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### Emulsifier effects on fat crystallisation

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DOI:

[10.1016/j.foostr.2014.11.002](https://doi.org/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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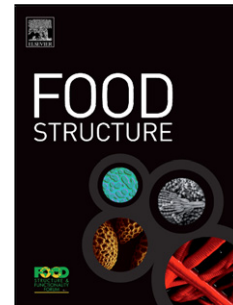
Title: Emulsifier effects on fat crystallisation

Author: G. Rizzo J.E. Norton I.T. Norton

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. Rizzo J.E. Norton I.T. Norton Emulsifier effects on fat crystallisation (2014), <http://dx.doi.org/10.1016/j.foostr.2014.11.002>

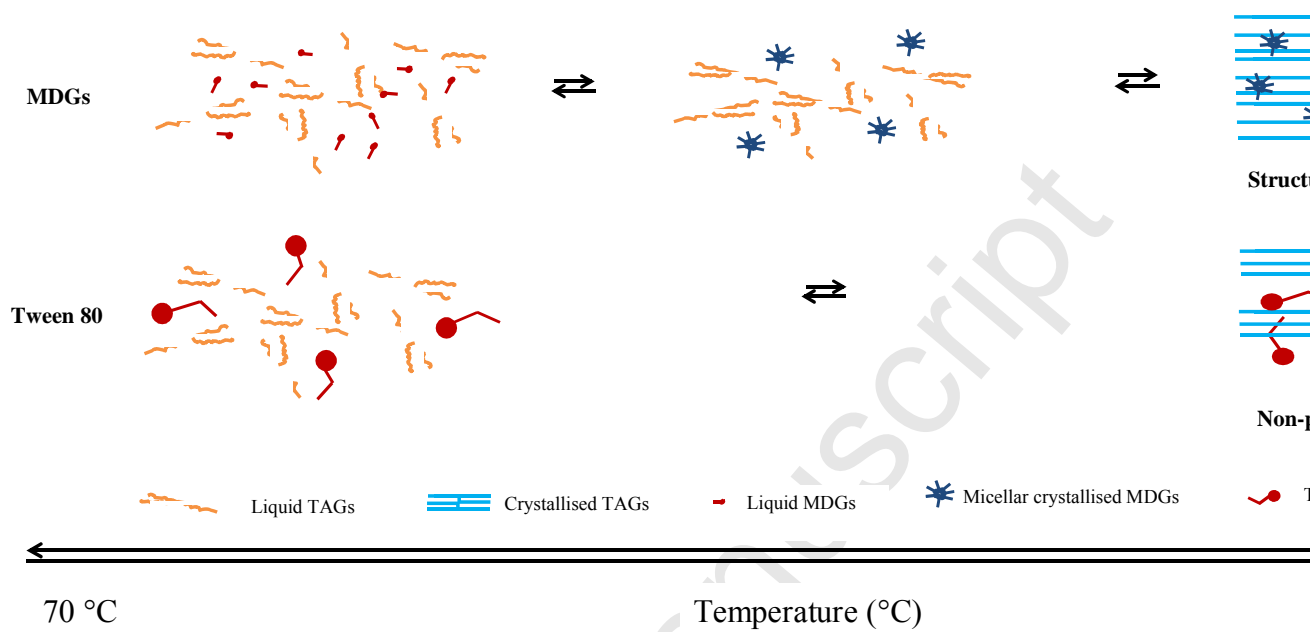
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1 **Highlights**

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

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## 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

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### 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 polyoxyethylenated 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).

