THE STABILITY OF RECOMBINED MILK FAT GLOBULES

Promotor: dr.ir. P. Walstra
hoogleraar in de zuivelkunde

Johannis P. Melsen

THE STABILITY OF RECOMBINED MILK FAT GLOBULES

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. C.C. Oosterlee,
in het openbaar te verdedigen
op maandag 21 september 1987
des namiddags te vier uur in de aula
van de Landbouwuniversiteit te Wageningen

ABSTRACT

Melsen, J.P. (1987) The stability of recombined milk fat globules. Doctoral thesis Agricultural University, Wageningen, 146 p, 19 figs, 46 tables. English and Dutch summaries.

The stability of the fat globules in recombined milk products against creaming, flocculation, clustering, partial coalescence and real coalescence, with the emphasis on partial coalescence, was studied. (partial) Coalescence was characterized by determining changes in globule size distribution and fat content. Without crystals the emulsions were mostly stable at rest and during flow. If crystals were present, natural cream and emulsions of milk fat-in-whey were unstable in a flow, while emulsions of milk fat and skimmilk or milk fat and buttermilk remained fairly stable and only gave partial coalescence if high shear rates were applied to emulsions with a high fat content and a large average diameter.
In some cases partial coalescence resulted in the formation of a few large clumps that coalesced into floating fat upon heating the emulsion to above the melting point of milk fat thus causing a reduction of the fat content of the underlying emulsion, in other cases partial coalescence resulted in the formation of many small clumps that coalesced into larger fat globules upon heating, thus causing an increase in average globule size. Coalescence course and rate appeared to depend on emulsion type and applied treatment. Partial coalescence of milk fat-in-whey emulsions nearly always resulted in a decrease of the fat content. With a model starting from a small fraction of reactive globules gradually growing into clumps during the treatment, the coalescence process of these emulsions was fairly good quantitatively described. The ideas whereupon this model is based were used to qualitatively explain the different partial coalescence processes observed with the other emulsions.

Free descriptors: partial coalescence; coalescence; creaming; clustering; aggregation; recombined milk products; emulsion stability, crystallisation; cream; Taylor vortices; Couette flow; flocculation; heat stability.

STELLINGEN

1. Partiële coalescentie van emulsies kan zeer verschillende gevolgen hebben.

   Dit proefschrift

2. De druppeldiameter heeft een zo grote invloed op de emulsiestabiliteit, dat het effect van andere variabelen daarop alleen bepaald kan worden door emulsies met een zelfde druppelgrootteverdeling met elkaar te vergelijken.

   Dit proefschrift

3. De conclusie dat een combinatie van Recodan RS (een preparaat van mono- en diglyceriden) en ondermelk veel effectiever werkt bij het stabiliseren van emulsies dan ondermelk kan nooit gebaseerd worden op onderzoek waarbij de stabiliteit van zuivere ondermelk-in-olie emulsies niet is onderzocht.

   M. Kako, P. Sherman, 1974. Milchwissenschaft 29 (12): 733-737

4. Op grond van hun resultaten mogen Thome en Eriksson niet concluderen dat de opklopbaarheid van room verbeterd wordt door toevoeging van karnemelk.

   K.E. Thome, G. Eriksson, 1973. Milchwissenschaft 28(8): 502-505

5. De veronderstelling dat een oplosmiddel door een verschil in porositeit van de grensvlaklaagjes gemakkelijker in een natuurlijk dan in een gehomogeniseerd melkvetbolletje kan binnendringen, ter verklaring van gemeten verschillen in de hoeveelheid extraheerbaar vet, is in strijd met het optreden van een Laplacedruk bij gekromde grensvlakken.

   A. Fink, H.G. Kessler 1985. Milchwissenschaft 40 (6): 326-328

6. Het dimensieloze kental waarmee Winsor de verschillende typen aggregaten, die amfifiele moleculen in polaire en apolaire oplosmiddelen kunnen vormen, kenmerkt en waarmee hij de overgang van het ene type aggregaat naar het andere karakteriseert, is zo slecht gedefinieerd dat het geen enkel inzicht geeft in de factoren die de vorm van het aggregaat werkelijk bepalen.

   P.A. Winsor, 1971. Molecular crystals and liquid crystals 12: 141-178

7. Ondanks het succes van het gebruik van computers in het rekenen met simulatiemodellen blijft een wiskundige analyse van de structuur van zulke modellen doorgaans noodzakelijk.

8. Bij het ontwikkelen van methoden, waarmee men het smeer en koelgedrag van koelvloeistoffen in praktijksituaties tracht te voorspellen dient rekening gehouden te worden met effecten veroorzaakt door het fors verkleinen van de schaal.

9. In een huis met alleen maar hoekstenen is geen ruimte om te wonen.

Proefschrift van J.P. Melsen.
The stability of recombined milk fat globules.
Wageningen, 21 september 1987.

VOORWOORD

Bij de voltooiing van dit proefschrift wil ik een ieder, die heeft bijgedragen aan het tot stand komen ervan, hartelijk bedanken.
Mijn promotor, Pieter Walstra, voor het kritisch doornemen van alle stukken en voor alle zaterdagen die hij heeft willen steken in de, naar mijn gevoel, zeer vruchtbare discussies over mogelijke modellen waarmee de belangrijkste resultaten beschreven konden worden.
Zijn vrouw, Paulien Walstra, die ons van de hiervoor benodigde energie heeft voorzien door middel van smakelijke lunches.
Henk v.d. Stege en Henk Jansen die voor mij muurvast zittende bouten met beheerst geweld los wisten te krijgen en de apparatuur die ik nodig had steeds weer verder verbeterden.
Henk v.d. Stege voor de proeven die hij gedaan heeft aan het verpoederen van gerecombineerde emulsies en de nuttige discussies over de interpretatie van de gegevens.
Hugo Stempher voor het steeds maar weer geduldig uitleggen van de microscoop en een aantal aanvullende proeven die hij voor mij gedaan heeft.
Herman Hooyer voor het in perfecte conditie houden van de apparatuur.
Alle andere leden van de vakgroep Zuivel en Levensmiddelennatuurkunde voor de prettige sfeer op het lab.

Het Nederlands Instituut voor Zuivelonderzoek (NIZO) heeft niet alleen het onderzoek gefinancierd maar ook de nodige menskracht geboden om het proefschrift tot een goed einde te brengen. Met name wil ik bedanken:
Johan Schaap, die mij als contactpersoon van het NIZO de weg naar de juiste personen gewezen heeft en die mij stimuleerde door zijn interesse in dit onderzoek.
Jaap de Wit, die mij vertrouwd en enthousiast gemaakt heeft met en over wei-eiwitten.

Klaas Leffring en Leo Cornelisse die een groot aantal emulsies gemaakt en gesteriliseerd hebben.
Wout Heinen die het onderzoek meegecoördineerd heeft.

Tevens wil ik bedanken:
De heer C. Rijpma voor de vakkundige wijze waarop hij de figuren heeft getekend en Elly Geurtsen voor de snelle en accurate wijze waarop zij het manuscript heeft getypt.

Tenslotte zou ik mijn vrouw Annemiek willen bedanken voor haar geduld en ondersteuning bij het schrijven van dit proefschrift.

CONTENTS

h_{cr}	thickness of the cream layer	(m)
$J(t)$	number of effective collisions per unit time	$(m^{-3}.s^{-1})$
$J_1(t)$	number of collisions between a globule and a clump	$(m^{-3}.s^{-1})$
$J_2(t)$	number of collisions between a globule and a large clump, consisting of many smaller clumps	$(m^{-3}.s^{-1})$
k_1	first order rate constant	(s^{-1})
k	a characteristic diameter relating the real diameter d to the parameter u via d=k.u	(m)
l	pathlength	(m)
$n_e(t)$	number of globules in an emulsion as function of treatment time	(m^{-3})
n_1	refractive index of disperse phase	(1)
n_2	refractive index of continuous phase	(1)
$N_{cl,m}$	number of fat globules in a clump, just before this clump is removed from the emulsion	(1)
$N_{cl}(t)$	number of fat globules in a clump as a function of time	(1)
P	polymer concentration	(mg/ml)
Q(t)	ratio of collisions between fat globules and reactive kernels and collisions between reactive kernels mutually as a function of time	(1)
Q*	light scattering coefficient corrected for forward scattering	(1)
R_{cl}	average reactivity of a clump	(1)
R_i	radius of the inner cylinder	(m)
R_o	radius of the outer cylinder	(m)
R_1	fraction of deformed globules changing into reactive kernels per unit time	(s^{-1})
R_2	fraction of collisions leading to the formation of reactive kernels	(1)
R_3	fraction of collisions leading to partial coacence	(1)
Re	Reynolds number	(1)
s	gap width	(m)
S_n	n^{th} moment of the frequency distribution	
S_o	total number of droplets per unit volume	(m^{-3})
Ta	Taylor number	(1)
u_i	circumferential speed of the inner cylinder	$(m.s^{-1})$
u_o	circumferential speed of the outer cylinder	$(m.s^{-1})$

LIST OF SYMBOLS

Symbol	Description	Unit
a	truncation parameter	(1)
a_{sp}	specific surface area of disperse phase	$(m^2.ml^{-1})$
B	number of reactive kernels (globules and clumps)	(m^{-3})
b	dilution factor	(1)
c	fraction of fat globules that is reactive or becomes reactive immediately after starting the experiment	(1)
c_1, c_2, c_3	constants	(1)
c_n	variation coëfficiënts	
c_s	relative standard deviation of the surface weighted distribution	(1)
d	diameter	(m)
d_{32}	volume-surface average diameter	(m)
d_f	initial average diameter of a fat globule	(m)
d_{cl}	average diameter of a clump	(m)
D_r	relative deformation	(1)
E	optical density	(1)
E_t	optical density after the treatment	(1)
f_c	phospholipid content of the original centrifuged buttermilk	$(mg.ml^{-1})$
f_o	phospholipid content of the skimmed emulsion	$(mg.ml^{-1})$
$f(d)$	number frequency distribution	(m^{-4})
$f(u)$	upper limit distribution function	(1)
F	fat content of the emulsion	(1)
F_o	fat content of the emulsion before treatment	(1)
F_t	fat content of the treated emulsion	(1)
$F(d)$	number of globules per unit emulsion volume with diameter $<d$	(m^{-3})
g	acceleration due to gravity	$(m.s^{-2})$
$g(d)$	differential (or frequency) distribution function	(m^{-4})
G	(apparent) shear rate	(s^{-1})
G_d	corrected Gerber reading of the diluted emulsion	(1)

$V_{cl,m}$	volume of a clump just before it is removed from the emulsion	(m^3)
x	protein-fat ratio	(1)
Z	reduced turbidity	(1)
γ	fat-plasma interfacial tension	($N.m^{-1}$)
Γ	surface load	($mg.m^{-2}$)
η_c	viscosity of the continuous phase	(Pa.s)
λ	wavelength	(m)
ν	kinematic viscosity	($m^2.s^{-1}$)
ρ	size parameter in spectroturbidimetry	(1)
ρ_{32}	volume-surface average size parameter	(1)
ρ_c	density of the continuous phase	($kg.m^{-3}$)
ρ_f	density of milkfat	($kg.m^{-3}$)
σ	coefficient of variation of size distribution	(1)
σ_{cr}	pressure at the top of the cream layer	($N.m^{-2}$)
τ	lifetime of an encounter	(s)
ϕ	volume fraction of fat	(1)
ϕ_{cr}	volume fraction of the cream layer	(1)
$\phi(t)$	fat content emulsion after heating and removal of floating fat as a function of time	(1)
$\phi'(t)$	time derivative of the fat volume fraction	(s^{-1})
ω_i	angular velocity of the outer cylinder	(s^{-1})

1 INTRODUCTION

1.1 General introduction

Recombination involves dissolving a powder, made by drying a low fat milk fraction, in water, followed by emulsifying milk fat into it. Most often skimmilk powder is used but buttermilk powder and whey powder can also be used. Sometimes milk fat is replaced by another, vegetable fat, to give "filled milk" products. The use of recombined products is becoming increasingly important because in many situations it is very advantageous. In areas where the supply of milk is very uneven or even absent, it is a way to provide the population during the year with milk products. If milk production is in areas remote from those were milk is consumed it may be too expensive to keep the milk in a good condition during transport. It is then advantageous to produce milk powder and anhydrous milk fat in plants in the production area and to recombine milk products where needed.
Since anhydrous milk components can be stored for years at ambient temperatures without further care, if packed well, whereas e.g. butter and cheese need lower temperatures and more care and still are more or less perishable, it is also a way to diminish storage cost in areas where milk production greatly exceeds the needs of the population.
Another aspect of recombination is the possibility to use other components and thus to make products with new properties. Products made of milk fat and whey are sometimes preferred to products made of milk fat and skimmilk. This means a broadening of the assortment of dairy products and a valorization of certain by-products of dairy industry (e.g. whey and buttermilk).

Because of the growing importance of recombination a lot of research, e.g. reviewed by Jensen & Nielsen (1982), is done on the various recombined products. But the sometimes crucial aspects of emulsion stability have received relatively little attention.

In this work the stability properties of the emulsion ob-

tained after emulsification of the milk fat into aqueous protein solutions are studied. It is meant to link the more fundamental research on oil-in-water emulsions to the development of recombined emulsions.

If milk is separated into skimmilk, buttermilk and milk fat and if the three components are mixed and homogenized, an emulsion results with properties rather different from milk, although the composition is kept the same.
During the process, however, the structure of the emulsion is changed:

1. The substances of the natural membrane are dispersed into the solution and replaced by plasma proteins adsorbed onto the fat globules.
2. Whereas in the original milk the composition of the fat differs between the droplets, it is identical in all droplets of the recombined emulsion.
3. Depending on the applied homogenisation pressure the size distribution of the fat droplets is more or less changed.

These modifications appear to have great influence on the stability properties of the emulsion.

When instead of the above combination of skimmilk and buttermilk other aqueous milk fractions are chosen, the surface layers of the fat droplets become different. The composition of the fat in the droplets does not alter and also the size distribution can be kept constant by adapting the homogenisation pressure. Consequently, the influence of the various interfacial layers on the stability properties of the emulsion can be determined independently.

1.2 Different types of instability

An oil-in-water emulsion is a dispersion of oil droplets in an aqueous solution. In this thesis the terms "oil" and "fat" will be used interchangeable, and refer to liquid or (partially) crystalline milk fat. Also the term "emulsion" is in this study

extended to systems wherein at certain temperatures crystallisation may occur in the disperse phase.

The fat globules in an oil-in-water emulsion may be subject to various kinds of (physical) instability:

Creaming:

Due to the difference in density between globules and continuous phase, the globules rise under the influence of gravity, which results in the formation of a cream layer. When no further changes occur, the original situation is easily restored by gently shaking the liquid.

Aggregation:

Globules can aggregate in various ways:

- We define floccules as aggregates wherein the globules only touch eachother, keeping their identity. The term flocculation is used here to describe this type of aggregation.
- Clusters then are aggregates wherein each globule keeps its identity but shares part of its interfacial layer with other globules. The term clustering is used to describe this kind of aggregation.
- In fat clumps globules have lost part of their identity, since the disperse phase has become continuous. The formation of this type of aggregates is called partial coalescence. Partial coalescence can only occur when both liquid and solid fat are present in the globules. When the solid fat is melted clumps completely coalesce to give large globules, which usually coalesce further to give eventually a fat layer floating on the emulsion.
- Real coalescence of emulsion droplets can occur if the globules only contain liquid fat. If coalescence goes on until a more or less complete separation of phases has occured, it is said that the emulsion breaks.

  Although partial coalescence and real coalescence both result in emulsions with larger fat droplets or even separation of fat, the mechanisms responsible for coalescence and partial coalescence may be completely different.

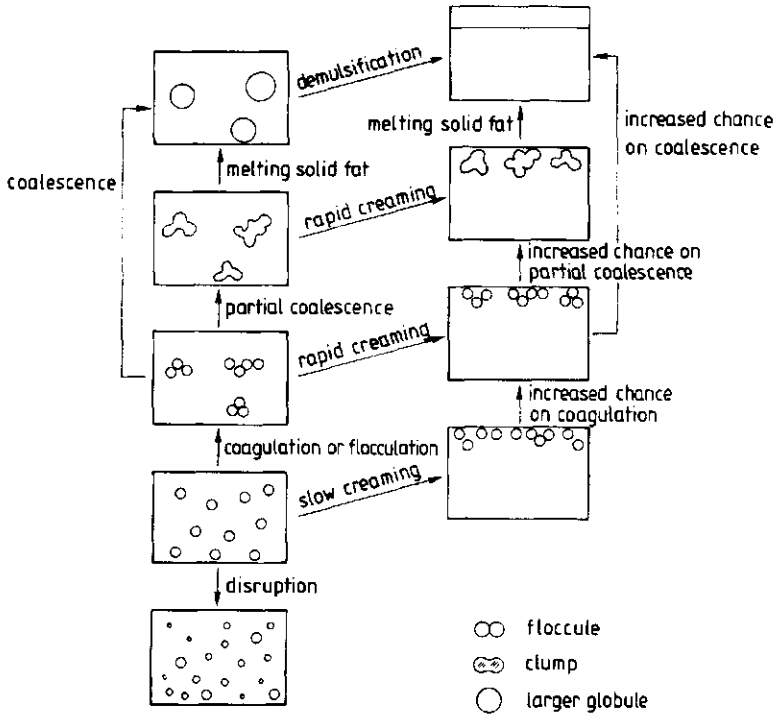

Fig. 1.1 Main types of instability in a fat-in-water emulsion. Interactions between the various forms of aggregation.

Whereas stability against real coalescence is predominantly determined by the properties of the interfacial layer, van Boekel (1980) clearly demonstrated that stability against partial coalescence is also determined by the shape and orientation of the fat crystals. Completely stable emulsions may become very unstable after a partial crystallisation of the fat.

The above classification, although workable, is not as regourous as it may look at first sight:

- The different aggregation processes influence eachother. Globules in floccules and cream layers often coalesce far more readily than do free globules which have to meet each

other before coalescence can occur. Creaming usually enhances flocculation and (partial) coalescence and vice versa.
Partial coalescence may lead to breaking of the emulsion after melting of the fat.
A survey of these interactions is given in fig. 1-1.

- It is sometimes difficult to discriminate between the different types of aggregation. Especially the distinction between floccules and clusters is to some extent arbitrary.
- Mixtures of the different types of aggregates may exist, e.g. clusters flocculated under the influence of electrostatic forces or floccules wherein a part of the globules have partially coalesced.

The counterpart of aggregation and coalescence is the disruption of floccules, clusters and globules. Disruption of small globules only occurs at very high shear rates but disruption of clusters may occur more easily, while floccules often need only very mild shearing to be (temporarily) disrupted (Mulder & Walstra 1974).

Instability of an emulsion against aggregation may depend on many parameters:

- Properties of the continuous phase like viscosity, concentration and type of surface active materials, ionic strength and pH.
- Properties of the disperse phase like viscosity, concentration and type of surface active materials and crystallisation characteristics such as the percentage of solid fat as a function of temperature and temperature history.
- The size distribution of the fat globules as characterized by the volume surface average diameter d_{32} and the width and shape of the frequency distribution.
- The properties of the surface layer around the fat globules
- The volume fraction of the disperse phase.
- The crystal habit of the globules, i.e. size, shape and orientation of the crystals in the globules.

