PARTIAL COALESCENCE IN OIL-IN-WATER EMULSIONS

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PARTIAL COALESCENCE IN OIL-IN-WATER EMULSIONS

Proefschrift

ter verkrijging van de graad van
doctor in de landbouw- en milieuwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
op woensdag 5 februari 1992
des namiddags te vier uur in de aula
van de Landbouwuniversiteit te Wageningen

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Stellingen

1. Men realiseert zich veel te weinig dat coalescentie in eetbare emulsies van gering belang is, terwijl partiële coalescentie daarin juist een prominente rol kan vervullen.

2. De term "rebodying" is ongelukkig gekozen, daar partiële coalescentie een duidelijker karakteristiek gevolg is van deze temperatuurswisselingen dan de, in sommige gevallen eveneens waargenomen, stevigheidstoename.
   Dit proefschrift.

3. Het gemak waarmee de term deegontwikkeling wordt gebruikt, zonder dat de betekenis ervan precies duidelijk is, geeft aan hoe empirisch het bakkerij-onderzoek nog altijd is.
   Dexter, J.E.; Kilborn, R.H.; Preston, K.R.; Cereal Chemistry 67 (1990) 46.

4. Het is verheugend dat analytisch chemici zich nu af gaan vragen wat de betekenis is van de door hen bepaalde moleculaire en microscopische structuren voor de eigenschappen van het onderzochte materiaal.
   Galan, L. de; Chemisch Magazine september 1991 blz 518.

5. Zolang Rogers et al. geen duidelijke correlatie kunnen aantonen tussen hun instrumentele test en sensorische waarnemingen, lijkt het nut van die test gering.
   Rogers, D.E.; Doescher, L.C.; Hoseney, R.C.; Cereal Chemistry 67 (1990) 188.

6. Het optreden van kristallisatie in onderkoelde emulsiedruppels tengevolge van de aanwezigheid van volledig gekristalliseerde druppels, zoals waargenomen door Mc Clements et al., moet zijn veroorzaakt door uitstekende kristallen in de vaste deeltjes die de onderkoelde druppels raken.
   McClements, D.J.; Dickinson, E.; Povey, M.J.W.; Chemical Physics Letters 172 (1990) 449.

7. De aanduiding "appellation d'origine contrôlée" op het etiket van een fles wijn geeft slechts garantie omtrent de herkomst en is geenszins een waarborg voor goede kwaliteit.

8. Hoewel het de overzichtelijkheid niet ten goede komt, is er toch veel voor te zeggen om de auteur van een proefschrift te vermelden boven het dankwoord en allen die in het dankwoord genoemd worden als auteurs van het proefschrift.

9. Het zou de sport (en de gezondheid van de sporters) ten goede komen indien voetballers, net als de leden van de Nederlandse Golf Federatie, met goed gevolg een examen "omgangsvormen" zouden dienen af te leggen alvorens te worden toegelaten tot de competitie.

Stellingen horende bij het proefschrift 'Partial Coalescence in oil-in-water emulsions' van Karin Boode.

VOOR YVES

ABSTRACT

Boode-Boissevain, K. (1992). Partial coalescence in oil-in-water emulsions. Ph.D. Thesis, Wageningen Agricultural University (159 pp, English and Dutch summaries).

The influence of crystals on the stability against partial coalescence at rest and during Couette flow was examined in emulsions of saturated triglycerides in SDS- or caseinate solutions and in natural cream. Partial coalescence was characterized by determining changes in globule size distribution and fat content. In the absence of crystals emulsions were stable at rest and in Couette flow.

At rest partially crystallized emulsions remained stable unless numerous large fat crystals were present or a temperature cycle was applied (= rebodying process). A theory was developed to explain this temperature controled phenomenon.

In Couette flow considerable partial coalescence was observed if the fat network inside the globules was continuous. Due to a lack of liquid oil crystals were sticking out of the globule further, thereby increasing aggregation. Aggregation could be nullified within a few hours after clumping by changing the wetting properties, so that the fat crystals became preferentially wetted by the aqueous phase. Deaggregation could occur also in a flow field if the solid fat fraction had exceeded the optimum, which depended mainly on the properties of the fat and on the velocity gradient applied.

A theoretical model was developed that accurately describes the course of the partial coalescence process up to the point where most of the fat creamed out of the emulsion, when warming it. The model is based on Smoluchowski's frequency equation and distinguishes between singlets and clumps with and without crystals. From the model it was deduced that the kind of fat, the solid fat content and the number of globules that contains crystals are the main factors that determine the instability of the emulsion globules.

Free descriptors: partial coalescence, coalescence, clumping, aggregation, Brownian motion, Couette flow, emulsion stability, cream, contact angle, fat crystallisation, aggregation kinetics, permeability, rebodying, triglycerides.

Woord vooraf

Wanneer slechts diegenen die een wezenlijke bijdrage hebben geleverd aan dit proefschrift aan de auteurslijst zouden worden toegevoegd dan zou deze lijst niet te overzien zijn. En dan noem ik nog lang niet iedereen die mij met raad en daad terzijde stond. Allen ben ik dank verschuldigd.

Pieter Walstra, jouw enorme kennis op ieder gebied dat ter sprake is geweest heeft grote indruk op mij gemaakt.

Iain Campbell, thank you for all the help you gave me. Our debats have always been very stimulating for me. I have met a dear friend.

Alle leden van de sektie Zuivel en Levensmiddelennatuurkunde ben ik dank verschuldigd voor de goede samenwerking, die onder alle omstandigheden een prettige basis is geweest. In het bijzonder wil ik Aliza de Groot, Mies de Haan, Henk van der Stege en Hugo Stempher noemen waar ik altijd terecht kon met een vraag of gewoon voor een praatje.

De studenten Chris Bisperink, Christel Keetels en Hette Bouma, alsmede de stagaires Marianne van Hal en Ron Slijster wil ik bedanken voor de bijdrage die zij leverden en voor de prettige samenwerking.

Unilever Research ben ik niet alleen dank verschuldigd voor de financiële ondersteuning van het onderzoek, maar ook voor de begeleiding. Met name Emmy Lucassen-Reijnders en Jan Benjamins waren een geweldige steun.

Het LEB-fonds wil ik bedanken voor haar financiële steun bij de afronding van dit proefschrift.

Ook Piet Quartel en Mari van der Giessen dank ik hartelijk voor de medewerking en de waardevolle suggesties, die de layout veel goed hebben gedaan.

Ook buiten de Landbouwuniversiteit zijn experimenten uitgevoerd. Mijn dank gaat uit naar Jan Baars van het ITAL voor de hulp bij het maken van de capillairen en naar Jan Klok en Peter van Mil (NIZO) voor de gastvrijheid en de hulp bij de bediening van de Malvern Particle Sizer.

CONTENTS

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1 OBJECTIVES AND MOTIVATION

The present study deals with the stability to coalescence of oil-in-water emulsions, in which part of the oil is crystallized. Many processes are known in which the stability of an emulsion is influenced by the presence of fat crystals. For example, the churning of cream to produce butter is impossible without crystals in the oil phase [10] and according to Berger & White [1] fat crystals are necessary for clumping of fat globules in ice-cream. During storage and transport, on the other hand, emulsions should remain stable. Control of the aggregation process is, therefore, a necessity and a basic understanding of the principles that underlie destabilisation of emulsions, caused by fat crystals, is required. Several workers have studied coalescence in partially crystallized emulsions. Labuschagne [7] studied the possibility of churning in the absence of air. Darling [5] worked on the instability of dairy creams. Van Boekel [2] investigated the influence of crystals in the oil phase on the stability of paraffin-in-water emulsions that were stable in the absence of crystals. Melsen [9] studied the stability of milk fat emulsions, in which the fat was recombined in skim milk or whey. Recently, Mc Clements et al. [8] reported on the behaviour of hydrocarbon emulsions containing a mixture of solid and liquid globules.

The above mentioned investigations have clearly shown that the course of the aggregation process and the rate at which coalescence occurs depends on the type of emulsion present. The crystals play a key role in it. Therefore, the objective of the present study was to investigate the effect of fat crystal properties on emulsion stability and to gain a more fundamental understanding of the variables that influence these properties. Special attention was paid to the kinetics of the process in an attempt to better differentiate between factors

that influence emulsion stability by their effect on the number of encounters (e.g. globule size and velocity gradient) and factors that change emulsion stability by causing a change in the efficiency of encounters (e.g. type of fat and fat crystal size).

2 DESTABILIZATION OF O/W EMULSIONS BY PARTIAL COALESCENCE.

2.1. Mechanism

An oil-in-water emulsion is a dispersion of oil globules in an aqueous solution. One of the processes that may occur in such a system is the rupture of the film between two approaching globules resulting in the merging of the globules. This is called coalescence. When crystals are present in the oil phase coalescence may be incomplete in the sence that the globules do not flow together completely, because a crystal structure prevents this. Instead, clumps of irregular size and shape are formed [10]. This process is called partial coalescence.

Partial coalescence is a form of aggregation that exhibits some important differences as compared to true coalescence of liquid globules [2, 7, 9]:

- Due to the irregular form of the aggregates, the viscosity of the emulsion may increase.
- The aggregation can go on until a continuous network is formed throughout the volume, thus giving the product solid properties (yield stress) and immobilizing other particles (e.g. air cells) present.
- The rate of aggregation greatly depends on agitation (i.e. velocity gradients in the liquid); the rate may be increased by e.g. a factor 11^6, while liquid droplets rarely show an appreciable dependence of coalescence on G.
- Under many conditions (in a cream layer, during flow or other agitation) the stability to partial coalescence is orders of magnitude smaller than would be the case for true coalscence (the globules containing no crystals). The most probable explanation is

that crystals, protruding from the O/W interface, pierce the thin aqueous film between closely approaching globules [3]. The film, that would have remained stable in the absence of crystals, ruptures and the globules will partially coalesce (figure 1-1).

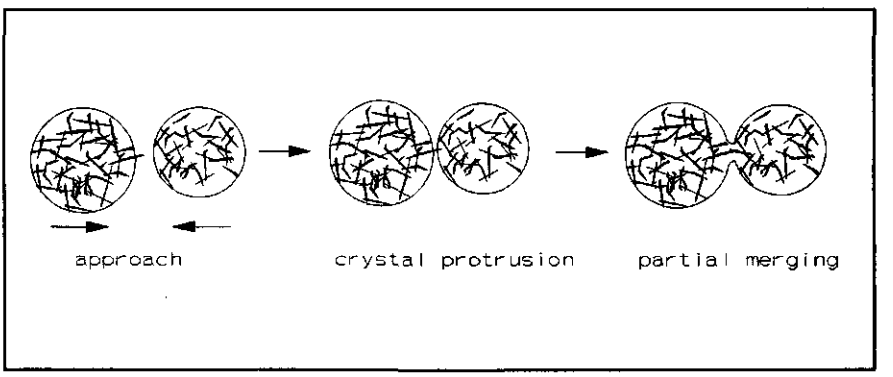
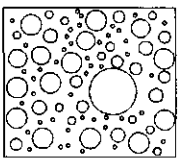


Figure 1-1. Partial coalescence of two fat globules (highly schematic).

2.2 Kinetics

The general problem of predicting the globule size distribution changes with time in suspensions and emulsions has been studied by many authors in various areas [11, 12, 13, 14]. In partially crystallized O/W emulsions the problem, however, is more complicated, since next to the encounter frequency aggregation depends on the properties of the fat crystals. For example, larger crystals may cause greater instability in a further unaltered emulsion. It is, therefore, not surprising that partial coalescence may occur in several ways. Figure 1-2 gives examples of the various types that have been observed. It clearly shows that in most cases a fat layer is produced. Consequently, description of the changes in globule size distribution, solely, is insufficient to describe the process. The course of the partial coalescence process can only be described accurately with the combination of changes in the globule size distribution and the total fat content.

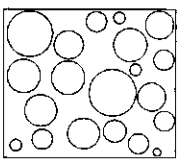
t = 0 min



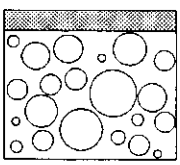
The experiments were all carried out with emulsions with some spread in globule size. Emulsions were warmed to 45°C before globule size distributions were determined. In this way spherical globules were obtained in all cases.

Figure 1-2.

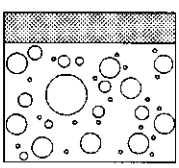
t = 30 min



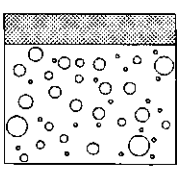
Type A: The fat globules that participate in partial coalescence form irregularly shaped clumps. On warming, an emulsion is obtained with globules larger than at the beginning of the experiment.
Example: paraffin mixture in PVA solutions [2].



Type B: In some instances the clumps become so large that they cream out of the emulsion when it is warmed. The remaining fat globules are larger than the original ones.
Example: natural cream [7].



Type C: Some fat globules participate in rapid partial coalescence, leading to clumps creaming out of the emulsion, while the remaining fat globules show an unaltered size distribution.
Example: milk fat in whey protein solutions [7].



Type D: As in types B and C, large clumps are formed that cream out of the emulsion on heating. This time, however, the remaining emulsion does show an altered size distribution with smaller globules [4].
Example: saturated triglycerides in SDS solutions.

Figure 1-2 Various types of partial coalescence (highly schematic). In some instances type A changes into type B in the course of the process, and similarly types C and D.

3 OUTLINE OF THIS THESIS

This thesis consists of five parts, that have already been published or will be published in the near future. The purpose of this study was to investigate the role of fat crystals in O/W emulsions. Most attention was directed to model systems of saturated triglycerides in solutions of SDS or caseinate.

Chapter 2 deals with thickening of O/W emulsions, caused by temperature cycling (this is called the rebodying process [6]). This process is well known for natural cream, but it is clearly shown that the same phenomena are valid for model systems as well. A theory is developped to explain the observed thickening. Fat crystallization appears to play a key role.

Chapters 3 and 4 are about the various ways in which partial coalescence can occur and the role of the fat crystals in it. Special emphasis is given to the properties of the fat. To that end measurements have been done on the bulk fat and on the emulsified fat globules.

In chapters 5 and 6 a kinetic model is presented that describes the course of the partial coalescence process up to the point where too much fat creams upon warming of the emulsion. The influence of various parameters has been investigated. Experimental results are compared to model calculations.

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DESTABILIZATION OF O/W EMULSIONS CONTAINING FAT CRYSTALS BY TEMPERATURE CYCLING.

ABSTRACT

The behaviour of model triglyceride oil in water emulsions during and after a temperature cycle was studied. As a surfactant either SDS or a protein was used. The behaviour appeared to be the same as in the case of (recombined) cream. The emulsions, though stable during storage at 5°C, exhibit considerable thickening when warmed to a temperature where most of the fat was melted and subsequently cooled again. From the results of microscopic observations, determination of the change in the globule size, and observations on the effect of dilution with deflocculating agents it was concluded that partial coalescence is the cause of thickening.

A theory is developed to explain the role of the fat crystals. Nucleation plays a key role. It appeared essential that the temperature treatment causes significant changes in the state of crystallization of the fat, without fully melting it.

Boode K., Bisperink C., Walstra P.; submitted for publication in Colloids and Surfaces.

DESTABILIZATION OF O/W EMULSIONS CONTAINING FAT CRYSTALS BY TEMPERATURE CYCLING.

1 INTRODUCTION

The presence of fat crystals in the oil can cause a considerable decrease in the stability of oil-in-water emulsions. The reason is that fat crystals may stick out into the water phase and if such a crystal is present in the film between approaching globules it may pierce the film, causing the globules to coalesce. The solid fat fraction prevents rearrangement to the spherical shape, so that the globules form weirdly shaped clumps, in which remnants of the original globules still can be distinguished. This process has been called partial coalescence and it has been particularly studied by van Boekel [1] and Melsen [11]. Generally and up to a certain limit, the higher the amount of crystals present the less stable the emulsion. An explanation for the influence of a higher solid fat fraction may be that more globules contain protruding crystals, while crystals also may stick out further if there are more crystals in the oil droplet, or if the crystals are larger. Attempts of van Boekel [1] to obtain smaller crystals *in the globules by cooling the emulsion very quick in ice water were unsuccessful.* The crystals had the same appearance under the microscope as when cooled in the normal way. Moreover, some stirring was inevitable when rapidly cooling a large amount of emulsion, and this caused instability.

In dairy science, a temperature treatment that results in aggregation of the oil globules in natural cream has been known since as long ago as 1932 [7]. This process may take several forms, but the essential features are:

- cooling the cream to 5 °C (figure 2-1,I)
- keeping it at that temperature for at least 2 hours (for maximum effect) (figure 2-1,II)

- warming the cream to 30 °C (T_{max}) (figure 2-1,III)
- keeping the cream at 30 °C for some time (figure 2-1,IV)
- cooling to 5 °C (figure 2-1,V)
- aging (figure 2-1,VI)

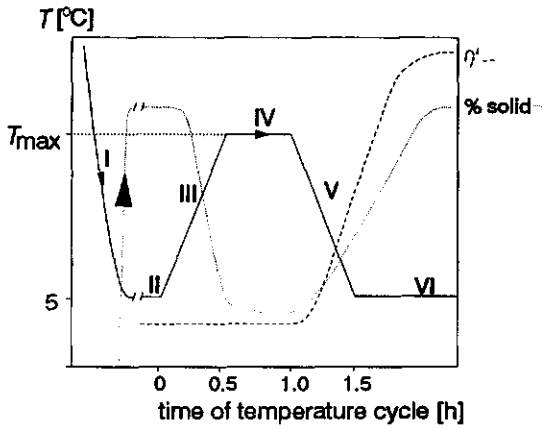

Figure 2-1. Rebodying effect. (——) temperature cycle, (----) apparent viscosity, as measured at 5°C (·····) % of the fat being solid.

In cream of 30% fat or more, tempering (i.e. a short term for temperature cycling) in this way can cause a very thick and plastic consistency to develop; this effect has been called rebodying. It is nullified by heating the cream above 40°C, but it can be induced anew. Commercially available UHT-cream, stored at ambient temperature, shows this rebodying effect if the storage temperature fluctuates. Recombined cream made of skim milk and butter fat with phospholipids dissolved in it, shows this viscosity effect in the same way as does cream. Recombined cream without phospholipids added to the fat can not be "rebodied" [8, 13]. We consider it very likely that neck-plug formation in cream liqueurs during temperature cycling [5] is the same phenomenon.

Several authors have attempted in vain to explain the rebodying process:

Hening & Dahlberg [7] said that the rebodying effect could be caused by what they call clumping of the milk fat globules, because the rebodying effect more or less disappears

when warming the sample to room temperature. This explanation was contradicted by the fact that micrographs of the treated samples did not show more or bigger clumps than the untreated ones. According to the authors the rebodying effect could also be caused by protein adsorption or hydration, but they did not explain how. Wiese et al. [25] came to the conclusion that the material in the surface layer of the milk fat globule and the composition of the milk fat play an important role in the rebodying process. They were, however, not able to give any further explanation.

Sommer [15] hypothesised that the temperature treatment during the rebodying process causes reorientation of the molecules in the milk fat globule and at its interface. He argued that upon warming the cream from 5°C to 30°C the lower melting triglycerides will melt first. The situation now is one of a continuous liquid phase of low melting triglycerides with the unmelted triglycerides in suspension. Since the lower melting triglycerides contain (per unit mass) more polar groups than higher melting triglycerides, he suggested that relatively more lower melting triglycerides will be lodged at the O/W interface. After a temperature treatment, the polar groups at the interface will dominate as compared to the O/W interface after merely cooling from the totally liquified state to a low temperature. The increased surface forces somehow cause adsorption which favours the cohesion of the globules. The effect of phospholipids in the fat phase on the response to the temperature treatment was explained by the same effect of the polar groups. However, the proportion of polar groups in triglycerides or other largely non-polar lipids has never been shown to correlate with their surface activity; contrariwise, factors like the possible chain packing density seem to predominate (for instance, stearic acid is much more surface active than either oleic acid or myristic acid). In itself, this invalidates Sommer's ideas, but some other statements neither fit with what is known about surface chemistry.

From earlier experiments [8] we have indications that if recombined cream with phospholipids dissolved in the oil phase is tempered, partial coalescence is the type of aggregation. In natural cream, on the other hand, clumping could not clearly be detected. This paper deals with the mechanism whereby a temperature cycle leads to aggregation of

the emulsion globules and the role of the fat crystals in it.

2 MATERIALS AND METHODS

2.1 Materials

Cream was obtained by centrifuging fresh cows' milk at 40°C to the desired fat content. To inactivate lipase it was heated for 15 min at 70 °C.

Skim milk was obtained by centrifuging fresh cows' milk at 40°C to a fat content of 0.07%. To inactivate lipase it was heated for at least 10 min at 64°C.

Sodium caseinate was prepared from fresh skim milk by repeated precipitation with hydrochloric acid and redispersion in weak NaOH (to pH 6.7). Afterwards it was spray-dried. It was used in 1% solutions.

Sodium dodecyl sulphate (SDS), was obtained from BDH chemicals, England; its grade was specially pure. The critical micelle concentration (CMC) in water is 0.23% at 20°C [4]. It was used in concentrations of 0.4%, unless stated otherwise.

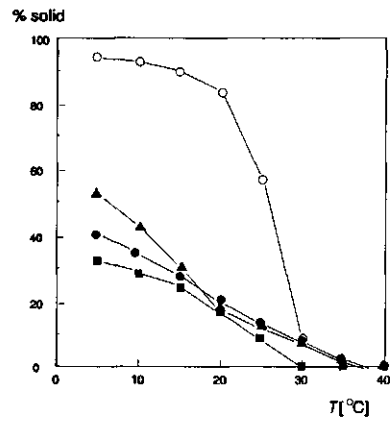

Figure 2-2. Solid fat content of several fat blends as a function of temperature.

(●): blend A (○): blend B (▲): milk fat (■): mixture of solid and liquid paraffin oil.

Anhydrous milk fat (> 99.8% pure fat, < 0.1% water) was stored at 7°C in sealed tins. The fat was fully melted before use.

Paraffin oil was obtained from OPG, Utrecht, The Netherlands. Viscosity 60 - 80 mPa.s; density about 860 kg m^{-3}. Solid paraffin was obtained from Merck A.G., Darmstadt, W-Germany. It had an apparent melting point of 42 - 44°C and a density of about 880 kg m^{-3}. Both paraffins were mixed in different ratios, which are indicated in the text.

The triglyceride blends A and B were kindly supplied by Unilever Research, Vlaardingen, The Netherlands. Both blends contained about 96.9% triglycerides, 3.0% diglycerides and 0.1% monoglycerides. The melting curves of the above mentioned fats are depicted in figure 2-2. The liquid fractions of both fat blends were obtained by fractionation at 5°C.

Tristearin was also obtained from Unilever Research, Vlaardingen, The Netherlands. It had a melting point of 69°C, somewhat below the pure compound's melting point of 72°C.

Soy lecithin was obtained in powder form from Du Lectin-Van Schuppen, containing 97% phospholipids; The powder (0.7%) was dispersed in the milk fat, in which it was well dispersible.

2.2 Emulsification.

Oil-in-water emulsions were made by mixing fat (oil) and surfactant solution at 60°C in the inlet vessel of a Rannie laboratory homogenizer (capacity 100 l/h), while stirring. The mixture (1l) was then homogenized at a homogenization pressure of 4 bar, circulating the emulsion for 20 minutes, cautiously avoiding any uptake of air. Fairly narrow globule size distributions are obtained in this way, the surface-weighted relative standard deviation c_s [19] being about 0.5; the volume surface average droplet diameter, d_{vs}, was about 2.5 μm.

2.3 Pretreatment of the O/W emulsions.

All emulsions were stored at least overnight at 4°C to ensure crystallization of fat in all globules [23]. Storage was shorter than a week so that bacterial spoilage was avoided. Creaming and subsequent partial coalescence were prevented by storing the emulsion in slowly rotating cylinders, end over end, under exclusion of air. The droplet size distribution was found not to change during storage.

2.4 Characterization of the emulsion.

For the characterization emulsions were split. In one part the amount of fat that was crystallized was estimated by wide-line proton pulse-NMR [2] and the appearance of fat crystals in the oil globules was observed by polarized light microscopy. Four different crystal habits were distinguished, in analogy with milk fat globules [18]: figure 2-3.

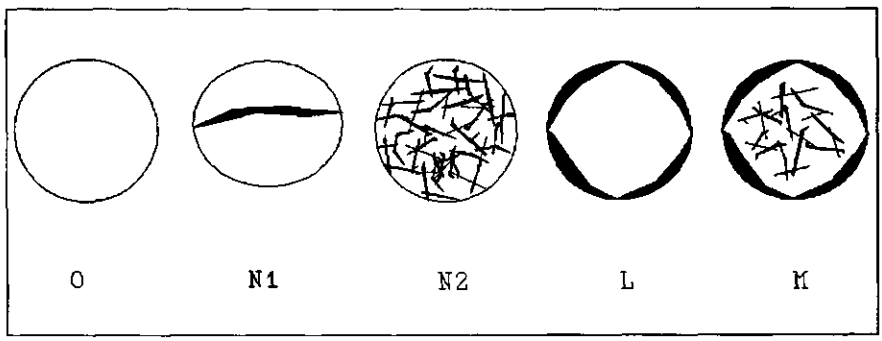

Figure 2-3. Habit of emulsion droplets containing fat crystals, as observed by polarized light microscopy. Modified after Walstra [18].

In the O type crystals are absent or too small to be visible. In the N type "needles" are seen, although in fact, most crystals are elongated platelets. In the L type crystals are tangentially oriented near the droplet boundary. The M type has the characteristics of both L and N types.

The other part of the emulsion was diluted with 5% solution A (a solution of 0.375% disodium ethylene diamine tetraacetate (EDTA) and 0.125% polyoxyethylene sorbitan monolaurate in water, adjusted to pH 10 with NaOH) to prevent globules from flocculation and heated (1 hour, 45°C) in a cylinder (of 0.15 m in height) to turn any clumps into (fully liquid) globules. Big aggregates (diameter > approximately 10 μm) cream, causing the separation of an oil layer on top of the emulsion. After removal of the oil layer, the fat content in the remaining emulsion was estimated by wide-line proton pulse-NMR [2] and the globule size distribution was determined by a spectroturbidimetric method [17, 19, 24]. For this purpose the emulsion was further diluted to a fat content of approximately 2% with

solution A.

In some cases emulsions were diluted with water or a solution of SDS (0.1 or 1%). If so, this is indicated in the text.

2.5 Couette flow.

Some O/W emulsions were subjected to Couette flow, i.e. flow between two concentric cylinders of which the outer one rotated and the inner one was fixed. The rate of rotation was about 100 s^{-1}, so that laminar flow developed [3]. After 30 minutes of rotation the apparatus was emptied and the samples were characterized as described in section 2.4.

2.6 Tempering.

Emulsions were stored at 5°C to ensure crystallization in all fat globules. Emulsions were carefully poured into test tubes. They were placed in a Haake D8 water bath at 5°C. With a Haake programming unit, PG20, connected to the water bath, temperature cycles were carried out. Each temperature cycle (figure 2-1) consist of warming of the emulsion from 5°C to T_{max} at a rate of 1°C min^{-1}, keeping the emulsion at T_{max} for half an hour and subsequently cool the emulsion to 5°C, again at a rate of 1°C min^{-1}. Between subsequent cycles emulsions where kept at 5° for half an hour. In some experiments a different temperature programme was applied, as indicated in the text.

Thickening of the samples was examined by pouring out the emulsion. The consistency varied from a thin liquid to a solid substance that no longer subsided under its own weight (strong thickening). In several cases, the emulsion started to flow if poured out, but the substance had become solid (so that the flow stopped) even before it reached the end of the test tube (moderate thickening). Hence it is useless to carry out quantitative viscosity measurements, since the mere filling of the viscometer would already cause considerable changes in the sample.

Afterwards the samples were treated as described in section 2.4, or they were stored for treatment in the Couette apparatus (Sec. 2.5).

3 RESULTS

3.1 Effect of tempering on natural cream

A temperature cycle was applied to natural cream of various fat contents. Before tempering and one day afterwards the emulsions were characterized as described in section 2.4, and thickening of the creams was examined (table 2-1). The crystals were situated inside the droplet (O- or N-type). Only rarely some crystals were observed at the boundary layer (L/M-type). The proportion of fat being solid appeared to be the same in all cases : 51% at 4°C.

Table 2-1. Characterization of natural cream of various fat contents before and after tempering.

t = 0 h		t = 24 h		
d_{vs} [μm]	fat [%]	d_{vs} [μm]	fat [%]	thickening
3.37	10.2	3.36	10.2	no
3.39	19.0	3.42	19.0	no
2.07	20.0	2.10	20.0	no
3.44	30.0	6.02	11.5	strong

From these results it becomes clear that 20% dispersed phase is insufficient to cause significant aggregation.

3.2 Influence of tempering on various O/W emulsions.

So far the effect of tempering has only been studied in dairy emulsions. To find out whether other emulsions can be rebodied as well, we examined several systems, of which the stability after storage at 5°C and in Couette flow are known. Compositional data and the behaviour of these emulsions under the conditions mentioned are given in table 2-2. In those

Table 2-2. The effect of stability of model O/W emulsions (35% dispersed phase) on (i) keeping at 5°C, (ii) tempering as shown in figure 2-1 or (iii) in Couette flow (30' at 100 s^{-1}, 20°C).

Oil-in-water emulsions	5°C	5-35-5°C	Couette flow
SDS - liquid part of blend A	stable	stable	stable
SDS - blend A	stable	unstable	unstable
SDS - liquid part of blend B	stable	stable	stable
SDS - blend B	unstable	unstable	unstable
SDS - paraffin (40% solid paraffin)	stable	stable[1)]	slightly unstable
Na-caseinate - blend A	stable	stable	stable
Na-caseinate - blend B	stable	stable	stable
Skimmilk - milk fat	stable	stable	stable[2)]
Skimmilk - milk fat - lecithin	stable	unstable	unstable[2)]
Natural cream	stable	unstable	unstable[2)]

[1)] T_{max} of 20, 25 and 30°C had the same result [2)] after Melsen & Walstra [12].

cases where the emulsion became unstable an oil layer appeared on top after heating the emulsion to 45°C. The d_{vs} sometimes changed and sometimes remained the same. Emulsions were considered stable if the droplet size and the fat content remained unaltered. It can be seen from table 2-2 that emulsions remain stable if the globules have no crystals

(by using the liquid fraction of the particular blend). It seems that the presence of fat crystals is essential in the aggregation process. On the other hand phospholipids do not seem to be essential although the results with recombined cream make clear that addition of lecithin can enhance the rebodying effect.