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

61

62 Fredrick and colleagues (2008) showed that unsaturated monoacylglycerols (MAGs) from  
63 sunflower oil did not have an effect on the nucleation of palm oil crystals, whereas saturated  
64 MAGs (derived from palm oil) promoted nucleation. These authors suggested that the  
65 homogeneity between the fatty acids of MAGs and palm oil and their degree of saturation  
66 were the principal causes of the acceleration of palm oil crystallisation. MAGs can associate  
67 as reverse micelles (Walstra and Vanberesteyn, 1975), which can decrease the energy barrier  
68 for the nucleation of triacylglycerols (TAGs). If the MAGs are from palm oil they can form  
69 micelles and crystallise because of their higher melting point compared to MAGs from  
70 sunflower oil. Subsequently, these MAGs micellar crystals may act as seeding material and  
71 are more effective than micellar structures alone at promoting earlier nucleation. Foubert *et al.*  
72 (2004) showed that the degree on saturation is an important factor in terms of the effect of  
73 the emulsifier on the fat. These authors investigated the influence of diacylglycerols (DAGs)  
74 and MAGs on the crystallisation of milk fat, showing that it was dependent on the acyl  
75 groups present in the additives. With stearic acyl chain the crystal growth rate was reduced,  
76 whereas an oleic acyl chain had no effect. The reason probably resides in the fact that stearic  
77 based MAGs and DAGs may be easily incorporated into the crystal lattice impeding further  
78 growth, whilst oleic based MAGs and DAGs are incorporated to a lesser extent due to their  
79 unsaturated carbon chain. The importance of the similarity between the fat and the emulsifier  
80 structure has also been highlighted by Smith *et al.* (1994) and Smith and Povey (1997) who  
81 discussed the effect of different additives on the crystallisation of a trilaurin model system.  
82 The crystal growth rate increased in the presence of monolaurin, while it was hardly affected  
83 by MAGs, whose chain length differs from lauric acid. This was probably due to the co-  
84 crystallisation of monolaurin with trilaurin, which was not possible for emulsifiers with a  
85 different carbon chain length due to structural diversity. More recently, Basso *et al.* (2008)  
86 showed that the addition of MAGs accelerated the crystallisation of palm oil by increasing  
87 the number of crystallisation seeds (heteronuclei).

88

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

93  
94 The aim of this study was to investigate the thermal behaviour of a fat blend of 75 % coconut  
95 oil and 25 % sunflower oil in presence of Tween 80 and MDGs. The intention for the work  
96 was to investigate both a bulk fat blend and emulsifiers that have relevance for the production  
97 of ice cream; as such this was considered a model system to understand the effect in an  
98 emulsified ice cream. This is a novel area of investigation for two reasons: 1. the thermal  
99 behaviour of this blend has not been investigated previously and the effect of the presence of  
100 liquid oil on the crystallisation of coconut oil is required as it can decrease its crystallisation  
101 and increase its melting temperature (Norton *et al.*, 2009); 2. the effect of these two  
102 emulsifiers on the thermal behaviour of this fat blend has also not been investigated  
103 previously, and the effect of chain length and hydrophobicity of the head is interesting and  
104 useful for the scientific community as it is likely to have an impact upon  
105 the microstructure of ice cream. Our hypothesis is that Tween 80 interferes with the fat  
106 crystallisation (due to the unsaturated carbon chain and large hydrophilic head), whereas  
107 MDGs co-crystallise with the fat (due to the structural homogeneity with the bulk fat),  
108 favouring its crystallisation.

109  
110 The results are likely to have many applications in the ice cream industry. This fat blend is an  
111 economic substitute to milk fat as it mimics milk fat it in terms of partial coalescence,  
112 meltdown behaviour and flavour.

113

## 114 **2. Material and methods**

### 115 *2.1 Materials*

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

### 123 *2.2 Preparation of the fat-emulsifier blends*

124 The fat blend used was a blend of coconut oil 75% and sunflower oil 25% (bulk fat).  
125 Emulsifiers, Tween 80 and MDGs were dispersed at different ratios (emulsifier / bulk fat of  
126 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  
127 at 80 °C for approximately 20 minutes, until a homogeneous sample was obtained.

### 128 *2.3 Differential Scanning Calorimetry*

129 The effect of the emulsifiers on the thermal behaviour of the bulk fat used was determined  
130 using differential scanning calorimetry (DSC), a Perkin Elmer DSC Series 7 (UK), with  
131 thermal analysis software (Pyris). Nitrogen was used as a purge gas, at a flow rate of 30  
132 ml/min. The thermal behaviour of MDGs was also measured. The samples (8-10  $\mu\text{g}$ ) were  
133 loaded into Perkin Elmer 40  $\mu\text{l}$  capacity aluminium pans, and sealed with aluminium covers;  
134 an empty pan was used as a reference. The following thermal program was used: holding  
135 isothermally at 70  $^{\circ}\text{C}$  for 10 min, cooling from 70  $^{\circ}\text{C}$  to -30  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  and then heating  
136 from -30  $^{\circ}\text{C}$  to 70  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$ . The  $\Delta\text{H}$  (J/g) was calculated using the thermal analysis  
137 software (Pyris). The DSC scans shown in all figures have been normalised according to  
138 total mass and mass of crystalline material (i.e. amount of coconut oil and MDGs). In order to  
139 determine if the  $\Delta\text{H}$  (J/g) of crystallisation and melting of MDGs were independent from  
140 those of the bulk fat, predicted (theoretical  $\Delta\text{H}$  according to the mass of crystallising  
141 material) and experimental enthalpies for samples containing different MDGs to bulk fat  
142 ratios were determined.