Not only the inherent properties of the emulsion but also the

treatment applied to the emulsion (notably agitation) determines aggregation. In fact both are decisive as to whether, which type and at what rate aggregation takes place.

1.3 Outline of this study

The purpose of this study was to investigate the influence of various emulsion parameters in combination with various treatments on the stability of oil-in-water emulsions. As oil-in-water emulsion common recombined dairy products as milk fat-in-skimmilk, milk fat-in-buttermilk and milk fat-in-(clarified) whey were taken. The most important variables were the globule size distribution, the fat content, the surface load and the pH. In some emulsions, these parameters could be varied independently, in others there is a relation between two or more of them. The most important treatments were storing at rest, storing under slow rotation to prevent creaming, various flow fields and various heat treatments before or after homogenisation. The influence of beating in of air falls outside the scope of this thesis. Since air bubbles are known to greatly influence emulsion stability, care was taken to exclude them.

It is clear that a combination of all possible values of the emulsion parameters with all possible treatments would lead to an endless number of experiments. Therefore those combinations of parameters and treatments were taken that are expected to give maximum information about the emulsion characteristics.

The study was mainly aimed at partial coalescence, which was estimated by comparing the droplet size distribution and the fat content of the original emulsion with those of the treated emulsion. As such, it is a continuation of the work of van Boekel (1980), although it is more practically oriented and it can also be viewed as an extension of the work of J. Labuschagne (1963) to recombined emulsions. Furthermore, the heat stability and stability against spray drying of some recombined emulsions was studied.

2 METHODS

2.1 The preparation of emulsions

Oil-in-water emulsions were made from anhydrous milk fat, sometimes with phospholipids dissolved in it, and an aqueous milk fraction like skimmilk, buttermilk, whey or clarified whey (see 2.1.1). Because of the large influence of the droplet size on the coalescence stability of emulsions, a method was developed in which a narrow size distribution can be obtained accurately and reproducibly. To achieve this, a preemulsion, i.e. a stirred mixture of milk fat and an aqueous milk fraction, was homogenized with continuous recycling during a fairly long time at constant pressure and temperature in a high-pressure homogenizer (Rannie, 100 l per h). The inlet receptacle of the homogenizer could be thermostatted. To avoid air inclusion during homogenizing, the outlet of the homogenizer was put below the liquid level in the receptacle. To allow the reproducible manufacture of emulsions with a large average droplet size a spring was put between the homogenizing head and the valve chamber to counteract the weight of the homogenizing head; an accurate manometer (protected against overpressure with a safety valve) and a flat homogenizing valve instead of the corrugated LW-type were installed. This made it possible to obtain emulsions with a narrow globule size distribution and a volume-surface average diameter up to 10 μm in a very reproducible manner. It appeared that the equation $\log d_{32} = -0.6 \log P + 0.9$ discussed by Walstra (1975), remained valid at very low homogenisation pressures (Fig. 2-1). These modifications were gradually introduced, and at the time that the emulsions of milkfat-in-skimmilk or buttermilk were studied, it was not yet possible to reproducibly obtain the largest average diameters.

2.1.1 Characterisation of materials

The following materials were used:

- Anhydrous milk fat made by Frico in 17 kg tins. It contained more than 99.8% pure milk fat and less than 0.1% water. To avoid the risk of fractionating the samples, the fat in the tins was completely melted, stirred and poured in 350 ml tins that were stored at 7°C. Before use each small tin was first completely melted and stirred.
- Skimmilk was obtained by centrifuging fresh cows' milk to a fat content of 0.07%. After centrifuging the skimmilk was heated to inactivate lipase; usually a temperature treatment of 20 minutes at 70°C was chosen, but sometimes other heat treatments were applied.
- Buttermilk was obtained by churning natural cream. Fresh cows' milk was separated at 40°C to obtain cream of 60% fat. The ream was heated to inactivate lipase and kept overnight at 4°C. The next day the cream was churned and butter and buttermilk were separated. The buttermilk was centrifuged to a fatcontent of 0.07%. In one case use was made of low-heat

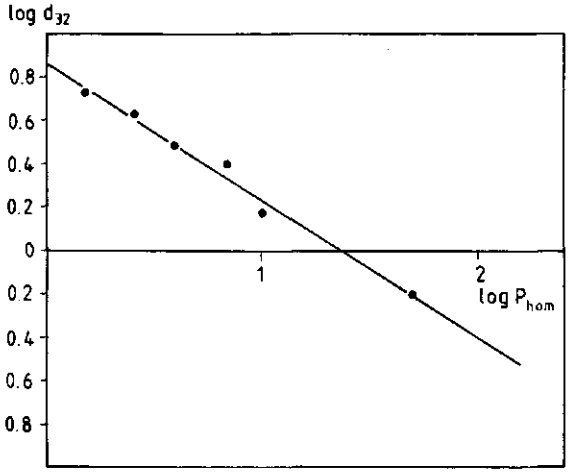

Fig. 2.1 The relation between the homogenisation pressure and the volume surface average diameter of emulsions with about 30% fat: d_{32} in μm, P_{hom} in bar.

buttermilk powder made by NIZO. This powder was dissolved in tap water up to the original dry matter content. Before making an emulsion the diluted solution was kept overnight to ensure equilibrium between solute and solvent.

- Whey: sometimes use was made of natural whey obtained by rennetting fresh milk. One part was immediately heated at 70°C for 20 min to inactivate rennet and to kill any starter bacteria. Another part was left during the rest of the day at room temperature, kept overnight at 4°C and the next day when the pH was decreased from 6.6 to 5.6 heated at 70°C during 20 min. Mostly, clarified whey powder made by NIZO (De Wit et al. 1978) was used. Clarified whey may be regarded a decaseïnated, defatted and demineralized cheese whey. The whey protein content is 12%, the rest of the dry matter is for the most part lactose. The powder was dissolved in tap or demineralized water, usually up to the original dry matter content, but sometimes other powder-water ratios were taken. Every solution was stirred for at least one hour to ensure equilibrium between the different components before fat was emulsified in it.
- Lecithin: use was made of egg lecithin and soya lecithin. The egg lecithin was from Merck (article 5331); it contained 50% phospholipids and was a paste that did not dissolve in milk fat. Two different kinds of soya lecithin were used: a paste called Bolex Z containing 50% phospholipids, 45% other lipids and 5% carbohydrates, and a powder from Du Lectin-van Schuppen containing 97% phospholipids. Both were well dispersible in milk fat, giving clear solutions at concentrations below 0.3% and turbid ones at higher concentrations.

Besides recombined emulsions, use was made of natural cream obtained from fresh cows' milk by centrifuging at 40°C. To inactivate lipase the cream was heated at 70°C for 20 min.

2.1.2 The adjustment of other variables affecting emulsion stability

An emulsion is not only characterized by its components, but also by other parameters of which the most important ones regarding emulsion stability are described in 1.2. Most of these parameters cannot be controlled independently but depend on the nature of continuous and disperse phases and are interrelated to eachother.

The content of the disperse phase was controlled by choosing a suitable mass ratio between milk fat and the aqueous phase or by diluting the emulsion afterwards. Dilution has the advantage of largely preventing unwanted variation in the surface layer, which may occur when the fat-protein ratio in the mixture is changed.

The volume-surface average diameter d_{32} was fully adjustable by varying homogenisation pressure, although the relation between homogenisation pressure and diameter is also affected by the nature of the continuous and disperse phases. In some emulsions d_{32} was correlated with surface excess (see 3.2.1 and 6.2.1). The shape of the size distribution of emulsions made from preemulsions by homogenizing with continuous recycling was hardly influenced by the constituents of the emulsion.

The properties of the surface layer naturally depend on the constituents of the emulsion and in some cases also on the ratio between aqueous and fat phase, the pretreatment of the aqueous phase, the homogenisation pressure (via d_{32}) and the homogenisation temperature. More specific information is given in 3.2.1 for emulsions made from skimmilk and milk fat and 6.2.1 for emulsions made from whey and milk fat.

Temperature and temperature history affect the proportion of crystalline fat. To exclude temperature history effects, all emulsions were rapidly cooled in an ice bath and stored for at least one night at 4°C. During this time equilibrium between solid and liquid fat is more or less reached (Walstra, van Bere-

steyn 1975). Before each experiment the emulsion was warmed to the desired temperature.

It was not possible to influence the crystallisation habit of emulsions with milk fat as disperse phase by modifying temperature or temperature history. In all cases these emulsions gave, when cooled below 40°C, for the greater part globules with many very small crystals inside the globule (the so called N-type crystallisation).

2.2 Storage of the emulsions

Most of the emulsions were prepared and tested during the same week. During this time the emulsions were stored at 2-4°C to prevent bacterial deterioration and to ensure crystallisation of fat in the globules. Use of a biocide was not necessary since storage time was short enough (3 days) to prevent outgrowth of psychrotrophic bacteria.

To avoid creaming during storage the emulsions were stored in 350 ml cylinders which were slowly rotated, end over end. These cylinders were carefully filled to exclude air although a few small air bubles did not significantly affect coalescence stability. Coalescence stability during storage was examined by comparing the size distribution of the emulsion immediately after preparation with that after storage. In hardly any case the size distribution did change.

2.3 Test conditions

2.3.1 At rest

As milk fat has a lower density than plasma, the fat globules rise under the influence of gravity when the emulsions are left at rest. Due to the same buoyancy forces the globules are pressed together in a cream layer. The pressure is maximal at the top of the cream layer and is there approximated by:

$$\sigma_{cr} = \phi_{cr} (\rho_f - \rho_c) g h_{cr} \qquad \text{(Eq 2-1)}$$

with σ_{cr} = pressure at the top of the cream layer ($N.m^{-2}$)
ϕ_{cr} = volume fraction of fat in the creamlayer (-)
h_{cr} = thickness of the creamlayer (m)
g = acceleration due to gravity ($m.s^{-2}$)
ρ_c = density of the continuous phase ($kg.m^{-3}$)
ρ_f = density of milk fat ($kg.m^{-3}$)

h_{cr} ϕ_{cr} is not only a function of the intrinsic parameters of the emulsion but does depend also on the size and shape of the container in which the emulsion is stored. To exclude these external effects all creaming experiments were done in 15 cm cylindrical tubes. When necessary 100 ppm thiomersal was added to prevent bacterial deterioration.

2.3.2 Different flow fields

The coalescence stability of the emulsions was estimated in laminar flow, flow with Taylor vortices and turbulent flow.

The laminar flow is a simple shear flow generated in a Couette equipment consisting of two coaxial cylinders of which the outer one could be rotated. It is the same as used by van Boekel (1980). The height of the outer cylinder, which was made of transparent perspex, is 87 mm and the radius 65 mm. The inner cylinder, which was made of stainless steel, has a radius of 63 mm. The gap width of the annular clearance is therefore 2 mm. Because gap width is small compared to the outer cylinder radius the shear rate is constant throughout the gap and is approximated for this device by

$$G = u_0/s \qquad \text{(Eq 2-2)}$$

with u_0 = circumferential speed of the outer cylinder ($m.s^{-1}$)
s = gap width (m)
G = shear rate (s^{-1})

In every experiment the circumferential speed was checked by means of a tachometer. At high circumferential speeds flow changes from laminar to turbulent. For the systems studied here the change from laminar to turbulent flow would take place between Re = 2000 and 3000.

Re (the Reynold number) is given by (Back 1975):

$$Re = u_o s/v \qquad \text{(Eq 2-3)}$$

with: u_o = circumferential speed of the outer cylinder ($m.s^{-1}$)
s = gap width of annular clearance (m)
v = kinematic viscosity ($m^2.s^{-1}$)

Although the dimensions of the equipment are chosen so that disturbances of the flow due to end effects are upon the whole negligible, this is certainly not the case locally. If coalescence occurred it started at the edges, gradually spreading to other parts of the annulus. If coalescence resulted in gradually breaking of the emulsion, which often happenend for the systems studied, laminar flow was disturbed shortly after starting.

After each experiment the emulsion was heated in the apparatus to above 40°C, to melt partially coalesced fat globules, and then completely removed and analysed (see 2.4.1).
Only in a few cases changes in size distribution and fat content of the emulsion were followed during an experiment by drawing at regular times small samples out of the apparatus.

Experiments were conducted at temperatures varying between 5°C and 40°C, with fat contents varying between 2% and 35%, during times varying between 1 and 100 minutes and with various circumferential speeds of the outer cylinder. In all cases the Reynolds number was kept below 2000. Because air blubles may have a large influence on coalescence stability, care was taken to exclude air uptake during an experiment.

Literature about flow with Taylor vortices is reviewed by Labuschagne (1963) and van Boekel (1980). Here only a summary is given: A flow with undisturbed Taylor vortices is characterised

by vortices with an axis perpendicular to the axis of rotation, with spacings equal to the distance between the inner and outer cylinder. The vortices are counter-rotating which locally results in elongational flow, which may cause disruption of large globules (Walstra 1980). Taylor vortices appear in a couette type equipment when the inner cylinder rotates with such a speed that the so called Taylor number exceeds the critical value 41.3. This Taylor number is defined as:

$$Ta = u_i s^{1.5} \nu^{-1} R_i^{0.5} \qquad \text{(Eq 2-4)}$$

with Ta = Taylor number (-)
u_i = circumferential speed of the inner cylinder ($m.s^{-1}$)
s = gap width (m)
ν = kinematic viscosity ($m^2.s^{-1}$)
R_i = radius of the inner cylinder (m)

At very high Taylor numbers the flow gradually changes, via a flow with wavy vortices, into turbulent flow. Disturbances in the flow also may occur as a consequence of the presence of fat globules and of fat coalesced after starting the experiment. Since only overall coalescence rates were measured and the flow is difficult to describe precisely, the flow of the emulsion may be characterised by some overall parameter, for instance an average power density (i.e. the work exerted by the inner cylinder per m^3 emulsion per second) or the apparent shear rate (i.e. the shear rate that would exist if the flow were laminar).

Flow with Taylor vortices was generated in a couette type equipment consisting of two coaxial cylinders of which the inner one can rotate. It is basically the same as used by Labuschagne (1963) and van Boekel (1980). The radius of the outer cylinder was 25,5 mm, and several inner cylinders with different radii were used. The height of the cylinders was 90 mm. The circumferential speed of the inner cylinder was variable. Almost all experiments were conducted with the same inner cylinder (radius 20 mm) and the same speed (3.0 $m.s^{-1}$). At this speed an emulsion

with 30% fat gave a flow with taylor vortices. This was verified by adding sudan 3: an emulsion with this fat soluble dye gave during treatment the red and white bands as described by Labuschagne (1963). The variation in experimental conditions and the treatment of the emulsion before and after the experiment were the same as described for laminar flow.

The flow is characterized by the apparent shear rate G. Since the gap width is not small compared to the outer cylinder the rigorous formula ought to be used:

$$G = \frac{2\omega_i R_i R_o}{(R_o^2 - R_i^2)} \qquad \text{(Eq 2-5)}$$

with R_o = radius outer cylinder (m)
R_i = radius inner cylinder (m)
ω_i = angular velocity of the outer cylinder (s^{-1})
G = apparent shear rate (s^{-1})

Turbulent flow may be generated in either Couette type equipment. In the equipment for laminar flow the Reynolds number given by eq. 2-3 has to exceed 2000 for a transition from laminar to turbulent flow. This value is reached at lower circumferential speed for a wider gap. Therefore use was made of an inner cylinder with a radius of 60 mm instead of 63 mm. In the equipment for Taylor vortices turbulent flow could only be achieved at very high circumferential speeds. Although both types of flow may be called turbulent the characteristics were in fact somewhat different.

Only a few experiments were done at turbulent flow; the treatment of the emulsions before and after the experiment were the same as described earlier.

2.3.3 Different heat treatments

When skimmilk or butter milk is used as aqueous phase a heat treatment is necessary to inactivate lipase. This enzyme, occur-

ring in these liquids, will otherwise hydrolyse the fat, leading to the formation of fatty acids, diglycerides and monoglycerides. These components influence the properties of the emulsion and cause a soapy, rancid flavour. The skimmilk was heat treated before adding the milk fat. When fresh buttermilk was used the natural cream was heat treated before churning. In case of skimmilk powder, buttermilk powder and clarified whey powder a heat treatment was not necessary since lipase was already inactivated, but was sometimes applied as a variable. For the same reason the cream and the skimmilk in some cases were more intensely heated than needed for the inactivation of the enzyme.
The applied temperatures were always below 100°C. Due to the small amount of liquid per batch (about 2 litres) the heat treatments were applied in a hot water bath ("stand pasteurisation").
In some cases a heat treatment was (also) given after homogenisation. If a temperature below 100°C was required, a stand pasteurisation was given but in a few cases the influence of temperatures above 100°C was studied. These so called UHT treatments were applied to larger quantities of emulsion (about 100 litres). These experiments are described in 3.1.3.

2.4 Characterization of instability

Globules can aggregate in various ways, as described in section 1.2. Each type of instability has its own pecularities and demands its own methods of study. Some of these are described in the following sections.

2.4.1 Characterization of coalescence

Coalescence results in a smaller number of globules. Consequently coalescence rate is logically expressed as the decrease in the number of globules per unit volume and time. There are, however, two complications:
- It is often difficult to accurately determine the number of

globules.

- Processes with the same coalescence rate may result in different emulsions. In some cases the average and the width of the globule size distribution change while fat content remains the same while in other cases the globule size distribution remains (almost) the same while fat content is reduced. In the latter case (partial) coalescence has resulted in globules that are so large as to immediately cream out of the emulsion. Sometimes size distribution as well as fat content change.

Because coalescence always results in a decrease of interfacial area between continuous and disperse phase it is also possible to express coalescence rate as the decrease in that area per unit emulsion (= specific surface area a_{sp}) per unit time. Since $a_{sp} = 6\ \phi/d_{32}$ it is necessary to measure the change in fat content and the change in d_{32} as a function of time. Often it is possible to calculate the change in specific surface area from the change of the optical density (see 2.4.1.4).

The most revealing way to characterize coalescence is to determine the complete size distribution and fat content at several moments after starting the experiment. In this way information is gathered, not only about the rate of coalescence but also about the type of coalescence. The characterization of a size distribution is described in 2.4.1.2. The determination of fat content and size distribution are described in 2.4.1.1. and 2.4.1.3 respectively.

In some older experiments (Labuschange 1963), churning time defined as the time needed to produce visible clumps, was used to characterize coalescence instability. The reciprocal of churning time may be called churning rate.

In this study coalescence stability is characterized by the rate of change of fat content and average globule size.

2.4.1.1 The estimation of fat content

After each treatment the emulsion was gently heated to at least 40°C. Large clumps then coalesce completely to give fat floating on the emulsion, but small clumps made up of only a few of the original globules will give larger globules remaining in the emulsion. Because the studied recombined emulsions are very stable if the globules contain only liquid fat, it is not expected that these globules coalesce with others to give floating fat when the emulsion is gently heated to just above 40°C. The boundary between large and small clumps is not exactly known, but lies for certain above 17 μm and is probably much higher. (The size distribution of a fat-in-whey emulsion with a maximum diameter of 17 μm did not change after cooling to 4°C, storing during one night and heating to above 40°C.)