The behaviour of the emulsions after a temperature cycle is in accordance with the behaviour of the O/W emulsions in Couette flow, paraffin excepted. Paraffin is the only oil with a deviating crystallization behaviour. In emulsion globules only one or two big crystals (N2-type) are detected microscopically, whereas normally many small crystals (N1-type) are observed. Since crystals are essential in the rebodying process and the number of crystals in paraffin oil globules is very small this may be the reason that paraffin is an exception. The instability in Couette flow, too is less than in all other emulsions containing crystals.

The stability of the emulsions in which caseinate or skimmilk is the only surface active material may be due to the film between approaching globules remaining thicker than the length over which crystals protrude into the aqueous phase, implying that the crystals cannot reach an approaching droplet. In the flow field the distance between globules may become slightly less [1], but the film presumably remains too thick for partial coalescence to occur.

3.3 Characterization of the type of aggregation as a result of tempering.

Hening & Dahlberg [7] only noticed a tempering effect if the emulsion contained about 25% dispersed phase or more and this was confirmed in our experiments (see Sec. 3.1). The average free distance between fat globules, assuming no colloidal interactions and purely spherical globules, is very small at these high concentrations [20]. Van Boekel [1] also found that above about 25% dispersed fat the aggregation rate (due to partial coalescence) of O/W emulsions in Couette flow steeply increased, presumably due to the close packing of the globules.

It remains to be answered whether the aggregation caused by tempering is due to flocculation or to partial coalescence. The latter seems more realistic. After all, globules

Table 2-3. Stability of temperature-treated emulsions and untreated ones before and after application of Couette flow (30 min, 100 s^{-1}), as derived from d_{vs} and fat content.

		before Couette flow		after Couette flow	
Temperature treatment		SDS-blend A	Natural cream	SDS-blend A	Natural cream
5-20°C	d_{vs}	2.07	3.39	2.31	4.22
	% fat	20.0	19.0	19.4	18.4
5-35-5-20°C	d_{vs}	2.10	3.42	4.05	6.23
	% fat	20.0	19.0	15.2	10.2

without crystals remain stable even in emulsions with over 30% dispersed phase. Furthermore, most emulsions that partially coalesce in Couette flow are also unstable after tempering; and emulsions that are stable in the applied flow field, remain stable after the temperature cycle as well. If partial coalescence is the aggregation type, emulsions with 20% dispersed phase or less should become more unstable in a flow field if a temperature cycle is applied to them beforehand. In the experiment reported in table 2-3, an SDS-blend A emulsion and unhomogenized natural cream were stored for one night at 5°C and then split into equal parts, one part being tempered while the other was kept at 5°C. After that, both parts were warmed to 20°C and Couette flow was applied. After each treatment the emulsion was characterized as described in section 2.4. The change in d_{vs} and fat content are measures for the proceeding of the aggregation (see e.g. Melsen [11]). Table 2-3 shows that both 20% emulsions remain largely unaltered after tempering. If, after that, a flow field

was applied, both emulsions became unstable, but the tempered emulsions were markedly less stable. Similar results were obtained with 10% emulsions (results not shown). It may thus be concluded that the temperature cycle has a detrimental effect on the stability of the oil globules in dilute emulsions.

As shown in table 2-4, dilution of the aggregated emulsions with deflocculating agents like 0.4% SDS or solution A did not cause any disaggragation. Dilution with high concentrations of SDS (over 1%) resulted in disaggregation, but this is known to change the wetting properties (we intend to report on this subject in more detail in a subsequent paper). The

Table 2-4. Influence of different diluents on the characteristics of natural cream and 0.4% SDS-blend A emulsion.

diluting agent	natural cream		SDS - blend A	
	d_{vs} [μm]	fat [%]	d_{vs} [μm]	fat [%]
before tempering				
solution A[1)]	3.49	30.0	3.41	28.0
after tempering				
H_2O	5.98	12.1	2.82	8.7
solution A[1)]	6.02	11.5	2.80	8.5
0.4% SDS	6.04	11.9	2.83	8.7
1.0% SDS	3.61	29.7	3.79	26.9

1) 0.375% disodium ethylenediamine tetraacetate and 0.125% polyoxyethylene sorbitan monolaurate in water, pH 10)

crystals then are better wetted by the aqueous phase than by the oil phase and they can migrate to the continuous phase; this is sometimes called the Lanza process [9]. Disaggregation was only observed if the dilution occurred immediately after collection of the sample from the Couette apparatus. The cause presumably is that the crystal that pierced the film between two aggregated globules, is removed from the aggregate. As a consequence, the bridge that kept the globules together has disappeared and the globules separate; these aspects is dealt with in chapter 3.

3.4 Effect of tempering on the fat crystals in the oil globules of O/W emulsions.

The 'rebodying' effect thus implies that emulsions can partially coalesce in the absence of a velocity gradient. In the temperature treatment causing this, three stages can be distinguished:

- Cooling of the (freshly made) emulsion to 5°C
- Tempering, i.e. warming, keeping, cooling
- Aging at 5°C

These three stages will be discussed below.

3.4.1 Cooling of the emulsion (stage 1).

Above 40°C, all globules are fully liquid. Figure 2-4 schematically illustrates crystallization curves of fat blend A and O/W emulsions of different average droplet sizes after cooling and keeping them at various temperatures for 24 hours. From this figure it can be seen that an emulsion needs supercooling for crystallization to occur, the more so for smaller globules [14]. If the globules are not too small, crystallization in all globules will have occurred at 5°C. Furthermore it was observed that the crystallization rate is high in all cases (at least 80% of the solid fat that is present after 24 h had crystallized within 1 h). After reaching sufficient supercooling many nuclei are formed, independent of the cooling rate. The resulting many small crystals soon flocculate to form a fat crystal network [14, 21].

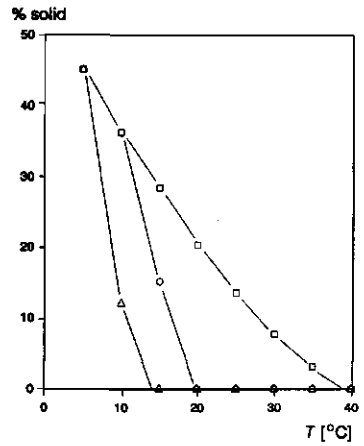

Figure 2-4. Solid fat content as a function of temperature for 0.4% SDS-blend A emulsions of different $\underline{d_{vs}}$ (○, ▲) and for blend A in bulk (□).

○) d_{vs} = 2.36 μm ▲) d_{vs} = 0.81 μm

3.4.2 Temperature cycle (stage 2).

3.4.2.1 Effect of the cooling and warming rate and of the time interval at T_{max}

So far the cooling and warming rate were 1 K min^{-1}, as Sommer [15] applied to cream. To find out whether this is also a good choice for other emulsions, several cooling and warming rates and interval times at T_{max} were tried for SDS - blend A and recombined cream with lecithin. The results are represented in table 2-5. Each time only one of the three stages was changed. The last column in table 2-5 gives the results for both emulsions, since no differences in change in consistency were observed. It appears that the rate at which the emulsion is heated to T_{max} is irrelevant.

The values taken so far for the other variables seem to give about optimum results. If the time interval at T_{max} was shorter or the cooling rate faster, the resulting thickening was less. Consequently, all further experiments were carried out in the same way: warming - and cooling rates of 1 K min^{-1} and a 30 min time interval at T_{max}.

Table 2-5. Influence of the warming/cooling rate and the interval time at 35°C on thickening of recombined cream with lecithin and of 0.4% SDS-blend A. d_{vs} = 2 μm

Heating time 5 -> 35°C	Holding time at 35°C	Cooling rate 35 -> 5°C	thickening
0.5 K min^{-1}	30'	1 K min^{-1}	strong
1.5 K min^{-1}	30'	1 K min^{-1}	strong
3 K min^{-1}	30'	1 K min^{-1}	strong
1 K min^{-1}	**0'**	1 K min^{-1}	little
1 K min^{-1}	**15'**	1 K min^{-1}	moderate
1 K min^{-1}	**30'**	1 K min^{-1}	strong
1 K min^{-1}	**60'**	1 K min^{-1}	strong
1 K min^{-1}	30'	**0.5 K min^{-1}**	strong
1 K min^{-1}	30'	**1 K min^{-1}**	strong
1 K min^{-1}	30'	**1.5 K min^{-1}**	strong
1 K min^{-1}	30'	**6 K min^{-1}**	no

3.4.2.2 Solid fat content of the emulsions during tempering

Several temperature cycles, in which T_{max} was varied, were applied to recombined cream and emulsions with SDS and blend A. The solid fat content during these cycles was followed using the pulsed-NMR method. In figure 2-5 the relationship between T_{max} and the solid fat content is represented. If, at T_{max}, only a little solid fat was left thickening of the

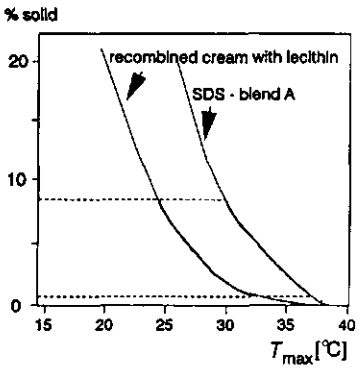

Figure 2-5. Relationship between T_{max} and the solid fat content (% of total fat). Between about 1.5 and 8% solid fat at T_{max} the emulsion showed increased thickening after tempering.

emulsion occurred upon cooling.

Since it is now clear that only little solid fat (between 1.5 and 8%) should remain at T_{max} for destabilization to occur, the effect of adding a little of a non-melting fat was studied. Therefore emulsions were made with 0.4% SDS as the water phase and paraffin, blend A or blend B as the oil phase, with or without 2% tristearin (SSS), added to the oil phase, before emulsification. Microscopically it was observed that in the case of blend A or paraffin in combination with SSS, the emulsion globules were of the L or M-type, whereas in the presence of blend B with SSS globules remained N2-type. Without SSS the emulsion globules were of the N-type, without any exception and irrespective of the cooling rate used. Only if the emulsion was poured out in ice water immediately after emulsification, the crystallization habit of the globules did not depend on the presence of SSS. Presumably, the crystallization of the other fat was not influenced by the presence of tristearin in this case. Another effect from the addition of minor amounts of tristearin was that the emulsions became much more stable against partial coalescence: see table 2-6. It seems as if the coverage of the interface of the droplet by SSS makes the droplet behave as if it is completely solidified, a rigid sphere; this is in agreement with earlier findings of Van Boekel [1], who observed that if the major part of the oil had crystallized, the emulsion became

Table 2-6. The influence 2% SSS on the stability of several 35% O/W emulsions. The aqueous phase was 0.4% SDS in all cases. The paraffin solid to liquid ratio was 20/80.

Dispersed phase	5°C	5-35-5°C	Couette flow; 30 min. 100 s^{-1}; 20°C
Paraffin	stable	stable	unstable
Paraffin + 2% SSS	stable	stable	stable
Blend A	stable	unstable	very unstable
Blend A + 2% SSS	stable	stable	stable
Blend B	unstable	unstable	no experiment possible
Blend B + 2% SSS	stable	unstable	unstable

more stable against partial coalescence (in Couette flow) again.

3.4.3 Aging (stage 3)

During aging at 5°C (after tempering) the emulsions become thicker. Under the microscope (using polarized light microscopy) aggregates of N-type globules were noticed. Only in the case of blend A as the oil phase, some bright layers were observed. It is remarkable that in spite of the aggregation hardly any changes were observed in the crystallization habit of the emulsion globules. On the other hand, the crystals are very small so that small changes may be hard to detect. Therefore it was tried to accentuate the effect by tempering the emulsions as described before, followed by several cycles with a maximum temperature that was 10 K below the original T_{max}. In this way many crystals are presumably remelted, so that reorientation of the crystals may be enhanced. The results are represented in table 2-7.

Table 2-7. The influence of repeated tempering (5-35-5-[25-5]$_n$) on the stability of several 35% O/W emulsions. During the first temperature cycle (n = 0) T_{max} was 35°C; during all other cycles (n ≥ 1) T_{max} was 25°C.

	Recombined cream with lecithin	0.4% SDS-blend A	0.4% SDS-blend B with 2% SSS
Before 1st cycle	no L/M-type	some L/M-type	no L/M-type
n = 0	no L/M-type	some L/M-type	no L/M-type
n = 1	some L/M-type	many L/M-type	no L/M-type
n = 2	many L/M-type	very many L/M-type	no L/M-type
n = 3	very many L/M-type	very many L/M-type	no L/M-type
n = 4	very many L/M-type	very many L/M-type	no L/M-type
Remarks:	Crystal size increases with n	No change in crystal size ?	Crystal size increases with n

Microscopically it was observed that emulsions, made with milk fat or blend A developed more L/M type crystallized globules, whereas the crystals obviously became bigger as well in recombined cream and SDS-blend B emulsions. In SDS-blend A emulsions enlargement of the crystal size was not observed.

4 DISCUSSION

4.1 Aggregation type as a result of tempering

From the experiments with concentrated ($\Phi > 0.25$) O/W emulsions, made of triglyceride blends or paraffin as the dispersed phase and SDS or caseinate solutions as the aqueous phase (see Sec. 3.1), it has become clear that it is possible to destabilize emulsions by

tempering, also in the absence of phospholipids. These results make clear that, in general, the stability of emulsions can markedly be affected by a temperature cycle provided that the temperature cycle is such that at T_{max} only little solid fat (between 1.5 and 8%) is left; this applies to emulsions that exhibit partial coalescence in a velocity gradient.

In dilute emulsions a temperature cycle does not result in spontaneous aggregation of the globules, although they do become more sensitive to aggregation: tempered emulsions show faster partial coalescence in Couette flow than do untempered emulsions. The aggregates that have formed can not be separated again with the use of deflocculating agents. After addition of a sufficiently concentrated SDS-solution(see Sec. 3.3), on the other hand, the crystals migrate to the water phase and this may result in the globules separating again. Furthermore, in the absence of fat crystals no thickening occurs whatever the concentration of dispersed phase. This makes clear that the globules are not flocculated but clumped, i.e. that the aggregates have at least one fat crystal linking two globules.

All experiments discussed above, are consistent with the postulate that the aggregation process is caused by partial coalescence. The destabilizing role of the phospholipids in the dairy emulsions fits this idea. Melsen and Walstra [12] reasoned that the phospholipids will, at least partly, displace the proteins from the interface of the fat globule. As a result the globules can now come closer on encountering each other, and protruding crystals will be able to bridge the thinner film more easily, so that partial coalescence is enhanced. So, contrary to the ideas of Sommer [15], the contribution of the phospholipids is in the reduction of the interparticle forces between approaching globules rather than in changing the fat distribution inside the globule.

The term rebodying is, strictly speaking, somewhat misleading at least in the case of systems with less than 25% fat. In this case, the globules do become more sensitive to partial coalescence, but because of the appreciable average distance between globules, no "body" formation will occur at rest. A better designation of the process is "tempering", which term accentuates that the temperature fluctuation is the driving force of the emulsion destabilization, although the role of the crystals is not represented in this way either. The

effect of tempering, being the altered crystallization habit of the globules (sometimes resulting in the body formation as a consequence of aggregation and sometimes only resulting in an increased reactivity to partial coalescence if a flow field would be applied) can better be described by the "sensitivity" of the globule to aggregation.

So far, the parameter to describe the effect of tempering, has always been some kind of consistency of the sample, because thickening of the cream was primarily considered. Now that it is known that the cause is partial coalescence, it is clear that apparent viscosity is not a good measure. Partial coalescence is greatly influenced by a flow field and viscosities can not be estimated without application of a velocity gradient. Instead of apparent viscosity it is more suitable to use changes in particle size and the fat content of the creamed emulsion to describe the proceeding of the aggregation process (see Sec 3.1).

4.2 Influence of tempering on the crystallization habit of the globules.

During the first stage of the tempering process the emulsion is cooled to 5°C in order to ensure (initial) crystallization in all globules. This is an essential step in the cycle since an emulsion that remains at temperatures above the temperature needed for crystal nucleation is not affected by a temperature cycle.

The initial crystallization in emulsion globules depends on the size and composition of the fat globules but always requires pronounced supercooling . Above 5°C, nucleation is predominantly heterogeneous, i.e. catalysed. From earlier calculations [23] it has become clear that in many situations only one or a few catalytic impurities can have been present in each droplet, while in fact there often are numerous crystals observed. As soon as a crystal has been formed, other crystals presumably will form in its vicinity. This so called secondary nucleation can occur if there is considerable supersaturation. From the emulsions examined (see Sec. 3.2), only those with paraffin were found to have only one or two (big) crystals inside each droplet. Apparently, appreciable secondary nucleation does not occur in the paraffin.

Although nucleation mainly occurs throughout the liquid (i.e. not at the droplet boundary)

for the emulsifiers applied [14, 21], the fat crystals may want to go to the boundary, since this may lead to the lowest thermal interfacial free energy. The energy state, in turn, depends on the wetting properties of the three phase system crystal-oil-water, as expressed by Young's equation:

$$\sigma_{co} - \sigma_{cw} = \sigma_{ow} \cos\theta \qquad (1)$$

σ denotes the interfacial tensions between the crystal (c), the oil(o) and the water(w) phase, whereas θ represents the angle that the surface of the crystal makes with the OW-interface, as measured in the water phase. From equation (1) it follows that in practical systems, where the condition $90 < \theta < 180°$ is fulfilled the interfacial free energy of the system is lowest when the crystals are situated in the OW-interface, preferentially wetted by the liquid fat. The energy gain, as compared with the state of complete wetting of the crystals by the oil, is larger for smaller θ. On the other hand crystals in oil globules, if large enough, are considered to be flocculated in a kind of network [16, 21], because of van der Waals attraction. The crystal network is embedded in the liquid fat; only crystals that become detached from this network have the opportunity to reach the OW-interface [10]. This is

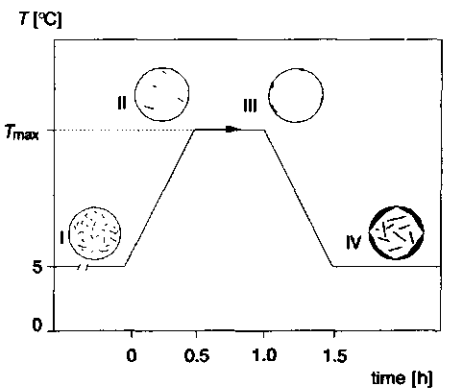

Figure 2-6. The influence of tempering of an O/W emulsion on number, size and orientation of crystals inside an oil droplet.

confirmed, microscopically, since most emulsions have N-type crystallized globules upon initial crystallization (figure 2-6,I). Upon warming to T_{max} solid fat will melt. As a result crystals can totally disappear or they can become smaller, because only part of the fat crystals melt. There may be a relation between these two ways of melting and the crystal modification. In addition, polymorphic transition from α to ß' or from ß' to ß may take place with increasing temperature. Anyway, far fewer crystals will be left.

From the NMR measurements (see Sec. 3.4.2.2) it has become clear that marked thickening of the samples only occurs if at T_{max} only little solid fat has remained (figure 2-6,II). This situation is achieved almost immediately after T_{max} is reached in the case the warming rate was 1 K/min. Some further melting of crystals may occur during the period that the emulsion is kept at T_{max}, if the warming rate of the emulsion was faster than the melting rate of the fat crystals.

The crystals that are left are no longer kept in a continuous network so that they can move around freely. If we consider the crystals to be spherical (with radius r_c), than the average time t that a crystal needs to diffuse from the centre of an oil droplet (with radius r_d) to the OW-interface, can be deduced according to Einstein [6]:

$$t = \frac{6\pi\eta_0 r_c r_d^2}{kT} \qquad (2)$$

in which η_0 is the viscosity of the liquid oil. From this expression, it appears that a spherical fat crystal (r_c = 0.1 μm) in an emulsion droplet (r_d = 1 μm, η_0 = 0.04 Pa.s) at 35 °C can reach the OW-interface within 20 seconds. Most crystals will deviate from spherical and are smaller than 0.1 μm, but it seems reasonable to assume that the crystals will meet the interfacial region at least a few times per minute.

Nevertheless, it becomes clear from variations in the time emulsions were kept at T_{max} (see Sec. 3.4.2.1.) that it takes some 15 minutes before crystals have had the chance to settle at the OW boundary (figure 2-6,III). We may conceive of some kind of energy barrier near the OW-boundary which hinders the crystals from reaching the interface. The differences in occupation of surfactant at the OW- and OC- interfaces will lead to interactive forces,

such as steric hindrance and electrostatic effects. From the above it can be deduced that approximately in one of 10^3 meetings of the crystal with the interfacial region the crystal has enough energy to overcome the boundary activation energy. The Gibbs activation energy G_a of those crystals that settle in the OW-interface can be estimated with the Boltzmann equation:

$$\frac{N_h}{N_o} = \exp\left(\frac{-G_a}{kT}\right) \quad (3)$$

where N_h/N_0 represents the ratio between the number of times a crystal permanently settles at the interface after meeting the interfacial region and the number of times the crystal goes back to the bulk oil inside the droplet. With a ratio of N_h/N_0 of $1/10^3$ G_a would be about 7 kT. In other words the thermal energy of a crystal must be 7 times its average to be able to reach the interface.

Cooling of the emulsion results again in crystallization. Since there are crystals in all globules no appreciable supercooling occurs, unless the cooling is very fast. As a result the supersaturation of the oil is less, hence secondary nucleation is less. As a consequence the number of crystals does not (greatly) increase, but the crystal size increases. The crystal shape may be influenced as well. As described above, polymorphic transitions may have occurred and it is not unlikely that this results in changes of the crystal shape. Whether such changes in crystal shape occur and whether they would favour partial coalescence or not, we could not find out.

Apart from the change in crystal size and possibly shape, the orientation of the crystals is altered. The remaining crystals serve as nuclei and as some of them are situated at the interface, the amount of crystals at the boundary layer increases. Consequently, more crystals may protrude from the interface and, in addition, may protrude further because they are bigger (figure 2-6,IV). Both phenomena must enhance partial coalescence. These observations are confirmed by microscopic studies of creams undergoing repeated cycling (see Sec. 3.4.3) which made clear that crystals become bigger and more situated at the interface.

5 CONCLUSIONS

Tempering of o/w emulsions, in the dairy literature described as the rebodying process, may induce partial coalescence in emulsions at rest. Essential is that the temperature treatment causes significant changes in the state of crystallization of the fat, without fully melting it. The repulsion between globules remains critical as well: if the distance between approaching globules remains larger than the reach of the protruding crystal, fat crystals cannot bridge the gap between globules. Thickening of an emulsion after tempering is not limited to dairy cream but can occur in other emulsions too, if the emulsion is sensitive to partial coalescence and if at T_{max} only little solid fat is left in the emulsion.

After tempering the crystals have become bigger and more of them are present at the o/w boundary. This way of tempering is the only temperature treatment known so far that changes the crystal size and position without changing any further system properties. From the results described in this paper, it appears that bigger crystals make emulsion globules more sensitive to partial coalescence and that orientation of the fat crystals at the o/w boundary enhances partial coalescence too.

The term rebodying has intentionally been changed into tempering effect because of the influence the temperature history has on emulsions, even in cases where no body is formed. It was further concluded that the extent of the process cannot meaningfully be characterized by apparent viscosity, since tempering causes the emulsion to become very sensitive to a velocity gradient. Instead, the changes in particle size can be used as a characteristic.

6 ACKNOWLEDGEMENTS

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PARTIAL COALESCENCE IN O/W EMULSIONS :

I. NATURE OF THE AGGREGATION.

ABSTRACT

The mechanism causing aggregation in triglyceride oil in water emulsions in which the droplets contain fat crystals is investigated. As a surfactant either SDS or a protein was used. The crystals must be situated at the O/W interface to cause partial coalescence; if the fat crystals are totally wetted by the oil phase or the aqueous phase they do not affect emulsion stability. Although a suitable contact angle (crystal, oil, aqueous phase) appears necessary for emulsion instability, it is obviously not sufficient. Additional conditions are a close enough approach of the globules, so that the protruding crystals can bridge the aqueous film between them, and the presence of sufficient solid fat. Crystals may have an approximately radial orientation at the O/W interface if they are kept in a continuous fat network. If, furthermore, the contact angle (as measured in the aqueous phase) is below 90° then the coalescence efficiency (α) is high (mostly $\alpha >> 10^{-6}$). If crystals can move around freely they can obtain a tangential orientation at the interface irrespective of the contact angle. Globules then are not very sensitive to partial coalescence ($\alpha < 10^{-6}$). Even if partial coalescence has already occurred, it can in some cases be nullified by changing the wetting properties so that the fat crystals become separated from the interfacial region. This reversibility only holds if carried out within a few hours after aggregation. After that the partially coalesced emulsion droplets are irreversibly merged into one bigger clump.

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PARTIAL COALESCENCE IN O/W EMULSIONS :

I. NATURE OF THE AGGREGATION.

1 INTRODUCTION

In the absence of fat crystals most oil-in-water emulsions are fairly stable to coalescence at rest and in a flow field, if the oil droplets are not more than a few microns in diameter [4]. In many emulsions of practical interest part of the oil may crystallize at a certain temperature. Strictly speaking, these emulsions have changed into three-phase systems, but as they originate from true emulsions in which crystals arise we still call them emulsions. The presence of crystals in the fat globules of an O/W emulsion can tremendously enhance the instability of the emulsion [2,8,13,17,19,24]. This destabilizing effect is similar to that of hydrophobic material in aqueous foams [10]. The presence of a crystal structure can prevent complete coalescence of oil globules, if the solid network is strong enough to resist the capillary forces involved. Instead of the energetically favoured spherical shape, clumps are formed of irregular size and shape [19]. Therefore, the process is called partial coalescence.

At rest, partial coalescence could only be observed so far if fat content was extremely high, like in a cream layer, or if a specific temperature treatment was applied, like in the rebodying process (see also chapter 1). The presence of velocity gradients in the emulsion greatly enhances partial coalescence. In general, turbulence is more effective than flow with Taylor vortices and that, in turn, is more effective than laminar flow to cause partial coalescence.

Van Boekel & Walstra [4] hypothesised that coalescence may be caused by fat crystals at the surface of the oil globule (figure 3-1). When two globules approach each other, a thin aqueous film usually remains between them due to repulsion forces. The stronger the repulsion, the thicker the aqueous film. Crystals in the interface stick somewhat out of the globule, the distance depending on crystal size and shape and on the wetting properties (i.e.

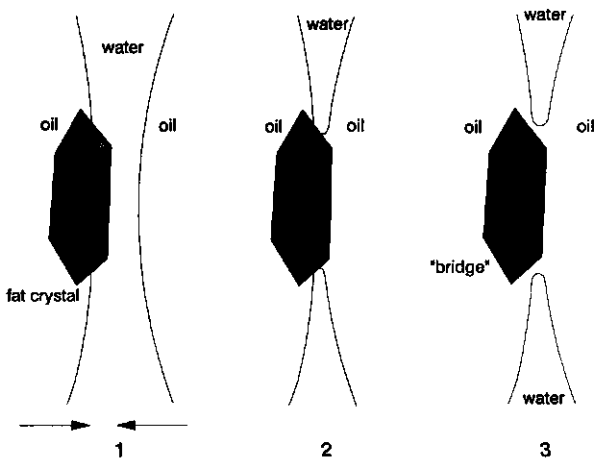

Figure 3-1. Schematic drawing of the hypothetical coalescence mechanism caused by a crystal.

the contact angle). On approach of a second globule, such a crystal may pierce the thin film between globules, if protruding far enough. If the globules orbit around each other, as frequently occurs in a shearing flow, the probability that a protruding crystal breaches the film between two globules is greatly enhanced. As soon as the crystal touches the oil phase of the other globule, coalescence is inevitable because the crystal is better wetted by oil than by water.

Van Boekel & Walstra [4] and Darling [8] tried to correlate contact angles and emulsion stability by examining systems with different surfactants. These variations in composition may, however, also influence the sensitivity to partial coalescence in other ways than by affecting the contact angle. Several authors have reported the (partial) displacement of one surfactant by another. Glycerol mono-oleate, e.g., displaces PVA 16-88 to some extent [20] and proteins can be removed by SDS [9,21]. Water soluble surfactants can thus influence colloidal interaction forces and thereby the distance over which the globules can approach each other. Oil soluble surfactants can, moreover, affect the fat crystallization and possibly decrease the tendency of crystals to flocculate [16]. In the present work it was tried to circumvent such complications.

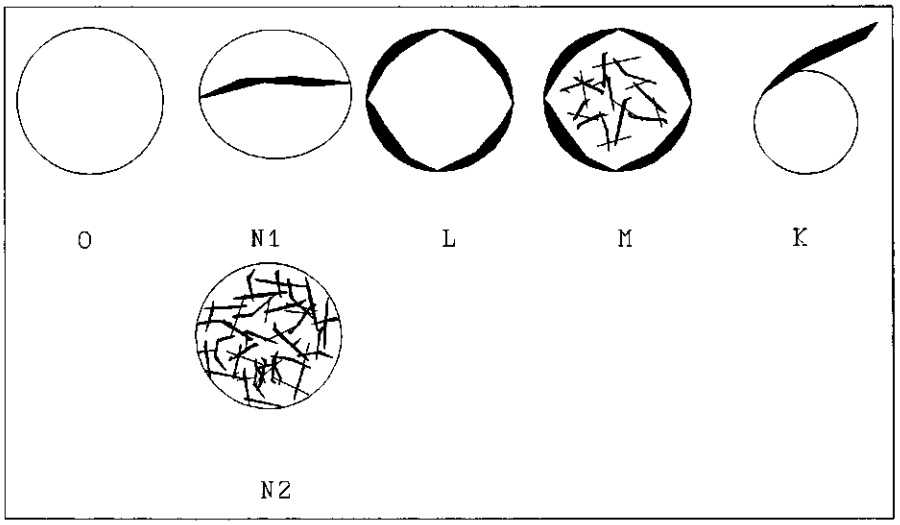

Figure 3-2. Habit of emulsion globules, containing fat crystals, as observed by polarized light microscopy. Mainly after Walstra [26].

Another factor that may influence partial coalescence is the orientation of crystals in the fat globules. Walstra [26] already reported the existence of four different types of crystallization in droplets (figure 3-2). Van Boekel & Walstra [4] suggested that partial coalescence only occurred if L/M-type globules were present. They observed microscopically that emulsions that were sensitive to partial coalescence nearly always had crystals tangentially oriented at the interface. Although the contact angle was always in favour of this, they observed that in a few emulsions the crystals did, nevertheless, not reach the interface, and these emulsions were stable. Following Lucassen-Reynders [16], they suggested that flocculation of the crystals into a network may have prevented their adsorption onto the interface. Only emulsions stabilized with caseinate showed no tangentially oriented crystals and yet partial coalescence occurred. Melsen [17] showed later that whey protein-milk fat emulsions also exhibited such behaviour. Consequently, the mechanism of partial coalescence may also be (partly) different from that proposed by van Boekel & Walstra [4]. To this we may add that some of our emulsions were much more sensitive to partial coalescence then those of van

Boekel and Walstra.