### 143 **3. Results**

144

#### 145 *3.1 Thermal behaviour of the bulk fat in presence of MDGs*

146

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

150

151 As can be observed, on cooling the bulk fat crystallised in two peaks, the first at  $\sim -5.5$   $^{\circ}\text{C}$  and  
152 the second at  $\sim -16.5$   $^{\circ}\text{C}$  (see **1** and **2** in Fig. 1) and on heating it began to melt at  $\sim 6$   $^{\circ}\text{C}$ , with  
153 the main peak at  $\sim 19$   $^{\circ}\text{C}$  (see Fig. 2). Very similar results were obtained by Tan and Che Man  
154 (2002) who studied the thermal behaviour of coconut oil with DSC using the same scan rate.  
155 Our melting and crystallisation peaks are slightly lower due to the effect that the liquid oil has  
156 on the crystallisation of solid fat, a phenomenon that is well known (Norton *et al.*, 2009). We  
157 can assume that the two crystallisation peaks and the presence of a shoulder in the melting  
158 curve is due to the presence of two different TAGs, a higher and a lower melting fraction,  
159 where the higher fraction exhibits slower melting and more rapid crystallisation (Tan & Che  
160 Man, 2002). The MDGs melted between  $\sim 50$   $^{\circ}\text{C}$  and  $\sim 60$   $^{\circ}\text{C}$  and crystallised between  $\sim 40$   $^{\circ}\text{C}$   
161 and  $\sim 53$   $^{\circ}\text{C}$  (see Fig. 1 and 2), thus at higher temperatures than the bulk fat.

162

163 The thermal behaviour of the bulk fat changed with the addition of different quantities of  
164 MDGs. In the crystallisation curves (see Fig. 1) the two exothermal peaks of the bulk fat were  
165 replaced by a single peak at around  $\sim 0$ - $5$   $^{\circ}\text{C}$ . Moreover, with the addition of greater quantities  
166 of MDGs a second peak appears on both melting and crystallisation, one in the position of the  
167 bulk fat peak (see 'A' in Fig. 1 and 2), and the other at a higher temperature representative of  
168 the MDGs ( $\sim 35$ - $50$   $^{\circ}\text{C}$  for the crystallisation and  $\sim 40$ - $57$   $^{\circ}\text{C}$  for the melting thermograms; see  
169 'B' in Fig. 1 and 2). The melting and crystallisation peaks in position 'B' (see Fig. 3B)  
170 shifted to higher temperature with the addition of MDGs (logarithmic  $R^2 = 0.97$  and  $0.93$  for



171 melting and crystallisation, respectively). However, the peak temperatures were always lower  
172 than the MDGs alone, probably due to the effect that the sunflower oil exerted on it.

173

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

179

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

190

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

204

205 MDGs are currently used in the ice cream production. In addition to providing understanding  
206 of the effect of this emulsifier on the thermal behaviour of the bulk fat, is useful in the  
207 context of ice cream production: with the addition on MDGs the fat crystallisation occurs  
208 earlier, so the fat will be completely crystallised by the end of the commercial freezing  
209 process ( $\sim 5$  °C to  $-8$  °C). Earlier crystallisation enhances the destabilisation phenomenon. It is  
210 likely that the fat droplets would have then large protruding crystals, which would easily  
211 interact with other crystals giving rise to the partial coalescence of the droplets. Partial  
212 coalescence is in turn important because it contributes to some of the characteristics of the  
213 final product, such as the speed of melting, the degree of shape retention during melting and

214 smoothness during consumption (Hartel & Goff, 2013). The effect of MDGs on the thermal  
215 behaviour and structure of ice cream would be an interesting area for future research.