After some 10 min. heating the emulsion was removed from the equipment, stirred thoroughly and poured into a separatory funnel. To avoid inhomogeneities in the emulsion layer due to creaming of larger globules the emulsion was separated from the floating fat after waiting a few minutes. The remainder of the floating fat was sucked away with a pump. The fat content of the thus separated emulsion was determined by the Gerber method (NEN 1964), often after a dilution. For an emulsion diluted with water the gerber reading ought to be multiplied with 1.03 to correct for the change in density.

Samples taken during the treatment of the emulsion were always diluted before heating and removing the coalesced fat. Since only the aqueous phase and not the fat phase is diluted, the relation between fat content in the diluted emulsion and in the original emulsion is not given by: $F_t = G_d\ b$ (Eq. 2-6)

but by: $$F_t = \frac{F_o G_d - bG_d}{F_o - 1 - bG_d + G_d} \qquad \text{(Eq. 2-7)}$$

with F_o = fat content of the emulsion before treatment (-)
F_t = fat content of the treated emulsion (-)

G_d = (corrected) Gerber reading of the diluted emulsion (-)
b = dilution factor = (weight diluted sample)/(weight original sample) (-)

2.4.1.2 Characterization of the globule size distribution

A globule size distribution can be characterized adequately by an average, a distribution width and often an upper size limit. With these three parameters almost any unimodal distribution can be described. If the number of globules per unit emulsion volume with diameter < d is given by F(d), then the number frequency distribution is given by $f(d) = \partial F(d)/\partial d$ and the volume frequency distribution by $(1/6)\pi d^3 f(d)$.

As an auxiliary parameter, the n^{th} moment of the frequency distribution is used, which is defined as:

$$S_n = \int_o^\infty d^n f(d)\, \partial d \qquad \text{(Eq. 2-8)}$$

Hence, S_o = the total number of droplets per unit volume.
With this auxiliary parameter any type of average diameter can be described:

$$d_{nm} = \left(\frac{S_n}{S_m}\right)^{\frac{1}{n-m}} \qquad \text{(Eq. 2-9)}$$

so d_{10} = number average diameter, d_{30} = volume average diameter and d_{32} = volume-surface average diameter.
With the same auxiliary parameter the variation coefficients are described:

$$C_n = \left(\frac{S_n\, S_{n+2}}{S_{n+1}^2} - 1\right)^{\frac{1}{2}} \qquad \text{(Eq. 2-10)}$$

Hence, c_0 is the number standard deviation divided by d_{10} etc. The most suitable parameter to describe a distribution is d_{32} because it relates the surface area of the fat to its volume. Then the width ought to be expressed as the relative standard deviation of the surface- weighted distribution which is c_2.

The shape of the globule size distribution of the studied emulsions could often be approximated with the upper limit distribution functions f(u) given by:

$$f(u) = \frac{a}{u^4(a-u)} \text{ Exp } - \frac{\ln^2 (au/(a-u))}{2 \ln^2 \sigma} \qquad \text{(Eq. 2-11)}$$

in which σ determines c_2 (the width of the distribution) and a determines the truncation of the distribution. If a is small (say < 2), the size distribution is severely truncated: few flobules larger than twice the average size occur. For large a the distribution function approximates the log normal distribution function. The shape of the distribution functions f(u) is determined by the combination of σ and a.

2.4.1.3 The estimation of the globule size distribution

The globule size distribution was always estimated by spectroturbidimetry. Sometimes a Coulter counter was used to verify turbidity measurements.

Spectroturbidimetry was developed by, amongst others, Walstra (1965, 1968, 1969) as a method for the determination of the globule size distribution in emulsions. Since this method is already described extensively, only a short description is given here. The theory was extended for emulsions with a known type of size distribution but with an unknown d_{32} that is larger than, say, 3.5 μm.

After the treatment described in 2.4.1.1 the emulsions were diluted with water to roughly 1% of the original concentration. An aqueous solution of disodium ethylene diamino tetra acetate

and poly(oxyethylene) sorbitan monolaurate was added to dissolve particles other than fat globules that may otherwise affect the turbidity measurements. The optical density of these strongly diluted emulsions was measured at nine wave lengths in a Zeiss spectrofotometer with an attachment for turbidity measurements. These optical densities were converted into reduced turbidities according to

$$Z = \frac{0.2443\ E\ \lambda}{l(n_1 - n_2)\ \phi} \qquad \text{(Eq. 2-12)}$$

with E = optical density (-)
λ = wavelength (m)
l = pathlength (= 5.10^{-3} m)
n_1 = refractive index of disperse phase (-)
n_2 = refractive index of continuous phase (-)
ϕ = volume fraction of fat (-)
Z = reduced turbidity (-)

The refractive indices of water and milk fat at various wave lengths are given by Walstra (1968). The refractive index of milk fat was sometimes checked with an Abbe refractometer.

These nine reduced turbidities were plotted against log y, giving a Z-spectrum, where

$$y = 2\pi\ (n_1 - n_2)/\lambda \qquad \text{(Eq. 2-13)}$$

Walstra (1965) has shown that for polydisperse emulsions:

$$Z = \left(\frac{\overline{Q^*}}{\rho}\right) = \frac{\lambda \int_0^\infty d^2\ g(d)\ Q^*(\rho(d))\delta d}{2\pi.(n_1-n_2) \int_0^\infty d^3\ g(d)\ \delta d} \qquad \text{(Eq. 2-14)}$$

Q^* = light scattering coefficiënt corrected for forward scattering. (-)
ρ = $2\pi d(n_1 - n_2)/\lambda$ (-)
d = diameter of sphere (m)

g(d) = differential or frequency distribution function (m^{-4})

Theoretical reduced turbidity functions (Q^*/ρ) were calculated for various distribution functions by Walstra (1965) with:

$$\left(\frac{\bar{Q}^*}{\rho}\right) = \frac{\int_0^\infty Q^* (\rho_k u)\, u^2\, f(u)\, \partial u}{\rho_k \int_0^\infty u^3\, f(u)\, \partial u} \qquad \text{(Eq. 2-15)}$$

Where f(u) is a differential distribution function belonging to a set of size distribution functions given by:

$$g_k(d) = \frac{1}{k} f\left(\frac{d}{k}\right) \qquad \text{(Eq. 2-16)}$$

k is a characteristic diameter that relates the real diameter d to the parameter u via d = ku; k is related to d_{32} according to:

$$k = d_{32} \cdot \frac{\int_0^\infty u^2\, f(u)\, \partial u}{\int_0^\infty u^3\, f(u)\, \partial u} \qquad \text{(Eq. 2-17)}$$

and ρ_k is a function of n_1, n_2, k and λ according to:

$$\rho_k = 2\pi\,(n_1 - n_2)k/\lambda \qquad \text{(Eq. 2-18a)}$$

ρ_k is related to ρ_{32} via

$$\rho_k = \rho_{32} \cdot \frac{\int_0^\infty u^2\, f(u)\, \partial u}{\int_0^\infty u^3\, f(u)\, \partial u} \qquad \text{(Eq. 2-19)}$$

ρ_{32} is a volume surface average size parameter given by:

$$\rho_{32} = 2\pi\ (n_1-n_2)d_{32}/\lambda \qquad \text{(Eq. 2-18b)}$$

The theoretical reduced turbidity functions were plotted as a function of log ρ_{32} for all kinds of distribution functions.

The size distribution function of an emulsion g(d) is determined by shifting the abscissa of the experimental Z versus log y plot over the theoretical (Q^*/ρ) versus log ρ_{32} plot until two plots coincide. When a good fit is found g(d) equals $k^{-1}f(d/k)$ for that particular f(u) and d_{32} is read from the shift of abscissa because log ρ_{32} = log y + log d_{32}. With these two results the globule size distribution is determined since k can be calculated from Eq. 2-17. This method gives good results in case of monomodal size distributions with d_{32} smaller than 3.5 μm.

From spectroturbidimetric measurements it became apparent that the spectra of our repeatedly homogenized emulsions that had a d_{32} lower than 3.5 μm precisely fitted the theoretical curve calculated for an upper limit function with a = 1 and σ = 2.7. The size distributions of these emulsions thus all belonged to one set of functions given by:

$$g_k\ (d) = \frac{1}{k}\ f(\frac{d}{k}) \text{ with:}$$

$$f(u) = \frac{1}{u^4\ (1-u)}\ .\ \text{Exp}\ -\ \frac{\ln^2\ (\frac{u}{(1-u)})}{2\ \ln^2\ (2.7)} \qquad \text{(Eq. 2-20)}$$

Only k is a variable, depending on the homogenisation pressure and the fat content. In other words: The parameter σ (= 2.7) corresponding to a variation coefficient c_s (= 0.56) and the truncation parameter a (= 1) of the repeatedly homogenised emulsions were independent of homogenisation pressure and fat content. d_{32} depended on fat content and homogenisation pressure in a way already described by Mulder & Walstra (1974), namely

log d_{32} = c - 0.6 log (homogenisation pressure), with c = 0.9 for mixtures containing 30% fat and slightly lower for mixtures with a low fat content.

For higher d_{32}, however, the Z-spectra increasingly differed from the theoretical curve. This must be due to the calculated correction for scattered radiation falling on the detector being incorrect for large particles (Walstra 1965). Hence, fitting the curve to a theoretical spectrum is not well possible, but they can be fitted to the curves obtained from Z-spectra of distributions with a lower d_{32}. By overlapping such spectra an experimental ($\bar{Q}^*/\bar{\rho}$)-curve was derived for large arguments (large ρ_{32}); see Fig. 2.2 (Using this procedure it was tacitly assumed that c_s and a remained the same).

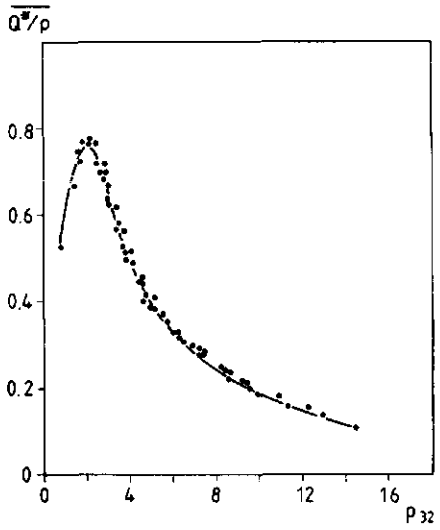

Fig. 2.2 The average reduced turbidity as function of the volume surface average size parameter used in spectroturbidimetry, valid for all emulsions described in this study

2.4.1.4 Optical density as a measure for coalescence stability

In some cases coalescence rate was estimated by measuring the optical density at one wavelength at regular time intervals (E_t). These values divided by the original fat content (F_o) can

be related to a decrease of interfacial area between continuous and disperse phase if:

1. The fat content changes while the size distribution remains the same. A change in E/ϕ calculated from the change in E/F then exactly represents the decrease in the number of globules and the decrease in specific surface area. (The emulsion can be viewed as diluted).
2. Only the volume surface average diameter d_{32} changes, while fat content and distribution shape (e.g. distribution width c_2 and truncation parameter) remain constant. In this case a change in E/F reflects a change in the average diameter and thus in specific surface area: In fig. 2-2 (Q^*/ρ) as a function of ρ_{32} is given. This relation holds for practically all emulsions made by homogenizing with continuous recycling preemulsions of milk fat and any aqueous milk fraction. (Exceptions are emulsions of mixtures with too low a protein content to cover all of the created fat-plasma interface.) For values of ρ_{32} larger than 3, $(\bar{Q}^*/\bar{\rho})\rho_{32}$ appears to be constant (see table 2.1 derived from fig. 2-2). Similar results were found by Walstra (1969) for natural unhomogenized milks.

Table 2.1 The relation between the average reduced turbidity and the volume surface average spectrotubidimetric size parameter.

ρ_{32}	$\overline{Q^*/\rho}$	$\rho_{32} \cdot \overline{Q^*/\rho}$
3	0.65	2.0
4	0.5	2.0
5	0.4	2.0
6	0.33	2.0
7	0.29	2.0
8	0.25	2.0
9	0.22	2.0
10	0.195	2.0
11	0.17	1.9
12	0.16	1.9
14	0.13	1.8

Since $\overline{(Q^*/\rho)} = \bar{Q}^*/\rho_{32}$, $\bar{Q}^*$ is constant. The optical density E then is proportional to the total cross sectional area of the globules. As fat content is proportional to the total volume of all the droplets, E/F is proportional to the volume-surface average diameter d_{32} (Walstra 1969). As a consequence of the requirement $\rho_{32}>3$, d_{32} should be higher than 1.5 μm when a wavelength of 400 nm is chosen.

2.4.2 Clustering

2.4.2.1 Characterization of clustering

Only clusters in emulsions made of skimmilk and milk fat were studied. When such an emulsion is heated for a few minutes to temperatures above 100°C fat globules may aggregate into clusters. Clusters may be characterized by their size, their composition (especially the amount of continuous phase enclosed), the strength and nature of the bonds between the different fat globules and the size distribution of the globules that make up the cluster in relation to the original size distribution.

A first impression about the extent of clusering can be obtained from microscopical studies. Rheological behaviour and creaming rate may provide additional information about size and composition of the clusters. Some idea about the strength of the bonds between the globules in a cluster may be obtained from the rheological behaviour of dilute emulsions by determining the shear rate at which the viscosity is no longer time independent but declines irreversibly. Information about the nature of the bonds in a cluster may be obtained from the possibility of breaking up the clusters in different reagents. If it is possible to dissolve the clusters into their component globules, the size distribution of these can be determined by spectroturbidimetry (see 2.4.1.2). If after dissolution of the clusters only single fat globules are seen and if the size distribution of these globules is the same as that of the original ones, it

is fairly certain that during heating and dissolution no coalescence of fat globules has occurred.

2.4.2.2 Viscosity measurements

The viscosities of clustered emulsions were measured in a Deer viscometer and a Haake Rotovisco.

The Deer was used with a coaxial cylinder geometry. The bottom of the inner cylinder had the shape of a flat conus to make end effects calculable. The inner and outer cylinder had radii of 28 mm and 29 mm giving a gapwidth s of 1 mm. The height of the cylinders was 70 mm. At the inner cylinder a variable torque can be applied and the resulting angular velocity registered; the Deer is thus a constant-stress viscometer.

The Haake Rotovisco was also used with coaxial cylinders. End effects are diminished by the bottom of the inner cylinder being hollow, so that an air bubble is trapped when the inner cylinder is let down in the outer one filled with emulsion. The radius of the outer cylinder was 21 mm and that of the inner cylinder 20 mm, giving a gap width s of 1 mm. The height of the annular clearance was 60 mm. the inner cylinder is made to rotate at a variable rate and the torque exerted by the emulsion is registrated; the Haake is thus a constant-shear rate viscometer. The sensitivity of the Haake Rotovisco was far smaller than that of the Deer viscometer.

If the relation between shear stress and shear rate is time independent the Haake rotovisco and the Deer should give the same results for identical geometries.

Because of the high viscosity or even plasticity of the clustered emulsions, it was difficult to obtain accurate and reproducible results. Disturbances were predominantly due to air bubbles between inner and outer cylinders and to creaming in the emulsion during the experiment. The best reproducible results were obtained when an excess of emulsion was poured in the outer cylinder first, left there to reach the desired temperature and

carefully mixed to undo any creaming before the inner cylinder was slowly let down. The surplus of emulsion was sucked away. To avoid creaming during a measurement it was kept as short as possible but minimal measuring time was still 30 min.

If the emulsions were diluted, skimmilk having had the same heat treatment as the emulsion was used.

2.5 The determination of the crystal habit in emulsion droplets

Fat globules at temperatures where part of the fat must be solidified, show different images in a microscope under polarized light. Based on these images, Walstra (1967) distinguished four types of crystallization habits; the habit describes the magnitude and orientation of the crystals in the globules.

Type O: crystals are absent or too small to be visible.

Type N: throughout the globule tiny crystals, often of an apparently needle like shape and widely variable in number and size are visible.

Type L: a birefringent outer layer, often along the total periphery of the globules, sometimes along a small part of the periphery, is visible. This layer is made up of tangentially oriented elongated crystals of which those in the outermost layer are oriented in the oil-water interface (Walstra 1967; van Boekel 1980).

Type M: a birefringent outer layer as well as crystals throughout the globule are visible.

The pictures as shown in fig. 2.3 appear when the polarization direction of the polarizer is perpendicular to that of the analyser: the birefringent layers appear as four bright sectors and crystals oriented parallel or perpendicular to the plane of polarization cannot be seen.

2.6 The estimation of the phospholipid content of the surface layers of recombined milk fat globules

The amount of a certain component adsorbed onto the interface of

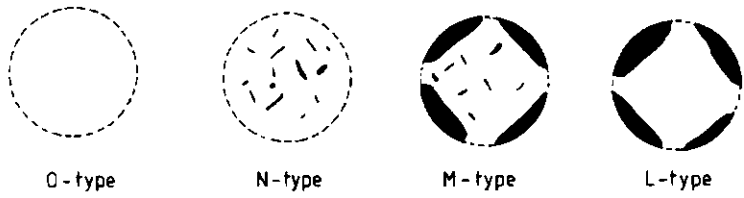

Fig. 2.3 Crystallisation types in emulsion droplets containing fat crystals, as observed under the microscope with polarized light. The globule boundary is indicated by a dotted line.

recombined fat globules is best studied by depletion experiments. The concentration of the component studied is determined in the aqueous phase before and after emulsification. (Oortwijn & Walstra, 1979)

First, the phospholipid content of the buttermulk used was determined. The buttermilk had to be centrifuged to remove natural globules containing phospholipids in their membranes. Anhydrous milk fat, which contains hardly any phopholipids, was emulsified into it and the resulting emulsion was sharply skimmed, but never so sharp as to obtain a skimmilk with a lower fat content than that of the original centrifuged buttermilk. Coalescence of globules during skimming was avoided by centrifuging in two or more stages, first under mild conditions and finally under more severe ones. The phospholipid content of the so obtained skimmilk was again determined. The difference in phospholipid content must be caused by the adsorption of phospholipids to the interface of the removed recombined fat globules.

When the skimmilk is devoid of recombined globules, surface concentration of phospholipids follows from:

$$\Gamma = \frac{(f_c - f_o).(1 - \phi)}{a_{sp}.\phi} \qquad \text{(Eq. 2-21)}$$

with Γ = The amount of phospholipids in the interface ($mg.m^{-2}$)

ϕ = The volume fraction of fat (-)

f_c = The phospholipid content in the original centrifuged buttermilk ($mg.ml^{-1}$)

f_o = The phospholipid content in the skimmed emulsion ($mg.ml^{-1}$)

a_{sp} = Interfacial area of the globules per unit volume disperse fat ($m^2.ml^{-1}$).

If skimming is incomplete (i.e. when some globules are very small) more complex formulae have to be used (see Oortwijn & Walstra, 1979). If f_c and f_o, reduced to fat globule free products, are equal, no phospholipids are adsorbed at all.