The aim of this work was to establish in more detail the factors governing partial coalescence. The involvement of the fat crystals and the role of the contact angle in partial coalescence are accentuated. The formation of a fat crystal network in emulsion globules was examined by microscopical observation of the behaviour of emulsion globules that are sucked onto the tip of a glass capillary. Special use is made of migration of fat crystals from the oil to the water phase due to changed wetting properties. Factors affecting the film thickness, i.e. the distance between approaching globules, are also considered, since substances that change the wetting properties may also affect film thickness.

2 MATERIALS AND METHODS

2.1 Materials

Triglyceride blends were stored at 4°C in tins. The fat was fully melted before opening the tin for use. Blend A(96.9% tri-, 3.0% di-, 0.1% monoglycerides) had solid fat fractions of 0.45 and 0.20 at 5 and 20°C, respectively. The final melting point was 38°C.

Blend B(96.7% tri-, 3.2% di-, 0.1% monoglycerides) had solid fat fractions of 0.95 and 0.84 at 5 and 20°C, respectively. The final melting point was 38°C.

Sodium dodecylsulphate (SDS) (also called sodium laurylsulphate) was obtained from BDH, England. Its grade was specially pure. The critical micelle concentration (CMC) in water is 8 mmol/l at 20°C and 1.5 mmol/l in 0.1 mol/l NaCl [6].

Cream was obtained by centrifuging fresh cows' milk at 40°C to the desired fat content. To inactivate lipase it was heated for 15 min at 70°C.

Anhydrous milk fat (> 99.8% pure fat, < 0.1% water) was stored at 7°C in sealed tins. The fat was fully melted before usage.

Skim milk was obtained by centrifuging fresh cows' milk at 40°C to a fat content of 0.07%. To inactivate lipase it was heated at least for 10 min at 64°C.

Sodium caseinate (1%) was prepared from fresh skim milk by repeated precipitation with hydrochloric acid and redispersion in water (pH7.6). Afterwards it was spray-dried.

ß-lactoglobulin (1%) M.W. 18,300, Serva Feinbiochimica, Heidelberg, F.R.G.

2.2 Wetting properties

Contact angles were determined by the method described by Campbell [5]. All measurements were made with fat solidified against air. The liquid oil phase always was a liquid fraction separated from the fat blend at 5°C. Contact angles were estimated of oil droplets formed at the fat surface-water interface (θ_w) and of water droplets formed at the fat surface-oil interface (θ_o). Since results appeared identical we have chosen to use the contact angles as measured in the aqueous phase (θ_w) only.

Interfacial tensions were measured by means of the Wilhelmy plate method.

2.3 Penetration of aqueous phase into fat blends

This method is an adaptation of the method as developed by Arcuri et al. [1]. Small amounts (30 mg) of a partially crystalline fat were deposited on a glass plate. A second glass plate was placed on the first one, and clamped on it at a distance of about 0.1 mm. With this procedure the crystal dispersion takes the form of a circular spot. Then the glass plates were immersed into the aqueous phase and the gap between the plates was instantaneously filled up with water. The region in which the aqueous phase has entered the crystal dispersion appears white, because of the large difference between the refractive index of fat crystals and water. On the other hand, the difference of refractive index between crystals and oil is so small that the regions where the oil is still present, appears transparent.

2.4 Emulsification

The emulsions were made by mixing the fat blend (varying from 5 to 30%) and aqueous solution at 60°C in the inlet vessel of a Rannie laboratory homogenizer (capacity 100 l/h), while stirring. The mixture was then homogenized at 4 bar by allowing it to recirculate through the homogenizer for 20 minutes, cautiously avoiding any uptake of air. In this way, fairly narrow globule size distributions were obtained, the surface-weighted relative standard

deviation c_s being between 0.2 and 0.6, and the shape of the surface-weighted distribution being near symmetrical; the volume-surface average droplet diameter, d_{vs}, was about 2 μm. The emulsions were free of aggregated globules, as was checked by microscopy.

2.5 Pretreatment of the emulsions

To ensure fat crystallization in all globules, emulsions, except those used for stability experiments at rest, were stored at least overnight at 4°C. To avoid creaming and thus partial coalescence, the emulsions were stored in 200 ml cylinders that were slowly rotated, end over end. The cylinders were carefully filled to exclude air. The globule size distribution was regularly examined before and after storage, and was not found to change. Stability experiments at rest were carried out with freshly made emulsions.

2.6 Characterization of the emulsions

Total fat content was determined by a pulse NMR method as reported by van Boekel [3]. Only the registration of the signal was slightly improved. Instead of measuring the signal only at two distinct times after the 90° pulse, the signal decay over an interval of 100 μsec was collected. The best horizontal straight line was fitted through the signal pattern from 30 to 100 μsec after the pulse and this line was taken as representative for the signal of the 'liquid' hydrogen nuclei at the measuring temperature. In this way the accuracy was increased (scattering of the signals measured were about 0.1%). These signals were compared to calibration curves made of the NMR signals of mixtures of SDS solution and fat blend as a function of the fat content.

The solid fat content of the bulk fat and the emulsions was also estimated by pulse NMR. For this purpose the indirect method, as described by van Boekel, was used, with the same modifications as described above for the determination of the total fat content, resulting again in scattering of the measured signals of about 0.1%.

Triolein (Fluka AG) was used in all cases as a reference oil.

The globule size distribution was determined by spectroturbidimetry [27] after heating the

samples for 30 minutes at 45°C to change possible aggregates into spherical globules.

2.7 Couette flow

O/W emulsions were subjected to Couette flow, i.e. flow between two concentric cylinders of which the outer one rotated and the inner one (diameter 60 mm) was fixed (gap width = 5 mm). The rate of rotation was about 100 s^{-1}, so that laminar flow developed [4]. After 30 minutes the apparatus was emptied and the emulsions were diluted with a solution of disodium ethylene diamino tetraacetate (EDTA) and polyoxyethylene sorbitan monolaurate in water, and heated to turn any clumps into globules. Any big aggregates (diameter > 10 μm) caused the separation of an oil layer on top of the emulsion. After removal of the oil layer the remaining emulsion was characterized as described in Sec. 2.6.

2.8 Microscopy

Polarized light microscopy was used to observe the appearance of fat crystals in the oil globules. In analogy to milk fat globules [26] several crystallization habits were distinguished (figure 3-2). Two main types were observed. In the N type "needles" are seen, although in fact, most crystals are elongated platelets. In the M-type a combination of tangentially oriented crystals near the droplet boundary and randomly distributed "needles" are observed.

2.9 Capillary method

This method has its origins in studies of the surface properties of biological cells [18]; since then it has been developed and used on several systems. It was used by Horwitz et al. [12] and Phipps & Temple [22] to study milk fat globules. The technique is based on microscopical observation of the behaviour of globules if sucked onto the tip of a glass micropipette (a schematic representation of the apparatus is given in figure 3-3). Glass capillaries (Clark Electromedical Instruments, type GC 150-15) were cleaned and pulled (Narashige Scientific Instrument. Lab., Tokyo, Japan; type PN-3), routinely yielding tip diameters of 0.4 - 1.0 μm. The capillary was held in a micromanipulator, its tip being

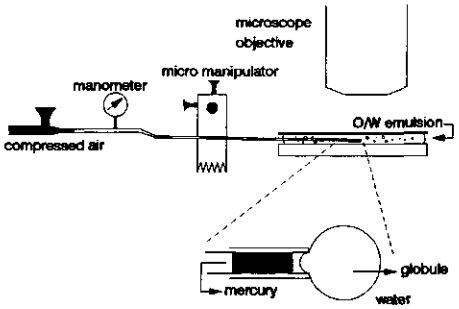

Figure 3-3. General overview of the equipment for the capillary method; see text.

immersed in the diluted emulsion on a microscope slide which was viewed under a light microscope with magnifications of x1000 to x1200. The other end of the pipette was connected to a bottle of compressed air. A mercury drop was brought into the capillary and by raising the pressure it was brought to the tip. Depending on the tip diameter an overpressure of 1 to 6 bar was needed. The tip was then placed in the vicinity of a globule and by reducing the overpressure the globule was sucked onto it. The deformation and further behaviour of the globules was observed.

3 RESULTS

3.1 Wetting properties

When a dispersion of fat crystals in oil is brought into contact with an aqueous solution of a surfactant, one can observe that, in some cases, the crystals separate from the oil. The industrial application of this technique of separation is known under the name of "Lanza process" after a patent by Lanza [14], who first reported the use of surfactant aqueous solutions to separate solid stearic acid from liquid oleic acid. From contact angle measurements on SDS - triglyceride blend A it appeared that SDS can induce this Lanza behaviour, if present in sufficiently high concentrations (figure 3-4). The following

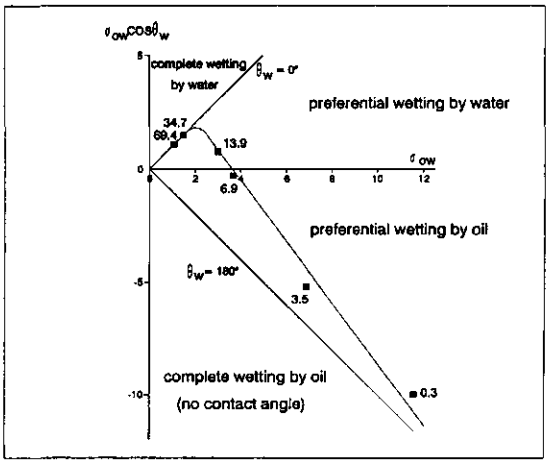

Figure 3-4. Adhesion tension ($\sigma_{ow}\cos\theta$) versus interfacial tension (σ_{ow}) for solid triglyceride blend A at SDS - liquid triglyceride blend A interface. The SDS concentrations (mM) are indicated near the corresponding measured points.

relationship between σ_{ow} and θ_w was found (for 0.05 mM < [SDS] < 28 mM) :

$$\sigma_{ow}\cos\theta_w = -1.26 * \sigma_{ow} + 4.22 \qquad (r^2 = 0.989) \qquad (1)$$

The slope of -1.26 is somewhat unusual. Nobody has ever reported a slope below -1 sofar [15]. We, however, did find it, although it must be atmitted that the slope may in reality be closer to -1, because of the limited accuracy of the measurements.

Wetting reversal, defined as taking place when the contact angle reaches the value of 90°, occurs at σ = 3.4 mNm^{-1}, i.e. at c = 8 mM (=c.m.c.), according to these results. Up to SDS concentrations of about 28 mM fat crystals will be in the oil-water interface, whereas above this concentration they will be in the aqueous phase. This wetting behaviour of SDS - triglycerides was confirmed for bulk systems by the use of the penetration method as described in section 2.3. Figure 3-5 (e.g.) shows that about half an hour after addition of a "Lanza inducing" SDS solution many small oil droplets were ejected from the bulk and fat crystals became wetted by water. One day later the liquid oil phase had totally been dispersed into small droplets with the fat crystals dispersed in the aqueous phase. Crystal migration in SDS - blend A emulsion was followed microscopically. At SDS concentrations

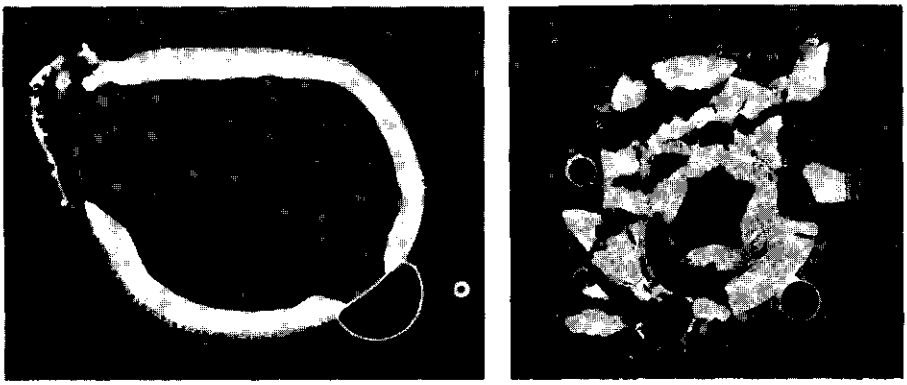

Figure 3-5. Ejection of oil droplets from fat crystal network 30 minutes (A) and one day (B) after addition of a 35 mM SDS solution to blend A.

above 28 mM crystals were no longer observed in the globules. Instead, they were lying on the bottom of the microscope slide. In most cases the shape of the originating droplets could still be recognized, so that it was concluded that complete crystal networks had come out of the globules.

3.2 Emulsion stability

3.2.1 At rest

Emulsions that had been kept at 5°C for at least several hours became unstable, if warmed to a maximum temperature between 20°C and 35°C, kept there for some 30 minutes, and subsequently cooled again to 5°C. Instability here means that the emulsion becomes very viscous or even solid-like. Conditions leading to this phenomenon are illustrated in figure 3-6; d_{vs} and Φ affect the results. Such a temperature treatment resulting in thickening of natural cream has been known since 1932 [11]. The process is called rebodying, after the solid body that is formed as a result of the treatment. It was shown in chapter 1 that partial coalescence is the cause of the thickening. It appeared that other O/W emulsions also show thickening if treated in the same way. This phenomenon is the only one described in literature, so far, where partial coalescence takes place at rest in emulsions that are perfectly stable in the absence of fat crystals.

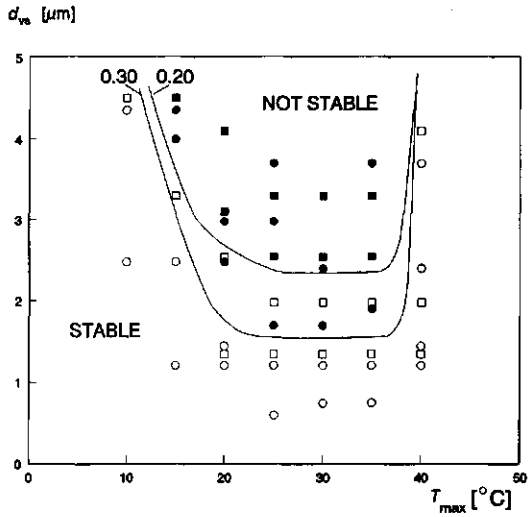

Figure 3-6. Thickening, caused by temperature cycling (5 - T_{max} - 5°C), as a function of d_{vs} [μm] and T_{max} [°C] for SDS(14 mM) - triglyceride blend A emulsions of variable fat content. The closed symbols correspond to emulsions that thicken during storage, whereas the open symbols represent emulsions that are stable under quiescent conditions. (□) 20% fat (○) 30% fat.

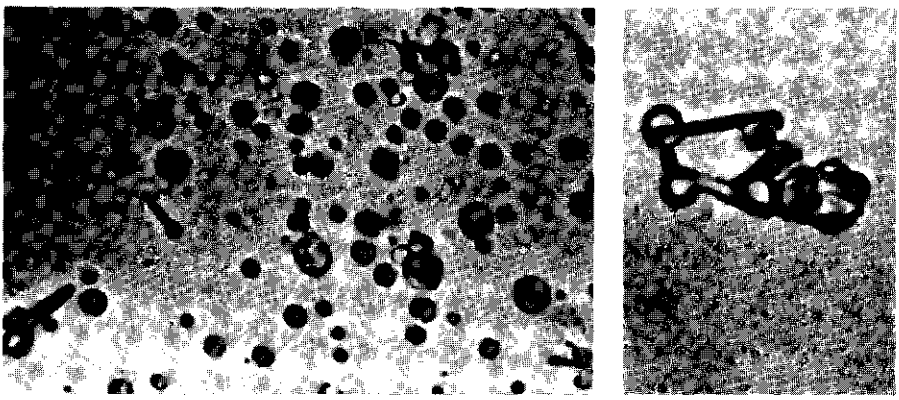

Figure 3-7. Crystals growing out of the oil globules; crystal dimensions exceeding the globule diameter. SDS (10 mM) - triglyceride blend B (0.5%) emulsion. (A) Single globules (B) Clump formed by partial coalescence in the previously mentioned emulsion.

The stability at rest of O/W emulsions of both triglyceride blends (described in section 2.1) with 14mM SDS in the aqueous phase was tested. From electron microscopy (by courtesy of I. Heertje) we observed that crystals of blend B are approximately 10 times as large as crystals of blend A in emulsion globules. Furthermore, it was observed that for blend B, every now and then, a large crystal grows out of a globule. The size of such a crystal is even larger than the diameter of the globule it came out of (figure 3-7A). If such an emulsion was stable at rest it could easily be destabilized. Even cautious pouring out of the, yet stable, emulsion resulted in a solid, partially coalesced mass, while clumps were seen even before the emulsions had reached the end of the vessel. The role of the crystals in this system is beyond questioning. It is obvious that it is not necessary for the film between two globules to become very thin in order to achieve partial coalescence (figure 3-7B). In most cases, however, blend B, having a high solid fat content (about 93% at 4°C) and large crystals, clearly shows N-type crystallization in emulsion globules. It can clearly be observed that several crystals protrude from the globule surface (figure 3-8) over a distance of several microns.

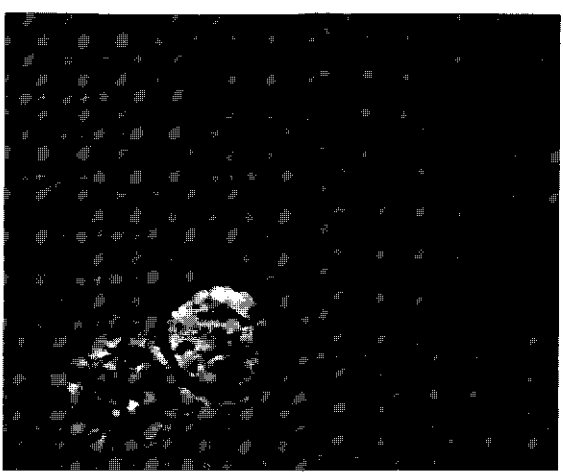

Figure 3-8. Triglyceride blend B globules in 14 mM SDS solution at 4°C. Note the crystals protruding from the O/W interface.

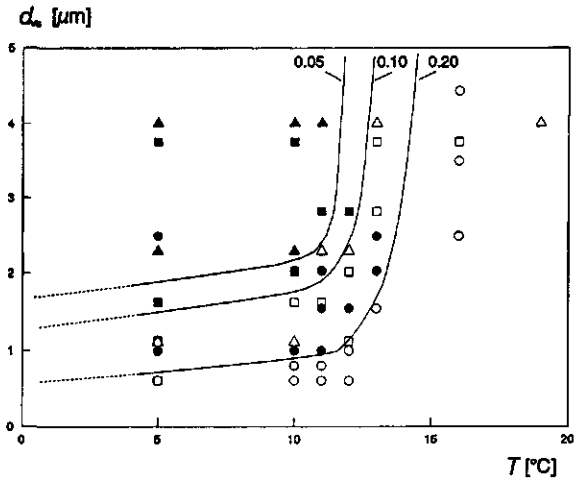

Figure 3-9. Emulsion stability during storage at rest as a function of d_{vs} [μm] and T [°C] for SDS (14 mM) - triglyceride blend B emulsions of variable fat content. The closed symbols correspond to emulsions that destabilize during storage, whereas the open symbols represent emulsions that are stable under quiescent conditions. (Δ) 5% fat (□) 10% fat (○) 20% fat.

Storage of SDS (14mM) - blend B emulsions at temperatures above 13°C did not cause instability. At temperatures below 13°C ,however, a homogeneous solid mass was attained for emulsions of sufficiently high d_{vs} and/or fat content (figure 3-9). Subsequent heating to 45°C caused the emulsion to demix. The upper layer consisted of partially coalesced clumps that creamed out of the emulsion, whereas the lower layer contained the part of the emulsion that remained stable. For a 20% blend B-emulsion (d_{vs} = 2μm) the upper layer amounted to 40% of the total fat content, if kept at 8°C for 3 hours. Similar to the thickening process described above, it was found that for a lower fat content the d_{vs} at which emulsions just became unstable was larger. SDS (14 mM) - blend A emulsions, stored at temperatures between 4 and 30°C were perfectly stable at rest, without any exception.

3.2.2 Couette flow

Emulsion stability was examined in Couette flow of emulsions with SDS or a protein and blend A. The solid fat content of the blend could be varied from 0% to 20% by diluting the original fat blend with its liquid fraction. All experiments were carried out at 20°C.

Table 3-1. The influence of salt addition to SDS (6.9 mM) - blend A (20%) systems on emulsion stability in Couette flow (10 min. at 125 s^{-1}; 20°C ; d_0 = 2.48 μm). Instability is expressed as the relative change in d_{vs} and fat content.

salt concentration [mM]	d_{10}/d_0 [-]	Φ_{10}/Φ_0 [-]
0.00	1.00	1.00
3.42	0.82	0.48
6.84	0.55	0.29

Emulsions were stable at rest and in Couette flow, if no crystals were present. In the presence of crystals emulsions were stable at rest too. In Couette flow they behaved differently. We will first consider SDS(14 mM) - 20% blend A emulsions with 20% solid fat in the oil phase at 20°C. Application of Couette flow during 10 minutes at a shear rate of 125 s^{-1} resulted in fast aggregation, so that the d_{vs} and the fat content, in the stable remainder of the emulsion after heating it at 45°C, decreased with time. Variation in ionic strength by varying the salt concentration markedly changed the observed emulsion instability (table 3-1). The more salt added the more unstable the emulsion becomes. Variation in the solid fat content appeared to give similar results. Emulsion instability increased with solid fat content (table 3-2). This is in accordance with findings of van Boekel & Walstra [4], who published similar results for paraffin emulsions in the presence of PVA 16-98 or SDS as the surface active material. Triglyceride blend A was also used to make emulsions with 1% ß-lactoglobulin or 1% sodium caseinate in the aqueous phase. In some cases the protein was displaced by SDS after emulsification. The stability of these emulsions in Couette flow at a shear rate of 500 s^{-1} is represented in table 3-3. The protein stabilized emulsions appeared perfectly stable. This is what one would expect, since the contact angles of crystals in these systems is high (for caseinate systems we have found a contact

Table 3-2. The influence of solid fat content in SDS (14 mM) - blend A (20%) emulsions on the stability in Couette flow (10 min at 125 s^{-1}; 20°C; d_0 = 2.45 μm). Instability is expressed as the relative change in d_{vs} and fat content.

Solid fat content [%]	d_{10}/d_0 [-]	Φ_{10}/Φ_0 [-]
13.5	1.00	1.00
16.2	1.02	0.99
20.3	0.89	0.77

angle (θ_w) of 141°, the contact angle of ß-lactoglobulin we did not estimate, but is likely to be approximately the same) and, furthermore, thick films remain between approaching globules due to the steric repulsion of the adsorbed protein. If, before cooling the emulsion to 4°C, 14 mM SDS was added to it extremely unstable emulsions were the result. The

Table 3-3. Influence of displacement of protein by SDS (14 mM) in 20% blend A emulsions on the stability in Couette flow. The volume fraction fat that creamed upon heating the treated emulsion at 45°C is taken as a measure of the instability. d_{vs} = 2.5 μm

Surfactant added		Fat loss after Couette flow (G=500 s^{-1}, 20°C, 10 min) and heating step (1h, 45°C)
before crystallization	after crystallization	
Protein[1)]	----	0%
Protein[1)] + SDS	----	85%
Protein[1)]	SDS	0%
SDS	----	90%

1) Sodium caseinate and ß-lactoglobuline gave identical results

decreases in d_{vs} and fat content were comparable to that of the SDS-blend A emulsions. Addition of 14 mM SDS after cooling the emulsion overnight at 4 °C did not cause instability of the emulsion. Now, the emulsion behaved in the same way as the protein stabilized emulsions did. This will be discussed later on.

3.3 Lanza effects in partly crystallized O/W emulsions

The role of the crystals was further examined by removing the crystals from the oil phase (by dilution with 35 mM SDS) at different times before and after induction of partial coalescence in Couette flow. For comparison, emulsions were also diluted with water. Natural cream, recombined cream and SDS-triglyceride blend A were tested in this way. Since the results with all systems were similar, we have chosen to discuss only the results with SDS - triglyceride blend A (figure 3-10). Emulsions appeared stable, if the crystals were removed from the oil phase before application of Couette flow, similar to emulsions that did not contain crystals in the first place. Application of Couette flow to emulsions with crystals in the oil phase, gave more complicated results. From the samples that were diluted with

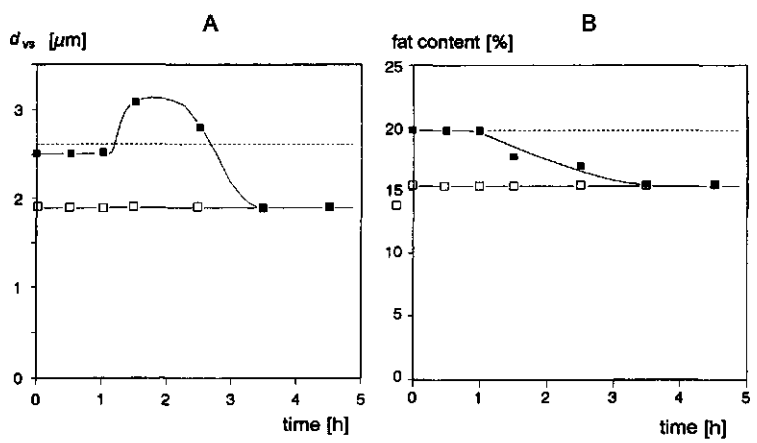

Figure 3-10. Effect of diluting SDS (14 mM) - triglyceride blend A (20%) emulsions with 35 mM SDS (■) or H_2O (□) at various times after applying Couette flow (10 min at $G \approx 125 s^{-1}$), on d_{vs} and fat content of the lower layer of the creamed emulsion. At $t=0$ the emulsion is just removed from the Couette apparatus. The dotted lines represent the situation of the emulsion before applying Couette flow.

water it can be seen that Couette flow resulted in partial coalescence, as reflected in a decrease in d_{vs} and fat content after creaming. Aggregation was almost nullified by removal of the crystals, if removal took place within about one hour after aggregation. The slightly smaller d_{vs}, found after dilution with 35 mM SDS, must have been due to the loss of material in the globules if the crystals migrate to the water phase. Addition of 35 mM SDS two hours after partial coalescence results in the highest d_{vs}. It was even higher than in the original emulsion. The fat content was in between that of the original emulsion and the emulsion diluted with water, two hours after partial coalescence. At this time, apparently not all crystal aggregates could be completely separated any more. Clumps appeared of which some still were so large that they creamed, whereas others were larger than the original globules but not so large that they creamed. If the time elapsed between partial coalescence and removal of the crystals from the oil phase exceeded four hours, no clumps could be separated any longer, so that d_{vs} and fat content were comparable to the results obtained after dilution with water.

3.4 Microscopic observations

From microscopic observations it appeared that in our experiments the fat crystals were more or less randomly distributed in the globules. Moreover, we commonly observed N-types (figure 3-2), irrespective of the particles being single globules or aggregates. This differs from the observations by van Boekel & Walstra [4]. They found that in their systems, containing either paraffin oil or tristearate, instability was almost always accompanied by tangentially oriented fat crystals, e.g. M-type globules (figure 3-2); a few exceptions were found where N-type crystalization was observed and nevertheless partial coalescence occurred. In these cases, the aggregates showed the M-type, without exception. This suggests that N-types may be transformed into M-types, e.g. after breakdown of the crystal network due to deformation of globules in a velocity gradient. However, van Boekel [2] has argued that this was very unlikely to happen in the flow field he used in his experiments, since the shearing stresses were too low.

We have tried to simulate this deformation process on blend A globules, dispersed in an

aqueous solution of caseinate or SDS, by the use of the capillary method as described in section 2.8. The suction pressure was adjusted to suck the N-type globules onto the opening of the capillary. A further increase of the pressure resulted in squeezing liquid oil out of the globule, but we could never change N-type into M-type globules, unlike earlier observations with milk fat globules [26]. What we did see, however, was that the shape of the globule changed into some sort of a 'porcupine', the quills being the crystals that protruded from the globule. Such a globule appeared extremely sensitive to partial coalescence, since immediately after formation of this weirdly shaped globule aggregation with globules in its vicinity was observed.

4 DISCUSSION

4.1 Influence of contact angle and film thickness on emulsion stability

Destabilization of O/W emulsions that are stable in the absence of crystals, can only occur if crystals are situated at the interface partly sticking out into the aqueous phase [3,8]. The presence of interfacial crystals seems governed by the contact angle at the O/W boundary. As crystals become preferentially wetted by the aqueous phase they are expected to stick out further, the corresponding emulsion globules thereby becoming more unstable. The effect of crystals at the interface, however, is complicated by other factors. The crystal shape will affect the equilibrium position at the interface and this and the crystal size will influence the protrusion distance (figure 3-11). The latter effect is at least one of the

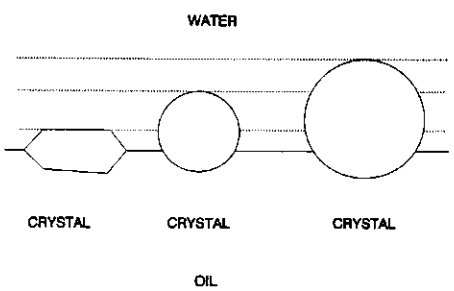

Figure 3-11. Influence of crystal size and shape on the protrusion distance into the aqueous phase (after [8]).