216

### 217 *3.2 Thermal behaviour of the bulk fat in presence of Tween 80*

218

219 In this section the effect of the addition of Tween 80 on thermal behaviour of the bulk fat  
220 (specifically the shape of the melting and crystallisation peaks, peak temperature and  
221 enthalpy) will be discussed.

222 Figures 7 and 8 show the thermal behaviour of the bulk fat with the addition of increasing  
223 amounts of Tween 80. As can be seen the general shape of the curves (i.e. two peaks) does  
224 not change with the addition of Tween 80. However, increasing the ratio of Tween 80 to bulk  
225 fat, the exothermic and endothermic energy of melting and crystallisation does differ. As can  
226 be seen in Figure 9 increasing the amount of Tween 80 decreased the amount of energy  
227 required to melt the fat (linear  $R^2 = 0.83$  indicating a strong relationship between Tween to  
228 bulk fat ratio and  $\Delta H$ ) and increased the amount of energy released during crystallisation  
229 (linear  $R^2 = 0.74$  indicating a strong relationship between Tween to bulk fat ratio and  $\Delta H$ ).

230

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

250

## 251 **5. Conclusion**

252

253 Both the emulsifiers investigated have an effect on the melting and crystallisation of the bulk  
254 fat. MDGs melt and crystallise independently from the bulk fat, but have an effect on its  
255 thermal behaviour, acting as templates for the crystallisation of the bulk fat. Tween 80 acts as  
256 an impurity, leading to the formation of less perfect crystals in the bulk fat. As this work has  
257 relevance due to the use of both the bulk fat blend and the emulsifiers in the production of ice

258 cream, future work should consider the effect of these emulsifiers on the thermal behaviour  
259 of an emulsified system, to determine the effect of additional ingredients (such as water and  
260 sugar) and consider interfacial effects. Further investigations should take into account their  
261 effect on the final ice cream product, in terms of fat destabilisation, meltdown properties,  
262 texture and sensory perception.

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336

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

338

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

341

342 **Fig. 3** Crystallisation and melting peak maximums in position **A** (A) and **B** (B) (see Fig. 1 and 2) as a function  
343 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  
344 of 10 °C/min. Error bars represent one standard deviation of the mean of six measurements.

345

346 **Fig. 4** Predicted and experimental  $\Delta H$ 's of the melting and crystallisation peaks in position **B** (see Fig. 1 and 2)  
347 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  
348 a scan rate of 10 °C/min. Error bars show the standard deviation of six measurements.

349

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

353

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

356

357 **Fig. 7** Thermal behaviour of bulk fat and different ratios Tween 80 to bulk fat during cooling from 70 °C to -30  
358 °C at a scan rate of 10 °C/min.

359

360 **Fig. 8** Thermal behaviour of bulk fat and different ratios Tween 80 to bulk fat during heating from -30 °C to 70  
361 °C at a scan rate of 10 °C/min

362

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

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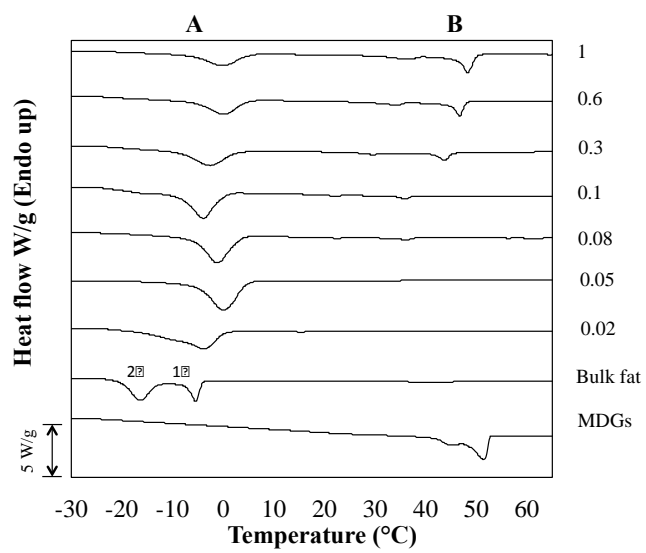
373 **Industrial Relevance**