The determination of the phospholipid content consists of three parts:

1. The extraction of the phospholipids.
   Phospholipids were extracted from the solution via a slightly modified Röse-Gottlieb procedure. The most important modification was the addition of 0.15 g NaCl per 10 ml sample before the extraction. (Walstra & de Graaf, 1962).
2. The digestion of the extracted phopholipids to phosphates by heating with sulfuric and nitric acids. Because of the influence of acid on the colorimetric determination of phosphates, the added amount of sulfuric acid was limited and accounted for in the next step of the determination. Nitric acid disappears during the digestion completely as nitric vapours.
3. The amount of phosphate (expressed as mg P per ml) was determined with a spectrometer. A mixture of sulfuric acid, amino naphthol sulphonic acid and sodium sulphate added to the sample, gives on heating a stable blue colour with an intensity proportional to the phosphate content of the sample. (B.L. Griswold, F.L. Humoller, A.R. McIntyre, (1951) and S. Lavee (1968)).

Phosphorus content was converted to phospholipid content by multiplying by 25.97, i.e. the ratio between the molecular mass

of an average phospholipid molecule and the atomic mass of phosphorus. With this method phospholipid contents as low as 0,01% can still be estimated within 10% accuracy.

3 STABILITY PROPERTIES OF EMULSIONS MADE FROM MILK FAT AND SKIMMILK

3.1 Adsorption of skimmilk components

The adsorption behaviour of components from skimmilk at a plasma - fat interface has been studied by Ogden et al (1973) and Walstra & Oortwijn and Oortwijn & Walstra (1977, 1979, 1982). The section gives a summary of their results.

When milk fat is emulsified into skimmilk that has been given such a treatment that lipase is inactivated but that serum proteins are not denaturated, adsorption of caseïn and serum proteïn occurs. On adsorption caseïn micelles partly are adsorbed as such onto the interface, partly spread in submicelles. Serum proteins give, because of their small size, a thin layer.

This difference in behaviour has of course its impact on the surface load of the globules. The surface load of a surface fully covered with serum proteïns amounts to 2-3 $mg.m^{-2}$, with intact casein micelles to some 40 $mg.m^{-2}$ and with casein submicelles to some 5 $mg.m^{-2}$. Therefore, surface load depends on the ratios between serum proteins and casein micelles and between intact casein micelles and micelles spread into submicelles.

The adsorption of these proteins is not proportional to their relative abundance in skimmilk. Only 5% of the mass (but 25% of the surface) in the surface layer is made up by serum proteins while their relative abundance in skimmilk amounts to 18%. Casein on the contrary makes up 95% of the mass. This effect is explained by Walstra & Oortwijn (1982) by taking into account that adsorption in the turbulent flow field existing in the valve of a homogenizer is governed by convection, not diffusion. The same theory predicts also that within one emulsion the surface layer of small droplets is thicker and contains relatively more casein than the surface layer of larger droplets.

At neutral pH the relative abundance of α_s, β and κ casein with regard to the total amount of casein is the same in the

surface layer and plasma. The same holds for the serumproteins β-lactoglobulin and α-lactalbumin.

The protein-fat ratio hardly influences surface load and composition until a critical ratio is achieved, below which homogenisation clustering occurs.

The influence of the pretreatment of the skimmilk and the homogenisation temperature is considerable: Heating skimmilk for a long time (30 min) at temperatures between 70°C and 95°C results in the (partial) denaturation of serum proteins. These serum proteins precipitate on the casein micelles. When milkfat is emulsified in high heated skimmilk a complex of serum proteins and casein micelles is adsorbed. Because of the absence of a thin layer of serum proteins, surface load is higher. The ratio between adsorbed intact casein micelles and adsorbed casein submicelles depends on the spreading rate of the casein and the flux of protein particles to the globules. A higher homogenisation temperature hardly influences this flux but goes along with an increased spreading rate. The surface load of a milk fat globule will therefore be lower when the preemulsion is homogenized at higher temperatures (see table 3.1).

Table 3.1 The influence of pretreatment and homogenisation temperature on surface load and composition.

pretreatment of the skimmilk	homogenisation temperature	Effect on composition and load of the surface layer of the fat globule
10 min. 64°C	65°C	No denaturation of serum proteins. Adsorption of casein micelles and serum proteins. Spreading rate of casein micelles is relatively high. Thus average surface load is low.
20 min. 90°C	45°C	Serum proteins are precipitated on casein micelles. Adsorption of a complex of serum proteins and caseïn. Spreading rate of casein micelles is relatively low. Thus average surface load is high.
20 min. 70°C	50°C	Denaturation of serum proteins is still slight. Spreading rate of casein micelles is relatively low. Thus average surface load is intermediate.

3.2 Results

3.2.1 Stability at rest

When an emulsion is stored at rest creaming occurs. The globules in the cream layer are pressed together, which may lead to coalescence (see 2.3.1).
Emulsions of milk fat and skimmilk proved to be very stable to coalescence. In experiments where creaming time was varied between 1 and 7 days, creaming temperature between 2 and 30°C, fat content between 5 and 30%, d_{32} between 0.8 and 8.5 μm, preheating of the skimmilk between 10 min at 64°C and 20 min at 90°C and homogenisation temperature between 40 and 70°C, the size of the globules proved to be by far the most important factor affecting coalescence.

Table 3.2 Influence of globule size on coalescence stability of emulsions left to cream at 2°C (preheating skimmilk 20 min 70°C)

homogenisation temp (°C)	creaming time (days)	changes in fatcontent (%)	d_{32} (μm)	c_s (%)	a (-)
40	2	6→ 6	1.3→1.3	52→52	2→2
50	2	32→32	2.1→2.1	56→56	1→1
40	3	13→13	3.3→3.3	64→64	1→1
50	2	27→27	5.5→5.5	56→56	1→1
70	4	15→0	8.3→ITD*	100→ITD	2→ITD

* ITD = impossible to determine

Emulsions with average globule sizes up to 5.5 μm gave after two days creaming at 2°C no coalescence at all, while an emulsion with d_{32} = 8.3 μm was completely broken after 4 days (table 3.2). Creaming was essential for coalescence to occur. The globule size distribution of an emulsion with d_{32} = 7.3 μm (preheating skimmilk 20 min 70°C, homogenisation temperature 50°C) did not change when it was kept overnight at 2°C slowly rotating, but broke within an hour on further leaving it to cream at 2 and 20°C.

Table 3.3 Influence of storage temperature on coalescence of emulsions left to cream for 2 days (preheating skimmilk 20 min 70°C, hom. temp 50°C)

storage temperature (°C)	Changes in fatcontent (%)	d_{32} (μm)	c_s (%)	a (-)
2	27→27	5.5→5.5	56→56	1→1
12	27→25	5.5→5.5	56→56	1→1
20	27→27	5.5→5.5	56→77	1→1
30	27→26	5.5→5.8	56→64	1→1

Table 3.4 Influence of storage temperature on coalescence of emulsions left to cream for 7 days (preheating skimmilk 10 min 64°C, homogenisation temp. 64°C)

storage temperature (°C)	Changes in fatcontent (%)	d_{32} (μm)	c_s (%)	a (-)
2	32→32	4.3→4.4	56→48	1→1
14	32→32	4.3→4.4	56→48	1→1
30	32→31	4.3→4.3	56→56	1→1

The storage temperature had a minor influence on the occurrence of coalescence. Emulsions with d_{32} = 5.5 μm gave small changes in the globule size distribution after 2 days storage at 30°C and 20°C, while fatcontent decreases somewhat at 12°C (tables 3.3 and 3.4) but emulsions with a slightly smaller d_{32} (= 4.3 μm) were even after 7 days storage at any temperature completely stable against coalescence.

Since the depth of the cream layer and therefore the pressure exerted on the globules, is proportional to the fat content, it is to be expected that for a given size and shape of the storage cylinder, coalescence rate is larger as fat content is higher. All emulsions with a $d_{32} < 5.5$ μm were stable for fat contents up to 30% and will therefore be stable at lower fat contents, but an emulsion with d_{32} = 7,3 μm broke before 10% of the fat reached the creamlayer.

Although the intensity of the heat treatment of the skimmilk prior to emulsifying and the homogenisation temperature influence the thickness and the composition of the surface layer (see 3.1), these effects are not clearly reflected in the coalescence stability (Table 3.5).

Table 3.5 Influence of skimmilk preheating and homogenisation temperature on coalescence stability of emulsions left to cream for 7 days at 2°C

preheating skimmilk	homogenisationtemp (°C)	Changes in fatcontent (%)	d_{32} (μm)	c_s (%)	a (-)
10'64°C	64	32→32	4.3→4.4	56→48	1→1
20'90°C	45	28→27	3.1→3.1	56→56	1→1

Consequently, any influence of storage time, storage temperature, fat content, shape and size of storage cylinder, preheating and homogenisation temperature is superseded by the influence of droplet size. Only for emulsions with a d_{32} between 5.5 and 6.5 μm an influence of one of these parameters cannot be ruled out. The lack of coalescence stability of the emulsions with globules larger than 6 μm probably goes along with a change in crystal habit of these emulsions in a cream layer. All the emulsions had N-type globules (small crystals without a common orientation) but only very large globules changed under the microscope after a certain time from type N to L (crystals tangentially oriented at the edge of the fat globules and probably in the oil-water interface (van Boekel 1980)), which is presumably a consequence of the pressure exerted on the liquid by the cover glass. A similar process probably occurs in the cream layer due to the buoyancy forces exerted on the globules. As van Boekel (1980) already pointed out, this transition leads to emulsions with gross instability against coalescence.

Temperature fluctuations during storage, that would induce "rebodying" if applied to natural cream, hardly resulted in any coalescence in the recombined emulsions (see table 3.6).

Table 3.6 The influence of rebodying experiments on the stability of milk fat in skimmilk emulsions.
Pretreatment skimmilk: 20 min 70°C
Homogenisation temperature: 60°C

Treatment	1d Ro 2°C 5h R 30°C 19h R 2°C	1d Ro 2°C 5h R 20°C 19h R 2°C	1d Ro 2°C 5h R 30°C 19h R 2°C	1d Ro 2°C 5h R 20°C 19h R 2°C
Changes in:				
Fatcontent (%)	29.3→29.3	29.3→29.5	27.4→27.0	27.4→25.7
d_{32} (μm)	3.9→ 3.9	3.9→ 3.9	5.5→ 5.8	5.5→ 5.8
c^{32}(-)	0.6→ 0.6	0.6→ 0.7	0.6→ 0.7	0.6→ 0.7
a^{s}(-)	1 → 1	1 → 1	1 → 1	1 → 1

Ro = stored in 350 ml cylinders which were slowly rotated end over end
R = stored in 15 cm cylindrical tubes.

3.2.1.1 Character of the cream layer

Emulsions with droplets in the size range (d_{32}) 2-5 μm gave within a few days very sticky cream layers when stored at rest. Emulsions with smaller droplets gave very sticky cream layers after centrifuging at low angular velocities. This stickiness is not the result of fat clumping, since after heating to above 40°C and redispersion of the cream layer, an emulsion with the original fat content and droplet size distribution was obtained. The stickiness of the cream layer was greatly increased when 0.6 $kg.m^{-3}$ $CaCl_2$ was added to the emulsion before creaming (this is only a fraction of the amount that causes flocculation of casein). Removal of Ca^{2+} with sodium oxalate or Dowex 50 W-X 8 (Visser 1977) resulted in cream layers without any stickiness.

In an attempt to characterize the stickiness, the elastic shear modulus G of the cream layer was measured in a Deer rheometer with plate and conus geometry. An emulsion with a d_{32} of 3 μm was left to cream for three days at 2°C. One part was left without any addition, to another part 1.2 $kg.m^{-3}$ $CaCl_2$ was added before storage and to a third part 0.45 $kg.m^{-3}$ sodium oxalate, which is enough to bind almost all the calcium and magnesium ions present in the emulsion. Before each measurement

the emulsion was heated to 40°C and the cream layer carefully collected while leaving it intact. This proved impossible for the emulsion containing sodium oxalate, since this cream layer exhibited no coherence.

Although the experiments were poorly reproducible, the cream layers of the two remaining samples showed such differences as to be significant:

Sample without any addition G = 60 ± 25 Pa

Sample with 1.2 $kg.m^{-3}$ $CaCl_2$ G = 660 ± 50 Pa

The stickiness in the cream layer is probably due to an interaction of the adsorbed caseins and can be explained with the existing ideas about the structure of the casein micelle as reviewed by Schmidt (1980). Casein occurs in cow's milk as roughly spherical particles, the casein micelles. These micelles are build out of submicelles cemented together by calcium phosphate that is finely divided between the submicelles. Submicelles consist of about 30 monomeric casein molecules. These are not all the same, but differ in casein composition. Some submicelles contain little or no κ-casein and high quantities of α_{s1}, α_{s2} and β casein; others contain high quantities of κ-casein. The former are much more sensitive to aggregation under the influence of Ca-ions than are the latter. It is believed that the various submicelles aggregate reversibely with calcium phosphate into micelles growing larger and larger until the surface of the micelle consists completely of κ-casein rich submicelles. Submicelles that are sensitive to calcium will therefore be buried into the interior of the micelles and micelles that are relatively calcium insensitive will make up the surface. As the micelles partially are spread onto adsorption at the interface into submicelles, some of these calcium sensitive submicelles turn up at the surface, making the fat globule sensitive for aggregation. If the globules are pressed together in the cream layer a submicelle at the interface of one globule is cemented with calcium phosphate to another submicelle at the interface of another fat globule. In this way the whole cream layer is cemented together, causing stickiness. Adding $CaCl_2$

will increase the number of calcium phosphate bridges and therefore increase the stickiness of the cream layer. Removal of calcium will prevent the formation of bridges and therefore cause a cream layer without any coherence.

3.2.2 Stability in flow fields

- Laminar flow

Emulsions made of milk fat and skimmilk are very stable in a laminar flow field. In experiments where shear rate was varied between 330 s^{-1} and 1500 s^{-1}, temperature between 10°C and 40°C, duration between 15 and 75 min, d_{32} between 1 μm and 7 μm and concentrations between 5% and 30%, this type of emulsion proved to be stable (see tables 3.7, 3.8, 3.9 and 3.10).

Even an emulsion with large droplets (d_{32} = 7.3 μm) was stable in laminar flow (shear rate 550 s^{-1}) at a temperature where maximum coalescence is to be expected (20°C), although

Table 3.7 Influence of temperature and duration of the treatment on coalescence of emulsions in a laminar flow field (shear rate 330 s^{-1})

temperature (°C)	duration (min)	changes in fatcontent (%)	d_{32} (μm)	c_s (-)	a (-)
25	30	9→ 9	1.1→1.1	0.4→0.4	1→1
40	30	9→ 9	1.1→1.1	0.4→0.4	1→1
25	75	12→12	1.7→1.7	0.6→0.6	1→1
40	75	12→12	1.7→1.6	0.6→0.7	1→1

Table 3.8 The influence of shear rate on coalescence of emulsions in a laminar flow field (duration 30 min, temperature 15°C)

shear rate (s^{-1})	changes in fatcontent (%)	d_{32} (μm)	c_s (-)	a (-)
450	13→13	3.3→3.3	0.6→0.6	1→1
1500	13→12	3.3→3.3	0.6→0.6	1→1

Table 3.9 The influence of temperature on coalescence of emulsions in a laminar flow field (shear rate 450 s^{-1})

temperature (°C)	duration (min)	changes in fatcontent (%)	d_{32} (μm)	c_s (-)	a (-)
10	30	13→13	3.3→3.3	0.6→0.6	1→1
15	30	13→12	3.3→3.3	0.6→0.6	1→1
30	20	30→30	4.0→4.0	0.6→0.6	1→1

Table 3.10 The influence of d_{32} on the coalescence stability of emulsions in a laminar flow field

shear rate (s^{-1})	temperature (°C)	duration (min)	changes in fatcontent (%)	d_{32} (μm)	c_s (-)	a (-)
550	20	15	28→28	7.3→7.3	0.6→0.6	1→1
450	30	20	30→30	4.0→4.0	0.6→0.6	1→1

such an emulsion shows rapid and extensive coalescence when it is allowed to cream. Only very long lasting treatments (>1h) at 40°C seemed to cause a slight broadening of the droplet size distribution. Although in these series of experiments the pretreatment of the skimmilk (20 min 70°C) and the homogenisation temperature (40 to 50°C) were kept constant, these variables will probably not affect coalescence stability, in view of their influence on coalescence rate in a cream layer and in a flow with taylor vortices.

- Flow with Taylor vortices

The results of these experiments, listed in table 3.11 are summarized as follows: Emulsions made of skimmilk and milk fat are stable in a flow with Taylor vortices at a moderate apparent shear rate for every pretreatment of the skimmilk between 10 minutes at 64°C and 20 min at 90°C, for every homogenisation

Table 3.11 Stability of emulsions of milk fat and skimmilk in a flow with Taylor vortices
apparent shear rate: 550 s^{-1}
treatment time: 30 min

pretreatment skim milk	homogenisation temp. (°C)	treatment temperature (°C)	changes in fatcontent (%)	changes in d_{32} (μm)	changes in c_s (-)	changes in a (-)
20'70°C	50	20	29→28	3.0→3.0	0.6→0.6	1→1
20'70°C	50	30	30→30	3.0→3.0	0.6→0.6	1→1
20'90°C	45	15	33→31	3.9→3.9	0.6→0.6	1→1
20'90°C	45	30	33→33	3.9→3.9	0.6→0.6	1→1
10'64°C	65	15	33→34	4.4→4.4	0.6→0.6	1→1
10'64°C	65	30	33→33	4.4→4.4	0.6→0.6	1→1

temperature between 45°C and 65°C, for fat contents up to 30% and for globule size distributions with a d_{32} up to 4.4 μm.

Only emulsions homogenized once at low pressures showed a little coalescence in a flow with Taylor vortices (Table 3-12). Coalescence was probably due to the very large globules which still exist in the emulsion after it is homogenized once. (For instance if two emulsions have a globule size distribution with the same d_{32} the emulsion that is homogenized once still contains droplets with a diameter of 18 μm while the maximum diameter in the repeatedly homogenized emulsion is about 8.2 μm.

Table 3.12 Stability of emulsions made by homogenizing a mixture of milk fat and skimmilk once, in a flow with Taylor vortices.
pretreatment skimmilk: 20 min. at 70°C
treatment time: 30 min.
temperature during treatment: 15°C
apparent shear rate: 550 s^{-1}

changes in fatcontent (%)	changes in d_{32} (μm)	changes in c_s (-)	changes in a (-)
29→28	4.8→5.1	0.8→0.8	2→2
19→19	2.3→2.3	0.8→0.8	2→2
18→16	3.1→2.7	0.8→0.8	3→2

But if the homogenisation pressure was increased, even emulsions made by homogenizing a preemulsion once, remained stable in this flow (table 3.12)

- Turbulent flow

The results of these experiments, listed in tables 3.13, 3.14, 3.15 and 3.16, are summarized as follows: Experiments in which apparent shear rate was varied between 730 s^{-1} and 2520 s^{-1}, temperature between 10 and 70°C, preheating of the skimmilk between 10 min at 64°C and 20 min at 90°C, homogenisation temperature between 45 and 65°C, fat content between 9 and 34%, and d_{32} between 1.5 and 4.5 µm showed that emulsions made of skimmilk and milk fat are rather stable in turbulent flow. Only emulsions with large globules ánd a high fat content undergo coalescence at high apparent shear rates.