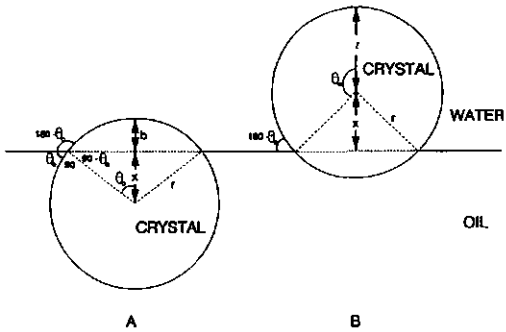

Figure 3-12. A spherical fat crystal at the O/W boundary. The protrusion distance of the crystal into the aqueous phase is equal to $r - x$ in case of an acute contact angle (A) and $r + x$ if the contact angle is obtuse (B).

reasons that with blend B, having large crystals (about 1 μm), far more unstable emulsions are produced (even under quiescent conditions) than with blend A (section 3.1). The number of crystals sticking out into the aqueous phase is important too. This is demonstrated by the influence of the solid fat content. The more solid fat present, the more likely it is that crystals stick out. Evidently, this would lead to faster partial coalescence, which indeed has been observed (section 3.2). It must be realized that changes in wetting properties in most cases are accompanied by other changes as well. The contact angle is related to the interfacial tensions in the system as given by Young's equation, and on the other hand the interfacial tensions are related to surfactant adsorption by virtue of Gibbs' law. Surfactant adsorption, in turn, influences the minimum film thickness (h_{min}) that remains between approaching droplets.Let us, for example, consider the situation of a spherical fat crystal at the O/W boundary as a function of the SDS concentration. We realize that a platelet shape is more realistic, but the simpler case of spheres serves to illustrate the trends. From figure 3-12 it becomes clear that the length (b) of that part of the crystal that sticks into the aqueous phase amounts to:

$$b = r\,(1 - \cos\theta_c) \qquad (2)$$

Whether the length b is sufficient to cause partial coalescence depends on the interaction energy V_{int} between approaching emulsion globules. V_{int} is composed of a repulsive, V_r, and an attractive energy, V_a. With ionic, low molecular weight, emulsifiers the DLVO-theory is

applicable. Usui et al. [25], who analyzed SDS-emulsions in terms of DLVO-theory, gave a useful approximation formula (if $\kappa h > 1$) for the repulsive force:

$$V_R = \frac{\epsilon d \psi_0^2}{4} \ln(1 + e^{-\kappa h}) \quad (3)$$

where ϵ is the dielectric constant of the medium, d is the diameter of the globule, ψ_0 is the potential at the interface and κ is the Debye reciprocal length parameter (for a detailed description of the calculations see the appendix). The Van der Waals attraction is given by:

$$V_A = -A \frac{d}{24h} \quad (4)$$

where A is the Hamaker constant.

In figure 3-13 both b and h_{min} are depicted as a function of the SDS concentration. The minimum distance between approaching globules is virtually constant above the critical micellar concentration (cmc), due to a constant ionic strength, whereas the protrusion

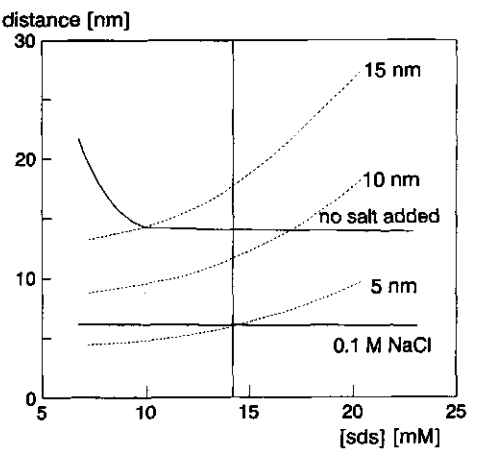

Figure 3-13. Influence of the SDS concentration on the distance of minimum approach h_{min} of two globules of identical size (——) and on the length (b) of that part of the crystal that sticks out into the aqueous phase (----). The numbers denote the radii of the three spherical crystals for which b was calculated. Calculated for $A = 2 * 10^{-20}$ J, $r = 1.5\ \mu m$, $\psi_0 = 80\text{-}100$ mV. For the values of κ see the appendix.

distance of a (spherical) crystal at the interface increases, so that emulsion instability is enhanced at higher SDS concentrations. Salt addition, too, decreases h_{min}, yet in this situation the contact angle remains almost constant. As a consequence, one expects emulsions to become more unstable, too, as the salt concentration increases and this is indeed observed (section 3.2).

From figure 3-13 it can be deduced that emulsions with 13.8 mM SDS in the aqueous phase would be stable ($b < h_{min}$), if crystals are not extremely large. It must, however, be realized that the above considerations are based on free moving spherical crystals. Yet in emulsion globules crystals may have a different shape. Furthermore, crystals are bound to be flocculated into a network, so that they are restricted in their movements. In time these flocculated systems will sinter into a strong network [23,28]. As a consequence, crystals may adopt an interfacial position that is significantly different from what is expected merely on the basis of wetting properties. This is confirmed by our adsorption displacement experiments. It is shown that the moment of protein displacement, i.e. before or after fat crystallization, is of great influence on emulsion stability (see section 3.2.2 and table 3-3). We found that upon SDS addition before crystallization the emulsion behaved as if no protein was present; the SDS had displaced the protein, in the way De Feyter et al. [9] describe. But then the question arises as to why the emulsion behaved so differently if SDS had been added after crystallization has occurred. One assumption may be that in the presence of crystals protein displacement by SDS would not occur, but that would imply that the protein is specifically adsorbed onto the crystalline fat and this appears very unlikely. A more plausible explanation in our opinion is that the displacement does take place in the same way De Feyter et al. describe, but that the crystals, being fixed in a strong network, cannot reorientate in reaction to the new situation. The supposition that the crystals have flocculated into a strong network is realistic, since the globules rather form 'porcupine' shaped globules than yield under the applied pressure (see section 3.2). This would mean that the extent of protrusion of the sintered crystals from the interface does not alter upon removing the protein.

This network rigidity would also imply that the sticking out must be established during the

period that the crystals still move around freely or the network still is dynamic, i.e. crystals rearrange by flocculation and deflocculation [16]. From the experiments described in section 3.3 we have indications that it may take several hours after crystallization before such a dynamic network changes into a strong fixed network (see section 4.3), although this will most likely depend on the fat composition.

4.2 Nature of the globules

In emulsions exhibiting partial coalescence, different types of globules with different characteristic crystal orientations at the O/W interface have been perceived so far:

- I - Globules with (some of the) crystals tangentially oriented at the O/W boundary (figure 3-2). The crystals are smaller than the globule diameter and attain their position at the interface after being formed. The larger part of such a crystal will probably not stick out of the globule, but the curved interface and the typical geometry of many fat crystals can possibly lead to a situation where an edge sticks out of the globule. This situation may occur in at least some globules depending on geometry, crystal size and contact angle and a protruding crystal may stick out by a few times ten nanometres. These emulsions show partial coalescence at moderate rate which can be described by first order kinetics [3]. Van Boekel and Walstra calculated a collision efficiency, α, being the fraction of encounters leading to coalescence. For their systems (containing crystals) α was approximately 10^{-6}, whereas in the absence of crystals $\alpha = 10^{-12}$ appeared realistic.

- II - Globules with crystals that are too large to follow the curvature of the boundary while growing (K-type). If the contact angle favours wetting of the relatively large crystals by the aqueous phase ($\theta_w \leq 90°$) the crystals will grow out of the oil globule. This behaviour was found in SDS(11-28 mM) - blend B emulsions; blend B crystals producing large crystals. On the other hand, the crystals in the globules of, for example, SDS (13.8 mM) - paraffin mixtures did not grow out of the globules, despite of the large crystal sizes. This must have been due to the unfavourable wetting properties ($\theta_w = 116°$, [4]); crystals were preferentially wetted by the oil

phase. As can be seen from figure 3-7B, globules with crystals growing out need not be close to each other in order to partially coalesce. Such an emulsion appears extremely sensitive to velocity gradients, turning into a solid mass by simply pouring it. In this case α approaches 1, i.e. all encounters lead to partial coalescence.

- III - Globules with (some of the) crystals roughly radially oriented at the O/W boundary. Three situations of free moveable crystals can be distinguished, based on the contact angle (θ_w) of a crystal at the

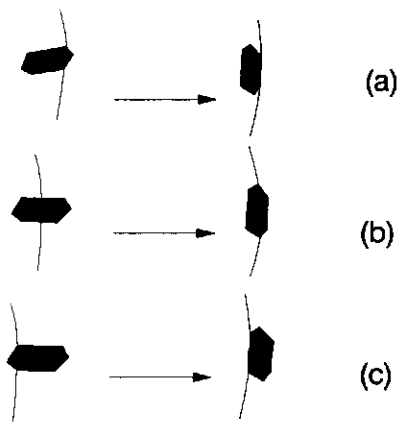

Figure 3-14. Possible reorientation of a free moveable crystal at the O/W boundary. The contact angle (as measured in the aqueous phase) was (A) larger than 90° (B) approximately 90° and (c) smaller than 90°.

interface (as measured in the aqueous phase):

- $\theta_w >> 90°$ (figure 3-14a). Crystals, being preferentially wetted by the oil phase, will move to the interior of the globule. Consequently the situation as described in I is attained.

- $\theta_w \approx 90$ (figure 3-14b). This seems a stable position for crystals, not being forced into either phase. Nevertheless, it is a metastable situation, since the interfacial forces will push the crystals into a tangential orientation. Again the situation as described in I is attained.

- $\theta_w << 90°$ (figure 3-14c). Crystals are preferentially wetted by the aqueous phase, so that they will become tangentially oriented at the outside of the globule in the O/W interface. This may, in principle, cause aggregation of globules by bridging, but partial coalescence has become unlikely.

From the above it becomes clear, that irrespective of the wetting circumstances, free moving crystals will be tangentially oriented at the interface (except if crystals are too large to bend along the curvature of the globule). Nevertheless, we observed crystals distributed at random throughout the globules (N-type) in most of our emulsions. At the globule boundary crystals with an approximately radial orientation were clearly observed . This orientation seems only to persist if the crystals are kept in a network. This supposition was confirmed by the experiments with the capillary method. A firm crystal network prevented the globules to be sucked into the capillary if solid fat was present. Instead, oil was squeezed out of the globule (see also sec. 3.4). Such a loss of oil causes a deficiency of liquid so that more crystals will protrude from the interface and over larger distances. A further suction of liquid oil will thus result in the sensitivity to partial coalescence to increase. We indeed observed rapid partial coalescence with globules in the vicinity of such a globule at the capillary tip.

The protrusion of crystals due to a lack of (liquid) oil from the globule, as caused by suction on a capillary, may be representative for the process occurring when globules crystallize. First of all, a continuous crystal network is developed. In the beginning the oil will be able to fully surround the network, but if more oil crystallizes, for example by lowering the temperature, the amount of material in the network increases, whereas the amount of oil decreases. If this process continues, globules will become short of liquid oil, so that crystals can no longer be completely wetted by the oil. They will start protruding the O/W interface. Furthermore, lowering of the temperature will cause shrinkage, the liquid oil shrinking more than the solid. This again will promote the protrusion of crystals. Let us, for example, consider emulsion globules of 20% solid fat in the oil, where the crystals have formed a solid network. The thermal expansion coefficients are about 10^{-6} m^3 kg^{-1} K^{-1} for the oil and $3.9*10^{-7}$ m^3 kg^{-1} K^{-1} for the solid fat [7]. The globules are cooled from 40 to 20°C, so that

the volume shrinkage amounts to 1.80% (if the reciprocal of the density of the oil at 40°C is 1.1 $dm^3\ kg^{-1}$). The volume shrinkage with regard to the crystals is 0.70%, so that the relative shrinkage of the oil, with regard to the crystals, therefore, is 1.10%. For a globule with a radius of 2 μm this comes down to an average (further) protrusion into the aqueous phase of 7 nm due to shrinkage. If due to the temperature decrease, more fat crystallizes the protrusion will even be larger and naturally, the latter effect may become quite large. In conclusion, microscopic observation of the crystal orientation does not give unequivocal information on the position of the crystals at the interface (crystals may stick out, irrespective of tangential or random orientation in the droplets), nor on the mechanism of partial coalescence. Furthermore, it must be concluded that crystals may stick out further from N-types than from L- or M-types, depending on the presence of a network and some other variables (solid fat content and changes therein, original crystal size, way of sintering, etc.). Such N-type crystallized globules may cover a wide range of coalescence efficiencies. In the (rather exceptional) case where there are only one or two crystals present per globule, for example in paraffin (liquid and solid) globules, α is approximately 10^{-6}. If N-type globules contain numerous crystals partial coalescence may become much more efficient ($10^{-6} < \alpha < 1$).

Knowing that globules may crystallize in various ways the question arises as to what factors cause crystals to become so differently oriented. We will discuss this aspect in more detail in a subsequent paper. Furthermore, it is clear that the different crystallization types greatly influence the rate of destabilization of O/W emulsions. We also studied the kinetics of partial coalescence, influenced by factors like kind of fat and surfactant, solid fat content, shear rate etc. and compared the results with those of a simulation model developed to provide a means of characterizing emulsion stability. We intend to report on this shortly.

4.3 Nature of the aggregates

Van Boekel & Walstra [4] designated partial coalescence an irreversible process. From the experiments described in section 3.3 we know now that this is not necessarily the case until some time (about 4 hours in the case of blend A) after partial coalescence. Changing the

wetting properties shortly after partial coalescence, so that crystals become better wetted by the aqueous phase, results in dispersion of the aggregates into globules of the original size (except for the crystals that are now in the aqueous phase). In our opinion this has to be explained as follows: directly after the occurrence of partial coalescence aggregates are kept together by an oil neck that covers the bridging crystal(s) (figure 3-15A). Upon addition

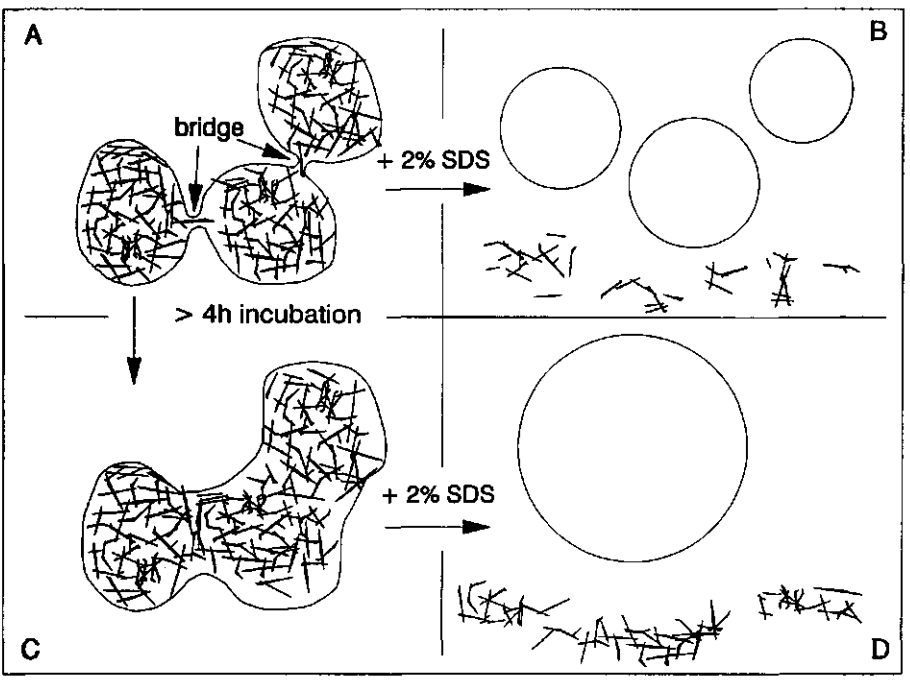

Figure 3-15. Structure of partially coalesced clumps (highly schematic).

of a "Lanza inducing" SDS solution crystals migrate to the aqueous phase. The oil neck between aggregated globules, that served to cover the bridging crystal, breaks. As a consequence globules will separate again (figure 3-15B). In time, more and more crystal

networks of the originating globules will sinter. These sintered aggregates can no longer be separated. After several hours (4 to 5 hours in the case of blend A) all clumps have become irreversibly attached by the sintering process (figure 3-15C). Addition of 35mM SDS removes the crystals from the oil phase and the liquid oil flows together into one, larger, droplet (figure 3-15D).

5 CONCLUSIONS

Partial coalescence caused by L/M-type crystallized globules (as described by van Boekel & Walstra [4]) was found to be an exception, caused by the absence of secundary nucleation in paraffin oil. In most cases crystals are kept in a network. Under these circumstances, some crystals can have a stable, approximately radial orientation at the globule boundary. This was observed for N-type crystallized globules in the case that the number of crystals was numerous. These globules appear very sensitive to partial coalescence (mostly $\alpha >> 10^{-6}$). In some cases rapid partial coalescence was observed even at rest.

The variation in α is mainly caused by variations in the distance over which crystals protrude into the aqueous phase. The further they protrude the more sensitive the globules are to partial coalescence. The main variables that influence the protrusion distance are the contact angle of the crystals at the O/W boundary at the moment of network formation and any further fat crystallization after formation of the network.

In some cases crystals in the globule can move around freely, and at least some become tangentially oriented at the O/W interface. The coalescence efficiency, α, depends on the wetting properties. If $\theta_w \geq 90°$, α will be small ($\alpha < 10^{-6}$), whereas at lower θ_w-values crystals, being tangentially oriented at the outside of the O/W interface, may cause globule aggregation, but not partial coalescence.

Partial coalescence can in some cases be reversed by changing the wetting properties to such extent that crystals become better wetted by the aqueous phase. If these alterations take place within a few hours after partial coalescence the crystal networks of the individual globules may come out of the globules as a whole and the remaining liquid droplets separate again. After a few hours the merging of globules has gone so far that the liquid droplets can

no longer be separated upon removal of the crystals.

6 ACKNOWLEDGEMENTS

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APPENDIX: IONIC STRENGTH OF MICELLAR SOLUTIONS (after unpublished results of E.H. Lucassen-Reijnders)

The Debye parameter, κ, represents the reciprocal of the electric double layer thickness of an ionic solution. For a surfactant, NaS, having a valence of 1, κ depends on the molar concentrations (c_{Na} and c_S) the following way:

$$\kappa \simeq \sqrt{10(c_{Na} + c_S)} \tag{5}$$

where κ is expressed in nm^{-1}. Micellisation of the ionic surfactant NaS can be represented as:

$$n[S] + (1-\alpha)n[Na] \rightleftarrows [M] \tag{6}$$

where α is the degree of dissociation of the micelles (M) and n the number of monomers per micelle. If also salt is present, the total concentrations of S and Na are given by:

$$c_T = c_s + nc_M \tag{7}$$

$$c_T + c_{Cl} = c_{Na} + (1-\alpha)nc_M \tag{8}$$

where c_{Cl} is the salt concentration of the added salt. If α can be assumed constant (i.e. independent of c_{Na} and c_S), c_{Na} and c_S can be expressed in terms of the critical micellar concentration in the absence of salt, c_0, since at this concentration we have $c_{Na} = c_S = c_0$:

$$\log c_S + (1-\alpha)\log c_{Na} = (2-\alpha)\log c_0 \tag{9}$$

A second relationship between the free concentrations c_{Na} and c_S follows from equations (7) and (8):

$$c_{Na} = (1-\alpha)c_s + \alpha c_T + c_{Cl} \tag{10}$$

c_{Na} and c_S can be evaluated from equations (9) and (10) as a function of c_T for any given values of α, c_0 and c_{Cl}. From the effect of added NaCl on the critical micellar concentration, α is mostly found to be 0.25 ± 0.05. In figure 3-16 κ is given as a function of the SDS concentration is given, using $\alpha = 0.25$ and $c_{Cl}/c_0 = 0$ or 12.5, taking into account that the addition of NaCl reduces the concentration at which micelles are first formed to 15% of c_0, according to equation (9).

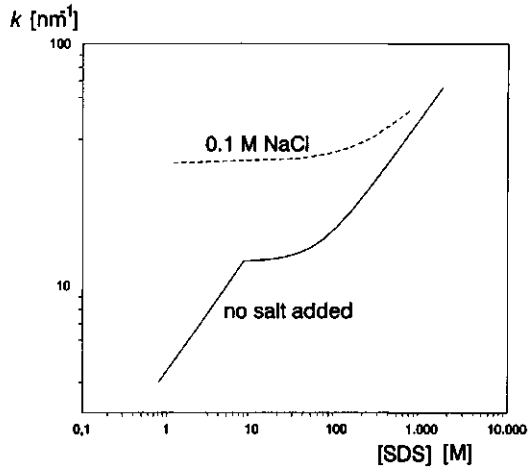

Figure 3-16. Ionic strength of an SDS solution with (0.1 M) and without salt as a function of the SDS concentration. The critical micelle concentration of SDS without salt is 8 mM and with salt 1.25 mM. The micellar degree of dissociation was 0.25.

PARTIAL COALESCENCE IN O/W EMULSIONS:

II. INFLUENCE OF THE PROPERTIES OF THE FAT

ABSTRACT

The influence of the properties of the fat in O/W emulsions on partial coalescence was investigated. As a surfactant either SDS or a protein was used. The presence of crystals in the fat globules of an O/W emulsion can tremendously enhance the instability of the emulsion. We found that in emulsions exhibiting partial coalescence a continuous fat network throughout the globules is present. The formation of such a network depends on the size of the crystals and of the globule: the larger the crystals and/or the smaller the globule the higher the solid fat content needed for a continuous fat network to be formed. Consequently, partial coalescence mostly considerable increased with increasing solid fat content. Above a certain amount of solid fat, the rate of partial coalescence decreased again. The optimum solid fat fraction for partial coalescence depended both on the properties of the fat and on the velocity gradient to which the emulsion was submitted: the higher the velocity gradient, the lower the solid fat content \at which the partial coalescence rate started to decrease again.

Boode K., Walstra P., de Groot-Mostert A.; to be published in colloids and surfaces.

PARTIAL COALESCENCE IN O/W EMULSIONS:

II. INFLUENCE OF THE PROPERTIES OF THE FAT

1 INTRODUCTION

Fat crystals in the oil globules of oil-in-water emulsions play an important role in emulsion instability, especially if streaming occurs. When crystals stick out through the O/W interface they may pierce the water film that remains between approaching globules. The crystal functions as a connection along which oil can flow from the one globule to the other, causing them to coalesce. The crystals inside both globules, often kept in a network, mostly prevent complete merging of the globules: they only partly flow into one another. This process, therefore, is called partial coalescence [2, chapter 3]. With this prominent role of fat crystals, it is obvious that the properties of the fat must be considerable in emulsion destabilization. Many reports in literature [1,8,13,17,18,19,22] mention the importance of the crystalline fat. Nevertheless, the knowledge of the influence of the properties of the fat on emulsion stability is rather scanty. What we do know is that the composition of the fat has considerable influence (see also chapter 3). It influences the amount of solid fat and this in turn influences emulsion stability. The more solid fat, the greater the number of crystals that may stick out, causing the emulsion to be less stable. It is, however, unclear whether there is a minimum and an optimum solid fat content with respect to emulsion instability. One can imagine that at a low solid fat content there may be a shortage of crystals that can induce partial coalescence, whereas a very high solid fat content leaves insufficient liquid fat to allow even the beginning of a merging of globules. The existence of an optimum temperature (hence, an optimum solid fat content) for churning of natural cream, as reported, for instance, by Labuschagne [13], is in accordance with this idea. Furthermore,

the size and shape of crystals may be important [3,8] by means of their influence on the protrusion distance into the aqueous phase. The influence of the size of the crystals (the shape may play a role as well) is essential in the so-called rebodying process (see chapter 2): emulsions that were stored at 4°C for at least two hours, then kept at, say, 30°C for at least half an hour and subsequently cooled back to 4°C, became extremely unstable. Above a fat content of, say, 20% partial coalescence then occurred even at rest. It was concluded that the larger size of the crystals is the main reason for the marked increase in instability.

The number of crystals present in fat globules differs widely. Walstra and van Beresteijn [26] reasoned that, for the case where the number of catalytic impurities is limiting for crystallization to occur in the emulsion, most individual globules would contain only one or two of these. Consequently, only one or a few crystals would then be expected in each globule. In practice, however, many fats produce numerous crystals per emulsion globule. The only explanation we can think of is secondary nucleation, a not yet fully understood phenomenon. It amounts to the spontaneous formation of nuclei in the vicinity of a (growing?) crystal. Since the number of crystals determines their size and the possibility of the formation of crystal networks, secondary nucleation may play an important role in partial coalescence.

Recently, Mc Clements et al. [15] observed a (very slow) crystallization of supercooled liquid globules in the presence of fully crystallized globules. In our opinion this can only be caused by protruding crystals of the solid globules that touch a supercooled globule during a collision. This may occasionally induce nucleation in the other globule, which then (partly) crystallizes. From the results of Mc Clements et al. we calculate that at most 1 in 10^8 Brownian encounters between a partly crystallized and a liquid globule would have led to crystallization in the latter.

The properties of a fat crystal network may thus have considerable effect on emulsion stability. Yet, we know only little about it. Some rheological measurements [11,12,21] have been done, but only in bulk fat. The properties of a fat network in bulk and in a globule

have, however, never been compared. In fact, the network in the globules itself has never been studied.

The aim of this study was to obtain a better understanding of the properties of the fat in relation to partial coalescence of emulsion globules. Experiments were carried out both in bulk fat and in emulsion globules. We have attempted to interpret some of the results by means of fractal flocculation theory.

2 MATERIALS AND METHODS

2.1 Materials

The triglyceride blends A and B were kindly supplied by Unilever Research, Vlaardingen, The Netherlands. Both blends were stored at 4°C in tins. The fat was fully melted before opening the tin for use. Blend A (96.9% tri-, 3.0% di-, 0.1% monoglycerides) had solid fat fractions of 0.45 and 0.20 at 5 and 20°C, respectively. The final melting point was 38°C. Blend B (96.7% tri-, 3.2% di-, 0.1% monoglycerides) had solid fat fractions of 0.95 and 0.84 at 5 and 20°C, respectively. The final melting point was 38°C.

The liquid fractions of both fat blends were obtained by fractionation at 5°C. The solid fat content of the fat blends was varied by mixing these fractions with the fat blends. This was preferred to changing the temperature, since other properties may also change with temperature.

Anhydrous milk fat (> 99.8% pure fat, < 0.1% water) had solid fat fractions of 0.45 and 0.18 at 5 and 20°C, respectively. It was stored at 7°C in sealed tins. The fat was fully melted before use.

Paraffin oil was obtained from OPG, Utrecht, the Netherlands. Viscosity 60 - 80 mPa.s; density about 860 kg m^{-3}. Solid paraffin was obtained from Merck A.G., Darmstadt, W-Germany. It had an apparent melting point of 42 - 44°C and a density of about 880 kg m^{-3}. Both paraffins were mixed in different ratios, which are indicated in the text.

Sodium dodecyl sulphate (SDS) was obtained from BDH, England. Its grade was specially

pure. The critical micelle concentration (CMC) at 20°C in water is 8 mM and 1.5 mM in 0.1 M NaCl [7].

Cream was obtained by centrifuging fresh cows' milk at 40°C to the desired fat content. To inactivate lipase it was heated for 15 min at 70°C.

Skim milk was obtained by centrifuging fresh cows' milk at 40°C to a fat content of 0.07%. To inactivate lipase it was heated at least for 10 min at 64°C.

Sodium caseinate (1%) was prepared from fresh skim milk by repeated precipitation with hydrochloric acid and redispersion in water (pH 7.6). Afterwards it was spray-dried.

2.2 Pretreatment of the O/W emulsions.

Oil-in-water emulsions were made using a Rannie Laboratory Homogenizer at 4 bar overpressure. All emulsions were free of aggregated globules as was checked by microscopy. They were stored at least overnight at 4°C to ensure crystallization of fat in all globules [26]. Storage was shorter than a week so that bacterial spoilage was avoided. Creaming and subsequent partial coalescence were prevented by storing the emulsion in slowly rotating cylinders, end over end, with exclusion of air. The droplet size distribution was found not to change during storage.

In some experiments an emulsion, containing partly crystallized oil globules, was mixed with an emulsion without crystals. Care was taken that the globule size distributions of both emulsions were similar, so that the fraction of globules that contained crystals was independent of the globule size.

2.3 Characterization of the emulsion.

Globule size distributions of the emulsions were determined by a spectroturbidimetric method [23,25,27].

Fat contents as well as the amount of fat that was crystallized were estimated by wide-line pulse proton NMR [2].

Polarized light microscopy was used to observe the appearance of fat crystals in the oil

globules [24] (see figure 2-3 and chapter 3).

2.4 Couette flow

O/W emulsions were subjected to Couette flow, i.e. flow between concentric cylinders of which the outer one rotated and the inner one was fixed. The rate of rotation was below 500 s^{-1}, so that laminar flow developed [3]. After 30 min the apparatus was emptied and the samples were diluted with a solution of disodium ethylene diamine tetraacetate (EDTA) and polyoxyethylene sorbitan monolaurate in water, and heated in a separation funnel to turn any clumps into globules. Big aggregates cause the separation of an oil layer on top of the emulsion. A few millilitres of the remaining emulsion were tapped and characterized as described in Sec. 2.3.

2.5 Permeametry

For permeametry use was made of the equipment as depicted in figure 4-1. The method is derived from that by de Jager et al. [10]. We intend to report on it in detail in a forthcoming paper. Before each experiment the bottom of the measuring vessel was covered with a filter paper. On top a layer of melted fat was brought and stored for at least 24 hours at 4°C, so

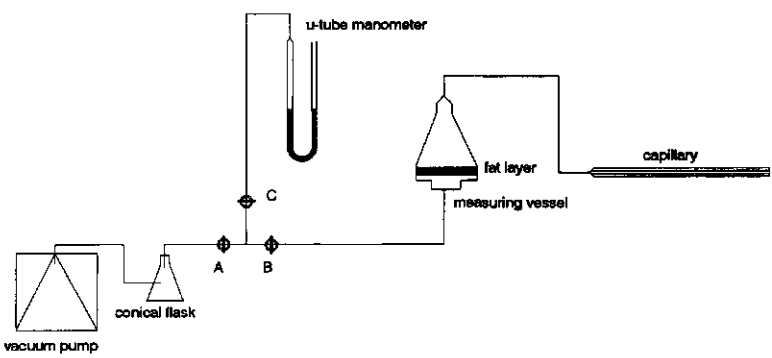

Figure 4-1. General overview of the equipment for permeametry; see text.

that a fat crystal network was formed. 16 hours before measurement the sample was put 20°C. Just before a measurement the vessel and the connected capillary were filled with liquid oil of 20°C. A constant pressure was adjusted to the desired value. Opening of tap B then resulted in the suction of oil out of the fat crystal network. The oil flux was measured during at least one hour. Measurements were done at several pressures (between 10^3 and 10^5 Pa) and after various storage times (between 2 and 19 days) at 4°C. After each experiment it was checked whether the network was still attached to the vessel. It appeared that, normally, the fat stuck to the wall. In those cases were we suspected that slip had occurred, the experiment was repeated.

2.6 Rheological measurements

Measurements were performed with a constant stress apparatus, a PDR 81 Rheometer from Deer Ltd. A stainless steel measuring body of concentric cylinder geometry was used. The diameter of the inner cylinder was 12 mm and that of the outer one was 15 mm; the height was 30 mm. The gap setting was done at 20°C. The measuring body was immersed in a thermostatting bath and the apparatus was placed in a perspex box to avoid interference by temperature gradients and air currents. A constant stress was applied to the inner cylinder by means of an induction type electric motor. The rolling friction was induced using an air bearing support. The angular displacement of the inner cylinder as a function of time was determined by a non-contacting electronic sensor. Stresses upto 0.0064 bar were used. Fat samples were fully melted at a temperature of 50°C and kept at 37°C until use. After filling with the fully melted fat the measuring body was rapidly cooled with ice water to a temperature of 4°C and left at that temperature for one hour. The sample was heated to 20°C at a speed of 0.25 K/min and aged for 1.5 hours at this temperature. A stress was applied during one minute and the relaxation of the sample in the following 1 min was registered. This was repeated with a somewhat higher stress and so on, until the sample started yielding.