374

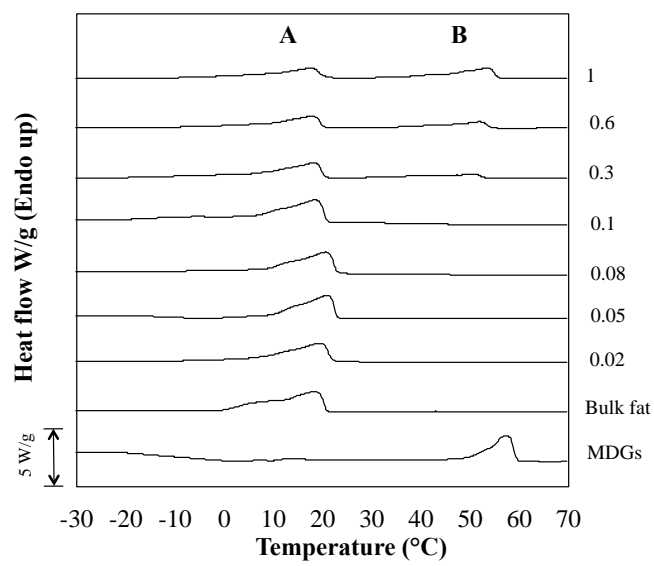
375 The fat blend studied in this work is a possible economic substitute for milk fat in the production of  
376 ice cream as it mimics milk fat in terms of partial coalescence, meltdown behaviour and flavour. As a  
377 consequence it is likely to be extensively used for this aim in the future. Studying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

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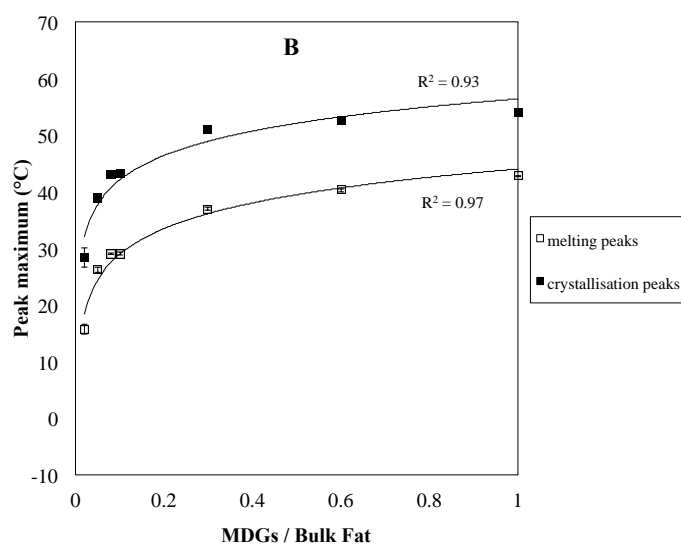
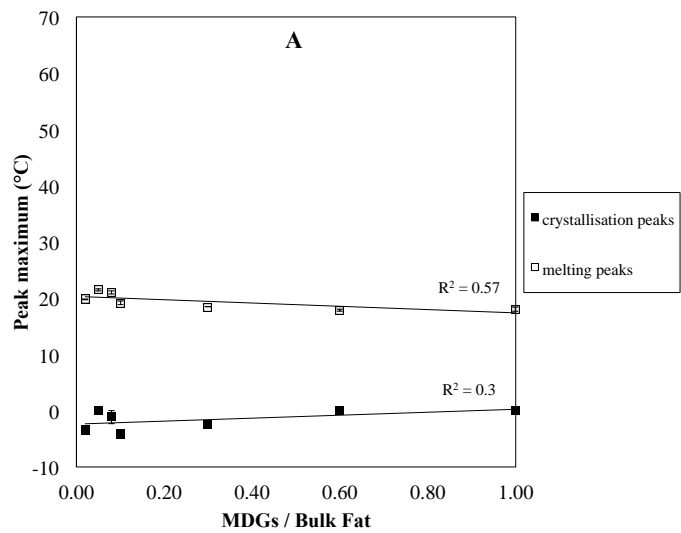