Temperature seemed to influence the course of coalescence: At 35 and 70°C turbulent flow resulted in coalescence characterized by a change in size distribution while fat content remained nearly the same; At 25°C coalescence caused a decrease in fat content (table 3.13).

At a lower apparent shear rate (1410 in stead of 2520 s^{-1}) the same trent, although much weaker, is seen. At 30°C coalescence was sometimes coupled with a change in droplet size dis-

Table 3.13 The influence of treatment temperature on coalescence rate of milk fat in skimmilk emulsions in a turbulent flow field.
pretreatment skimmilk: 20 min at 70°C
homogenisation temperature 40°C average shear rate: 2520 s^{-1}

treatment-time (min)	treatment temperature (°C)	changes in fatcontent (%)	d_{32} (µm)	c_s (-)	a (-)
30	25	34→24	3.9→4.0	0.6→0.8	1→2
30	35	34→34	3.9→7.1	0.6→1.5	1→5
25	70	34→33	3.9→5.3	0.6→0.8	1→2

Table 3.14 The influence of treatment temperature on coalescence rate of milk fat in skimmilk emulsions in a turbulent flow field.
pretreatment skimmilk: 20 min at 70°C
homogenisation temperature 50°C average shear rate: 1410 s^{-1}

treatment-time (min)	treatment temperature (°C)	changes in fatcontent (%)	changes in d_{32} (μm)	changes in c_s (-)	changes in a (-)
30	15	34→33	3.9→4.6	0.6→0.8	1→3
15	20	28→23	4.9→5.2	0.5→0.8	1→1
15	30	29→29	4.1→4.6	0.5→0.8	1→1
30	30	29→27	4.0→4.2	0.5→0.9	1→1

Table 3.15 The influence of fat content and treatment temperature on the coalescence rate of milk fat in skimmilk emulsions in a turbulent flow field.
pretreatment skimmilk: 20 min at 70°C
homogenisation temperature: 40°C average shear rate: 2520 s^{-1}

treatment-time (min)	treatment temperature (°C)	changes in fatcontent (%)	changes in d_{32} (μm)	changes in c_s (-)	changes in a (-)
30	70	13→13	3.3→3.3	0.6→0.9	1→1
25	70	34→33	3.9→5.3	0.6→0.8	1→2
30	20	13→13	3.3→3.3	0.6→0.6	1→1
30	25	34→24	3.9→4.0	0.6→0.8	1→2

tribution, sometimes with both a change in size distribution and a small decrease in fat content, at 20°C coalescence predominantly resulted in a decrease in fat content but at 15°C coalescence resulted again in a change in the size distribution (table 3.14). Similar effects were found, at lower shear rates, for natural cream (chapter 4).

Emulsions of lower fat content were stable in turbulent flow (table 3.15) at all applied apparent shear rates. The apparent shear rate had some influence on coalescence rate (table 3.16): Emulsions that coalesced in turbulent flow fields with apparent shear rates of 1410 and 2520 s^{-1} did not at 750 s^{-1}. Two remarks have to be made about this series of experiments:

Table 3.16 The influence of average shear rate and treatment temperature on the coalescence rate of milk fat in skimmilk emulsions in a turbulent flow field.
treatment time: 30 min.

pretreatment skimmilk	homogenisation temp. (°C)	average shear rate (s^{-1})	treatment temp. (°C)	changes in fat content (%)	changes in d_{32} (μm)	changes in c_s (-)	changes in a (-)
10'64°C	65	730	15	33→33	4.4→4.4	0.6→0.6	1→1
20'90°C	45	750	15	30→31	3.6→3.6	0.6→0.7	1→1
20'70°C	40	1410	15	34→33	3.9→4.6	0.6→0.8	1→3
20'90°C	45	760	30	33→33	3.9→3.8	0.6→0.7	1→1
20'70°C	50	1410	30	30→27	4.0→4.2	0.6→0.9	1→1
20'70°C	40	2520	35	34→34	3.9→7.1	0.6→1.5	1→5
20'70°C	40	2520	25	34→24	3.9→4.0	0.6→0.8	1→2

1) The equipment in which apparent shear rates of 2520 and 1410 s^{-1} were generated consisted of two coaxial cylinders with the inner one rotating, while an apparent shear rate of about 750 s^{-1} was generated in an equipment consisting of two cylinders with the outer one rotating. This may have caused slight differences in the type of turbulence.
2) It is impossible to exclude from these experiments a possible effect of skimmilk preheating or homogenisation temperature. In view of their influence on coalescence rate in a cream layer and in a flow with Taylor vortices such effects will probably be marginal.

In two cases coalescence in turbulent flow was followed by measuring E_t/F_o in samples taken at several moments during the experiment. At the end of each experiment, size distribution and fat content of the treated emulsion were determined and compared with those of the original emulsion.
An emulsion in turbulent flow at an apparent shear rate of 1410 s^{-1} and a temperature of 30°C, coalesced in such a way that d_{32} changed while fat content and shape of distribution remained about the same. (E_t/F_o) then is more or less proportional to the specific interfacial area. Ln (E_t/F_o) varied fairly lineair with

Table 3.17 Ln (E_t/F_o) measured at 420 nm of two milk fat in skimmilk emulsions in a turbulent flow field as a function of treatment time.

pretreatment skimmilk	20 min 70°C	20 min 70°C
homogenisation temperature	50°C	45°C
average shear rate	1410 s^{-1}	1410 s^{-1}
treatment temperature	30°C	20°C
maximum treatment time	15 min	20 min
Changes in: fatcontent	29.3% → 29.3%	28.2% → 23.3%
d_{32}	4.1 μm → 4.6 μm	4.9 μm → 5.2 μm
c_s	0.56 → 0.77	0.56 → 0.77
a^s	1 → 1	1 → 1

treatment time (min.)	ln (E_t/F_o)	ln (E_t/F_o)
0	-1.74	-1.96
2.5	-1.79	-1.98
5	-1.80	-2.03
7.5	-1.82	--
10	-1.91	-2.17
15	-1.97	-2.28
coalescence rate (k_1)	2.6×10^{-4} s^{-1}	3.8×10^{-4} s^{-1}

time, indicating first order kinetics as often is encountered if coalescence itself is rate determining (van den Tempel 1953, 1957). The reaction constant is 3.10^{-4} s^{-1} (Table 3.17).
The same flow field at a temperature of 20°C caused a type of coalescence characterized by a reduction of the fat content as well as a change in size distribution. Since the shape of the size distribution remained fairly (but not completely) constant and $\rho_{32} > 3$ for $\lambda = 420$ nm a change in E_t/F_o measured at this wavelength still reflects a decrease in specific surface area. During the first 15 min ln (E_t/F_o) varied again fairly linear with time (table 3.17). The reaction constant was about $4.10^{-4}s^{-1}$).

More systematic studies at high shear rates were impossible since the equipment did not endure the high forces needed.

3.2.3 Effect of heat treatment on stability

Emulsions made of skimmilk and milk fat were heat treated in two

ways: D.U.H.T. and I.U.H.T.
D.U.H.T. = direct ultra high temperature treatment:
The emulsion is heated to about 75°C in a heat exchanger. Under high pressure hot steam is injected in the emulsion so that the desired temperature is immediately reached. The liquid is kept at that temperature for a desired time and is then flash cooled to 75°C by withdrawing the same amount of steam in an expansion flask (adiabatic expansion). The emulsion is further cooled in the heat exchanger.
I.U.H.T. = indirect ultra high temperature treatment:
The emulsion is heated in a heat exchanger to about 75°C by hot water and then by hot steam to the desired temperature, kept at that temperature during a desired time and gradually cooled to the desired end temperature.

The most striking differences between D.U.H.T. and I.U.H.T. are:
- Because of the possibility to change the temperature almost instantaneously by injecting or withdrawing steam in D.U.H.T. equipment the emulsion is not longer exposed to temperatures above 100°C than for the choosen heating time. In a I.U.H.T. equipment it takes considerable time to heat and cool the emulsion. Consequently, the time during which the emulsion is exposed to temperatures above 100°C is (much) longer than the established heating time, certainly for high temperatures.
- In D.U.H.T. the emulsion is diluted with condensed steam, in I.U.H.T. steam does not reach the emulsion.
- In the expansion flask belonging to the D.U.H.T. equipment the emulsion is exposed to hot steam bubbles which is known to cause disruption of fat globules (Mulder & Walstra, 1974).

The effect of these two treatments on a recombined emulsion is, as expected, completely different. If the emulsions were subjected to D.U.H.T. (max. 30 sec at 135°C) the globules were disrupted, the more as temperature was higher, while absolutely no clustering occurred (table 3.18).

If the emulsions were subjected to I.U.H.T. (max. 120 sec. at

Table 3.18 The influence of various heat treatments on recombined fat-globules in milk fat-in-skimmilk emulsions

treatment	changes in				clus-tering
	fatcontent %	d_{32} µm	c_s	a	
D.U.H.T. 30'136°C	31→31	4,4→2,2	0,7→1,1	1→3	-
D.U.H.T. 30'126°C	31→31	4,4→3,3	0,7→1,0	1→2	-
D.U.H.T. 30'115°C	31→29	4,4→4,1	0,7→0,8	1→2	-
I.U.H.T. 30'135°C	31→31	4,4→4,5*	0,7→0,9	1→1	++**
I.U.H.T. 30'126°C	31→29	4,4→4,5*	0,7→0,9	1→1	+
I.U.H.T. 30'115°C	31→30	4,4→4,5	0,7→0,9	1→1	-

* after dilution in a solvent that disperses the clusters
** ++ = extensive clustering (microscopical examination)
+ = clustering
- = no clustering

135°C) neither disruption nor coalescence occurred. Instead globules aggregated to clusters, the more as the temperature was higher (see table 3.18). Immediately after this type of heat treatment no conspicuous macroscopic changes were visible, but after the emulsion was cooled it set into a kind of paste with a high apparent viscosity. This change in rheological behaviour must be a consequence of clustering. Although setting of the emulsion takes some time, microscopical examination showed that clustering occurred already during or immediately after the heat treatment.

For I.U.H.T. the effects of treatment conditions (heating time and temperature) and emulsion properties (globule size distribution) were further studied, since this technique is in wider use than D.U.H.T. As an index for clustering the apparent viscosity at 40°C and at a shear rate of 100 s^{-1} was taken. This shear rate is suitable as it appeared high enough to avoid irregularities due to slip or plug flow and to low to cause flow patterns deviating from laminar flow. The apparent viscosities are summarized in table 3.19. The given values are an average of the values obtained with the Rotovisco and the Deer Viscometer of emulsions subjected earlier to higher and lower shear rates. If the experiments were carried out as described in 2.4.2.1 the

results differed by less than 10%. In all cases fat content was about 28%, the heating of the skimmilk a few min. at 70°C (just enough to inactivate lipase) and the homogenisation temperature 55°C.

Table 3.19 The apparent viscosity of an I.U.H.T.-treated milk fat-in-skimmilk emulsion at a shear rate of 100 s^{-1}, Gap width: 1 mm
preheating skimmilk 5 min at 70°C
homogenisation temperature: 55°C

treatment time (s)	treatment temp. (°C)	original fat content (%)	original d_{32} (μm)	apparent viscosity (mPa.s)
influence of temperature				
30	115	28.6	1.2	30
30	125	28.6	1.2	78
30	135	28.6	1.2	113
30	125	27.5	3.3	12
30	135	27.5	3.3	31
Influence of globule size distribution				
30	125	27.5	3.3	12
30	125	26.2	2.8	13
30	125	26.5	1.3	86
30	125	28.6	1.2	78
30	125	27.8	0.7	106
30	135	27.5	3.3	31
30	135	26.8	1.4	114
30	135	28.6	1.2	113
Influence of duration of treatment				
10	135	26.8	1.4	113
30	135	26.8	1.4	114
55	135	26.8	1.4	135
120	135	26.8	1.4	138

In fig. 3.1 the apparent viscosity of an emulsion heated for 30s at 125°C is plotted against d_{32} of that emulsion.
Assuming that the differences in apparent viscosity of the emulsion reflect the extent of flocculation, the effect of a heat treatment of a recombined emulsion may be summarized as follows:
- Clustering occurs within a fraction of the time needed to

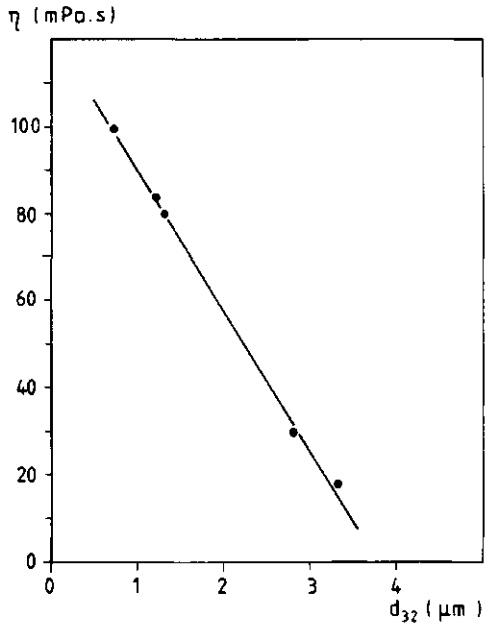

Fig. 3.1 The apparent viscosity of a I.U.H.T. treated (30s 125°C) emulsion (27% fat) as function of d_{32}

induce coagulation in the original aqueous phase (i.e. skimmilk). A similar decrease in heat stability was also observed after a homogenisation of normal and concentrated milk (Sweetsur and Muir, 1982) The decrease is tentatively explained by Oortwijn et al. 1977): during homogenisation casein micelles are adsorbed onto the milk fat globules. Since a milk fat globule covered with casein micelles can be viewed as a large casein particle, homogenisation has the same effect as increasing the protein content.

- Clustering is more extensive for a higher heating temperature. Similar results were found by Fink and Kessler, (1985) who measured the globule size distribution of a homogenized cream with a coulter counter before and after a heat treatment. Since this behaviour is as expected, it is not further discussed.
- The duration of the treatment hardly had any influence on the apparent viscosity. The selected temperature was probably so high that clustering was already complete within 10 s. Fink and

Kessler also observed that for homogenized cream the extent of clustering reached its ultimate value within 9 s at temperatures above 130°C while at 125°C the ultimate value was not reached within 40 s. On the basis of their results we may expect that an influence of the duration of the treatment on the extent of clustering will become measurable at temperatures below 125°C.
- The original droplet size has a strong influence on the apparent viscosity of a treated emulsion. Fig. 3.1 shows that the apparent viscosity after a given heat treatment varies linearly with d_{32} of the distribution. This phenomenon can not be explained via the apparent casein concentration, since the latter should little depend on droplet size. But apart from the increase in apparent casein concentration the structure of the casein micelle is changed after its adsorption onto the interface. The interface that has to be covered is inversily proportional to the d_{32} of the emulsion and a larger part of the micelles is spread into submicelles as d_{32} is lower. (Walstra & Oortwijn 1982). Since the outer layer and the inside of a casein micelle differ in composition (particularly in concentration of κ-casein), it is to be expected that the properties of the adsorbed casein particles differ from those of the native micelles (Schmidt 1980).

The pH of treated and original emulsions were measured and appeared always to be the same. This stresses the fact that coagulation occurred within very short times and did not depend on acid production from lactose. Acid production from lactose, resulting in a lowering of the pH, appears to be the main factor leading to heat coagulation in unconcentrated milk (Fox & Morrisey, 1977).

Information about the strength of the bonds between the fat globules in a cluster was obtained from the rheological behaviour of diluted emulsions. A few emulsions were diluted with skimmilk (that had had the same heat treatment as the emulsion) to half the original fat content. For the diluted emulsions proportionality was found between shear rate and shear stress, which was virtually time independent up to the highest shear

Table 3.20 The viscosity of a treated emulsion after dilution with (treated) skimmilk to 50% of the original fat content, as a function of treatment time

pretreatment skimmilk: 5 min 70°C
volume surface average diameter: d_{32} = 1.4 μm
fat content before dilution: 26.8%
treatment emulsion: I.U.H.T. at 135°C
fat content after dilution: 13.4%

treatment time (s)	viscosity at 40°C (mPa.s)
0	1.7
10	3.1
30	3.2
55	3.2
120	3.4

rates applied (800 s^{-1}). So the determined viscosity was independent of shear rate and shear time. The values are summarized in table 3.20. Again the influence of the duration of the heat treatment appeared almost absent, as the selected temperature was too high. One other emulsion was diluted to 75% of the original fatcontent. Also for this emulsion a linear time independent relationship was found. The highest applied shear stress was now about 6 Pa resulting in a shear rate of about 700 s^{-1}. So up to shear stresses of 6 Pa and shear rates of 800 s^{-1} no break up of clusters was found. In this respect the clusters formed at heat treatments are completely different from clusters made in a homogenizer as the latter are disrupted in these flow fields (Walstra & Ogden, 1970). Neither type of cluster, however, could withstand the much more effective elongational flow present in a flow field with Taylor vortices (average shear rate 600 s^{-1}). Both types of clusters were almost fully disrupted in such a flow field within 30 minutes.

Microscopic studies showed that heat induced clusters are not spherical but more like an ellipsoid. Their volume surface averaged (equivalent) diameter was between 10 and 20 μm but clusters with diameters of 50 μm and more were also found. (The number of counted clusters proved to be too low to establish

significant differences in size distribution between different emulsions). When the clusters are dispersed in water with at least 0.375% disodium ethylene diamino tetraacetate and 0.125% poly(oxyethylene) sorbitan monolaurate they fall apart into single globules. The size distribution of these resulting globules never deviated markedly from the original size distribution. (The applied concentrations of the dispersants did not influence Gerber readings nor turbidity spectra of unclustered emulsions.)
This demonstrates that during an I.U.H.T. treatment hardly any coalescence or disruption of droplets takes place. The clusters dissolve also completely in aqueous solutions of 0.13 molar sodium oxalate or of 6 molar urea. These results imply that between the fat globules in a cluster no covalent bounds (such as S-S bridges) are involved. Hence clustering is probably not a consequence of an interaction between α-lactoglobulin and κ-casein which has been considered to be crucial in the coagulation of homogenized concentrated milk (Sweetsur and Muir 1983).

The rate of clustering, the invariableness of the pH and the properties of the clusters suggest that in recombined creams other reaction(s) are responsible for aggregation than in homogenized concentrated milk. A more accurate description leading to an explanation of these phenomena will require much more research.

3.2.4 The effect of spray drying on the stability of the emulsion

Recombined emulsions made from skimmilk and milk fat were spray dried to study whether they yield good quality powders. Since the minimum amount of emulsion necessary to obtain a reasonable quantity of powder, exceeded the capacity of the beaker of the homogenizer, we did not make the emulsion in the way described in 2.1. In stead emulsions used for spray drying were made by first homogenizing the fat and skimmilk mixture one time at 1 MPa, and subsequently in a two-stage homogenizer at the de-

sired pressures. The droplet size distributions of these emulsions were somewhat broader and less reproducible than those of the emulsions made by repeatedly homogenizing a fat and skimmilk mixture.