2.7 Contact angle measurements

Contact angles were determined by the method described by Campbell [6]. All measurements were made with fat solidified against air. The liquid oil phase always was a liquid fraction separated from the fat blend at 5°C. Contact angles were estimated of oil droplets formed at the fat surface-water interface (Θ_w) and of water droplets formed at the fat surface-oil interface (Θ_o). Since results appeared identical we decided to use the contact angles as measured in the aqueous phase (Θ_w) only.

2.8 Capillary method

The technique is based on microscopical observation of the behaviour of globules if sucked onto the tip of a glass micropipette (tip diameters between 0.4 and 1.0 μm). For a detailed description see chapter 3.

3 RESULTS

3.1 Bulk fat properties

In principle, information about the structure of a network of fat crystals in oil can be obtained from the permeability coefficient, *B*. We applied Darcy's law

$$v = \frac{B}{\eta}\frac{dP}{dx} \qquad (1)$$

v = the superficial liquid velocity [m s^{-1}]

η = the viscosity of the flowing liquid [Pa s]

dP/dx = the pressure gradient [Pa m^{-1}]

to determine *B* for the triglyceride blends A and B, milk fat and paraffin-paraffin mixtures. In figure 4-2 the permeability coefficient of some fats is depicted as a function of the time the fat dispersions aged at 4°C before the measurement at 20°C. It can be seen that *B* significantly differs for the various kinds of fat. Furthermore, *B* slightly increases with

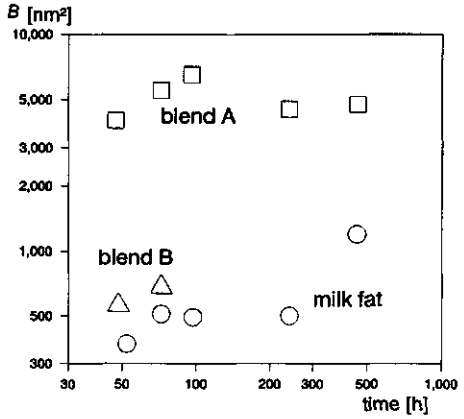

Figure 4-2. Permeability coefficient, *B*, of fat networks of various fats as a function of the time, the samples were stored at 4°C. Sixteen hours before a measurement the sample was placed at the measuring temperature of 20°C.

storage time; it is likely that this is due to one or more of the following changes:

- 1 - enlargement of the units (crystals or clusters of crystals) caused by:
    - Ostwald ripening
    - recrystallization due to polymorphic and compound crystal transitions
- 2 - crystal rearrangement (although sintering may soon stop this process).

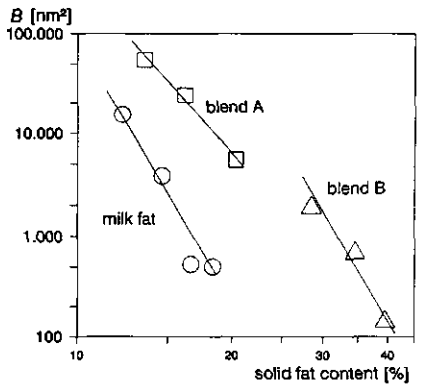

Figure 4-3. Permeability coefficient, *B*, of fat networks of various fats as a function of the solid fat fraction. Blend B was diluted with it's own liquid fraction to a solid fat content of 34.5%. The samples were stored at 4°C for 72 hours. They were placed at 20°C 16 hours before the measurement.

Furthermore, the influence of the fraction solid, Φ_s, on B was studied. In figure 4-3 the permeability coefficient is given as a function of the solid fat fraction, both on a logarithmic scale. The amount of solid fat was varied by adding liquid fraction to the fat dispersion (section 2.1). As can be seen, the permeability exhibited a strong dependence on Φ_s. Approximately straight lines were found, which suggests a fractal nature of the aggregates (see section 4). The slope of these lines is approximately -8, whereas the equation of Kozény-Carman (see equation 10) suggests that the slope should be inbetween -2 and -4. This deviating behaviour for fractal structures was also found by Bremer [4].

The results of the measurements of the shear modulus, G, as a function of the solid fat content, Φ_s, for triglyceride blend A and milk fat, are depicted in figure 4-4, both yielding roughly straight log-log plots.

The yield stresses, σ_y, of the fat dispersions are summarized in table 4-1.

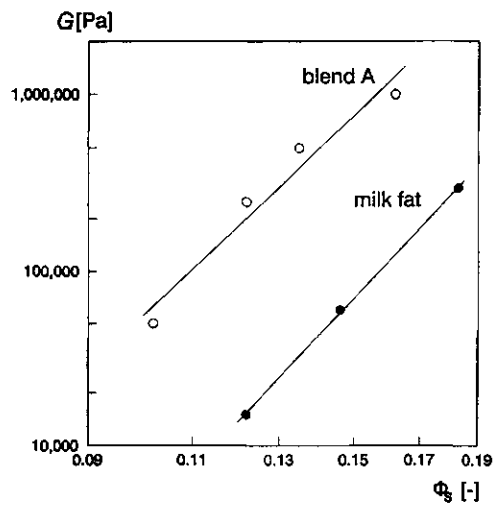

Figure 4-4. Modulus of bulk fats as a function of the solid fat fraction. Measurements were carried out at 20°C after crystallization (in the measuring device) at 4°C for 1 hour.

3.2 Properties of emulsion globules

Emulsion globules, with a diameter varying from 2 to 8 μm, were examined by suction onto the tip of a capillary as described in chapter 3. The method appeared not suitable for totally

liquid globules, since we were not able to sufficiently control the fluctuations in the pressure adjustment at the beginning of an experiment. Without exception, globules were completely sucked into the capillary directly after making contact with the tip. In the presence of sufficient solid fat this problem was overcome, as the initial fluctuations in pressure were too small to affect the globules.

Emulsion globules of paraffin (solid and liquid paraffin were mixed), milk fat and the triglyceride blends A or B in SDS solution were tested. The solid fat content was varied by mixing the fat blends with their own liquid fractions, but milk fat was diluted with the liquid fraction of triglyceride blend A. The behaviour of the globules was similar for all fats except paraffin globules, which were the only ones showing only one or two large crystals. As a result the liquid paraffin was easily squeezed out of the globule until the one or two paraffin crystal(s) in the globule blocked the opening; at that stage a pressure difference of 500 kPa was insufficient to squeeze out more oil.

The other fats behaved in the following manner. If the amount of solid fat was too low, no crystal network had formed and the globule behaved like a liquid one. If a crystal network had formed in the globules, oil could be squeezed out. This continued until the network was no longer completely wetted by oil. The capillary then started to suck on new emulsion globules, which immediately coalesced with the emaciated globule at the tip. The main differences between milk fat and both triglyceride blends was the amount of solid fat needed to obtain a network and the (negative) pressure that was needed to start squeezing out oil. Triglyceride blend B showed an extreme behaviour. At a solid fat content of 50%, a pressure of 500 kPa was not enough to suck any oil out of blend B globules, whereas at 28% solid fat no continuous network was detected. The behaviour of the various fat globules is summarized in table 4-1.

Crystal sizes were examined by polarized light microscopy. The primary fat crystals of blend A and milk fat were too small to be observed, although a fat crystal network structure could more or less be observed. The primary crystals of triglyceride blend B could just be observed, whereas the paraffin crystals were almost of the same size as the globules

Table 4-1. Influence of the type of fat and the solid fat content on the yield stress of the bulk fat, on the presence of a fat network in an emulsion globule (< 10 μm) and on the minimum pressure, P_o, that is needed to squeeze oil out of such a fat network.

		σ_y [Pa]	Fat network in an emulsion globule	P_o [Pa]
Milk fat	Φ_s = 0.092	0	No	0
	Φ_s = 0.120	46	No	0
	Φ_s = 0.146	71	No	0
	Φ_s = 0.180	>>642	Yes	< 5 10^2
Blend A	Φ_s = 0.102	65	No	0
	Φ_s = 0.135	470	No	0
	Φ_s = 0.162	>>642	Yes	3 10^4
	Φ_s = 0.203	>>642	Yes	6 10^4
Blend B	Φ_s = 0.091	0	No	0
	Φ_s = 0.193	2.5	No	0
	Φ_s = 0.285	47	No	0
	Φ_s = 0.836	>>>642	Yes	> 10^5

containing them, so that their size could easily be observed.

Because of the high number of crystals present in triglyceride blend B (presumably due to secondary nucleation) and the possibility to observe them by light microscopy, this blend was used to study the crystal orientation in emulsion globules in solutions of SDS (13.8 mM)or caseinate. The contact angle of crystals at the O/W interface greatly differed

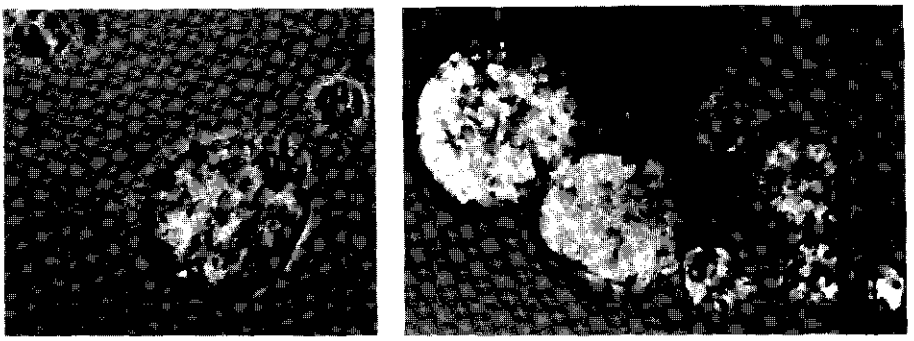

Figure 4-5. Crystallization habit of blend B globules in a 0.4% SDS solution (a) or a 1% caseinate solution (b) as perceived by polarized light microscopy.

between these aqueous solutions. With a contact angle of 154° (as measured in the aqueous phase) in the caseinate solution, the crystals were preferentially wetted by the oil. In the SDS solution a contact angle of 41° was observed, so that the crystals were preferentially wetted by the aqueous phase. This is in accordance with what we observed microscopically. If the solid fat content was not too high, crystals were hardly or not observed piercing the globule boundary in caseinate solutions, whereas in the SDS solution crystals were clearly situated at the O/W interface, partly sticking out into the aqueous phase. In globules with a solid fat content of about 90% at 4°C (pure triglyceride blend B) the amount of solid fat is so high that there is not enough liquid oil left to wet all crystals. The globules in the SDS solution had a porcupine like appearance., i.e. numerous thin spikes protruded from the surface, the more so for larger globules (figure 4-5a). In the caseinate solution it was the other way around; the globules remained approximately spherical and without bulges if they were large enough, and the smaller the globules the more porcupine like they were (figure 4-5b).

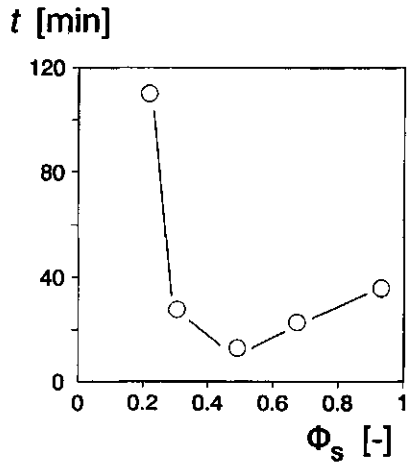

Figure 4-6. The time, until a column of 10 cm SDS (0.4%) - blend B (20%) emulsion no longer subsides under its own weight, is represented as a function of the solid fat content. Measurements were carried out at 4°C. Variations in Φ_s were achieved by diluting blend B with its liquid fraction (see further section 2.1).

3.3 Emulsion stability

Emulsion stability at rest and in Couette flow was studied for milk fat or triglyceride blends A or B in SDS (13.8 mM) or caseinate solution. The SDS containing emulsions made with triglyceride blend B showed extensive partial coalescence during storage at 4°C, as a result of which the emulsions became solid. The rate of partial coalescence for SDS (0.4%) - 20% blend B emulsions at rest was examined by filling several 10 cm high cylinders with an emulsion of 20°C and placing them at 4°C. Every 2 minutes, an emulsion was removed from its cylinder. In figure 4-6 the time, *t*, needed to form a solid emulsion, that no longer subsided under its own weight, is depicted as a function of the solid fat content, Φ_s. It can be seen that *t* sharply declines with Φ_s until approximately half the oil has become solid. Above Φ_s = 0.50, *t* slightly decreased again with increasing amount of solid fat. All other emulsions remained stable at 4°C under quiescent conditions. Emulsions made with caseinate were stable even in Couette flow up to a shear rate of, at least, 500 s^{-1}. The SDS containing emulsions behaved differently, and the degree of instability depended both on the kind of fat and on the solid fat content. Milk fat emulsions (figure 4-7) were more stable

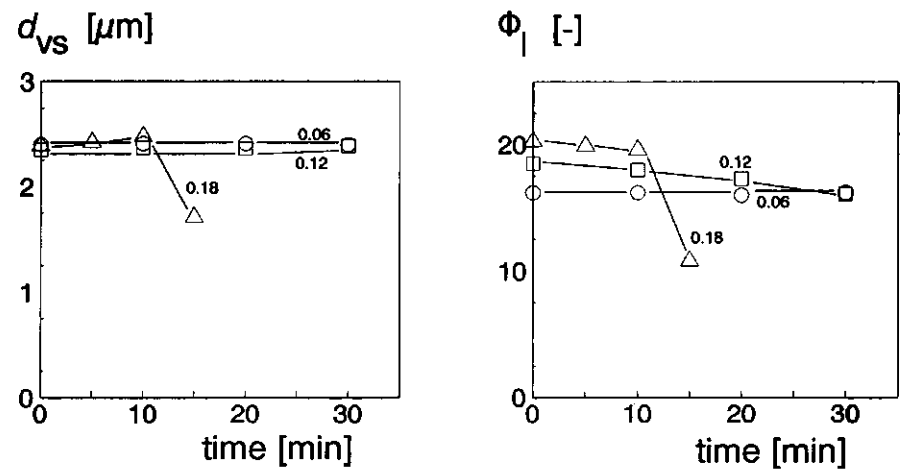

Figure 4-7. Effect of Couette flow (G = 250 s^{-1}, 20°C) on d_{vs} and fat content (Φ_l) as a function of time for SDS (0.4%) - milkfat emulsions of various solid fat contents (as indicated near the lines).

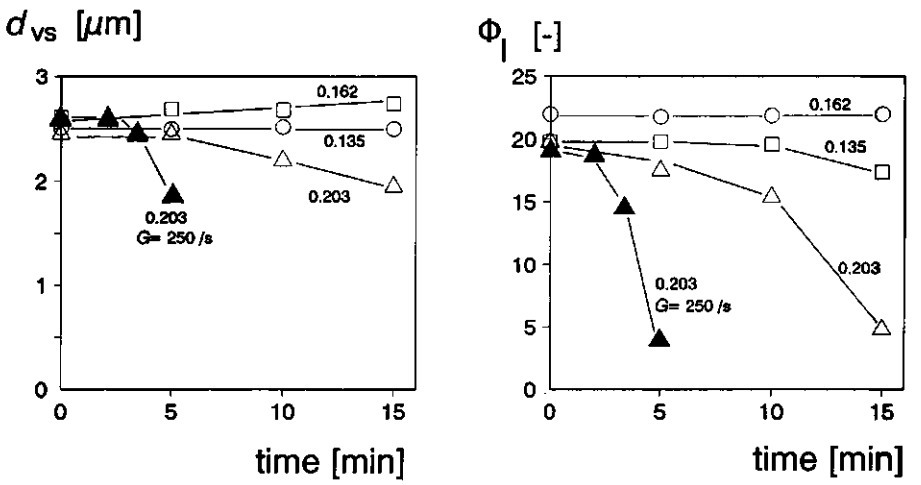

Figure 4-8. Effect of Couette flow (G = 125 s^{-1} unless stated otherwise, 20°C) on d_{vs} and Φ_l as a function of time for SDS (0.4%) - blend A emulsions of various solid fat content (as indicated near the lines).

than blend A emulsions (figure 4-8). The rate of partial coalescence increased with the amount of solid fat in both emulsions. No maximum was found for these emulsions, yet this may be the cause of the relatively low solid fat fractions of these fats.

4 DISCUSSION

The solid fat fraction, Φ_s, in O/W emulsions was observed to have a strong effect on emulsion stability. In general, the more solid fat present the more unstable the emulsion becomes; the number of crystals that can stick out presumably increases and so does the probability that at least one crystal protrudes from the globule surface over a sufficient distance to bridge the gap between two approaching globules. Hence, the probability for partial coalescence to occur increases. On the other hand, emulsions with the same solid fat content do not necessarily have the same emulsion stability. Emulsions with only one or two crystals per globule (like in emulsions of paraffin mixtures) mostly are only slightly unstable. There is only a small chance that the protruding part of the few crystals is in a favourable position for inducing partial coalescence to occur. In some cases, however, crystals grow into the aqueous phase (K-type), so that the effective diameter of the globule increases greatly. In that case emulsions were formed that were extremely unstable [9]. Mostly, however, the globules contain numerous crystals. Since the wetting properties of the crystals favour positioning of crystals at the O/W interface (at least in the systems studied here), one would expect L/M-type globules to be present. Nevertheless, we mostly observed N_2-type globules. So far, we only observed L/M-type clumps in some cases if the disperse phase was milk fat.

Apparently, flocculation of crystals occurs faster than the adsorption of crystals at the interface. As reasoned in chapter 2 the average time for diffusion of a crystal to the interface is about:

$$t_{ads} = \frac{3\pi\eta l_c d^2}{4kT} \qquad (2)$$

where η is the viscosity of the oil, d is the globule diameter and l_c is the crystal size. The time needed for flocculation to occur is, in a rough estimate [14]:

$$t_{floc} = \frac{1\pi\eta l_c^3}{16kT\Phi_s} \qquad (3)$$

so that the ratio between t_{ads} and t_{floc} is:

$$\frac{t_{ads}}{t_{floc}} = 12\phi_s\left[\frac{d}{l_c}\right]^2 \quad (4)$$

From equation (4) it follows that even in the rare situation where the emulsion globule is only 10 times larger than the crystals, the ratio between t_{ads} and t_{floc} equals 1200 Φ_s, so that only in a situation where $\Phi_s < 0.0008$ adsorption at the interface could occur before flocculation. Consequently, most crystals cannot move around freely to find the energetically most favourable orientation. L/M-type globules will only be formed if crystals near the interface can deflocculate and reach the globule boundary [24]. So, mostly N-type globules are formed with the crystals flocculated into a fat network. If the network is smaller than the globule, it will touch the O/W boundary. Only few crystals may stick out a little if, furthermore, $\Theta_w \leq 90°$. In this case no substantial partial coalescence will occur. If, however, the fat network size equals that of the globule, crystals may stick out at many places and they may stick out further too (see chapter 3). We, thus, expect a continuous fat network to cause considerable partial coalescence. This expectation is confirmed by our observation that a minimum solid fat fraction ($\Phi_{s,min}$) is required to destabilize emulsions and that $\Phi_{s,min}$ is comparable with the minimum solid fat fraction that appeared necessary for the formation of a continuous fat network in emulsion globules, as became clear from the capillary experiments. The minimum fraction of fat solid at which a continuous network was detected varied among fats.

The question now arises as to what factors determine whether a continuous network is formed in a globule. From the above it becomes clear that fat crystals in oil, once formed, rapidly flocculate. The flocs formed must be of a fractal nature [16]. Fractal theory for flocculation due to Brownian motion of monodisperse spherical particles of radius a predicts that the average number of spheres N in a floc of radius R (i.e. the radius of the smallest sphere that can contain the floc) is given by:

$$N = \left[\frac{R}{a}\right]^D \quad (5)$$

where D is called the fractal dimensionality, a parameter which always turns out (either from

computer simulations or from experiments) to be less than 3. Since the number of particles that could be present in the same sphere if closely packed is given by

$$N_t = \left(\frac{R}{a}\right)^3 \tag{6}$$

we have for the average volume fraction Φ_p in a floc

$$\Phi_p = \frac{N}{N_t} = \left(\frac{R}{a}\right)^{D-3} \tag{7}$$

The flocs become thus even more rarified while growing (since $D-3 < 0$) and as soon as Φ_p equals the volume fraction of spheres in the system, Φ, a continuous network or gel forms [5,28].

Is this theory applicable to networks of fat crystals? Theory predicts, for instance, that the permeability of the network B is proportional to $a^2\Phi^{2/(D-3)}$. Figure 4-3 shows indeed about lineair plots of log B versus log Φ_s, but the values of D obtained from the slope are irrealistic: D = 2.4 - 2.8, whereas theory for rapid flocculation of particles forming a gel that does not rearrange appreciably afterwards would predict D to be between about 1.8 and 2.1 [16]. Also log-log plots of the modulus versus Φ should give straight lines and figure 5 shows this not to be the case; neither are the slopes realistic.

Why does the theory fit the results so poorly? We can think of two main reasons:

1. The particles are not spheres: they are anisometric. For such particles no theory is available, but one would assume the relations to be similar to those for spherical particles, albeit with different constants.
2. The fat crystals undoubtedly grow while flocculating. The time for growth at low temperature is presumably of the order of 100 s [26], and during that time they can diffuse over a few μm, i.e. clearly further than the average interparticle distance. In our view, this must lead to a higher fractional dimensionality of the particle network, especially at high Φ_s. To be sure, equation (7) would not be applicable, certainly not up to the gel point.

Nevertheless, the concept of fractal flocculation of the fat crystals may lead to an important

qualitative conclusion. Equation (7) would predict that the floc size at the moment of gelation (formation of a continuous network) is given by [4]:

$$R_g = a\Phi^{\frac{1}{D-3}} \tag{8}$$

But formation of a network throughout the whole volume is only possible if $2R_g$ is greater than or equal to the size of the vessel. In our case, this would lead to the condition

$$\Phi_s > \left[\frac{2a}{d}\right]^{3-D} \tag{9}$$

where d is the globule diameter [28]. Although (9) will not hold precisely and although we do not know the effective D, qualitatively we may conclude that there is a certain minimum Φ_s needed for formation of a network throughout a globule and that $\Phi_{s,min}$ is larger for a larger crystal size and a smaller globule size.

The permeability coefficient is a reasonable measure for the average crystal size in fat networks, in which the pores are filled with liquid oil. From the equation of Kozeny-Carman [20]:

$$B = \frac{\epsilon^3 a^2}{180(1-\epsilon)^2} \tag{10}$$

where ϵ is the porosity of the fat network, it follows that B is proportional to a^2, other conditions being equal, which particularly means at constant solid fat content; this proportionality also follows from fractal theory [4]. From figure 4-3 it can, therefore, be concluded that blend A has on average 4 to 7 times larger crystals than has milk fat. Therefore, $\Phi_{s,min}$, is expected to be higher for blend A than for milk fat. We found with the capillary experiments (section 3.2) and emulsion stability tests (section 3.3) that for emulsions of triglyceride blend A the solid fat fraction must be above 0.15 to destabilize emulsions and to form a continuous fat network, whereas for milk fat, $\Phi_{s,min}$ is less than 0.12: at $\Phi_{s,min} = 0.12$ the emulsion just became unstable, whereas no strong crystal network was yet observed.

From the above it has become clear that the number of crystals and their size will greatly affect emulsion stability by determining the possibility for approaching globules to make

contact. After all, approaching globules will only make contact if there are crystals in the interfacial region and if the protrusion distance of such crystals is sufficient to bridge the aqueous film between globules. After making contact the formation of a strong liquid neck will depend on the amount of oil released from the network in the time available. The stress σ on the oil inducing neck formation will be of the order of γ/r, where γ is the interfacial tension and r is the radius of the globule. The stress must be large enough to force liquid out of the fat network. In our case, having globules of approximately 2 μm in diameter and an interfacial tension of about 4 mN m^{-1}, σ is in the order of 40 kPa. From the capillary experiments we have learned that the crystal network in a globule, once formed, is mostly very strong, so that it will not subside under the stress exerted on the globule. According to equations (1) and (10), the volume flow of oil out of the network increases with increasing porosity (i.e. decreasing solid fat content), with increasing crystal size and with decreasing liquid viscosity. It may thus be imagined that there is an upper limit to the solid fat fraction at which sufficient oil can be released from the network. The increased stability at higher solid fat fractions, as described by Labuschagne [13] for cream in Taylor vortice flow, has been explained by the lack of oil release to form an oil neck. It can be deduced from our capillary experiments on milk fat, at room temperature, that σ exceeded the pressure, P_o, needed to squeeze oil out of the fat network. For blend A, on the other hand, σ would not in all cases be larger than P_o. In the presence of more than about 17% solid fat oil could then only be released in the case of small globules. We indeed found a decrease in the partial coalescence rate of blend A emulsions above this particular solid fat content. We intend to report on this in more detail shortly.

Nevertheless, triglyceride blend B emulsions having a solid fat content of 90% or more were extremely unstable at rest. This seems in contradiction with the above, since a large pressure (much larger than σ) would be needed to squeeze oil out of a blend B fat network (see table 4-1). For an explanation we have to consider deaggregation of partially coalesced blend B clumps. In Brownian motion disruption of the aggregates is not very likely to occur. Even a single crystal piercing the aqueous film has an energy that is far larger than kT. After

first contact, the available time may thus suffice for the sintering of the crystals, so that oil neck formation may no longer be a necessity. In a flow field stronger forces will act on the doublets; especially at higher shear rates (G). Consequently, there will only be a short time encounter, namely proportional to G^{-1}. Only if an oil neck can be formed in this limited period of time a permanent doublet can be formed. It may thus be that blend B emulsions of such high solid fat contents would remain stable in a flow field, because than neck formation will be the time limiting step. Unfortunately, the extreme instability of these type of emulsions at rest prevented us from doing the experiment.

Disruption of aggregates depends on the velocity gradient. In Brownian motion sintering of the crystals seems to occur, whereas in a flow field the formation of an oil neck determines whether disruption will occur or not. Apparently, globules do coalesce provided that the time to release oil from the fat network exceeds the collision time. Aggregates with a high solid fat fraction seem to be disrupted before an oil neck can cause the merging of the globules.

The above considerations are only valid for emulsions with crystals that are preferentially situated at the interface (figure 4-5a). If crystals are completely wetted by the disperse phase (like in caseinate emulsions) crystals, in general, do not stick out far enough into the aqueous phase. Only if the amount of solid fat is so large that (at least) some crystals are forced into the interfacial region and the ratio between crystal size and emulsion globule becomes large, crystals may no longer be able to bend along the curvature of the globule (figure 4-5b). They will start protruding the interface (see further chapter 3); the more so for smaller globules and/or larger crystals.

5 CONCLUSIONS

- Emulsion stability at rest and in Couette flow decreases with increasing crystal size; large crystals, if sufficient in number, may even destabilize emulsions at rest.
- Secondary nucleation of fat crystallization promotes emulsion instability. The numerous crystals in each globule form a continuous network and this enhances partial coalescence considerably. If, on the other hand, no secondary nucleation occurs globules contain, at the

most, one or two crystals (e.g. paraffin). No network is formed and even though the crystals are larger these globules are less sensitive to partial coalescence.

- Fat crystal dispersions have a fractal nature, and thus have a fractal dimensionality, *D*. Quantification of *D*, however, remains impossible since the crystals are far from spherical, while a theory for anisometric particles is not available and because crystals may still grow during flocculation.

- Partial coalescence only occurs at a significant rate if the crystals in an emulsion globule are flocculated into a continuous network. According to the fractal theory just mentioned, the formation of a continuous fat network is limited by both crystal and globule size; the smaller the globules and the larger the crystals, the more solid fat is needed to achieve a continuous network. This agrees with our observations on the effect of crystal size.

- The optimum in the solid fat content with respect to partial coalescence seems to depend on the flow field. At rest, globules with higher Φ_s may still partially coalesce, whereas in a flow field disruption of just formed doublets may have taken place before the merging of globules is accomplished.

6 ACKNOWLEGEMENTS

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KINETICS OF PARTIAL COALESCENCE IN O/W EMULSIONS: I. DEVELOPMENT OF A SIMULATION MODEL

ABSTRACT

A simulation model is developed to describe the course of the partial coalescence process in polydisperse O/W emulsions in a shear field. The model is based on the Smoluchowski equation, modified to account for colloidal interactions and for the influence of the presence of fat crystals in the oil globules. The unknown parameters are the coalescence efficiencies of clumps and singlets (with crystals). By dividing the globules into clumps and singlets with and without crystals, the model can accurately describe the course of the partial coalescence process, as long as it has not gone too far. If partial coalescence had proceeded far enough for most of the fat to cream out of the emulsion when warming it, the model appeared inadequate.

The four different types of kinetics that have been observed experimentally, can be characterized by three parameters: (1) the initial coalescence efficiency, α_{init}, expressing the rate at which aggregation starts, (2) the ratio between the coalescence efficiencies of clumps and singlets P_c/P_s and (3) m, expressing the dependence of partial coalescence on the globule size.

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KINETICS OF PARTIAL COALESCENCE IN O/W EMULSIONS :

I. DEVELOPMENT OF A SIMULATION MODEL.

1 INTRODUCTION

It was shown before by van Boekel & Walstra [5] that the presence of crystals in the oil phase can induce considerable coalescence in O/W emulsions, especially in a velocity gradient or in a cream layer. This is, however, not true coalescence, since irregular clumps of fat globules rather than large spherical droplets are formed. Therefore, the process was designated partial coalescence. It only occurred if fat crystals were observed at the O/W boundary, hence, a mechanism based upon piercing of the thin film between approaching droplets by slightly protruding crystals was postulated. They observed in emulsions subjected to Couette flow, where the dispersed phase was paraffin oil containing solid paraffin or tristearate, that the rate of partial coalescence was (initially) independent of time, almost exactly proportional to of oil volume fraction squared and strongly increased with shear rate, average droplet size and proportion of solid fat; it also depended on the emulsifiers used.