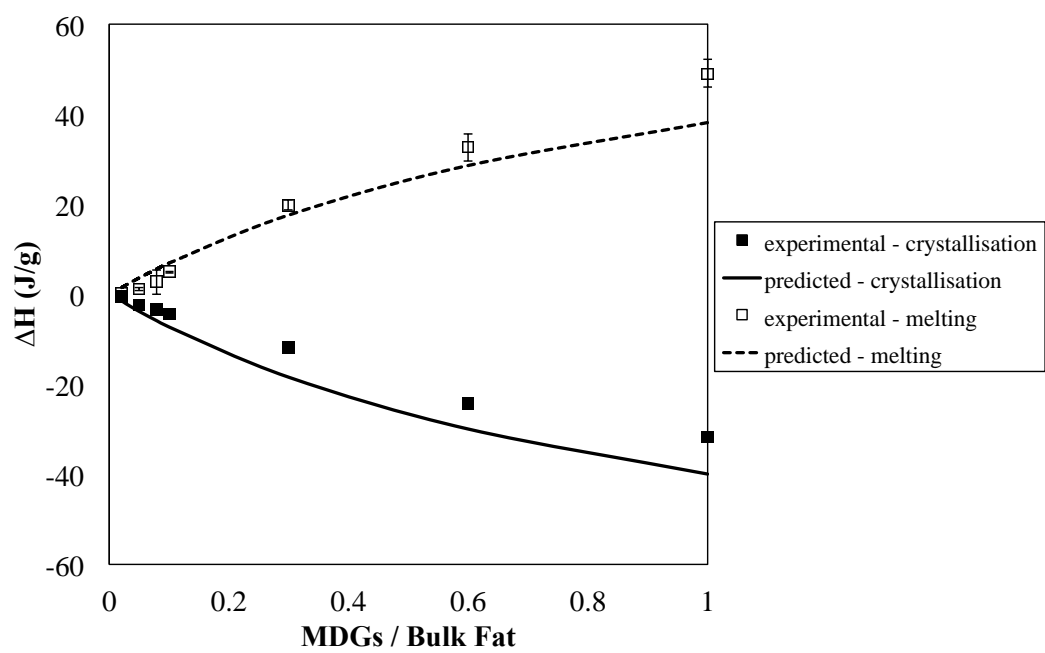
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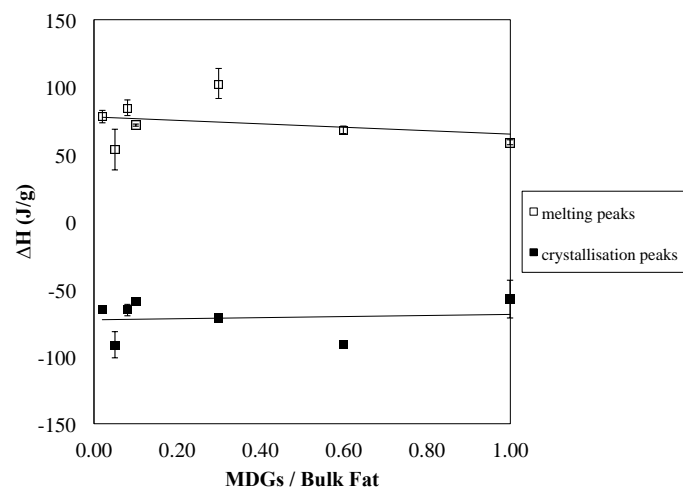