Since the dry matter content of most emulsions was rather high (about 40%) evaporation before spray drying was omitted. Spray drying occured so as to avoid heat coagulation of protein, the inlet temperature and the outlet temperature being rather low (140°C and 80°C respectively). A disk was used at 300 revolutions per second to obtain small droplets. The temperature of the emulsion before spray drying was below 50°C. The formation of vacuoles during spray drying was minimized by deaerating the emulsion and using a special disk constructed so as to prevent inclusion of air before droplet formation (van der Stege, Walstra, 1987). During atomization of the emulsion, however, inclusion of air is inevitable and a large proportion of the powder particles contained vacuoles.

The obtained powders gave upon dispersion in water clustered emulsions despite the mild conditions under which the emulsions were spray dried. The smaller the average fat globule size in the original emulsion and the lower the protein to fat ratio, the more clustering was observed (see tables 3.21 and 3.22).

Some powders gave emulsions with some fat floating on top. This "loss" of fat was more if the average fat globule size of the emulsion before spray drying was larger. The powder appeared also to change during storage. Powders stored for two or three weeks were harder to disperse and gave more floating fat. The storage temperature had only a minor influence on the physical deterioration of the powder.

The clusters could be separated into single fat globules, by dispersing the powder into an aqueous solution of disodium ethylene diamine tetraacetate and poly(oxyethylene)sorbitan monolaurate; this was done to allow comparison of the size distribution before and after spray drying. From other measurements it appeared that this solvent does not influence the globule size distribution of emulsions with single and clustered

Table 3.21 The effect of spray drying on the stability of recombined fat globules. Influence of d_{32}
pretreatment skimmilk: 5 min 70°C
homogenisation temperature: 50°C
ratio solids-not-fat/fat: about 0.25

situation	fat content (%)	d_{32} (μm)	c_s (-)	a (-)	clustering	visual appearance of powder
E1	25	1.5	0.6	1	--	
E2	25	1.3	0.8	1	--	
E3	24	-	-	-	++	
E4	21	0.5	1.5	3	++	
E(1,4°C)	19	-	-	-	++	changed
E(1,20°C)	21	-	-	-	++	changed
E1	26	1.0	0.6	1	--	
E2	26	0.9	0.8	1	--	
E3	25	0.6	0.8	5	++	
E4	24	0.5	1.3	5	++	
E/1,4°C)	22	0.4	1.2	∞	++	hardly any change
E(2,4°C)	22	0.4	1.2	∞	++	hardly any change
E(1,20°C)	23	0.5	1.3	5	++	hardly any change
E(2,20°C)	24	0.5	1.3	5	++	hardly any change
E1	27	0.5	0.6	1	--	
E2	27	0.4	1.1	3	--	
E3	27	0.4	0.9	3	+++	
E4	27	0.4	1.1	∞	+++	
E(1,4°C)	27	0.4	1.2	∞	+++	no visible change
E(1,20°C)	27	0.4	1.2	∞	+++	no visible change

E1: original emulsion
E2: emulsion after passing disk but before drying
E3: emulsion made of fresh powder that has not passed the cyclone
E4: emulsion made of fresh powder that has passed the cyclone
E(x,T°C): emulsion made of powder stored for x weeks at T°C.
cluster formation:
--: no clustering, + = slight clustering, ++ = clustering, +++ = extensive clustering

globules nor the determination of the fat content (see 3.1.3). Any changes in the size distribution of the fat droplets must therefore have occurred during the spray drying proces or during the storage of the powder, but not during the dispersion of the powder in the solvent. Care was taken to disperse about the same

Table 3.22 The effect of spray drying on the stability of recombined fat globules. Influence of ratio solids-not-fat/fat (s.n.f/f)
pretreatment skimmilk: 5 min 70°C
homogenisation temperature: 50°C

situation	fat content (%)	s.n.f./f (-)	d_{32} (μm)	c_s (-)	a (-)	clustering	changes in appearance during storage
E1	26	0.25	0.8	0.8	1	--	
E2	26		0.8	0.8	1	--	
E3	26		0.6	1.2	2	++	
E4	25		0.5	1.5	∞	++	
E(1,4°C)	25		0.5	1.5	∞	++	yes
E(1,20°C)	23		-	-	-	++	hardly any
E1	18	0.42	0.9	0.6	2	--	
E2	18		0.7	0.9	1	--	
E3	18		0.8	0.9	∞	++	
E4	18		-	-	-	++	
E1	10	0.84	0.7	0.9	1	--	
E2	10		0.7	0.9	1	--	
E3	10		0.8	1.0	5	+	
E4	9		0.8	1.2	∞	+	
E1	20	1.0	0.9	0.8	1	--	
E2	20		0.8	0.9	1	--	
E3	20		1.0	0.7	2	--	
E4	20		0.9	0.8	2	--	
E(1,4°C)	20		0.9	0.8	2	--	no
E(1,20°C)	20		0.9	0.8	2	--	no

for explanation of symbols see table 3.21

amount of dry matter in tap water as the original emulsion contained. Any differences in dry matter content measured before the removal of floating fat were corrected for in the figures denoting the fat content. Differences thus imply that the dispersed powder gave an emulsion with floating fat as this fat was removed before determination of fat content. The results are summarized in tables 3.21 & 3.22.

When an emulsion is spray dried, there are three stages in the proces during which changes in the size distribution may occur:

1 The atomisation of the emulsion at the outlet of the disk.
2 The drying of the emulsion droplets.
3 The separation of the air and the transport and collection of the powder particles at the end of drying.

Also during storage of the powder changes in the size distribution may occur.

Changes during atomizing were determined by taking samples in the tower while the in- and outlet temperature were kept on room temperature. In a few cases the emulsion was completely atomized and collected at the bottom of the tower.

During atomizing the size distribution of the fat droplets hardly changed; only if the average globule size exceded 1μm, it was slightly decreased. In this respect a disk obviously differs from a nozzle which is known to homogenize an emulsion during spraying. (T.J. Buma (1971)).

During drying of the droplets and collecting of the powder particles changes occurred resulting in considerable modifications of the size distribution and in clustering. A typical example of a changing size distribution during processing is given in fig. 3.2. Some of the fat globules seemed to be disrupted into smaller ones, while others were coalesced into larger fat globules. Disruption and coalescence appeared to continue during transport and storage of the powder. The physical deterioration during storage can also be seen by eye: especially powder stored at 4°C became very sticky and gave upon dispersing a larger part of floating fat. If the results summarized in tables 3.21 and 3.22 are compared, it seems that for low protein-to-fat ratios the obtained globule size distribution did not depend on the original one but changed during drying, transport and storage into a log-normal size distribution with $d_{32} \tilde{\sim} 0.5$ μm. If the protein-to-fat ratio (= s.n.f./f) was higher, d_{32} became higher: d_{32} rised from 0.5 μm for s.n.f./f = 0.25 to 0.9 μm for s.n.f./f = 1.0.

It is obvious that during the drying proces several changes occur in the droplet: The overall change of the size distribution (which was confirmed by Coulter countings) points to the

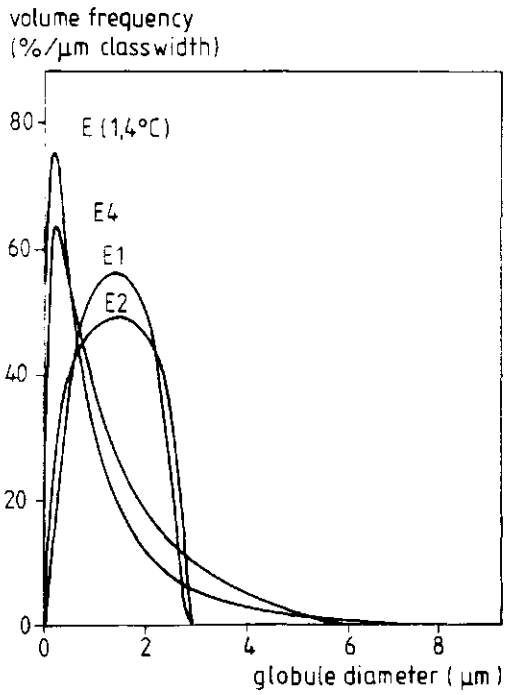

Fig. 3.2 The change in the globule size distribution of a milk fat-in-skimmilk emulsion after atomizing and drying (see table 3.21 for explanation of symbols).

possibility that during the evaporation of water considerable coalescence of the original fat droplets occurs. It may be that the dried droplets immediately after the evaporation of water consist to some extent of liquid fat with proteins and other non-fat components dispersed into it, as was observed after the evaporation of water from a similar system in an evaporator. When the dried droplet is cooled the dispersion solidifies, thereby entrapping most of the fat in protein layers. The average diameter of these new fat globules then only depend on s.n.f/f. Part of the fat remains uncovered, particularly at the edges of the particles or near vacuoles. After dispersing the powder in tap water, this part coalesces to fat floating on the surface. The formation of clustered emulsions during drying is not necessarily (only) a consequence of heat coagulation of

protein, but may also be caused by protein particles becoming shared by two partly denuded fat globules. The clusters in the dispersed powder would then resemble homogenisation clusters rather than heat coagulation clusters.

3.3 Discussion

Interactions of fat globules in emulsions made of skimmilk and milk fat

Milk fat-in-skimmilk emulsions are very stable with regard to coalescence; only in strongly turbulent flow fairly rapid partial coalescence may be expected, but such a flow is difficult to achieve for a long time in large quantities of a viscous liquid. It appeared to be difficult to reduce this stability by merely varying process conditions; only emulsions made at extremely low homogenisation pressures gave immediate coalescence after cooling and creaming.
The influence of beating in air was not systematically studied but in those cases where air was erratically beaten in, it appeared to enhance partial coalescence, certainly if the emulsions contained larger globules ($d_{32} \geq 3\mu m$). Emulsions with a globule size distribution with $d_{32} < 1\mu m$ were fairly stable under these conditions.

The stability against creaming, which is important when these emulsions are stored, is of course closely related to droplet size. Emulsions with droplets around 3 μm cream within one week, giving rise to tough and hardly dispersable cream layers, a situation which can only be ameliorated by adding calcium sequestering agents. If the emulsion has been homogenized strongly, some droplets are so small that the weight of the surface layer more than compensates the buoyancy of the fat; these droplets therefore do not cream but sediment on standing.
Consequently, there is a droplet size where the weight of the surface layer counteracts the buoyancy of the fat. Since by

means of repeated homogenisation very narrow globule size distributions can be obtained, it may be worthwhile to look for an optimal droplet size (which will, of course depend on other process conditions), to obtain a longer shelf life of the product.

The stability against coagulation during heating is poor, at least when indirect U.H.T. heating is applied. Although the effects of a direct U.H.T. treatment were not studied in detail, the results showed that it is possible to obtain sterile unclustered emulsions. Another, far more complicated treatment would be to sterilize the milk fat, treat the skimmilk by I.U.H.T. and aseptically emulsify the fat-skimmilk mixture afterwards.

During the spray drying process the size distribution of the fat globules changes radically. Moreover other forms of aggregation of fat droplets occur, resulting in clustered emulsions after the powder is dispersed. In 3.2.4 I have suggested that clustering is caused partly by heat coagulation of adsorbed protein during drying of the droplet, partly by the formation of fat globules with shared casein micelles during solification of the droplet. Clustering caused by heat coagulation can be opposed by starting with a suitable emulsion, obtained by emulsifying fat in concentrated skimmilk (high protein to fat ratio) at low homogenisation pressures (fairly large d_{32}). In this manner the fat surface area per amount of protein is low, resulting in a low fraction of micelles spread into a layer of the more heat-coagulation sensitive submicells. The apparent casein concentration is hardly increased. Heat coagulation, and probably clustering, can also be diminished by drying at low outlet temperatures, in view of the strong dependence of the coagulation rate on the temperature.
Clustering caused by sharing of casein particles is prevented by increasing the protein-to-fat ratio; the chance that an adsorbed casein particle adorbes onto a partly denuded fat globule before

a free casein particle is adsorbed is then lowered.
Modification of the size distribution of the fat globules during spray drying of the emulsion seems to be inevitable. Changes leading to a sticky powder that gives upon dispersing in water an emulsion with fat floating on top are of course not acceptable. The only way to oppose these undesired modifications is to start with an emulsion containing not to large fat globules, say 1 μm, and a high protein to fat ratio.

4 STABILITY OF NATURAL CREAM AND MIXTURES OF NATURAL CREAM AND RECOMBINED CREAM

Coalescence stability of natural cream in a flow with Taylor vortices was extensively studied by Labuschagne (1963). In this study only a few experiments were done with natural cream, merely to serve as a kind of reference for recombined emulsions.

Labuschagne expressed coalescence stability of natural cream as the time necessary to produce visible clumps in the emulsion. He observed that under different conditions different modes of clumping occur. Mode of clumping depended on temperature and the intensity of the Taylor vortices, as characterized by the circumferential velocity of the inner cylinder at a given annular clearance.
In 3.1.2 it was established that emulsions made from skim milk and milkfat can coalesce in various ways resulting in a decreased fat content, a modified size distribution or both. Experiments with natural cream showed that this emulsion also can coalesce in various ways (see 4.1).

To find a correlation between the observations of Labuschagne and the present results, a series of his experiments was more or less imitated. The results are not expressed as churning time and clumping behaviour, but as changes in droplet size distribution and fat content.

4.1 Results

Table 4.1 shows that natural cream almost completely coalesced at circumstances among which emulsions of milkfat and skimmilk were completely stable.
Temperature had a strong influence on type of coalescence (table 4.2): At 30°C coalescence resulted in an increase of d_{32} and a decrease of fat content by 28% of its original value. At 15°C coalescence resulted in a decrease of d_{32} and a sharp decrease of fat content by 87%.

Table 4.1 The stability of natural cream with regard to that of an emulsion made of skimmilk and milk fat.
Treatment: 30 minutes flow with Taylor vortices, average shear rate 600 s^{-1} temperature 15°C.

type of emulsion	changes in			
	fat content (%)	d_{32} (μm)	c_s (-)	a (-)
Recombined	33→31	3.9→3.9	0.6→0.6	1→1
Natural cream	30→ 4	4.0→2.9	0.4→1.3	2→5

Table 4.2 The influence of treatment temperature on course of coalescence in natural cream
Treatment: 30 minutes flow with Taylor vortices, average shear rate 600 s^{-1}

Temperature (°C)	changes in			
	fat content (%)	d_{32} (μm)	c_s	a
15	30.0→4.0	4.0→2.9	0.4→1.3	2→5
30	30.0→21.7	4.0→8.4	0.4→1.0	2→5

It is unlikely that a prolongation of the treatment at 30°C would ultimately result in the same size distribution and fat content as obtained after 30 min at 15°C, in other words: the size distribution and fat content reached after 30 mintues at 30°C would not be an intermediate state between the original ones and those after the same treatment at 15°C (see also 4.2 and 6.1).
The influence of type of flow was not investigated systematically. The experiments described in table 4.3 suggest that this influence is limited. Both in turbulence and with Taylor vortices coalescence was almost completed.

Cream repeatedly homogenized at such a low pressure that the size distribution was hardly altered, remained as unstable in a flow with taylor vortices as was natural cream (table 4.4). This result would imply that during homogenisation no or hardly any exchange of caseïn micelles or whey proteins with natural membrane material is taking place. Only when a new interface be-

Table 4.3 The influence of flow type on coalescence in natural cream

Temperature (°C)	flow type	average shear rate s^{-1}	changes in: fatcontent (%)	d_{32} (μm)	c_s	a
15	Taylor vortices	600	30→4.0	4.0→2.9	0.4→1.3	2→5
20	turbulent flow	765	30→2.9	4.0→2.2	0.4→1.3	2→5

tween fat phase and continuous phase is created, for instance when a mixture of milkfat and skimmilk is emulsified, adsorption of material takes place.

Table 4.4 The influence of homogenisation at very low pressures (3 bar) on coalescence stability of natural cream.
Treatment: 30 minutes flow with Taylor vortices, apparent shear rate 600 s^{-1} temperature 15°C.

	changes in fat content (%)	d_{32} (μm)	c_s	a
not homogenized	30→4	4.0→2.9	0.4→1.3	2→5
30 x homogenized	31→5	3.9→2.6	0.4→1.1	2→3

Table 4.5 The coalescence stability of mixtures from recombined emulsions and natural cream
Treatment: 30 minutes flow with Taylor vortices, apparent shear rate: 600s^{-1}; Temperature 15°C.

weight percentage globules from (%)		d_{32} Rec. emulsion (μm)	d_{32} cream (μm)	change in fatcontent (%)
cream	rec. emulsion			
50	50	5.4	3.4	30→11
20	80	5.4	3.4	31→2
50	50	2.8	3.4	29→25
20	80	2.8	3.4	29→28
10	90	2.8	3.4	27→27
73	27	0.23	3.4	26→22

Mixtures of cream and emulsion made from milk fat and skimmilk were tested in a flowfield with Taylor vortices (table 4.5). If the size of the recombined fat globules is large, say 4 μm, these mixtures are very unstable. They proved even to be more unstable if the proportion of natural cream was quite low, but if the natural cream was completely replaced by recombined emulsion this emulsion hardly gave any coalescence.
For recombined emulsions with smaller fat globules this mixture effect did hardly occur and if d_{32} of the recombined emulsion was very low, a mixture of cream and that emulsion was even more stable than was cream diluted with the same amount of skimmilk.

The influence of natural cream added before homogenisation to the fat-skimmilk mixture on coalescence stability of the resulting emulsion is summarized in table 4.6. If the mixture was homogenized at low pressure, coalescence stability decreased with natural cream content but if the homogenisation pressure was somewhat higher the emulsions were stable again, despite the addition of natural cream.

Table 4.6 The coalescence stability of emulsions made by homogenizing a mixture of natural cream, skimmilk and anhydrous milk fat. Treatment: 30 minutes flow with Taylor vortices, average shear rate 600 s^{-1}; temperature: 15°C

homogenisation pressure (bar)	weight percentage globules originating from		changes in	
	cream (%)	milkfat (%)	fatcontent (%)	d_{32} (μm)
2.5	10	90	28→28	6.0→6.3
2.5	20	80	29→25	5.2→6.8
2.5	30	70	29→12	5.0→8.9
8	10	90	28→28	2.2→2.2
8	20	80	29→28	2.2→2.4

4.2 Correlations with the observations of Labuschagne

Labuschagne (1963) observed that under different conditions different modes of coalescence occur. The type of aggregation depended for a given gap width on the circumferential velocity

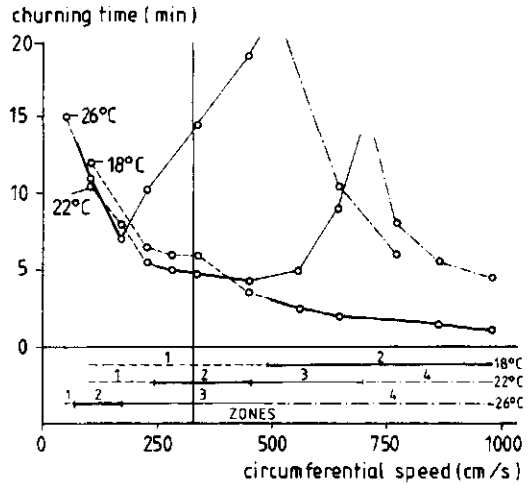

Fig. 4.1 The influence of the temperature on the relative position of similar aggregation characteristics with respect to the speed. (1) Irregular aggregation. (2) Uniform aggregation. (3) Tendency of "mechanical" emulsion. (4) "True" water-in-fat emulsion. (fat 39.8%; Annulus 0.45 cm) (Figure taken from Labuschagne 1963).

of the inner cylinder and the temperature of the cream during treatment. His observations are summarized in fig. 4.1, a reprint of fig. 9 of his thesis.