Since then it has become clear that partial coalescence also may occur in emulsions where there are no crystals observed at the globule boundary. Nevertheless, the same mechanism of piercing crystals appeared responsible [12]. The dependence of the partial coalescence rate on the proportion of fat solid was found to be quite variable: in some emulsions partial coalescence is not observed anymore if over half of the fat is solid [11], whereas in others much more of the fat can be crystallized. Furthermore, the kind of fat present in the globules appears to have a great effect on the type of partial coalescence occurring. Presumably, amount, size, shape and arrangement of the crystals are important. Moreover, the contact

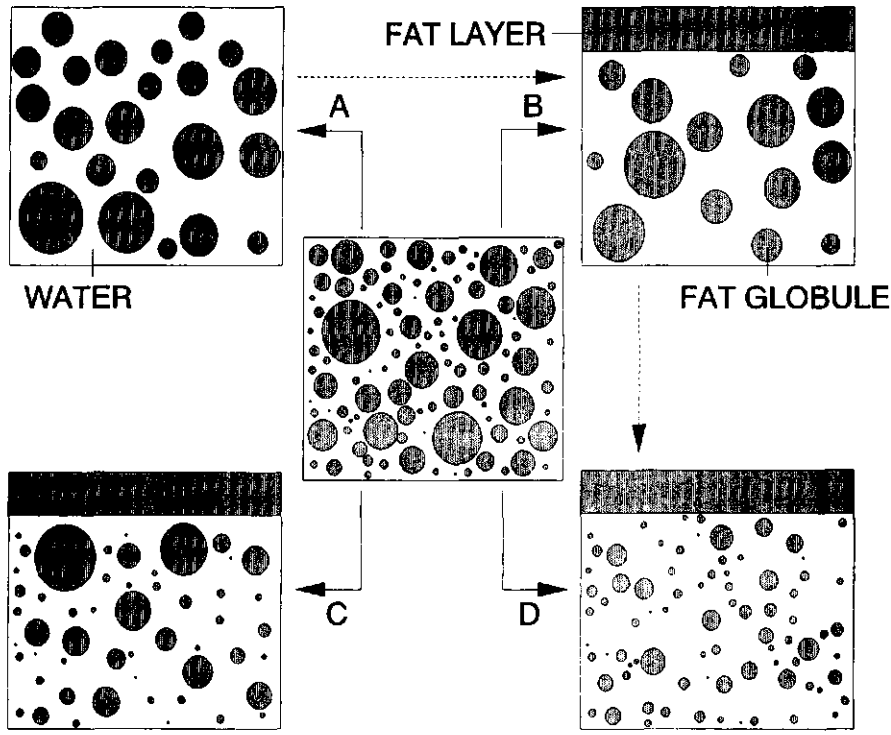

Figure 5-1. Various types of partial coalescence (highly schematic). In some instances these types change into one another during the partial coalescence process.

angle (crystal, oil, water) may play a part [7]. In figure 5-1 examples are depicted of the 4 types of change in globule size distribution observed:

- **type A:** The fat globules that participate in partial coalescence form irregularly shaped clumps. Upon warming, an emulsion is obtained with droplets larger than at the beginning of the experiment. Emulsions that behave according to this pattern are, among others, paraffin mixtures in SDS solutions [4].
- **type B:** In some cases clumps become so large that they cream out of the emulsion

when it is warmed. The remaining fat globules are bigger than the original ones. Examples of this type of instability are natural cream [2] and milk fat in SDS emulsions [see chapter 3].

- type C: Some fat globules participate in rapid partial coalescence, leading to clumps creaming out of the emulsion, while the remaining fat globules show an (almost) unaltered size distribution. Milk fat globules in whey protein solutions initially behave in this way [10].
- type D: As in the previous two cases, big clumps are formed that cream out of the emulsion upon heating. This time, however, the remaining emulsion does show an altered size distribution with smaller globules. This is, among others, the case in emulsions of fairly saturated triglycerides in SDS solutions (see chapter 3).

Up till now, no clear pattern has manifested itself. Consideration of accepted theories of coagulation kinetics [14, 15], even if taking hydrodynamic and colloidal interactions into account [8, 17, 18], does not lead to an explanation. A possible reason may be that in the models described so far monodispersity is assumed. Yet, polydispersity is considerable in emulsions and is known to enhance the number of encounters [12]. Even if the globule size distribution is narrow at the beginning, broadening of the distribution will occur during aggregation. Furthermore, several authors [1, 4, 9] reported emulsion stability to be strongly dependent on globule diameter, whence it must depend on size distribution width. The assumption of monodispersity thus seems to be an oversimplification and it cannot be ruled out that the spread in globule size has an overriding effect on the course of the coalescence process.

The aim of this work was to develop a mathematical model to describe the changes in globule size distribution of polydisperse crystal containing O/W emulsions subject to Couette flow, and to compare the results with the changes observed. In our endeavour we, fruitfully, used elements from the model by Melsen [10], who first attempted to simulate the kinetics of partial coalescence.

2 THEORY

We proceed from the following presumptions. The emulsion is brought in a simple shaer field and emulsion droplets can collide due to the velocity gradient. Partial coalescence can only occur if globules contain crystals. These are the reactive globules, which may collide with one another or with liquid globules. A certain proportion of these collisions is effective in that they lead to partial coalescence. Collisions between liquid globules have no effect.

The collision or encounter frequency of spherical particals has originally been described by Smoluchowski. For monodisperse systems the equation can be solved analytically . Emulsions, however, show considerable polydispersity, which means that the collision frequency can not simply be calculated. It can only be approached by fitting the experimentally obtained results, so that a finite-difference method had to be applied. Therefore, the globule size distribution of the starting emulsion was divided into classes of 0.5 μm width. The changes in the size distribution have been calculated for several conditions and several assumed reactivities. The results obtained were compared to experimental results.

2.1 Frequency of encounters

The model, describing the changes in the globule size distribution, is based on the collision frequency, b_{ij}, among globules with diameter d_i and d_j in a simple shear flow as described by Smoluchowski [14] for dilute dispersions:

$$b_{ij} = \frac{G}{6}(d_i + d_j)^3 N_i N_j \qquad (1)$$

where N_i and N_j are the number of globules in class i and j respectively and G is the shear rate. In simple shear flow, however, hydrodynamic and colloidal interactions have to be taken into account as well. Van de Ven & Mason [17, 18] have presented a theory for permanent doublet formation in monodisperse systems by introducing the orthokinetic capture frequency α_o:

where b_o is the actual capture rate, taking interparticle forces into account. For

$$\alpha_o = \frac{b_o}{b_{ij}} \quad (2)$$

monodisperse spheres in simple shear flow α_o can be derived from trajectory analysis. Van Boekel found that in SDS-stabilized emulsions permanent doublets are not formed unless salt is present. Furthermore, we have to deal with polydisperse systems in which, moreover, the shape of the clumps deviates from the spherical, so that only a very rough prediction of α_o would be possible. Taking the above into account, we decided not to try to approximate the effects of colloidal and hydrodynamic interactions, but to accomodate them in the coalescence efficiency J, where J is the ratio between the number of collisions leading to aggregation and the total number of collisions (see further section 2.2).

It was assumed further that Brownian encounters were negligible. If the translational Péclet number, Pe_t, is much greater than unity, Brownian encounters can be ignored [16]:

$$Pe_t = \frac{Gr^2}{D_i} \quad (3)$$

where D_i is the translational diffusion coefficient of a globule of size class i. For the lowest shear rate used ($G \approx 125\ s^{-1}$) and the smallest (mean) globule radius ($r_i = 0.5\mu m$) with $D_i = 4.4*10^{-13}\ m^2 s^{-1}$, $Pe_t = 71$ and the condition is fulfilled.

2.2 Reactivity of the globules

The initial globule size distribution, containing singlets, changes due to partial coalescence. In time the emulsion becomes a mixture of different types of particles, all referred to as globules. In the model the globules in class i have been divided into singlets with crystals (S_i), singlets without crystals (s_i) and clumps (C_i) (by definition containing crystals, since globules without crystals do not aggregate). At the beginning of an experiment the number of clumps $N_{C,i,t=0} = 0$ for all i, whereas the number of reactive singlets $N_{S,i,t=0} = R*N_i$ (R being the proportion of globules that contain crystals) and the number of singlets without crystals $N_{s,i,t=0} = (1-R)*N_{i,t=0}$. The number balance at any time during an experiment is:

$$N_i = N_{s,i} + N_{S,i} + N_{C,i} \quad (4)$$

The three types of globules, s_i, S_i and C_i, can collide with one another as follows, considering only two-body encounters:

$$s_i + s_j \rightarrow s_i + s_j \quad (5)$$

$$S_i + s_j \rightarrow S_i + s_i \quad (6a)$$

$$S_i + s_j \rightarrow C_k \quad (6b)$$

$$S_i + S_j \rightarrow S_i + S_j \quad (7a)$$

$$S_i + S_j \rightarrow C_k \quad (7b)$$

$$C_i + s_j \rightarrow C_i + s_i \quad (8a)$$

$$C_i + s_j \rightarrow C_k \quad (8b)$$

$$C_i + S_j \rightarrow C_i + S_j \quad (9a)$$

$$C_i + S_j \rightarrow C_k \quad (9b)$$

$$C_i + C_j \rightarrow C_i + C_j \quad (10a)$$

$$C_i + C_j \rightarrow C_k \quad (10b)$$

It is assumed (see the above equations (5) to (10b)) that partial coalescence can only occur if at least one globule contains crystals (marked with a capital). Furthermore, the presence of at least one (partly) crystallized globule does not necessarily lead to aggregation. Aggregation only takes place if at least one crystal protrudes through the interface, and if such a crystal is in the interfacial region between approaching globules and, furthermore, if the protrusion distance exceeds the thickness of the interparticle water film (chapter 3). A clump, formed upon aggregation, is added to class k, where the clump diameter, d_k, is given by:

$$d_k^3 = d_i^3 + d_j^3 \quad (11)$$

assuming the clump to be spherical. This is to some extent realistic, since globule size distributions have always been estimated on spherical globules, by melting the crystals beforehand. Yet, the effective (collision) diameter of the clumps during the partial coalescence process is likely to be larger. Until the emulsion is warmed the clumps may be far from spherical. The participating fat globules are not completely fused, the clumps contain enclosed aqueous phase. Therefore, if d_i and/or d_j in equation (1) refers to a clump, the diameter has been multiplied by an expansion factor of 1.5.

The ratio between the number of collisions leading to aggregation and the total number of collisions is represented by a coalescence efficiency, J, which may be influenced by factors both dependent and independent of the globule size (distribution):

$$J_i \sim (d_i^*)^m \quad (12)$$

where $d_i^* = d_i/d_{min}$ (d_{min} being the diameter of the smallest globules being present) if the smaller globules are the more 'efficient' ones ($m < 0$) and $d_i^* = d_i/d_{max}$ (d_{max} being the diameter of the largest globules the model takes into account, i.e. 9.75μm) if the larger globules have the higher efficiency ($m > 0$). Furthermore, the efficiencies of singlets and clumps may differ, so that we decided to distinguish between them; the efficiency of singlets, J_s, depending on P_s and m_s, and the efficiency of clumps, J_c depending on P_c and m_c. Hence, the coalescence frequency for singlets, b_{ij}^s, is:

$$b_{ij}^s = RJ_s\frac{G}{6}(d_i+d_j)^3[N_{s,i}(N_j-N_{c,j})+N_{s,j}(N_i-N_{c,i})-N_{s,i}N_{s,j}] \quad (13)$$

If clumps are involved in partial coalescence, the coalescence frequency b_{ij}^c can be described as:

$$b_{ij}^c = RJ_c\frac{G}{6}(d_i+d_j)^3[N_{c,i}N_j+N_{c,j}N_i-N_{c,i}N_{c,j}] \quad (14)$$

Considering the overall coalescence frequency, b, being the summation of b_{ij}^s and b_{ij}^c, the following expression can be derived for the rate of change of the concentration of globules

N_i, in a discrete spectrum of globule sizes :

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{j=i-1} b_{jk} - \sum_{j=1}^{\infty} b_{ij} \qquad (15a)$$

The first term on the right hand side represents the number of globules of size N_i formed by coalescence of smaller globules; the second represents the number of globules N_i lost by coalescence with other globules.

Analogous to equation (15a) the rates of change of the concentration of singlets containing crystals, S_i, and clumps, C_i, can be estimated by the following expression:

$$\frac{dN_{s,i}}{dt} = \frac{1}{2}\sum_{j=1}^{j=i-1} b_{jk}^{s} - \sum_{j=1}^{\infty} b_{ij}^{s} \qquad (15b)$$

$$d\frac{N_{c,i}}{dt} = \frac{1}{2}\sum_{j=1}^{j=i-1} b_{jk}^{c} - \sum_{j=1}^{\infty} b_{ij}^{c} \qquad (15c)$$

The finite steps in time (Δt) were initially set to 1 second. If Δt is taken too large, the number of globules disappearing from a class may exceed the number present. Since this is physically impossible, the time step has to be re-adjusted. Therefore, for every class i a correction factor α_i is calculated for the number of reactive singlets $N_{s,i}$, and clumps $N_{c,i}$ and the total globule number N_i:

$$\alpha_{s,i} = \frac{dt}{d\ln N_{s,i}} \qquad (16a)$$

$$\alpha_{c,i} = \frac{dt}{d\ln N_{c,i}} \qquad (16b)$$

$$\alpha_{N,i} = \frac{dt}{d\ln N_i} \qquad (16c)$$

If any $\alpha_i < 1$ second, more globules would disappear from class i than present and thus α_{min} is determined for every time step:

$$\alpha_{min} = \min(1, \alpha_{s,i}, \alpha_{c,i}, \alpha_{N,i}) \qquad (17)$$

Now the numbers per size class can be re-adjusted:

The time step becomes α_{min} instead of 1 second and the next time step can be calculated,

$$N_{s,i}[t+\Delta t] = N_{s,i}[t] + \alpha_{min}\frac{dN_{s,i}}{dt} \quad (18a)$$

$$N_{c,i}[t+\Delta t] = N_{c,i}[t] + \alpha_{min}\frac{dN_{c,i}}{dt} \quad (18b)$$

$$N_{i}[t+\Delta t] = N_{i}[t] + \alpha_{min}\frac{dN_{i}}{dt} \quad (18c)$$

starting at Δt = 1 second. In this way the changes in globule concentration as a function of time, depending on several process parameters can be calculated.

3 MATERIALS AND METHODS

3.1 Materials

Cream was obtained by centrifuging fresh cows' milk at 40°C to the desired fat content. To inactivate lipase it was heated for 15 min at 70 °C.

Anhydrous milk fat (> 99.8% pure fat, < 0.1% water) was stored at 7°C in sealed tins. The fat was fully melted before use.

Paraffin oil was obtained from OPG, Utrecht, Netherlands. Viscosity 60 - 80 mPa.s; density about 860 kg m^{-3}.

Solid paraffin was obtained from Merck A.G., Darmstadt, Germany. It had an apparent melting point of 42 - 44°C and a density of about 880 kg m^{-3}.

The triglyceride blends A and B were kindly supplied by Unilever Research, Vlaardingen, Netherlands. Both blends contained about 96.9% triglycerides, 3.0% diglycerides and 0.1% monoglycerides.

Tristearate was also obtained from Unilever Research, Vlaardingen, Netherlands. It had a melting point of 69°C, somewhat below the pure compound's melting point of 72°C.

Soy lecithin was obtained from Du Lectin-Van Schuppen, as a powder containing 97% phospholipids; The powder (0.7%) was dispersed in the milk fat, in which it was well dispersible.

Skim milk was obtained by centrifuging fresh cows' milk at 40°C to a fat content of

0.07%. To inactivate lipase it was heated for at least 10 min at 64°C.

Sodium dodecyl sulphate (SDS), was obtained from BDH chemicals, England; its grade was specially pure. The critical micelle concentration (CMC) in water is 0.23% at 20°C [6]. It was used in concentrations of 0.4%.

Sodium caseinate was prepared from fresh skim milk by repeated precipitation with hydrochloric acid and redispersion in weak NaOH (to pH 7.6). Afterwards it was spray-dried. It was used in 1% solutions.

3.2 Emulsification

Oil-in-water emulsions were made by mixing melted fat and surfactant solution at 60°C in the inlet vessel of a Rannie laboratory homogenizer (capacity 100 l/h), while stirring. The mixture (1l) was then homogenized at a previously adjusted homogenization pressure, circulating the emulsion for 20 minutes, cautiously avoiding any uptake of air. Fairly narrow globule size distributions are obtained in this way, the surface-weighted relative standard deviation c_s being about 0.5;the volume-surface average droplet diameter, d_{vs}, ranged from 1 to 5 μm according to the homogenization pressure applied [10].

3.3 Pretreatment of the o/w emulsions

All emulsions were stored at least overnight at 4°C to ensure crystallization of fat in all globules [23]. Storage was shorter than a week so that bacterial spoilage was avoided. Creaming and subsequent partial coalescence were prevented by storing the emulsion in slowly rotating cylinders, end over end, with exclusion of air. The droplet size distribution was found not to change during storage.

In some experiments an emulsion, containing partly crystallized oil globules, was mixed with an emulsion without crystals. Care was taken that the globule size distributions of both emulsions were similar, so that the fraction globules that contained crystals was independent of the globule size.

3.4 Characterization of the emulsion

Globule size distributions of the starting emulsions were determined by a spectroturbidimetric method [19, 21, 22]. This accurate method is only applicable to a limited set of unimodal size distributions. This is the case for freshly homogenized emulsions, but during the partial coalescence process the shape of the globule size distribution may change, and the formation of a bimodal shape is not unlikely. If so, spectroturbidimetry can no longer be used. Therefore, we decided to estimate the globule size distribution of the emulsions during the kinetics experiments with a Malvern 2600D particle size analyzer. The sizer was operated in the Model Independent mode (version 3.0) and equipped with a lens of 63 mm focal length detecting globules with a diameter between 1 and 118 μm. Each measurement was repeated three times and the average result reported.

For the unimodal starting emulsions both methods gave essentially the same results, so that we decided to use the spectro turbidimetric method to obtain the size distribution of globules below a diameter of 1 μm.

Fat contents as well as the amount of fat that was crystallized were estimated by wide-line proton pulse-NMR [3].

Polarized light microscopy was used to observe the appearance of fat crystals in the oil globules [20].

3.5 Couette flow

O/W emulsions were subjected to Couette flow, i.e. flow between two concentric cylinders of which the outer one rotated and the inner one was fixed. The rate of rotation was about 100 s^{-1}, so that laminar flow developed [4]. At pre-set timeintervals the apparatus was emptied and the samples were diluted with a solution of disodium ethylene diamine tetraacetate (EDTA) and polyoxyethylene sorbitan monolaurate in water, and heated in a separation funnel to turn any clumps into globules. Big aggregates cause the separation of an oil layer on top of the emulsion. A few millilitres of the remaining emulsion were taken and characterized as described in Sec. 3.4.

3.6 Details of data processing

Numerical simulation of the partial coalescence process in Couette flow was implemented on an IBM-compatible 80386-computer, using Pascal as the programming language. Model calculations were performed on globules of discrete sizes divided into 20 classes of fixed width (0.5 μm), the diameter of the first (d_{min}) and the last (d_{max}) class being 0.25 and 9.75 μm. Division of the globule size distribution into more classes did not significantly improve the result, nor did larger values of d_{max}. In the last class all globules with a diameter above 9.5 μm were collected. It was further assumed that upon heating of the emulsion, globules of class 12 and larger ($d_i \geq 6.25$ μm) cause the formation of an oil layer on top of the emulsion (see section 3.5).

4 RESULTS

4.1 Models tested

Numerous models have been tested, constructed to describe the partial coalescence process of polydisperse, partly crystallized, O/W emulsions in Couette flow. We will here discuss the four models, that gave the best results (table 5-1). In two models (I & II) reactive and non-reactive globules were distinguished (after Melsen [10]), conceiving reactive globules as globules with at least one crystal having a larger protrusion distance (δ) than the shortest distance (h) remaining between approaching globules. Consequently, all reactive globules can cause partial coalescence, whereas non-reactive globules can only aggregate upon collision with a reactive globule. Since emulsion stability greatly depends on globule diameter [4], we reckoned with the possibility that some variables that influence δ and/or h depend on globule size, whereas others do not. Therefore, the proportion globules being reactive at the beginning of an experiment, R_1, is as described in

table 5-1. In two other models (III & IV) globules with and without crystals were distinguished. As already described in section 3.3 emulsions were prepared in such a way that the fraction of globules containing crystals (R) was independent of globule size.

We assumed further that not all collisions in which globules with crystals are involved, lead

Table 5-1. Four simulation models, developed to explain the course of the partial coalescence process. g.s.d. = globule size distribution.

Model	Reactivity of globules	Coalescence efficiency	Results
I	$R_1 = P(d_i^*)^m$ proportion of globules with $\delta > h$	J_S = constant$_1$ J_C = constant$_2$	Dependency of R and J_S g.s.d. did not fit
II	$R_1 = P(d_i^*)^m$ proportion of globules with $\delta > h$	$J_{II,-}$ = constant$_3$ if $d_i < d_{crit}$ $J_{II,+}$ = constant$_4$ if $d_i \geq d_{crit}$	Dependency of R and $J_{II,-}$ g.s.d. did not fit
III	R = constant$_5$ proportion of globules with crystals	$J_S = P_S\left[d_i^*\right]^{m_S}$ $J_C = P_C\left[d_i^*\right]^{m_C}$	good g.s.d. fit
IV	R = constant$_6$ proportion of globules with crystals	$J_{IV,-} = P_{IV,-}\left[d_i^*\right]^{m_{IV,-}}$ $J_{IV,+} = P_{IV,+}\left[d_i^*\right]^{m_{IV,+}}$	g.s.d. did not fit

to partial coalescence (see section 2.2). The coalescence efficiency of encounters is described in all four models by an efficiency, J. The value of J in model I depends on the involvement of singlets or clumps. If two singlets partially coalesce, then $J = J_S$, whereas $J = J_C$ in case at least one clump is involved, even if a reactive singlet collides with a clump. In model II a critical diameter, d_{crit}, was defined such that if the diameter of the reactive globule was below d_{crit} then $J = J_{II,-}$, whereas otherwise $J = J_{II,+}$. In models III & IV the efficiency J depends on globule size. In model III an efficiency for singlets, J_S, representing the fraction of the collisions in which singlets caused partial coalescence, was

distinguished from J_c, representing the fraction of collisions in which clumps caused partial coalescence. As in model I, the coalescence efficiency of a clump is assumed to exceed the coalescence efficiency of a reactive singlet, so that $J = J_c$ if a reactive singlet collides with a clump. In model IV all globules below a critical diameter, d_{crit}, aggregate with an efficiency $J_{IV,-}$, whereas above d_{crit} the efficiency was $J_{IV,+}$. In the models I & II it was impossible to change R_1 independently of J. Furthermore, in all models except model III the fitted globule size distributions differed markedly from the experimentally determined ones. Especially in those cases where the unimodal size distribution changed into a bimodal one, changes could not be accurately described by the models I,II and IV. Model III, however, appeared to give a good description of the partial coalescence process, so that we decided to use this modelfor further study. As an example, figure 5-2 depicts the calculated and the

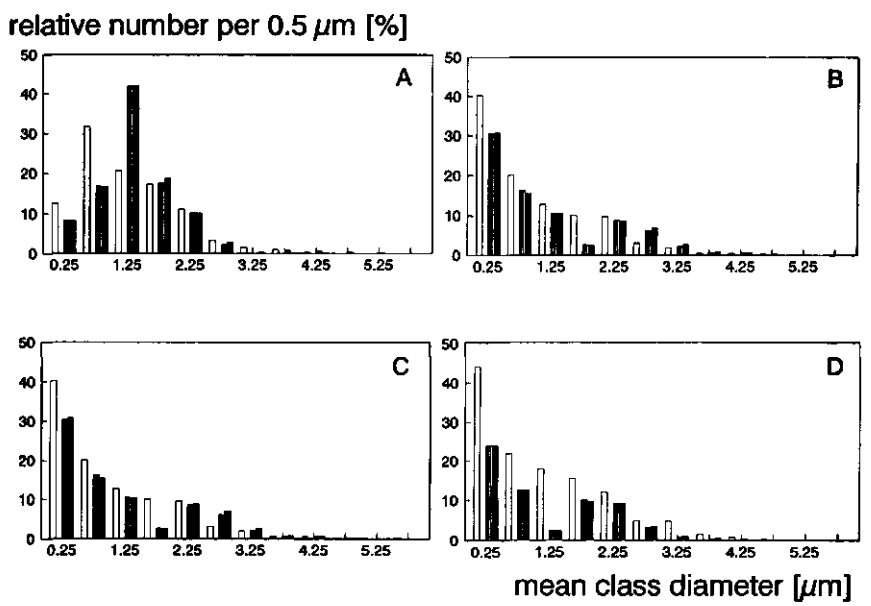

Figure 5-2. Frequency distributions as found on emulsions of different kinds of fat, after application of Couette flow (■) and as calculated with model III (▨). (A) paraffin (of which 25% was solid; G = 165s^{-1}); SDS-triglyceride blend with 33% (B) or 67% (C) of the globules containing crystals (G = 250s^{-1}); (D) SDS-milk fat (G = 190s^{-1}). The initial globule size distribution is represented by □.

experimentally determined changes in globule size distribution of emulsions of SDS (0.4%) with various kinds of fat after a treatment in Couette flow. It can be seen that the globule size distribution of some O/W emulsions changed from a unimodal into a bimodal distribution. Even the second peak was described accurately by model III; yet, in these cases d_{vs} is no longer a good representative of the globule size distribution. Therefore, we have chosen not to compare d_{vs} and fat content, but to judge the closeness of fit by comparing the whole size distribution, using χ^2 with 11 degrees of freedom:

$$\chi^2 = \sum_{i=1}^{i_{max}-1} \frac{(N_i - M_i)^2}{M_i} + \frac{\left(N^*_{i_{max}} - M^*_{i_{max}}\right)^2}{M^*_{i_{max}}} \qquad (21a)$$

with:

$$N^*_{i_{max}} = \max\left[N_{i_{max}},\ N_{i_{max}} + \sum_{i=1}^{i_{max}} N_i - \sum_{i=1}^{i_{max}} M_i\right] \qquad (21b)$$

$$M^*_{i_{max}} = \max\left[M_{i_{max}},\ M_{i_{max}} + \sum_{i=1}^{i_{max}} N_i - \sum_{i=1}^{i_{max}} M_i\right] \qquad (21c)$$

where N_i and M_i are the number of globules in each class i (but the last), as estimated experimentally and by model calculations respectively. N^*_{imax} and M^*_{imax} are the number of globules in the last class, corrected for the differences in total number of calculated and estimated globules. In most cases, χ^2 ranged from 0.1 to 5, which would mean, if the distributions were stochastics, that there is more than 95% probability that the similarity between the measured and the calculated globule size distribution is not an accidental one. Only in the case where the greater part of the fat is creaming during the heating step the fitted distributions appeared to deviate from the measured ones. This was reflected by a χ^2, rising to values in the range of 40 - 300. These values would suggest that the probability of the calculated size distributions agreeing with the measured ones is smaller than 1%. Possible reasons for the poor fit are discussed in section 4.2.

4.2 The course of the coalescence process

In most experiments the changes in globule size distribution were followed as a function of time. For a SDS (0.4%) - milk fat (20%) emulsion the globule size distributions obtained at four moments of the experiment are represented in figure 5-3. It can be seen that the kinetics change from one type (as described in section 1) into another. The larger globules are the more reactive, producing a second peak of globules with larger diameter.

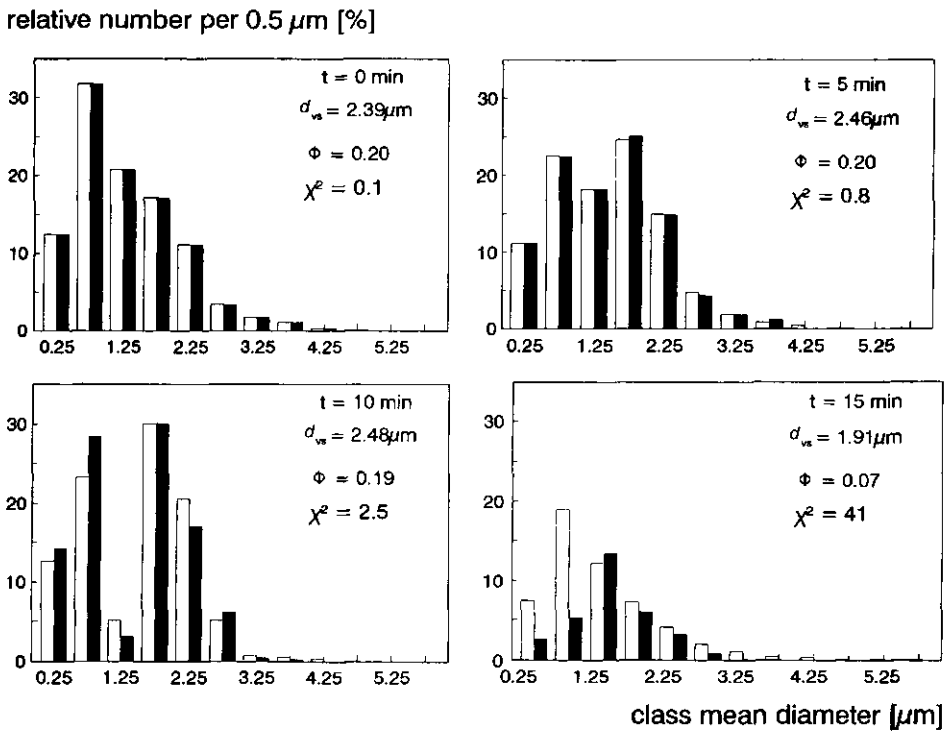

Figure 5-3. Frequency distributions as calculated with model III (□) and as found on SDS-milk fat emulsions after application of Couette flow at a shear rate of 250 s^{-1} during several time intervals (■). Abscissa: mean class diameter [μm], ordinate: relative number of globules per 0.5μm class width.

Consequently, d_{vs} increases, whereas the fat content initially remains unaltered (type A) and then gradually starts decreasing (type B). Globules in the second peak gradually grow; the second peak shifts to larger globule diameters. Eventually, this results in a decline in fat content when globules become so large that they cream upon warming of the emulsion (type D). The emulsion almost completely breaks; about 90% of the fat is in the fat layer. The remaining emulsion again has a unimodal size distribution. The changes in the globule size distribution are accurately described by the model ($\chi^2 < 2.5$) until the amount of creaming fat becomes too large: then the fitted data significantly deviate from the experimental ones ($\chi^2 > 41$). The amount of fat that has creamed upon heating is much larger than is calculated by the model. The reason for this discrepancy may be twofold. First, the coalescence efficiency for larger clumps may be higher than accounted for. This could be due to inertial forces, which are negligible for colliding small globules but may come into play for the larger clumps. Rotating anisometric aggregates have an inertial energy, E_{inert}, but if this is less than, say, 5 kT inertial effects are certainly negligible. Let us, in a first approximation, consider an aggregate consisting of two spherical globules of equal radius r, then

$$E_{inert} = \frac{1}{2} m_{eff} v^2 \qquad (22)$$

When the aggregate rotates in a simple shear flow with shear rate G, the average velocity v relative to the centre of mass is roughly:

$$v = \frac{1}{2} rG \qquad (23)$$

and the effective mass:

$$m_{eff} = \frac{4}{3} \pi r^3 \Delta\rho \qquad (24)$$

where $\Delta\rho$ is the density difference between the oil phase and the aqueous phase, amounting to about 100 kg.m^{-3}. Substitution of equations (23) and (24) into equation (22) leads to the following equation for E_{inert}:

$$E_{inert} = \frac{\pi}{6} r^5 \Delta\rho G^2 \qquad (25)$$

From figure 5-4 it can be seen that inertial effects are absent at the shear rate,at which almost all experiments were carried out (G = 125 s^{-1}). At the highest shear rate used (G = 250 s^{-1}) inertial effects may just come into play for the larger clumps. On the other hand, the relative change in d_{vs} and fat content of a SDS(0.4%) - blend A (20%) emulsion at a shear rate of 125 and 250 s^{-1} appeared to differ only in that aggregation proceeded faster at higher shear rates (table 5-2), so that it seems justified to neglect inertial forces even at the highest shear rate used.