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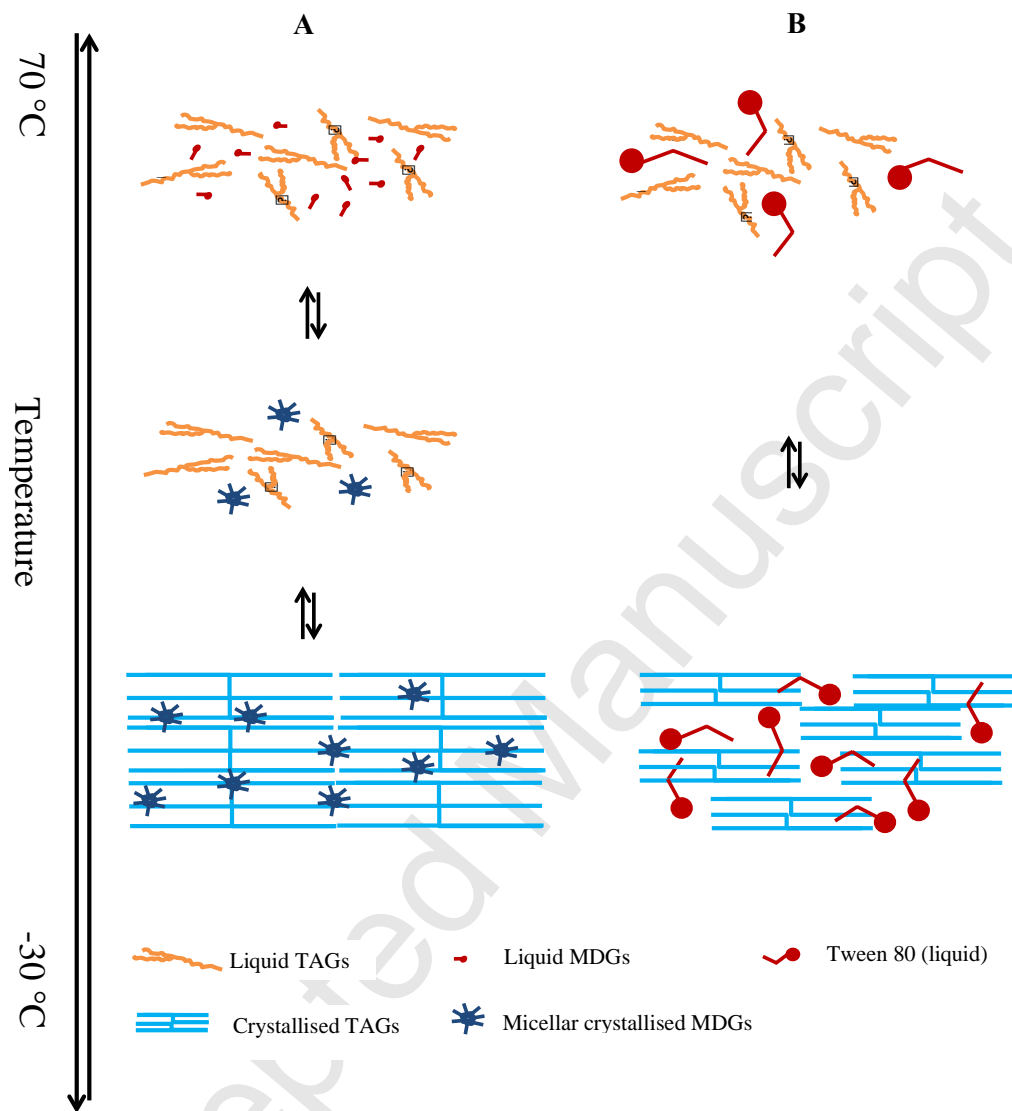