He descerned four types of aggregation:

1 At low temperatures and low circumferential speeds irregular aggregation occurs; only certain globules participate in aggregation and during the churning proces aggregates are in various stages of formation. Since small aggregates grow more slowly than larger ones do, differences between the aggregates enlarge during the churning proces and butter forms gradually.

2 When circumferential speed or temperature is raised, irregular aggregation is replaced by regular aggregation; all globules participate immediately in aggregation and all aggregates are more or less even sized and grow faster and faster until the proces ends in "instantaneous" butter formation.

3 At still higher temperatures or circumferential speeds Labuschagne observed that the cream had the tendency to form what he called a mechanical emulsion. Due to the weaker bonds between the aggregates (when temperature is raised) or to the larger forces working on the aggregates (when circumferential speed is raised) disruption of aggregates occurs. As a consequence butter formation is seriously retarded or even prevented.

4 At very high speeds the fat-in-water emulsion is converted into a water-in-fat emulsion and no buttermilk is released at all. This is a typical example of a true phase inversion.

We did a few experiments under the same conditions as Labuschagne applied. These experiments were all carried out at one circumferential speed (denoted by the vertical line in fig. 4.1) and at five temperatures, to obtain a better idea of the course of coalescence as a function of temperature. The results are summarized in table 4.7. These results are commented upon and compared with the results found by Labuschagne in table 4.8.

Table 4.7 Coalescence of natural cream in a flowfield with Taylor vortices. Repetition of Labuschagne's experiments.
apparent shear rate: 550 s^{-1}
annulus: 0.55 cm
circumferential speed of inner cilinder: 3 $m.s^{-1}$

temperature (°C)	treatment time (min)	changes in: fat content (%)	d_{32} (μm)	c_s	a
14	5	42→42	3.4→4.7	0.4→0.7	2→3
14	15	42→36	3.4→5.8	0.4→0.7	2→5
18	5	41→10	3.4→7.2	0.4→1.5	2→5
18	15	42→31	3.4→15.9	0.4→1.3	2→3
18	15	41→23	3.4→12.0	0.4→1.3	2→3
22	5	42→40	3.4→14.1	0.4→1.2	2→2
22	15	38→ 6	3.4→5.0	0.4→1.3	2→2
26	5	40→41	3.4→8.1	0.4→0.6	2→1
26	15	40→42	3.4→12.0	0.4→1.2	2→2
30	5	40→41	3.4→5.6	0.4→1.0	2→3
30	15	41→42	3.4→6.0	0.4→0.8	2→3

Table 4.8 A comparison between the present results and those obtained by Labuschagne

Temp.	Description of our results	Description of Labuschagne
14°C	Size distribution gradually wider d_{32} increases slightly Hardly any decrease in fat content	Irregular aggregation Long churning time
18°C	Increase in d_{32} Widening of size distribution Decrease in fat content Results are poorly reproducible.	Irregular aggregation short churning time
22°C	After a short time: increase of d_{32} After a longer time: decrease of fat content Widening of size distribution	Uniform aggregation short churning time
26°C	d_{32} increases strongly The width of the size distribution increase only slightly No decreases in fat content (at least within 15 minutes)	A mechanical emulsion A rather long churning time
30°C	d_{32} increases only slightly. Hardly any change in distribution width. No decrease in fat content.	A mechanical emulsion A very long churning time

From table 4.8 a few conclusions may be drawn:

- The observation of Labuschagne that in the case of irregular aggregation only certain globules start to aggregate and at all stages during the churning proces the variations between the aggregates are considerable is reflected in the formation of wide globule size distributions with long tails.
- The observation that in the case of uniform aggregation all globules are involved in the aggregation and the aggregates are more evenly sized is reflected in a gradual increase of d_{32} while the shape of the size distributions (if the diameter is plotted on a logarithmic scale) changes less than at irregular aggregation.
- The observation that butter formation is "instantaneous" in case of uniform aggregation is reflected in a sudden decrease

in fat content between 5 and 15 minutes when the emulsion is treated at 22°C.

- Labuschagne observed that in the case of formation of a so called mechanical emulsion aggregation was initially rapid and involved all globules but somehow stopped before butter was formed. This is reflected in our observation of a large increase in d_{32} during the first 5 min followed by a further but slower increase during the next 10 min while the fat content remained at the original level. Presumably, any larger aggregates formed are broken up again in the flow field. At 30°C the same trend is seen, but less pronounced.

4.3 Discussion

Natural cream is far less stable against coalescence than is recombined cream made of milk fat and skimmilk, provided that the globule size distribution is similar.
Mixtures of natural cream and milk fat-in-skimmilk emulsions are under certain conditions very unstable which makes it possible to regain some of the instability properties of milk. By adding a small proportion of natural cream to a recombined emulsion, the mixture can be made churnable, which may imply that a butter with a texture similar to that of natural butter but with an adjustable solid fat content can be obtained. Emulsions made of milk fat and skimmilk are presumably stable because they contain no globules unstable enough to start partial coalescence. If natural fat globules are added, these coalesce, thus giving clumps. These clumps appear to be capable to coalesce with the recombined fat globules. The same process may occur after inclusion of minor portions of air, that can have a considerable effect on the stability of milk fat-in-skimmilk emulsions, certainly if d_{32} is fairly large. A few clumps, originating from globules coalescing after adsorption onto the air-plasma interface, then initiate further coalescence. If the droplet sizes are small, such an induction of coalescence apparently does not occur.

Additional information is obtained about the behaviour of natural cream after homogenizing. If homogenizing pressure is too low to cause disruption of the fat droplets, adsorption of plasma proteins does not occur, at least the stability of the globules remains unaltered. This means that, even in a turbulent flow field, no significant loss of original membrane material occurs. In other words, it is much more difficult to damage the natural membrane than often is assumed, unless air is incorporated.

Treatment conditions not only determine coalescence rate but also the course of coalescence, which varies between a rapid change in globule size distribution while the fat content remains constant and a rapid decrease in fat content while the shape of the distribution hardly alters: Partial coalescence in this kind of emulsions apparently does not fit first or second order kinetics, as van den Tempel (1953, 1957) applied to emulsions without crystals in the disperse phase. There may be several reasons for this discrepancy: due to elongational flow occuring locally in a flow field with Taylor vortices, disruption of weak aggregates may occur, as Labuschagne already pointed out. But also differences in globule size and crystal habit may cause, under certain circumstances, large differences in reactivity of the droplets, resulting in an irregular aggregation.

5 THE EFFECT OF PHOSPHOLIPIDS ON THE STABILITY OF RECOMBINED EMULSIONS

5.1 Emulsions of buttermilk and milk fat

Buttermilk and skimmilk differ in their phospholipid content, which is in buttermilk much higher than in skimmilk, especially if the cream from which the buttermilk is obtained had a high fat content. If these phospholipids (often called lecithins) would adsorb onto the fat-plasma interface during or after recombination with milk fat, the properties of the resulting fat globules would be influenced and the stability of milk fat-in-skimmilk emulsions would differ from that of milk fat-in-buttermilk emulsions. We therefore carried out two depletion experiments, as described in 2.5, to see whether adsorption of phospholipids occurs during or after emulsifying.

Table 5.1 The adsorption of phospholipids on plasma-fat interfaces during or after emulsification of mixtures of milk fat and buttermilk.

Fat content original natural cream:	~ 30%	~ 60%
pretreatment of cream before churning:	5 min 80°C	30 min 55°C
fat content of buttermilk:	0.29%	0.61%
phospholipid content of buttermilk plasma:	0.041 ± 0.002%	0.140 ± 0.004%
fat content of recombined emulsion:	28.4%	26.2%
d_{32} of recombined emulsion:	4.5 μm	3.1 μm
- skimming immediately after preparing emulsion		
fat content after skimming:	1.36%	2.09%
fraction of milk fat removed:	96%	94%
phospholipid content after skimming:	0.041 ± 0.001%	0.141 ± 0.006%
- skimming after storage for one day at 2°C		
fat content after skimming:	-	2.29%
fraction of milk fat removed:	-	93%
phospholipid content after skimming:	-	0.138 ± 0.003%

The results, summarized in table 5.1, clearly show that the phospholipid content of the skimmed milk fat-in-buttermilk emulsion equals that of the original buttermilk. In other words: removal of about 95% of the fat globules immediately after

emulsifying or after storage for one day at 2°C did not significantly change the amount of phospholipids in the plasma. Consequently, adsorption of phospholipids from the buttermilk on the fat-plasma interface must be negligible (at most 0.05 $mg.m^{-2}$). Emulsions made of buttermilk and milk fat were, as was thus to be expected, just as stable as emulsions made of skimmilk and milk fat. Only emulsions with large droplets and a high fat content showed some coalescence on creaming and in flows with (locally) high shear rates (Table 5.2).

Table 5.2 The coalescence stability of emulsions made of buttermilk and milk fat
Homogenisation temperature: 50°C

Continuous phase	pretreatment cream before churning	treatment	time	temperature (°C)	changes in: fatcontent (%)	changes in: d_{32} (μm)
Buttermilk	5'80°C	at Rest	8 days	2	32→29	5.4→5.2
Buttermilk	5'80°C	at Rest	8 days	15	32→28	5.4→5.4
Solution of buttermilk powder	-	Taylor 600 s^{-1}	30 min	15	35→35	3.9→3.9
Buttermilk	5'80°C	Taylor 600 s^{-1}	30 min	15	32→31	5.4→5.6
Buttermilk	30'55°C	Taylor 600 s^{-1}	30 min	15	27→26	3.1→3.1
Buttermilk	5'80°C	Turbulent 785 s^{-1}	30 min	20	32→26	5.4→5.0

Koops (1967) found that the heat stability of natural cream increased more due to dilution of the cream with buttermilk than with skimmilk before homogenizing. He ascribed the increased heat stability to the adsorbtion of phospholipids, protecting the globules against clustering when the emulsion is heated. From our experiments we cannot completely exclude adsorption of phospholipids when, as a consequence of high homogenisation pressure and fat content, the created plasma-fat interface is so large that the amount of protein is insufficient to cover it, because in the two described experiments homogenisation pressure and fat content were such that the amount of protein was amply

sufficient to cover the interface.
Other authors (Hardy et al. 1985), however, found that added soya-lecithin improved the heat stability of natural cream whether it was homogenized or not, or whether the soya-lecithine was added before or after the homogenisation step. From these results the authors derived that phospholipids do not adsorb during the homogenisation process, but they could not exclude the possibility of a displacement of the adsorbed proteins by the phospholipids after the homogenisation. However, this proces is unlikely since we found no adsorption of phospholipids after a night storage of emulsions made from milk fat and skimmilk. Phospholipids may without being adsorbed in the fat-plasma interface also influence the formation of complexes between κ-casein and β-lactoglobulin (Korver & Meder 1974), a formation that plays an important role in the destabilisation of homogenized concentrated milk (Sweetsur & Muir, 1983). Phospholipids in buttermilk, although partly associated with lipoproteins, may act similar as added phospholipids. The suggestion of Hardy et al. (1985) that the stabilizing effect of added phospholipids is associated with above mentioned interaction, therefore ties in better with the present results. Other differences between skimmilk and buttermilk, e.g. the higher copper content of buttermilk, cannot be excluded as possible causes.

5.2 The influence of lecithin, dissolved in milk fat before emulsifying, on the stability of milk fat-in-skimmilk emulsions

Milk fat, to which several types of phospholipids were added, was stirred for at least one hour at about 60°C to dissolve or disperse the phospholipids. The selected egg lecithin (Merck art. 5331) was not dispersable at all and gave a tough sediment even after one hour stirring. The soya lecithins Bolex (a paste) and Du Lectin van Schuppen (a powder) dissolved, but gave at a concentration of 0.7% a turbid fat; 0.23% Bolex gave a clear solution. Emulsions were made with skimmilk as described in 2.1.

Table 5.3 The influence of added lecithine on coalescence stability of emulsions made from skimmilk and milk fat.
Pretreatment skimmilk: 10 min 65°C
Homogenisation temperature: 60°C
Treatment: Leaving at rest during 2 days
100 ppm thiomersal added.

Additions to milkfat	tempe-rature (°C)	changes in: fatcontent (%)	d_{32} (μm)	c_s	a
0.7% Bolex	20	31→31	2.3→2.3	0.6→0.6	1→1
0.7% Bolex	14	31→31	2.3→2.3	0.6→0.6	1→1
0.7% Merck	20	29→29	3.2→3.2	0.5→0.6	1→1
0.7% Merck	14	29→29	3.2→3.2	0.5→0.6	1→1
0.23% Bolex	20	31→31	1.6→1.6	0.5→0.6	1→1
0.23% Bolex	14	31→31	1.6→1.6	0.5→0.6	1→1
0.7% Lectin	20	30→29	2.2→2.2	0.6→0.6	1→1
0.7% Lectin	14	30→29	2.2→2.2	0.6→0.6	1→1
0.7% Lectin	2*	30→30	2.2→3.3	0.6→1.0	1→5

Bolex = Soya lecithin (paste)
Lectin = Du Lectin - v. Schuppen = Soya Lecithin (powder)
Merck = Egg-Lecithin
* Stored while rotating

All emulsions proved to be stable when they were left at rest for two days at 14°C and 20°C (table 5.3).
The emulsions with 0.7% soya lecithin (containing 0.35% phospholipids when the paste was used and 0.65% phospholipids when the powder was used) were very unstable in a flow field with Taylor vortices and coalesced almost completely, resulting in a sharp decrease in fat content (table 5.4), but an emulsion with 0.23% soya lecithin in the fat phase (corresponding to 0.12% phospholipids) was fully stable under the same circumstances. The emulsion with 0.7% powdered soya lecithin also coalesced when kept from creaming by rotation during one night at 2°C; under these circumstances coalescence resulted in a marked increase of d_{32} (see table 5.3). The fat with the undispersable egg lecithin gave, as expected, emulsions that were stable in a flow with Taylor vortices.
Emulsions made of skimmilk and milk fat can thus be made very sensitive to coalescence by adding phospholipids to the milk fat

Table 5.4 The influence of added lecithine on coalescence stability of emulsions made from skimmilk and milk fat.
Treatment: 30 min Taylor vortices
apparent shear rate: 550 s^{-1}, temperature 15°C
pretreatment skimmilk: 10 min 65°C
homogenisation temperature: 60°C

additions to milk fat	changes in:			
	fatcontent (%)	d_{32} (μm)	c_s	a
0.7% Bolex	31→3	2.3→I.T.D.	0.6→I.T.D.	1→I.T.D.
0.7% Merck	29→26	3.2→3.4	0.5→0.7	1→1
0.23% Bolex	31→31	1.6→1.6	0.5→0.5	1→1
0.7% Lectin	30→2	2.2→I.T.D.	0.6→I.T.D.	1→I.T.D.

I.T.D. = impossible to determine

prior to emulsifying. The phospholipid content has to exceed a certain level, lying between 0.12% and 0.35%, that might well correspond with the transition from clear to turbid fat.

5.3 Obtaining anhydrous milk fat containing milk phospholipids

Since phospholipids above a certain concentration in the fat phase markedly change the stability properties of a milk fat-in-skimmilk emulsion, while an emulsion of milk fat-in-buttermilk is just as stable as one of milk fat in skimmilk, it may be worthwhile to treat natural cream in such a manner that the phospholipids remain in the fat. A cream with 30% fat contains enough phospholipids to give, if all the phospholipids would dissolve in the fat phase during separation, an anhydrous milk fat containing 0.6% phospholipids, which would be more than enough to destabilize an emulsion made of skimmilk and this milk fat.

It was tried to obtain a phospholipid containing milk fat in the following way: 3 l of cream with 30% fat was washed twice at 40°C with 10 l of a weak NaCl solution with a ionic strength equal to that of milk and heated for 10 min at 70°C to inactivate lipase. (This procedure minimizes the loss of phospholipids as the membrane proteins containing the lion's share of the

phospholipids remain in the cream while the plasma proteins are washed away (Anderson et al 1972)). The washed cream was condensed at 55°C under reduced pressure. After two hours all water had evaporated and the emulsion was broken. The fat contained coagulated protein particles. The larger part of this flocculated material was removed by filtering the fat through a cheese cloth. The remainder was removed by heating the fat to 80°C and filtering it through a coarse paper filter. The resulting fat was completely clear but appeared to contain hardly any phospholipids: 0.015% ± 0.002%, i.e. at most 5% of the phospholipids present in the cream. Such a result was already in 1947 predicted by Mulder but quite opposite to the results obtained by Solms zu Baruch (1975). An emulsion made from this milk fat and skimmilk was, as was to be expected, almost completely stable in a flow field with Taylor vortices.

Others (Timmen, 1967) tried to separate a phospholipid containing anhydrous milk fat from butter. When butter is dried a product results with a content of phospholipids ranging from 0.14% to 0.17%. A large part of the phospholipids has then already been removed with the buttermilk. But when the fat is filtered to separate the protein, the remainder of the phospholipids is also lost and a clear fat remains with a phospholipid content of only 0.010% (Timmen, 1967). So in both cases the phospholipids were removed together with the proteins.

Dobers (1969), who tried to release the phospholipids from the proteins, found that in dried butter or ghee that is heated for a fairly long time at temperatures far above 100°C, proteins are removable without complete loss of phospholipids. A heating time of e.g. 60 min at 120°C increased the phospholipid content of clarified milk fat from 0.03% to 0.13%. Also the experiments of Pruthi (1979) clearly showed a proportional relation between the phospholipid content of anhydrous milk fat and the intensity of the heat treatment of the ghee. To prevent undesirable reactions during heating such as Maillard reactions, Dobers replaced the severe heat treatment by a milder one (1 hour at 90°C) whilst adding 4% potassium hydrogen phosphate to the aqueous

phase. This treatment resulted in the same rise of phospholipid content. These phospholipid contents probably are still too low to give, after recombination with skimmilk, emulsions that would coalesce in a flow field with Taylor vortices, but if the procedure described by Dobers is as effective for cream as it is for butter, an anhydrous milk fat containing about 0.3% phospholipids could be obtained from cream. This level should be high enough to influence coalescence stability of the recombined emulsions. Due to lack of time this procedure was not tried for cream.