Secondly, the heating step may cause the difference between the calculated and the experimentally determined fat content, which is mainly caused by a considerable divergence in the amounts of smaller globules (see also figure 5-3). Since the size distributions were very accurately predicted by the model until the amount of creaming fat became appreciable, the discrepancy in the size distributions is likely to be related with the loss of fat when warming the emulsion. On their way to the fat layer the large globules may coalesce with,

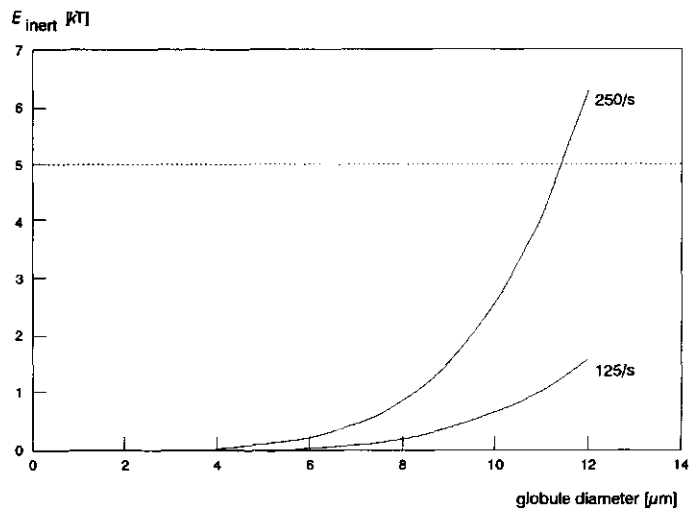

Figure 5-4. Inertial energy as a function of the globule diameter for two shear rates. Calculated from equation (23) assuming the density difference, $\Delta\rho = 100 kg.m^{-3}$.

Table 5-2. The influence of shear rate in SDS (14mM) - triglyceride blend A emulsions on the stability in Couette flow (20°C). Stability is depicted as the relative change in d_{vs} and fat content. $d_{vs,0}=2.5\mu m$ $\Phi_0=0.19\mu m$

t	$G = 125s^{-1}$		t	$G = 250s^{-1}$	
[min]	$d_{vs,t}/d_{vs,0}$	Φ_t/Φ_0	[min]	$d_{vs,t}/d_{vs,0}$	Φ_t/Φ_0
0	1.00	1.00	0	1.00	1.00
5	1.00	0.93	2	1.00	0.90
10	0.99	0.75	3	0.89	0.77
20	0.76	0.26	5	0.77	0.21

preferably, small globules, since they have the largest mutual difference in velocity. The average distance of overtake of the large globule with respect to the small one is:

$$H = 0.5\left[h - h\frac{v_1}{v_2}\right] \tag{26}$$

where v_1 and v_2 are the velocities of the small and the large globules, respectively, whereas h represents the rising height. Consequently the average volume of overtake is:

$$V = (1/4)\pi(d_1+d_2)^2 H \tag{27}$$

Combination of equations (26) and (27) results in a total creaming volume :

$$V_{tot} = N_2 V = (1/8)\pi N_2 (d_1+d_2)^2\left[1-\frac{d_1^2}{d_2^2}\right] \tag{28}$$

where N_2 is the number of large globules. It should be realized that part of this volume is occupied by small globules (d_1). The volume of creaming fat that originates from d_1 globules is:

$$V_1 = N_1(1/6)\pi d_1^3 V \tag{29}$$

where N_1 is the number of small globules. From equation (29) it follows that the volume

fraction of small globules, V_1, that is captured by large globules equals:

$$V_1 = (4/3)\Phi_1\Phi_2(1+a)^3(1-a)h/d_2 \quad with \quad a = \frac{d_1}{d_2} \tag{30}$$

If $V_1 = \Phi_1$, one encounter will occur between d_1 and d_2. If, on the other hand, $V_1 >> \Phi_1$, many encounters will occur and, thus, the probability of partial coalescence will increase. For the most unfavourable situation, where d_2 is just large enough to cream (6.75 μm), the ratio V_1/Φ_1 is approximately 355, so that it is rather likely that small globules are caught during creaming, resulting in additional coalescence after the partial coalescence in Couette flow. Our models do not account for the occurrence of coalescence during the heating step, so that the discrepancy in the globule size distributions is likely to increase.

4.3 Parameters to describe the course of the coalescence process

From the above it has become clear that the course of the partial coalescence process can be accurately simulated. By applying model III it is possible to determine whether the differences in the course of the partial coalescence process are only determined by differences in the number of collisions (e.g. caused by differences in G and/or globule size distribution) or also by the properties of the fat globules, as expressed in the efficiencies J_s and J_c.

Naturally, the course of the process is determined by the ease at which singlets and clumps partially coalesce. First of all, the singlets must be able to aggregate to destabilize an emulsion. The aggregation of singlets determines the rate at which the coalescence process starts. An impression of the 'initial coalescence efficiency', α_{init}, the fraction of encounters leading to partial coalescence at the beginning of the process, can be gained from:

$$\alpha_{init} = t^*/t \tag{31}$$

in which t^* is the time that would be needed to reach the same change in globule size distribution as observed in the first t minutes of the experiment, if all collisions would lead to partial coalescence. Normally t was taken to be 1 minute. The coalescence efficiency, α_{init}, is comparable to the coalescence efficiency, α_m, for monodispersed emulsions as

described by van Boekel [5]. α_m was calculated as the ratio of the measured (k_1) and the theoretically determined coalescence rate (k_{theor}, after Zeichner & Schowalter [24]:

$$\alpha_m = \frac{k_1}{k_{theor}} = \frac{k_1 \pi}{4 G \Phi_V N} \qquad (32)$$

where Φ_V is the volume fraction of the globules.

For SDS - paraffin emulsions van Boekel found α_m to be 10^{-4} and $2*10^{-6}$ in case the total amount of paraffin amounted to 1 and 19%, respectively. We have fitted the same data (kindly provided by van Boekel) to our model (table 5-3) and we found α_{init} to be smaller than the coalescence efficiency α_m by about a factor of 3. This was to be expected since the theoretical number of collisions, k_{theor}, is underestimated if a polydispersed emulsion is assumed to be monodisperse [12]. To study the progression of the coalescence process after initiation by singlets, the reactivity of the clumps has to be considered. Naturally, the reactivity of the clumps greatly depends on the reactivity of the singlets they are built of. An impression of the course of the process can be calculated by using the ratio P_C/P_S, provided that this dependence on globule size is the same ($m_S = m_C$). This seems a realistic assumption for those cases where all singlets have the same coalescence efficiency, J_S. In

Table 5-3. The initial coalescence efficiency for SDS (14mM) -paraffin emulsions with (α_m) and without (α_{init}) assuming monodispersity.

d_{vs} [μm]	Φ [-]	α_m [1)] [-]	α_{init} [-]
4.97	0.010	$1*10^{-4}$	$3*10^{-5}$
2.99	0.155	$2*10^{-6}$	$7*10^{-7}$
2.54	0.186	$2*10^{-6}$	$5*10^{-7}$

1) after van Boekel (1980)

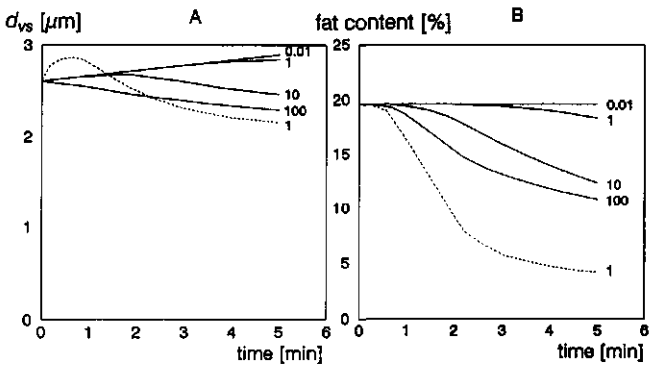

Figure 5-5. Changes in d_{vs} (a) and fat content (b) as a function of time as influenced by the ratio P_C/P_S (indicated near the curves) for $m_S = m_C = 0$; (————) $P_S = 10^{-5}$, (----) $P_S = 10^{-4}$.

figure 5-5 changes in d_{vs} and fat content are given for several values of the ratio P_C/P_S and it is clearly shown that the type of kinetics is greatly influenced by P_C/P_S. The smaller P_C/P_S the longer kinetics will remain of type A and type B. The singlets will form doublets, but these will not aggregate further very fast. If P_C/P_S is larger, newly formed doublets coalesce further, so that soon after the beginning of the process large clumps have formed that cream during the heating step. Both d_{vs} and fat content will decrease. Kinetics will soon change from type A and type B into type D. Naturally, the higher the absolute values of $P_S$and P_C, the lower the ratio at which kinetics will change into type D.Furthermore, the dependence of partial coalescence on globule size has a great impact on the changes in globule size distribution with time. The larger m (with a maximum of 4 in our calculations), the stronger the preference for large globules to aggregate and the unimodal size distribution will soon change into a bimodal one (figure 5-6). The newly formed second peak shifts to higher values, whereas the original peak only shows a diminishing volume but a change in mean diameter is not observed.

The actual values of the above discussed parameters will depend on such emulsion properties as the nature of the continuous and the disperse phase, type of surfactant and its surface load, solid fat content and the treatment conditions that determine the nature of collisions such as the presence (or absence) of a flow field and the applied shear rate. We

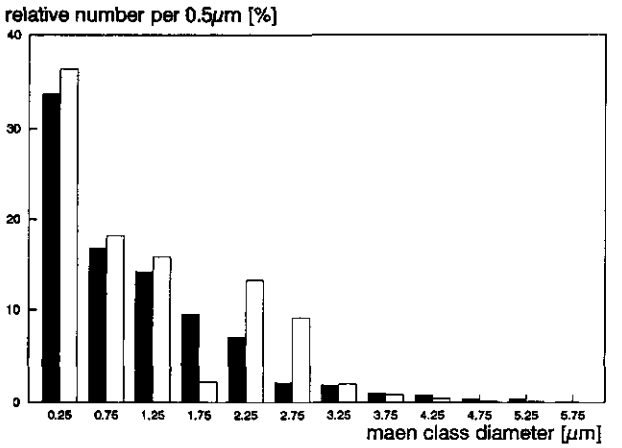

Figure 5-6. Frequency distributions as calculated with model III for $m_s = m_c = 0$ (■) and $m_s = m_c = 4$ (□) for an emulsion after application of a shear rate of 250 s^{-1} during 5 minutes; $R = 1$; $P_s = P_c = 10^{-5}$.

extensively studied the influence of emulsion properties and treatment conditions and we intend to report on this shortly.

5 CONCLUSIONS

The simulation model accurately describes the course of the partial coalescence process in polydisperse emulsions. Taking polydispersity into account made it possible to explain the four types of kinetics. Only in the special case where type A kinetics persists (e.g. paraffin emulsions) the simplification of assuming monodispersity seems to give reasonable results, although the underestimation of the total number of collisions leads to coalescence efficiencies that are too high.

All four types of coalescence kinetics found experimentally (see section 1), can be fitted by the model and seem mainly determined by (1) the ratio between the coalescence efficiencies of clumps and singlets (P_c/P_s) and (2) dependence of the coalescence efficiencies of singlets (m_s) and clumps (m_c) on globule size. The rate of coalescence seems to be determined by (1) the proportion of reactive singlets (R), (2) the coalescence efficiencies of collisions (J_s and J_c), and (3) the total number of collisions, i.e. Φ, d and G.

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KINETICS OF PARTIAL COALESCENCE IN O/W EMULSIONS:

II. EFFECT OF SOME VARIABLES.

ABSTRACT

The destabilization due to partial coalescence of an O/W emulsion under shear is quantitatively described by means of a kinetic model. Several process (e.g. shear rate) and product parameters (e.g. composition, content and fraction solid of fat, globule size, surfactant) were varied. The change in globule size distribution during the process was determined and the results fitted to the model by computer simulation. In this way we were able to distinguish between the effects of encounter frequency and emulsion characteristics. It was found that the composition of the fat, the solid fat content, the contact angle (fat crystal-oil-aqueous phase) and the number of globules that contain crystals are the main factors that determine the instability of the emulsion globules. Furthermore, partially coalesced aggregates appear to be disrupted under some conditions, even at the fairly low shear rate of 125 s^{-1}.

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KINETICS OF PARTIAL COALESCENCE IN O/W EMULSIONS: II. EFFECT OF SOME VARIABLES

1 INTRODUCTION

Partial coalescence in O/W emulsions is the aggregation of partly crystalline globules and is initiated by fat crystals that stick out of the disperse phase into the aqueous phase, rupturing the aqueous film between two approaching globules; it occurs especially when the emulsion is sheared [3]. The crystals initiate the coalescence process, yet, at the same time they mostly prevent the occurrence of full coalescence, in the sense that they prevent the aggregates from becoming spherical. Protruding crystals may tremendously enhance the instability of emulsions. O/W emulsions that are stable in the absence of crystals may be very unstable (some even at rest) if crystals are present.

In systems as described by van Boekel [1], the kinetics of partial coalescence was similar to that of normal coalescence, namely a gradual increase in average globule size with time until a critical size is reached above which coalescence rate is accelerated and the emulsion breaks. Yet, there are situations where partial coalescence proceeds in a different manner. From studies on paraffin emulsions [3], milk fat emulsions [8], natural cream [6, 7] and emulsions of a triglyceride blend (see chapter 3), it has become clear that the combination of emulsion characteristics (aqueous phase and fat composition, fat content, globule size) and the applied treatment (including pretreatments), is decisive as to whether, how and at what rate aggregation occurs. For example, a milk fat in skimmilk emulsion remained stable in a laminar flow field, whereas the emulsion exhibited rapid coalescence in such a flow field, if phospholipids had been dissolved in the milk fat prior to emulsification. An emulsion of a triglyceride blend-in-SDS was unstable at rest if the emulsion, after storage for at least

two hours at 4°C, had been warmed to 20°C and subsequently cooled back to 4°C. A paraffin emulsion, on the other hand, was not affected by such a temperature treatment. These examples make clear that comparison between various systems is difficult, as long as it has not been established what factors cause these differences. Furthermore, globule size distributions vary. As a consequence the frequency of encounters, greatly influenced by the globule size distribution, varies and thereby the instability. In order to provide a means to characterize emulsion stability, the factors that influence the reactivity of the emulsion globules (i.e. the probability that two globules closely encountering each other will partially coalesce) must be distinguished from factors affecting the frequency of encounters. To that end, we developed a simulation model and in the previous chapter on the kinetics of partial coalescence (chapter 5) this model was tested and discussed in general.

The model was extensively described in chapter 5. It attempts to describe the course of the partial coalescence process in simple shear. It is based on the Smoluchowski equation for orthokinetic aggregation, describing the encounter frequency of two-body encounters in polydisperse systems:

$$b_{ij} = \frac{G}{6}(d_i + d_j)^3 N_i N_j \qquad (1)$$

where G the velocity gradient, d is the globule diameter and N the number of globules. It has been modified to account for the colloidal interactions and for the influence of the presence of fat crystals in the oil globules. (N.B. We denote all emulsion droplets and aggregates, whether or not containing crystals, as globules.) The model distinguishes between singlets containing crystals, S_i, singlets without crystals, s_i, and clumps, C_i (by definition containing crystals, since crystals are necessary for partial coalescence to occur). Globules with crystals ('reactive' globules, denoted with a capital) can cause partial coalescence (although this will not occur for all encounters), whereas singlets without crystals can only become part of a clump by reaction with a reactive globule. Normally, the fraction of reactive globules, R, was equal to 1. Only if emulsions without solid fat were mixed with emulsions that did contain crystals, R was between 0 and 1.

The partial coalescence efficiency, J, of collisions in which (at least) one reactive globule is involved, is affected by some factors that depend on globule size (fit parameter is m) and some that do not (fit parameter is P):

$$J = P\left(d_i^*\right)^m \tag{2}$$

where $d_i^* = d_i/d_{min}$ (d_{min}, being the globule diameter of the smallest globules) if the smaller globules are the more efficient ones ($m < 0$), and $d_i^* = d_i/d_{max}$ (d_{max}, being the globule diameter of the largest globules (i.e. 9.75 μm) the model takes into account) if the larger globules have the higher efficiency ($m > 0$). The model distinguishes between the efficiencies of singlets, J_s (by means of the fit parameters P_s and m_s) and of clumps, J_c (fit parameters P_c and m_c). The coalescence frequency for singlets, b_{ij}^s, now becomes:

$$b_{ij}^s = RJ_s\frac{G}{6}(d_i+d_j)^3[N_{s,i}(N_j-N_{c,j}) + N_{s,j}(N_i-N_{c,i}) - N_{s,i}N_{s,j}] \tag{3a}$$

If clumps are involved in partial coalescence then the coalescence frequency, b_{ij}^c, can be described by:

$$b_{ij}^c = RJ_c\frac{G}{6}(d_i+d_j)^3[N_{c,i}N_j + N_{c,j}N_i - N_{c,i}N_{c,j}] \tag{3b}$$

where the overall coalescence frequency, b_{ij}, is the sum of b_{ij}^s and b_{ij}^c. The rate of change of globules per size class i equals:

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{j=i-1} b_{jk} - \sum_{j=1}^{\infty} b_{ij} \tag{4}$$

Analogous to equation (4) the rates of change of reactive singlets and of clumps are estimated, so that for all kind of globules the changes in the size distribution can be followed as a function of time.

This model is used to evaluate the course of the coalescence process, i.e. the ease at which singlets and clumps partially coalesce. Instability of an emulsion can only occur if singlets are able to aggregate and this ability is expressed by the 'initial coalescence efficiency' (α_{init}), the fraction of encounters leading to partial coalescence at the beginning of the process:

$$\alpha_{init} = t^*/t$$

where t^* is the time needed to reach the same change in globule size distribution as observed in the first t minutes of the experiment, provided that all collisions would lead to partial coalescence.

The progress of the coalescence process is represented by the dependence on globule size (represented by m) and by the ratio P_c/P_s, provided that the dependence on globule size is the same for singlets and clumps ($m_s = m_c$, which appeared to be the case for all experiments, except for the one experiment where $R < 1$). The larger m, the greater the preponderance for larger globules to aggregate, causing the formation of a bimodal size distribution. The larger P_c/P_s, the sooner newly formed doublets will coalesce further, so that big aggregates will soon be formed that cream during the heating step.

The goodness of fit can accurately be calculated by the use of χ^2 (11 degrees of freedom). Normally, its values were between 0.1 and 5, suggesting a more than 95% probability that model calculations and experimental results were in good agreement. Only if the amount of creaming fat became substantial, χ^2 sharply increased to values of 40 and higher, so that the calculated globule size distribution did not match the experimentally determined one.

In our previous article we showed that the model can accurately describe the partial coalescence process up to a certain stage. In this paper we will compare model calculations with experimental results obtained at a wide range of conditions. In this way it can be checked whether (differences in) the values of the fit parameters are reasonable and consistent. If so, the factors that are important in partial coalescence can be established.

2 MATERIALS AND METHODS

The experimental procedure is only briefly summarised in this paper. For a detailed description see chapter 5.

2.1 Materials

Anhydrous milk fat (> 99.8% pure fat, < 0.1% water) was fully melted before use.

Paraffin oil was obtained from OPG, Utrecht, Netherlands. Viscosity 60 - 80 mPa.s; density about 860 kg m^{-3}.

The triglyceride blend was kindly supplied by Unilever Research, Vlaardingen, Netherlands. The blend contained about 96.9% triglycerides, 3.0% diglycerides and 0.1% monoglycerides.

Tristearin was also obtained from Unilever Research, Vlaardingen, Netherlands. It had a melting point of 69°C, somewhat below the pure compound's melting point of 72°C.

Sodium dodecyl sulphate (SDS), was obtained from BDH chemicals, England; its grade was specially pure. The critical micelle concentration (CMC) in water is 7.9 mM at 20°C [4]. It was mostly used in concentrations of 13.8 mM.

2.2 Methods

Oil-in-water emulsions were prepared using a Rannie Laboratory Homogenizer. The aqueous phase consisted of 13.8 mM SDS, whereas the disperse phase consisted of one of the above mentioned fats. The globule size distributions of all emulsions were measured using a Malvern 2600D particle size analyzer. The total fat content and the solid fat fraction were both estimated by wide-line proton NMR. All emulsions were stored at least overnight at 4°C to ensure crystallization of fat in all globules. The globule size distribution was found not to change during storage. In duplicate experiments we usually found reproducable results (± 2%).

O/W emulsions were subjected to Couette flow at variable shear rate. At the end of the experiment the apparatus was emptied, the emulsion was warmed to 45°C and left to cream for about 1 hour; in the lower layer the globule size distribution and fat content were estimated. The results were fitted with the simulation model as described in section 1 and the goodness of fit was expressed by χ^2, calculated for the distribution at the end of the experiment. In those cases where the amount of creaming fat had become so large that a

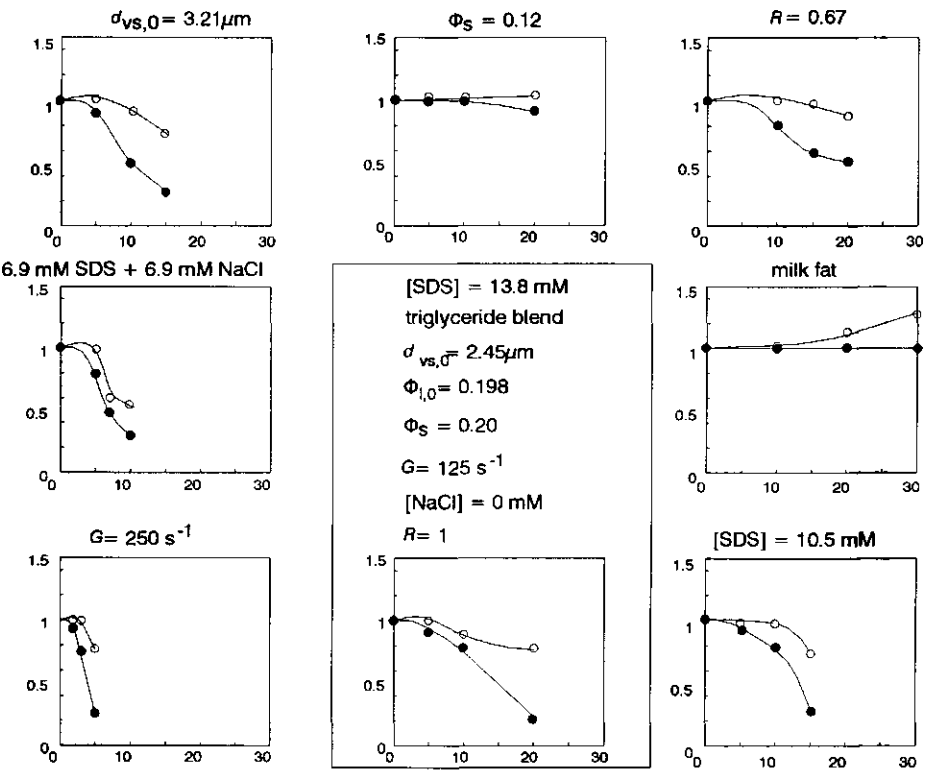

Figure 6-1. Effect of several variables on emulsion stability in Couette flow. In the large box in the middle the standard emulsion is represented. The seven other boxs represent the changes found for emulsions that deviated in one respect (as given at the top of each box) from the standard emulsion. Abscissa: time [min], ordinate: relative normalized globule size ($d_{vs}/d_{vs,0}$) (o) and normalized fat content ($\Phi_l/\Phi_{l,0}$) (●).

good fit was no longer possible, χ^2 was also calculated for the situation half-way the experimental time (and is given between brackets in the tables).

3 RESULTS AND DISCUSSION

In this section the results are described of kinetic experiments on SDS emulsions subjected to Couette flow. Figure 6-1 briefly summarizes the effects of some of the variables applied.

At first consideration, the instability seems to be affected by all variables in a different way. From these results few conclusions can be drawn on the effect of the variables on emulsion properties. We therefore fitted the experimental results to the simulation model as described in detail in chapter 5. For all emulsions the initial mean globule diameter ($d_{vs,0}$), initial fat content ($\Phi_{l,0}$) and applied shear rate (G) are reported. The fit parameters P_s, m_s and m_c and the emulsion characteristics α_{init} and P_c/P_s are tabulated, next to the goodness of fit as expressed by χ^2.

3.1 Influence of the composition of fat

Emulsions were made in SDS (13.8 mM) with the triglyceride blend, milk fat or liquid paraffin with tristearin (SSS) dissolved in it. Furthermore, some results of van Boekel (who kindly provided the data) for SDS - paraffin (a mixture of liquid and solid paraffin) emulsions were used as well. The above mentioned fats, except the paraffin-paraffin mixture, produce numerous crystals per globule, although it is well known that only one or a few catalytic impurities can have been present in each globule; as soon as a crystal has been formed, other crystals presumably form in its vicinity. This so called secondary nucleation is not well understood; it is likely that copious secondary nucleation only occurs at considerable supersaturation. Apparently, there is little or no secondary nucleation in paraffin mixtures, since this material only produces one or two crystals per globule. In figure 6-2 the changes in mean globule diameter and fat content are depicted as calculated by the simulation model and as determined experimentally. As discussed in chapter 5, the model accurately fits the experimental results until most of the fat is creaming during the heating step. In that situation the creaming fat globules presumably coalesce with globules they encounter on their way to the cream layer.

It can be seen from figure 6-2 that all four emulsions have different instabilities. The fat content of the emulsions that contain solid paraffin or milk fat remains constant, whereas d_{vs} increases; the more so for milk fat. The emulsions made with paraffin-tristearin or triglyceride blend both exhibit a decrease in d_{vs} and fat content, the triglyceride blend being

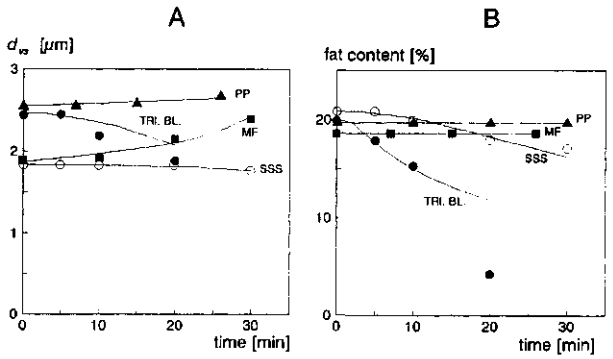

Figure 6-2. d_{vs} (A) and fat content (B) after being subject to Couette flow for various times as calculated (by the simulation model, lines) and experimentally determined (dots), in SDS stabilized emulsions with paraffin-solid paraffin (PP), milk fat (MF), triglyceride blend (TRI. BL.) or paraffin-tristearin (SSS) as the disperse phase. The shear rate used was 125 s^{-1}, except for the emulsion with paraffin-solid paraffin where a shear rate of 168 s^{-1} had been used.

Table 6-1. Effect of the composition of fat in emulsions with 13.8 mM SDS on the parameters obtained in the simulation model. For an explanation of the symbols see the text.

Kind of fat, Φ_s	$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_C/P_S	P_S	$m_S = m_C$	χ^2
Paraffin-paraffin, 0.20	2.54	0.186	168	0.5	8.10^{-04}	4.10^{-07}	2	0.4
Milk fat, 0.18	1.89	0.196	125	1	0.5	2.10^{-07}	2	0.1
Paraffin-tristearin, 0.20	2.44	0.208	125	6	1.4	7.10^{-04}	4	2.5
Triglyceride blend, 0.20	2.45	0.198	125	34	3	2.10^{-03}	4	198 (2.0)

the less stable one. These differences in emulsion stability are expressed by the fit parameters m and P_C/P_S that vary considerably with kind of fat (table 6-1). With increasing

emulsion instability (i.e. higher a_{init}) the ratio P_C/P_S increases. Furthermore, it appears that larger globules are more reactive in all emulsions ($m > 0$), and m is lower for the more stable emulsions.

3.2 Influence of the volume fraction of fat

On first consideration, one would expect the fat volume fraction, Φ_l, not to affect the fraction of collisions leading to partial coalescence. The encounter frequency will be proportional to Φ_l and so will the coalescence rate. However, some other factors may play a role as well. Disturbance of the Couette flow may occur and partial plug flow is likely to occur above $\Phi_l = 0.25$ [5]. Furthermore, the number of multiple-globule encounters may not be negligible any more. If so, the coalescence rate will be no longer proportional to Φ_l. We observed that the coalescence efficiencies of emulsions, made of SDS (13.8 mM) with triglyceride blend, were all similar, irrespective of the fat volume fraction (table 6-2). This is in accordance with results of van Boekel [1], who found a similar behaviour for emulsions with paraffin oil as long as Φ_l did not exceed about 0.25. It was concluded that disturbance of the flow field can be left out of consideration and that the destabilization of the O/W emulsions was not significantly affected by multiple-globule interactions.

Table 6-2. Effect of the fat volume fraction on the parameters in the simulation model for emulsions with 13.8 mM SDS and triglyceride blend ($\Phi_s = 0.20$). For an explanation of the symbols see the text.

$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot a_{init}$	P_C/P_S	P_S	$m_S = m_C$	χ^2
2.29	0.098	125	32	4	1.10^{-03}	4	163 (4.8)
2.61	0.151	125	32	2.5	2.10^{-03}	4	71 (1.8)
2.45	0.198	125	34	3	2.10^{-03}	4	198 (2.0)

3.3 Shear rate

Emulsions of SDS with triglyceride blend or milk fat were subjected to Couette flow at various shear rate and some typical results are shown in table 6-3. Both emulsions were stable at low shear rates. The transition from stable to unstable emulsions was very sharp; the triglyceride blend emulsion remained stable at $G = 96\ s^{-1}$, whereas at $G = 125\ s^{-1}$ the emulsion was very unstable. (It should be realized that the rate of aggregation is proportional to G if all the parameters of the model remain the same.) A further increase of the shear rate did not result in higher values for the fit parameters. The milk fat emulsion behaved in a similar way. At $G = 125\ s^{-1}$ the emulsion was slightly unstable, whereas a steep decline in stability was observed if G was increased to 190 s^{-1}; the fraction of encounters leading to partial coalescence at the beginning of the experiment (α_{init}) increased from 10^{-6} to 10^{-5}. Beyond $G = 190\ s^{-1}$ coalescence efficiency increased only slightly.