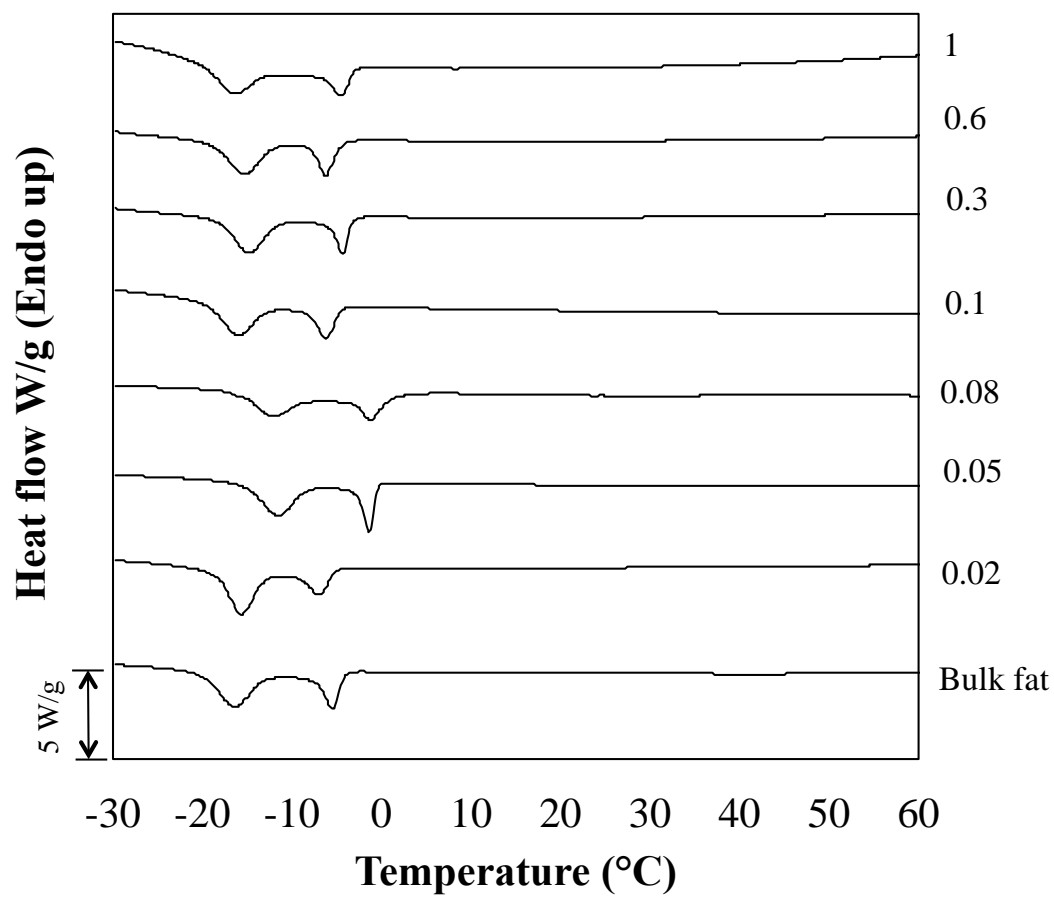


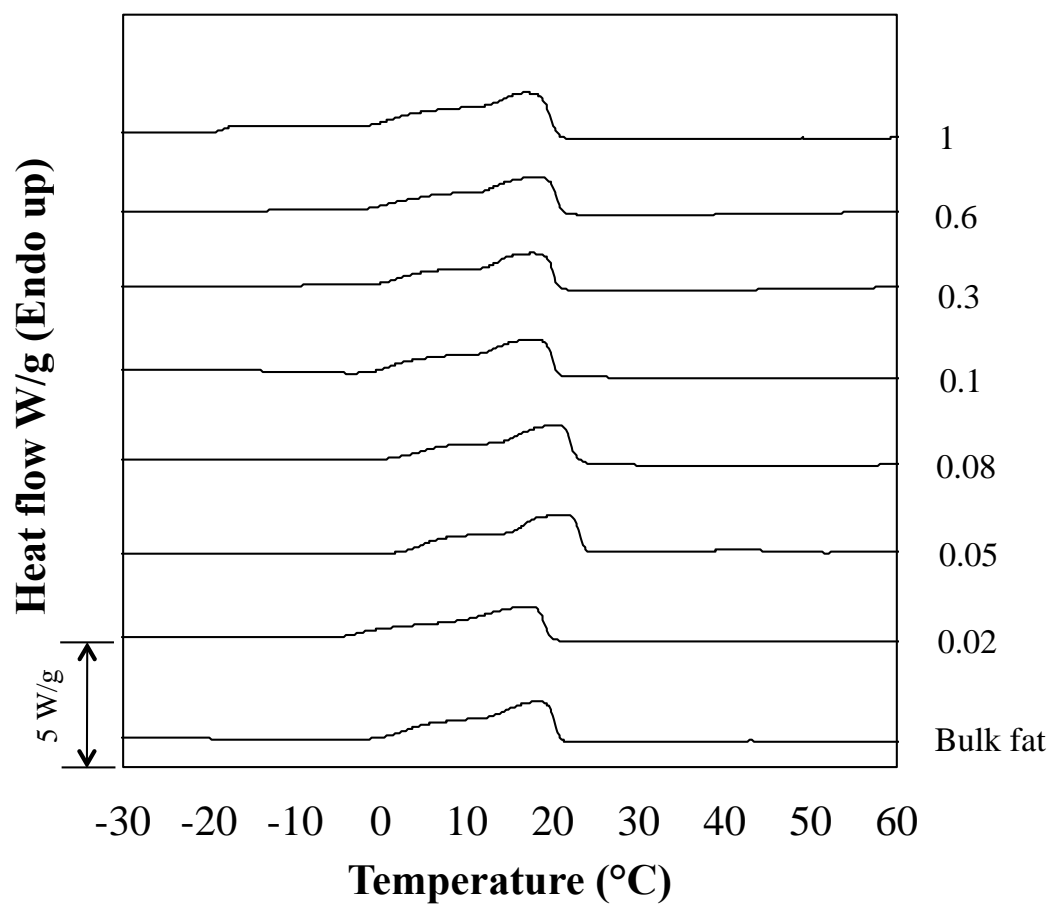




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