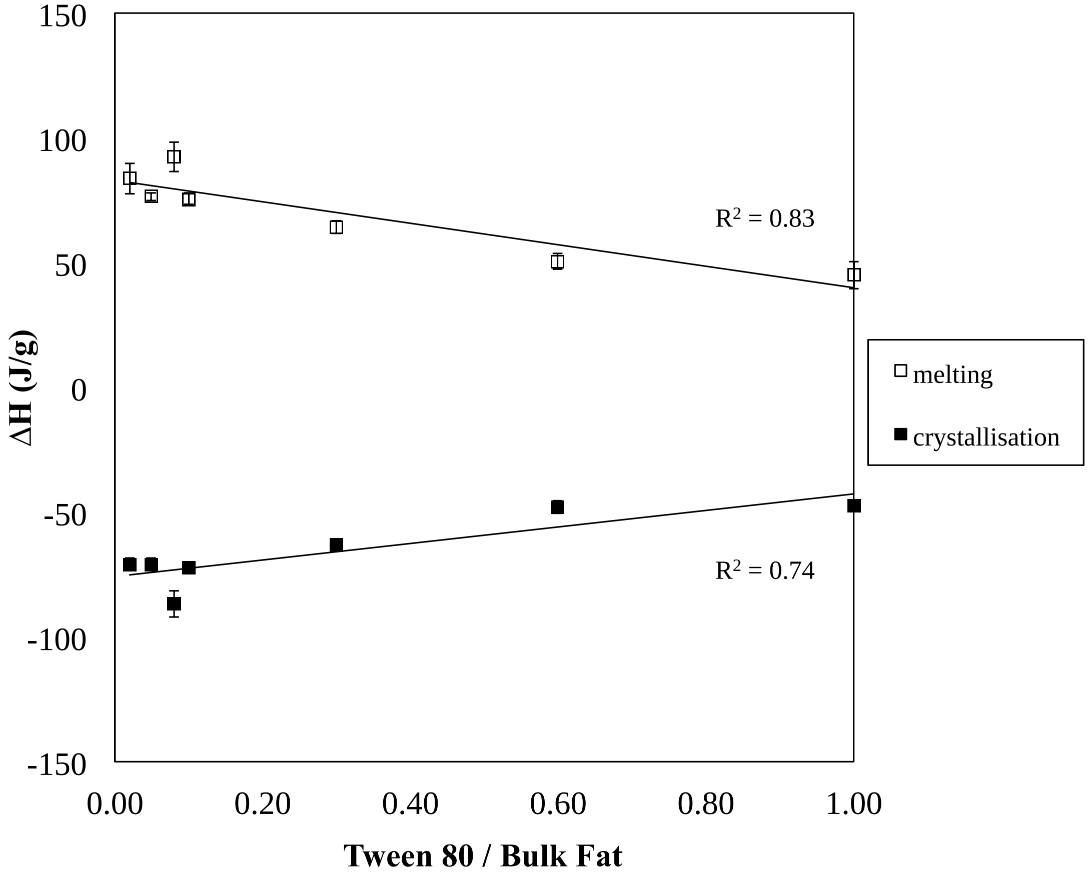

150
100
50
0
-50
-100
-150
ΔH (J/g)
0.00
0.20
0.40
0.60
0.80
1.00
MDGs / Bulk Fat
□ melting peaks
■ crystallisation peaks

Figure 6


A
B
70 °C
Temperature
-30 °C
Liquid TAGs
Liquid MDGs
Tween 80 (liquid)
Crystallised TAGs
Micellar crystallised MDGs


Heat flow W/g (Endo up)
1
0.6
0.3
0.1
0.08
0.05
0.02
Bulk fat
5 W/g
-30
-20
-10
0
10
20
30
40
50
60
Temperature (°C)


Heat flow W/g (Endo up)
5 W/g
1
0.6
0.3
0.1
0.08
0.05
0.02
Bulk fat
-30
-20
-10
0
10
20
30
40
50
60
Temperature (°C)


150
100
50
0
-50
-100
-150
ΔH (J/g)
0.00
0.20
0.40
0.60
0.80
1.00
Tween 80 / Bulk Fat
R2 = 0.83
R2 = 0.74
□ melting
■ crystallisation