Table 6-3. Effect of the shear rate on the parameters in the simulation model for emulsions with 13.8 mM SDS. For an explanation of the symbols see the text.

Type of fat, Φ_s	$d_{vs,0}$	$\Phi_{t,0}$	G	$10^6 \cdot \alpha_{init}$	P_c/P_s	P_s	$m_s = m_c$	χ^2
Triglyc. blend, 0.20	2.55	0.195	96	<5	-	$<10^{-6}$	4	-
	2.45	0.198	125	34	3	2.10^{-3}	4	198 (2.0)
	2.60	0.195	250	44	2.5	2.10^{-3}	4	256 (0.7)
Milk fat, 0.18	1.89	0.196	125	1	0.5	2.10^{-7}	2	0.1
	2.38	0.200	190	8	1	5.10^{-5}	2	6.3
	2.39	0.203	250	16	1	5.10^{-5}	2	66 (3.1)

3.4 Solid fat content

Again emulsions of SDS (13.8 mM) with triglyceride blend or milk fat were made. Both fats were used either undiluted or diluted with a fraction of the triglyceride blend remaining liquid at 20°C.

From table 6-4 it can be seen that the proportion of solid fat (Φ_s) is of great influence on the emulsion behaviour. At the lowest solid fat fractions examined the emulsions remained stable in shear. There appear to be insufficient crystals present to form a continuous network and therefore partial coalescence does not occur (see chapter 4). For both fats α_{init} increased with increasing solid fat content in the oil globules. Furthermore m increased, i.e. larger globules became relatively more sensitive to partial coalescence, with increasing Φ_s. This behaviour is observed for singlets as well as clumps. The most likely explanation is that

Table 6-4. Effect of the solid fat content on the parameters in the simulation model for emulsions with 13.8 mM SDS. For an explanation of the symbols see the text.

Type of fat, Φ_s	$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_C/P_S	P_S	$m_S = m_C$	χ^2
triglyc. blend, 0.14	2.50	0.217	250	<0.9	-	$<2.10^{-7}$	0	-
triglyc. blend, 0.17	2.65	0.197	250	4	0.25	4.10^{-4}	2	1.0
triglyc. blend, 0.20	2.60	0.195	250	44	2.5	2.10^{-3}	4	256 (0.7)
milk fat, 0.06	2.40	0.162	400	<0.03	-	$<10^{-10}$	0	-
milk fat, 0.12	2.37	0.185	250	0.03	1.4	7.10^{-8}	1	1.4
milk fat, 0.18	2.39	0.203	250	16	1	5.10^{-5}	2	66 (3.1)

more crystals will protrude from the O/W interface if more solid fat is present. The increase in α_{init} with increasing Φ_s is in accordance with this. The course of the partial coalescence process, as represented by P_c/P_s, is influenced differently for either fat. If milk fat globules partially coalesce ($\alpha_{init} > 3 \cdot 10^{-8}$), the reactivity of singlets and clumps is about equal. For triglyceride blend emulsions the ratio P_c/P_s increases with solid fat content. It may well be that these differences are caused by the structure of the crystal network and/or by the network strength. Furthermore, the variation in crystal size may be decisive. Unfortunately, we were not capable to distinguish between these variables.

3.5 Fraction of globules containing crystals

SDS - triglyceride emulsions were mixed with emulsions in which the liquid fraction of the blend was the disperse phase ($0 < R < 1$) before they were subjected to Couette flow. In this situation all singlets that can cause partial coalescence (S_i) have the same properties and, as we already mentioned in section 3.4, the singlets without crystals (s_i) are not reactive at all. This leads to a situation where α_{init}/R is almost constant, whereas P_c/P_s, i.e. the reactivity of the clumps relative to that of the singlets, sharply decreases with increasing proportion of liquid globules present (table 6-5), since the ratio solid fat / oil in the clumps decreases. Consequently, the crystals will become more and more wetted by oil, so that the protrusion distance decreases.

Table 6-5. Effect of the fraction of globules that contain crystals on the parameters in the simulation model for emulsions with 13.8 mM SDS and triglyceride blend ($\Phi_s = 0.20$). For an explanation of the symbols see the text.

R	$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_c/P_s	P_s	m_s	m_c	χ^2
0.33	2.61	0.200	250	10	1.10^{-4}	1.10^{-3}	4	0	0.6
0.67	2.66	0.203	250	29	2.10^{-3}	2.10^{-3}	4	2	0.3
1.00	2.60	0.195	250	44	2.5	2.10^{-3}	4	4	256 (0.7)

3.6 Initial globule size distribution

Several authors [1, 3, 7, 8] have observed a positive correlation between emulsion instability and globule size; the larger the globules the more reactive they are for partial coalescence. It appeared, indeed, from the model calculations that the coalescence efficiency of encounters increases with globule size (table 6-6). In nearly all conditions we found m values in almost all cases above zero. One would thus expect emulsions with larger $d_{vs,0}$ to result in higher α_{init} values, since the fraction of globules with a higher reactivity is higher. For paraffin emulsions we did find a very steep increase in α_{init} with increasing $d_{vs,0}$, for SDS - triglyceride blend emulsions α_{init} increased less spectacularly.

The fit parameter P_C/P_S, on the other hand, is expected to remain constant, since the globule size dependency is already incorporated in m. For the triglyceride emulsions this was indeed the case. For the paraffin emulsions a slight difference was found in the ratio P_C/P_S, but one should realize that paraffin shows little or no secondary nucleation. The number of catalytic impurities and, consequently, the number of crystals per globule may thus increase with

Table 6-6. Effect of the initial globule size distribution on the parameters in the simulation model for emulsions with 13.8 mM SDS. For an explanation of the symbols see the text.

Type of fat, Φ_s	$d_{vs,0}$	$c_{s,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_C/P_S	P_S	$m_S = m_C$	χ^2
Triglyceride blend, 0.20	1.66	0.27	0.181	125	26	3	2.10^{-3}	4	2.1
Triglyceride blend, 0.20	2.45	0.31	0.198	125	34	3	2.10^{-3}	4	198 (2.0)
Triglyceride blend, 0.20	3.21	0.71	0.231	125	43	3	2.10^{-3}	4	106 (4.2)
Paraffin, 0.20	2.55	0.61	0.186	168	0.5	8.10^{-4}	4.10^{-7}	2	0.4
Paraffin, 0.17	4.79	0.38	0.010	168	25	4.10^{-4}	1.10^{-6}	2	0.8

globule diameter, thereby increasing the reactivity of a globule, especially a singlet. One would also expect the instability (e.g. α_{init}) to increase with the relative spread in globule size distribution, but we have insufficient results to check this.

3.7 Surfactant concentration

The effect of increasing SDS concentration may be twofold. First the minimum distance of approach decreases by the increase in ionic strength. Second, the contact angle Θ_w (as measured in the water phase) of a fat crystal at the O/W interface decreases, so that the crystal will protrude further into the aqueous phase. Due to these factors α_{init} should increase; the difference between 6.9 and 10.4 mM SDS is indeed striking, but the further increase to 13.8 mM had a fairly small effect. The emulsions that were unstable in Couette flow showed the same fit parameters (table 6-7). Both singlets and clumps became more reactive at higher SDS concentrations, so that the ratio P_c/P_s remained constant, as expected.

Table 6-7. Effect of the surfactant concentration on the parameters in the simulation model for emulsions with triglyceride blend (Φ_s = 0.20). For an explanation of the symbols see the text.

SDS conc.	$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_c/P_s	P_s	$m_s = m_c$	χ^2
6.9mM	2.48	0.194	400	<0.3	-	$<7.10^{-7}$	4	-
10.4mM	2.62	0.196	125	36	3.3	9.10^{-4}	4	40 (0.6)
13.8mM	2.45	0.198	125	34	3	2.10^{-3}	4	198 (2.0)

3.8 Ionic strength

SDS is an ionic surfactant and the interaction between droplets stabilized by SDS depends

on ionic strength, as follows from the DLVO-theory. The presence of NaCl in a SDS stabilized emulsion may influence its stability. Yet, the salt containing emulsions remained stable if no crystals were present. In the presence of crystals, the addition of salt had no measurable effect if the emulsions were kept at rest. In Couette flow, salt content did affect emulsions containing crystals. The experiment made use of SDS (6.9 mM) - triglyceride emulsions, that were stable at the conditions applied. In some cases NaCl was present (N.B. added before emulsification) in such concentrations that the ionic strength was comparable with emulsions with SDS concentrations of 10.4 and 13.8 mM. The resulting fit parameters were, however, different (table 6-8). Although the reactivity of the singlets appeared almost the same, α_{init} and the reactivity of the clumps were smaller in the case salt was added. Similar to addition of SDS an increasing salt concentration results in an increase in ionic strength, so that the minimum distance of approach, h, between globules decreases. As a result emulsions are expected to be less stable. The contact angle, however, is not materially influenced by salt addition, in contrast to the increasing contact angle upon increasing SDS concentration. Consequently, emulsions are expected to be more stable than in the case SDS is added. Since we are not able to quantify the influences of both effects on emulsion destabilization we are not capable to quantitatively explain the results.

Table 6-8. Effect of the ionic strenght on the parameters in the simulation model for emulsions with 6.9 mM SDS and triglyceride blend (Φ_e = 0.20). For an explanation of the symbols see the text.

NaCl added	$d_{vs,0}$	$\Phi_{l,0}$	G	$10^6 \cdot \alpha_{init}$	P_c/P_s	P_s	m_s	χ^2
0	2.48	0.194	400	<3	-	$<7.10^{-7}$	4	-
3.4 mM	2.54	0.225	125	5	0.1	1.10^{-3}	4	123 (0.5)
6.8 mM	2.74	0.238	125	26	0.1	1.10^{-3}	4	125 (3.2)

4 DISCUSSION

For partial coalescence to occur, it is a necessary (though not a sufficient) condition that the closest approach (h) of encountering globules is less than the protrusion distance (δ) of crystals from the O/W boundary. Any emulsion ingredient or process variable that influences h or δ may thus influence the partial coalescence process (see chapter 3).

The protrusion distance, δ, and thereby the reactivity of globules depends on the fat crystals. The results show that in most cases the reactivities, P, of singlets (with crystals) and clumps of a given size are constant during the aggregation process and they are reproducible. P_c/P_s was about 1 for emulsions with milk fat and mostly 3 for emulsions with the triglyceride blend. Even the dependence on globule size was the same for singlets and clumps ($m_s = m_c$). Only in the case of paraffin (solid and liquid) emulsions, where only a few crystals are present in each globule (presumably because no secondary nucleation occurs), the clumps were far less reactive than the singlets. Here, the crystal length, being approximately equal to the diameter of the singlet, is small compared to the clump diameter; this is the more so for larger clumps, so that crystals become more and more engulfed by the liquid paraffin oil. Consequently, the protrusion distance decreases. On the other hand, the number of crystals in a clump and, thereby, the probability of partial coalescence may increase, but the effect of a decreased protrusion distance appears to predominate.

In addition to the differences between the different kinds of fat the reactivity of the singlets (and consequently of clumps) was especially influenced by the solid fat content; the reactivity increased with increasing solid fat fraction (table 6-4). This may be explained by the size, shape and number of crystals, which, in turn, depend on fat composition and especially on the fraction of the fat being solid. It is these characteristics that are important as to whether or not a continuous network, with crystals that stick out into the aqueous phase can be obtained. The reactivity of clumps also depends on the fat composition and the amount of solid fat present, but clump reactivity can also be influenced, selectively, by mixing emulsions with different reactivities of the singlets. For example, in the case where there are globules with and without crystals ($R < 1$, table 6-5), the reactivity is not the

same for all singlets. The reactivity of globules with crystals depends on the properties of the fat, whereas the globules without crystals are not reactive at all (partial coalescence of these globules only occurs with globules that contain crystals). Consequently, the reactivity of a clump is larger if the proportion of reactive singlets making up a clump is larger. The more reactive singlets present in a clump (e.g. higher R values), the more the reactivity of a clump will approach the reactivity of a singlet (with crystals). Van Boekel & Walstra [3] did similar experiments with paraffin containing emulsions. They found higher α_{init} values and another dependence of α_{init} on R. We cannot explain the differences found, although we feel that it must have something to do with the fact that globules of paraffin emulsions contain only a few crystals, whereas the triglyceride globules contain numerous (smaller) crystals. In addition to variables that influence δ there are variables that influence the partial coalescence process by their effect on h. Concentration of ionic surfactant (table 6-7), salt concentration (table 6-8) and shear rate (table 6-3) are such variables. The variation of the closest distance of approach (h) with shear rate has a distinct effect on emulsion stability. At shear rates up to about 100 s^{-1} our triglyceride emulsions were stable, whereas at 125

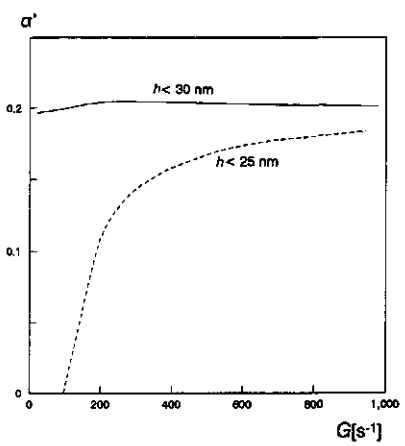

Figure 6-3. Calculated fraction of encounters α' for which either $h < 30$ nm (———) or $h < 25$ nm (----) as a function of the shear rate G, valid for SDS stabilized emulsion globules with $d = 3$ μm. No salt added. (After van Boekel & Walstra [3]).

s^{-1} the emulsions became extremely unstable. Figure 6-3 (after van Boekel & Walstra [3]) shows that below G = 100 s^{-1} no encounters with h < 25 nm would occur in SDS - emulsions, whereas above this shear rate the number of encounters with h < 25 nm rapidly increases. This presumably implies that protruding crystals were sticking out over a distance of about 25 nm in this particular (SDS-triglyceride) emulsion. For the milk fat emulsions the transition occurred at slightly higher G values, so that it was concluded that the protrusion distance of milk fat crystals must have been less than 25 nm. Melsen [8] found a similar transition point for milk fat in whey emulsions at about 500 s^{-1}. For this type of emulsion, we do not know the interaction energies, so that we cannot calculate h (it is presumably smaller). The crystals probably protrude over another (presumably smaller: see chapter 4) distance, but the situation may be similar in a qualitative sense.

At shear rates above 125 s^{-1}, however, the (apparent) reactivity of the globules did not in all cases become larger with decreasing h. Something similar was found for surfactant and salt concentration: there is a maximum above which the fraction of encounters resulting in partial coalescence is constant. This would imply that emulsion stability decreases as a result of an increase in the number of encounters, not by an increase in the coalescence efficiency of encounters. This situation of maximum coalescence efficiency may be the result of the fact that the globules have reached optimum reactivity. For example, because a shorter minimum distance of approach between globules would not result in more globules with crystals for which $\delta > h$. This is, however, very unlikely because in that situation one would expect P_s and P_c to equal 1 and that is not nearly the case. It is more likely, that the number of aggregates that are formed increases, but that part of the clumps disaggregate again due to the shear forces acting on them (disruption is not taken into account in our model; see chapter 5). The shear force (F_s) acting on a doublet of equal spheres is approximately given by:

$$F_s = G\eta d^2 \qquad (6)$$

where G is the velocity gradient, η the dynamic viscosity of the aqueous phase and d the sphere diameter. These shear forces are counteracted by interfacial forces. The force (F_b)

needed to pull two droplets apart that are bridged by a single crystal is, in first approximation, given by:

$$F_b = \frac{\gamma A (1 - \cos\theta_w)}{s} \quad (7)$$

where γ is the interfacial tension at the O/W interface, A is the area of that part of the crystal that pierced the O/W interface of the opposite globule, θ_w the contact angle of the crystal at the interface (as measured in the aqueous phase) and s the distance over which the crystal protrudes into the opposite globule. From equations (6) and (7) it can be seen that higher shear, larger globules and smaller crystals favour disruption. Furthermore, the interfacial tension must be low. Smaller values of cos θ_w favour disruption also. If, however, cos θ_w is negative, i.e. $\theta_w > 90°$, the situation may be different. Since crystals, in this situation, are better wetted by the oil phase, a liquid oil neck may be formed between both globules involved and this hampers disruption. If, on the other hand, the crystals are kept in a network, the outflow of oil is hindered by capillary forces, so that the formation of an oil neck may be hampered too. The latter becomes more significant at a smaller pore diameter of the crystal network, hence at a higher solid fat content and/or smaller crystals.

From the above it can be seen that disruption may be significant for SDS (13.8 mM) - triglyceride emulsions, having a γ_{ow} of 2 mN m^{-1} and cos θ_w being approximately zero (θ_w = 85°). If we assume that s equals $\sqrt{A}$ and that $A \approx 10^{-18}$ m^2, than it can be deduced from equations (6) and (7) that the resultant force ($F_s - F_b$), acting on a doublet in shear (G = 125 s^{-1}) would cause disruption for globules above approximately 4 μm. This is even more so for large aggregates, made up of two clumps that are only connected by one bridge between singlets.

In paraffin containing emulsions crystals are considerably larger (of the order of 1 μm). The contact angle at the SDS - paraffin interface is 116° (van Boekel & Walstra [3]). Furthermore paraffin globules contain only few crystals, so that it is likely that a liquid oil neck is readily formed between partially coalesced globules followed by the rapid merging of the paraffin globules. Disruption of newly formed aggregates, thus, is not very likely to

occur in the case of paraffin emulsions at the applied shear rates. We, indeed, did not find a maximum in the fit parameters for paraffin emulsions in laminar flow. Neither is this expected for protein containing emulsions, having an even higher contact angle.

5 CONCLUSIONS

The simulation model appears to be a helpful tool to unravel the factors affecting partial coalescence of emulsion globules in a shear field, be it emulsion properties or other effects, like encounter frequency and the distance of approach of the globules.

The following factors appeared of significant influence:

1. Shear rate, G, causing an increase in the contact area by the orbiting around each other of the globules. Therefore emulsions are far more sensitive to partial coalescence in shear than in Brownian motion. If all parameters of the model remain constant clumping rate is proportional to G. A minimum G may, however, be necessary to obtain a film thickness that is smaller than the protrusion distance of the crystal in the aqueous phase in order to get partial coalescence (film thickness decreases with increasing G values). Furthermore at some higher G freshly formed aggregates can be disrupted again in some cases. Presumably, this occurs only if $\theta_w \leq 90°$ in combination with a low interfacial tension. Such disruption may even occur in some conditions at a shear rate as low as 125 s^{-1}.

2. Fraction of dispersed phase, Φ_l. Up to a Φ_l of (at least) 0.25 partial coalescence can be described by orthokinetic aggregation without correction for the effect of the decreased volume of continuous phase on the encounter frequency, which effect increases steeply with Φ_l. It was concluded that disturbance of the flow field can be left out of consideration and that the aggregation rate in the O/W emulsions was not significantly affected by multiple-globule interactions.

3. Composition and fraction solid of the fat. The number of crystals, their size and shape and the protrusion distance into the aqueous phase determine globule reactivity. It appears essential whether there is a continuous crystal network in the globule or not. Unfortunately, it is not possible to accurately predict from the fat composition whether such a network will

be formed under the given circumstances (see chapter 4).

4. Globule size. For a given fraction of solid fat the possibility of formation of a continuous fat network in a singlet (and thereby the reactivity for partial coalescence) depends on its size. The larger the singlets relative to the crystals the less solid fat is needed to achieve this.

The effect of clump size can be twofold. In the case of only a few large crystals per singlet they become more and more engulfed by liquid oil with increasing clump size. Consequently the reactivity for partial coalescence decreases. If, on the other hand, singlets with crystal networks are present partial coalescence causes the squeezing out of liquid oil in order to form a neck between adjacent globules. Less oil remains to enclose the network, implying that crystals may protrude further; consequently, the clumps become more reactive with size.

5. Type of surfactant. The distance of approach of the globules is determined by this factor in combination with solvent quality (in the case of a polymer surfactant) and ionic strength (in case of an ionic surfactant). Moreover, it affects the contact angle of a crystal with the O/W interface and thereby the protrusion distance of crystals in the aqueous phase. If the surfactant is oil soluble, fat crystallization and network formation can also be influenced (see further conclusion 3).

Consequently, lowest reactivity of emulsion globules for partial coalescence is obtained if the following qualifications are met: small globules, a surfactant that causes a high interfacial tension and a high θ_w (e.g. protein), as little solid fat as possible (sometimes to be achieved by allowing supercooling to persist), small crystals.

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SUMMARY

The stability of triglyceride-in-water emulsions, with part of the fat crystallized, was investigated. These crystals may tremendously enhance aggregation of the oil globules. This aggregation process is called partial coalescence. In some cases a certain instability is desired (e.g. during whipping of cream), yet in other cases stability is needed (e.g. during storage and transport). The role of the fat crystals in emulsion stability has been investigated in some detail.
In the second chapter an industrial problem, called the 'rebodying process', is dealt with that has been observed in natural cream. Thickening of the emulsions occurs due to temperature cycling. The same phenomenon occurred in model emulsions with a fat content above 25%. At lower fat contents the emulsions did not thicken at rest (nor did dilute natural cream), yet they had become more sensitive to partial coalescence in a flow field after such a temperature cycle. It was concluded that rebodying is due to partial coalescence. It was shown that crystals become larger due to a temperature cycle, thereby making the emulsion more prone to partial coalescence.
Chapter 3 deals with the nature of the aggregation of partially crystallized O/W emulsions. The wetting properties of crystals at the O/W boundary were investigated. Although it appears to be necessary that the contact angle is such that crystals are preferentially at the O/W interface,this is obviously not the only condition that has to be fullfilled to destabilize the emulsions. The formation of a continuous crystal network throughout the globule also appeared of importance. It was clearly shown from displacement experiments that crystal orientation at the O/W boundary occurs before a crystal network is established. After network formation, the crystal orientation appeared to be fixed and thereby the sensitivity to partial coalescence. It was also found that aggregates can be disrupted again by changing the wetting properties such that crystals migrate from the oil phase into the aqueous phase. Within a few hours after aggregation disaggregation resulted in the return of the emulsion to the globule size distribution at the beginning of the experiment. After that time the merging of the globules had gone too far to regain the starting situation.
The specific role of the fat is described in chapter 4. The permeability of bulk fats was investigated, as well as stability measurements of emulsions (with the same fats) in Couette flow and the crystal network strength in individual globules. The latter was done with a capillary suction method that was specially developed for this purpose. It appeared that emulsion instability steeply increases when the crystal network has become continuous, in other words when it extends throughout the whole globule. It appeared further that the rate of aggregation increased with solid fat content up to a certain limit. Above that the aggregation rate decreases again with increasing amount of solids. The permeability of the fat plays an important role.
In the fifth chapter the development of a mathematical model is described that simulates the

course of the partial coalescence process in polydisperse systems in Couette flow. It is based on the Smoluchowski encounter frequency equation and is adapted to account for the influence of fat crystals in the oil globules. The model accurately describes the partial coalescence process by distinguishing between clumps and single globules with and without crystals. Only when too much fat creams on warming the emulsion, the model is no longer adequate. With this model the course of the partial coalescence process can be characterized by three parameters: (1) the initial rate of partial coalescence, (2) the ratio between the efficiencies at which single globules and clumps aggregate and (3) the dependence of partial coalescence on globule size.
The model was used to test the influence of various process variables (e.g. shear rate) and product variables (e.g. type, amount and solid fraction of the fat). The results are represented in chapter 6. The calculated changes in the globule size distribution and the fat content were compared with the experimental results. It appeared that the type of fat, the solid fat content and the number of globules that contain crystals are the main factors that determine emulsion stability. It was found that even at shear rates as low as 125 s^{-1} disruption can already occur, depending on the type of emulsion.

SAMENVATTING

In dit onderzoek werden olie-in-water emulsies onderzocht, waarbij de oliedruppels meestal vetkristallen bevatten. Deze kristallen kunnen een enorme toename in de aggregatie van de oliedruppels veroorzaken. Ten gevolge van de aanwezige kristallen vloeien de geaggregeerde druppels niet geheel samen, vandaar dat het proces partiële coalescentie wordt genoemd. Soms is deze instabilisteit gewenst (zoals bij het opkloppen van room), maar vaak ook niet (tijdens opslag en transport van de emulsies). Onderzocht is welke rol de vetkristallen spelen in dit proces.

In hoofdstuk 2 is een praktijkprobleem nader onderzocht dat zich voordoet bij natuurlijke room. Dit proces, 'rebodying' genaamd, houdt in dat ten gevolge van een temperatuurscyclus verdikking ('body'-vorming) van de emulsie optreedt. Het zelfde verschijnsel bleek zich ook voor te doen bij modelemulsies met een vetpercentage boven 25%. Bij lagere vetpercentages vond in rust geen verdikking plaats (evenals in verdunde room), maar het bleek dat emulsies na zo'n temperatuursbehandeling wel gevoeliger voor partiële coalescentie in een stromingsveld zijn. Er werd dan ook geconcludeerd dat rebodying een vorm van partiële coalescentie is. Aangetoond kon wordent dat ten gevolge van de temperatuurscyclus de vetkristallen groter worden, waardoor aggregatie makkelijker kan optreden.

Het mechanisme dat ten grondslag ligt aan de aggregatie in een gedeeltelijk gekristalliseerde O/W emulsie is beschreven in hoofdstuk 3. Hiertoe werden allereerst de bevochtigings-eigenschappen van de kristallen aan het grensvlak olie-water bestuudeerd. Een zodanige randhoek, dat de kristallen gedeeltelijk in de waterige fase uitsteken, blijkt noodzakelijk voor partiële coalescentie. Maar dit is niet de enige voorwaarde voor aggregatie. Ook de vorming van een vet netwerk is van groot belang gebleken. Verdringingsexperimenten hebben duidelijk gemaakt dat de orientatie van de kristallen in het grensvlak O/W plaats vindt voor dat zich een kristalnetwerk heeft gevormd. Zodra er zo'n netwerk is, verandert er weinig meer aan deze orientatie en aan de gevoeligheid van de druppels voor partiële coalescentie. Voorts bleek dat door verandering van de bevochtigingseigenschappen (zodanig dat de kristallen van de oliefase overgaan naar de waterfase) aggregaten weer uit elkaar getrokken kunnen worden, mits dit gebeurt binnen enkele uren na partiele coalescentie. Daarna is de samensmelting van druppels zo ver gevorderd dat de beide druppels niet meer van elkaar kunnen worden verwijderd.

In het vierde hoofdstuk wordt ingegaan op de specifieke rol van het vet. Hiertoe zijn permeabiliteits metingen gedaan aan bulk-vetten en tevens zijn de stabiliteit van de emulsie en de stevigheid van het kristalnetwerk in de emulsiedruppels bestudeerd. Voor dit laatste doel werd gebruik gemaakt van een speciaal voor dat doel ontwikkelde capillair. Gebleken is dat de

instabiliteit van een emulsie snel toeneemt als het kristalnetwerk continu is geworden, m.a.w. dezelfde diameter heeft als de druppel waarin het vet zich bevindt. Verder is gebleken dat de aggregatiesnelheid van de druppels groter is voor een hoger gehalte aan kristallijn vet, totdat een optimum bereikt is. Daarboven is de snelheid weer geringer. De permeabiliteit van het kristalnetwerk in de druppel speelt hierbij een belangrijke rol.

In hoofdstuk 5 is de ontwikkeling beschreven van een wiskundig model dat het verloop van partiële coalescentie in polydisperse systemen in a laminair stromingsveld simuleert. Het is gebaseerd op de Smoluchowski vergelijking voor de ontmoetingsfrequentie van kolloidale deeltjes en is aangepast voor de invloed van de vetkristallen in de oliedruppels. Het uiteindelijke model beschrijft accuraat het partiële coalescentieproces door onderscheid te maken tussen emulsiedruppels en aggregaten daarvan, met en zonder kristallen. Alleen als er te veel vet oproomt tijdens opwarming van de emulsie is het model niet langer bruikbaar. Met dit model kan het verloop van het partiele coalescentie proces worden gekarakteriseerd met behulp van drie parameters: (1) de initiële partiële coalescentiesnelheid, (2) de verhouding tussen de efficientie waarmee afzonderlijke druppels en aggregaten verder coalesceren en (3) de afhankelijkheid van partiële coalescentie van de deeltjesgrootte.

De invloed van diverse procesvariabelen (zoals afschuifsnelheid) en produktvariabelen (zoals type, hoeveelheid en fraktie kristallen in het vet) zijn getest en worden beschreven in hoofdstuk 6. De berekende veranderingen in de deeltjesgrootteverdeling en het vetgehalte zijn steeds vergeleken met de experimenteel verzamelde waarden. Het bleek dat het type vet, het vetgehalte en het aantal deeltjes met kristallen de belangrijkste faktoren zijn die de stabiliteit van O/W emulsies bepalen. Verder werd geconstateerd dat zelfs bij een lage afschuifsnelheid van 125 s^{-1} al disruptie van aggregaten plaats kan vinden, afhankelijk van het type emulsie.

CURRICULUM VITAE

De auteur van dit proefschrift werd geboren op 3 mei 1959 te s'Gravenhage. Na 6 jaar op het Stedelijk Gymnasium te Apeldoorn te hebben doorgebracht, begon zij in 1977 aan de HBO-B opleiding tot chemisch analiste aan de OLAN te Arnhem. Na het behalen van het diploma in 1980 was de auteur gedurende enkele jaren werkzaam als analiste. Daarnaast begon zij in 1981 met een studie levensmiddelentechnologie aan de Landbouwuniversiteit te Wageningen. In november 1986 slaagde zij met lof voor het doctoraalexamen, met als hoofdvakken levensmiddelennatuurkunde en informatica en als bijvak levensmiddelenchemie. Als vervolg van deze studie startte zij in die zelfde maand met een vierjarig, door Unilever Research Laboratorium Vlaardingen gefinancierd, promotieonderzoek bij de sectie zuivel en levensmiddelen-natuurkunde aan de Landbouwuniversiteit. Gedurende deze periode werd het in dit proefschrift beschreven onderzoek uitgevoerd. Vanaf januari 1991 werkt zij bij de sectie Bakery Products van het Unilever Research Laboratorium te Vlaardingen.