6 STABILITY OF EMULSIONS OF MILK FAT AND CLARIFIED WHEY

6.1 Differences between sweet cheese whey, acid casein whey and clarified whey

When milk is curdled with rennet or acidified the casein flocculates into a gel entrapping the fat globules. After formation of a gel (called curd), this network starts to shrink expelling liquid. This proces is called syneresis, the hazy yellow liquid that is expelled sweet cheese whey and acid casein whey, respectively.
Sweet cheese whey and acid casein whey both contain lactose (5%), some milk fat (~ 0.3%) protein (~ 0.7%, comprising 0.3% β-lactoglobulin, 0.15% α-lactalbumin, 0.04% serum albumin and 0.10% immunoglobulins) and some small curd particles, disrupted from the gel during separation of gel and liquid. Both contain proteose pepton, a part of the casein that remains soluble at low pH values, and calcium, magnesium and phosphate ions, but acid casein whey contains more of these compounds. Only sweet cheese whey contains whey proteose, a splitting product of κ-casein. If whey is demineralized and subsequently adjusted to a pH of about 4.6, a flocculent material is formed that slowly precipitates. These floccules contain the casein particles, the fat globules and most of the immunoglobulins. After removal a transparent yellow solution results, the so called clarified whey, that still contains most of the whey proteins and lactose (De Wit et al, 1978).
After evaporation and drying of this solution a yellow, easily dispersable and fully soluble fine powder results, that contains 12.5% whey protein, the so called clarified whey protein CWP.

6.2 The adsorption behaviour of whey proteins

6.2.1 The amount of adsorbed protein

The amount of protein adsorbed onto fat globules from a solution

of clarified whey powder was estimated by Walstra & Oortwijn (1979) as a function of fat and protein contents. They showed by means of depletion experiments that the average surface load of these emulsion droplets made at a given homogenisation pressure and temperature only depended on the ratio of fat to protein and hardly or not on their absolute values.
They concluded that the relation between surface load and the fat-protein ratio can be expressed for emulsions with d_{32} = 0.9 μm and Γ > 0.5 mg/m² as:

$$\Gamma = -0.4 + 1.5 \log x \qquad \text{(Eq. 6.1)}$$

where x = protein /fat ratio (mg/ml) and Γ = surface load (mg/m²)

The influence of homogenisation pressure was not studied by them.

Table 6.1 The influence of C.W.P. content and homogenisation pressure on the stability of milk fat-and-whey emulsions. fat content: 33%, homogenisation temperature: 50°C.

	CWP content (kg.m^{-3})	5		15		20		25		40		70	
	x	1.2		3.6		4.8		6.0		9.6		16.8	
P_{hom}	d_{32}	Γ		Γ		Γ		Γ		Γ		Γ	
0.4	3.1	0.5	N	1.2	S	1.4	S	1.6	S	1.9	S	2.2	S
1.0	1.5	<0.5	N	0.8	N	1.0	S	1.1	S	1.4	S	1.8	S
2.0	1.1	<0.5	N	0.6	N	0.7	N	0.8	N	1.3	S	1.6	S
5	0.6	<0.5	N	<0.5	N	<0.5	N	0.5	N	-	-	1.2	S
7	0.5	<0.5	N	<0.5	N	<0.5	N	<0.5	N	-	-	-	-
17	0.3	<0.5	N	<0.5	N	<0.5	N	<0.5	N	-	-	0.7	C

x = protein/fat ratio (mg/ml)
Γ = surface load (mg/m²), calculated with Eq. 6.4
N = not stable at rest
S = stable at rest
C = clustered
- = not determined
P_{Hom} = homogenisation pressure (MPa)

In testing the influence of the protein/fat ratio on the coalescence stability, emulsions were made at various homogenisation pressures with various protein/fat ratios. Some of these emulsions were stable while others broke within half an hour,

giving a floating layer of oil. A survey of these results is given in table 6.1; d_{32} and the protein/fat ratio are also given. d_{32} of the stable emulsions was determined with spectro turbidimetry. d_{32} of the unstable emulsions was calculated from the equation: $\log d_{32} = -0.63 \log P + 0.87$ (see 2.1). Neither the globule size nor the protein/fat ratio determined the stability: the combination appeared decisive.

The most obvious reason for instability to occur is an insufficient surface load. To prevent rapid coalescence, the plasma-fat interface created during emulsification ought to be fully covered with whey proteins which agrees with a surface load of about 1 mg/m² (Bull 1947). The surface load of polymer stabilized emulsions as a function of polymer/disperse phase ratio has been frequently studied (Lankveld & Lyklema 1972, Böhm & Lyklema 1976, Tornberg 1980). Their results can be summarized (Walstra 1980) in the equation

$$\Gamma = C_1 \log (p/a_{sp}) + C_2 \qquad \text{(Eq. 6.2)}$$

where Γ = surface load ($mg.m^{-2}$)
p = polymer concentration ($mg.m^{-3}$)
a_{sp} = specific surface area of disperse phase (m^{-1})
c_1 and c_2 are constants

This formula can be rewritten in terms of polymer/disperse phase ratio, in this case the protein/fat ratio x (mg/ml), and d_{32} (μm).

$$\Gamma = C_1 \log (xd_{32}) + C_3 \qquad \text{(Eq. 6.3)}$$

The constants C_1 and C_3 can be derived from the formula obtained by Walstra & Oortwijn (Eq. 6.1), resulting in a more general formula for emulsions of milk fat and clarified whey.

$$\Gamma = 1.5 \log(xd_{32}) - 0.33 \qquad \text{(Eq. 6.4)}$$

The values of Γ, calculated with this equation, are also quoted in table 6.1. If the critical value of Γ for coalescence stability is assumed to be 1 mg/m², both results match precisely.

Consequently, this approximate formula is not conflicting with the results. A more exact relation between surface load, homogenisation pressure and protein/fat ratio is to be established only by means of painstaking depletion experiments.

If a mixture of clarified whey and milk fat is homogenized at a high pressure (20 MPa) and the value of Γ calculated with Eq. 6.4 lies below 1 mg/m^2 not an unstable emulsion but a thick paste is obtained. This paste appeared to be a highly clustered emulsion. Based on the experiences of Ogden et al (1976) this clustering is unexpected in two respects:

- Ogden et al only observed clustering if homogenizing mixtures of milk fat and skimmilk with too low a protein concentration, but never in systems of milk fat and clarified whey. Based on these experiments they even defined casein as "shareable" and the whey proteins as "unshareable".
- In systems of milk fat and skimmilk Ogden et al found that a shortage of protein always led to clustering irrespective of homogenisation pressure, while we found that with mixtures of milk fat and clarified whey a shortage of protein led to unstable emulsions at low homogenisation pressures and to a clustered paste only at high pressures.

Contrary Ogden et al, we always made the emulsions by continuously homogenizing the mixture for a fairly long time. Possibly, clustering is a consequence of this procedure. Since this phenomenon falls outside the scope of this study, it was not examined further.

6.2.2 The composition of the surface layer

The adsorption behaviour of the proteins of sweet whey on coconut oil was studied by Shimuzu et al (1981) as a function of the pH of the mixture before homogenizing. Their results are summarized in table 6.2. Two remarks have to be made:

- They used coconut oil in stead of milk fat. These two fats may have a slighly different interfacial tension in a whey solution resulting in a different behaviour of the adsorbed

protein.

- After homogenisation they washed the emulsion with water, which may have led to removal of low molecular weight proteins, since these are reversibly adsorbed onto the interface (McRitchie 1977).

Despite these differences, table 6.2, which is a summary of their results, may give some indication of the composition of the surface layers in emulsions of milk fat in clarified whey. Surface load and composition appeared to vary strongly with the pH. At pH = 5 the found surface load was more than twice that at the other pH's. Yet these emulsions appeared to be far less stable at pH = 5 than at any other pH. Consequently, a high surface load is not always a guarantee for a stable emulsion. Shimuzu et al tried to find a correlation between the properties of the various proteins as function of pH and their abundance in the surface layer, but they did not find any relation between the average hydrophobicity or the surface hydrophobicity of a protein and its abundance in the surface layer.

Table 6.2 The composition of whey adsorbed on the fat-serum interface during homogenizing a mixture of milk fat and whey, as a function of the pH of the whey. (Experimental values taken from Shimuzu et al 1981)
protein/fat ratio: 2.5 mg/ml
homogenisation temperature: 50°C

pH	3	5	7	9
d_{32} (μm)	4.0	4.4	4.1	4.0
Γ(exp) (mg/m^2)	2.3	7.6	3.0	2.8
Γ(calc)*	-	-	3.2	-
α-lactalbumin (%)	48.3	24.4	11.0	9.9
β-lactoglobulin (%)	12.9	16.6	46.1	61.6
Casein + Immunoglobulins (%)	34.1	40.0	31.3	20.1
Serumalbumin (%)	1.0	10.6	2.7	1.0
Transferrin and lactoferrin (%)	3.7	8.4	8.9	7.4

* calculated with equation 6.4

However, there appears to be some correlation between the abundance of a protein in the surface layer and its association behaviour. At pH = 5 the surface load was more than twice as

high as at the other pH's. At this pH β-lactoglobulin occurs in small aggregates, α-lactalbumin is rather insoluble and so is any casein present.
In table 6.2 is seen that at other pH the total surface load was more or less constant, but composition of the surface layer was still variable.
At pH = 3 the surface layer contained mainly α-lactalbumin, while at other pH its relative abundance was far smaller. This protein forms at pH below 4 small aggregates, while it is non associated and soluble above pH = 5.5.
At pH = 9 the surface layer consisted mainly of β-lactoglobulin which aggregates at pH values around 9 and is completely soluble at the other pH values, except between pH 4 and 5.
At pH = 3, 5 and 7 roughly 30% of the surface layer consisted of remnants of the paracasein gel, at pH = 9 its value was less than 20%. At the same pH these paracasein gel particles dissolve. (Data about the behaviour of various proteins as function of pH were taken from R.L.J. Lyster 1972.)
These phenomena would support the idea that the quantity of a certain protein in the surface layer not only depends on its relative concentration but also on its state of dispersion: single molecules, small or large aggregates. Although washing of the globules after homogenisation can lead to a partial desorption of protein molecules (McRitchie 1977) and therefore to a higher relative content of aggregates, it is also possible that large aggregates are preferentially adsorbed over small ones. Walstra & Oortwijn (1982) showed that larger particles are preferentially adsorbed if the adsorption is determined by the transport rate of the proteins to the fat globule and if the flow is turbulent, which is always the case inside a homogenisation valve. However, clear effects are only to be expected if the size of these aggregates is of the same order of magnitude as that of the fat globules.

If this idea is correct, it means that the composition of the surface layer in an emulsion which is acidified after homogenisation, differs from that in an emulsion acidified before homo-

genisation. Since the coalescence stability seemed to be largely independent of the moment of acidifying (de Wit et al, 1976), not the composition of the surface layer is decisive for its stability but other properties that immediately modify with the pH.

6.3 *The course of the coalescence process*

If the emulsions were treated at temperatures between 2°C and 10°C partial coalescence always occurred in a very definite way, resulting in the formation of only a few, very large clumps. On heating these treated emulsions to above 40°C, the clumps melted and coalesced further into large fat droplets, creaming within a few minutes to form a layer of oil on top of the emulsion. The remaining emulsion thus had a reduced fat content. At small reductions of the fat content, by at most 30% of the original value, the size distribution of the remaining fat droplets was nearly the same as that of the original emulsion. A larger reduction led to a decrease in d_{32}, while c_s increased somewhat. Examples of the modification of the size distribution due to partial coalescence are given in fig. 6.1 to 6.4.

The influence of fat content on the stability of the emulsion is given in fig. 6.1 for an initial size distribution with d_{32} = 3.2 μm and in fig. 6.2 for d_{32} = 5.5 μm. The fat contents of the remaining emulsions were multiplied with the dilution factor to facilitate comparison of the various emulsions. It is seen that an emulsion with d_{32} = 3.2 μm and a fat content of 6.1% was almost stable, while an emulsion with the same size distribution but a fat content of 18.4% was fairly unstable in a flow with Taylor vortices. Also the average droplet size had a large influence. At the same fat content an emulsion with d_{32} = 3.2 μm was much more stable than one with d_{32} = 5.5 μm. In fig. 6.3 the influence of droplet size is also clearly demonstrated. These figures show that the way in which coalescence proceeds is quite different from what is normally expected and e.g. observed by Van Boekel (1980). Not a gradual increase of

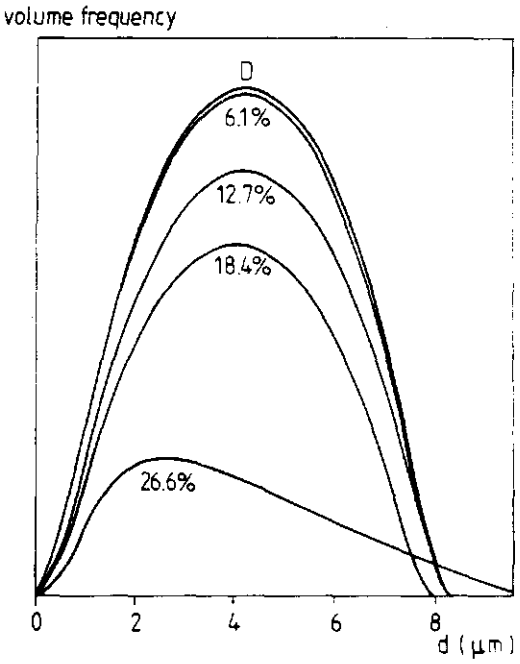

Fig. 6.1 The influence of the initial fat content on the globule size distribution, after treatment. (the frequencies are multiplied with the dilution factor so that the size distributions of the original emulsions (D) coincide).
Emulsion: milk fat in clarified whey, d_{32} = 3.2 μm
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min.

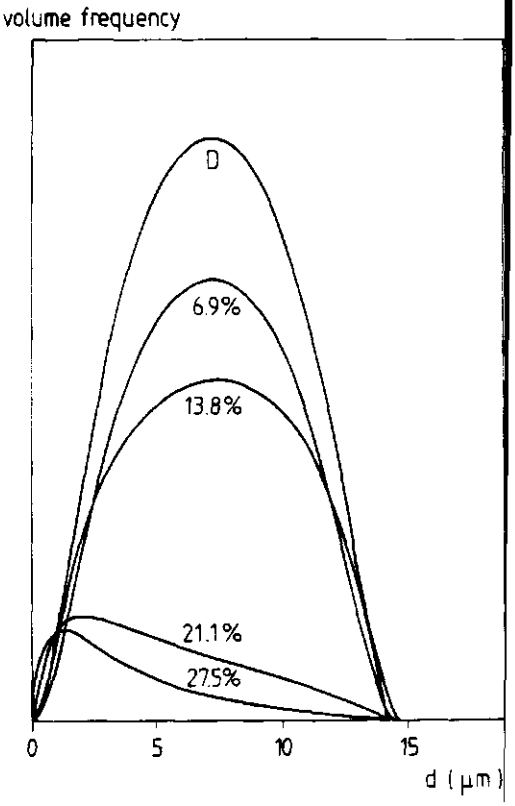

Fig. 6.2 The influence of the initial fat content on the globule size distribution after treatment. The frequencies are multiplied with the dilution factor so that the size distributions of the original emulsions (D) coincide.
Emulsion: milk fat in clarified whey, d_{32} = 5.5 μm
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min.

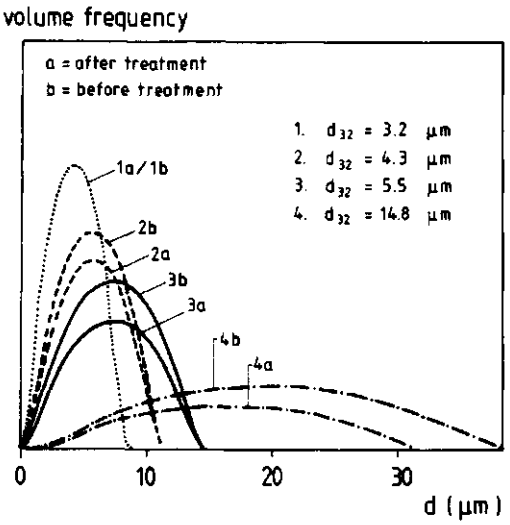

Fig. 6.3 Influence of initial d_{32} on the globule size distribution of emulsions of milk fat and CWP after treatment in a flow with Taylor vortices.
treatment: Taylor vortices
T = 10°C, G = 550 s^{-1}, t = 20 min
initial fat content: 7%

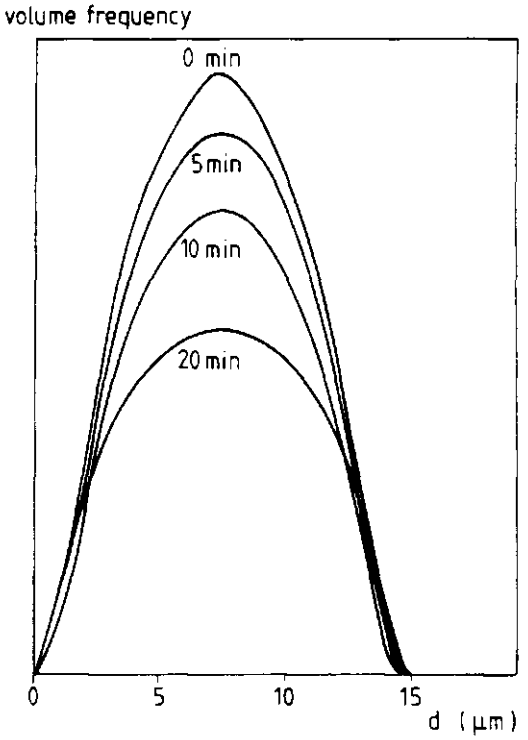

Fig. 6.4 Influence of treatment time on the globule size distribution.
Emulsion: milkfat in clarified whey, d_{32} = 5.5 µm, fat content 13.8%
Treatment: flow with Taylor vortices, T = 10°C, G = 550 s^{-1}

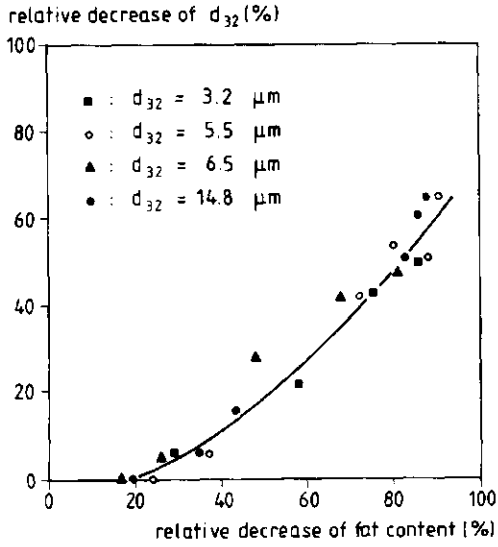

Fig. 6.5 The relation between the relative decrease of d_{32} and the relative decrease of the fat content during partial coalescence of emulsions of milk fat in CWP.

Table 6.3 The influence of treatment temperatures on the relation between the relative decrease in fat content and the relative decrease in d_{32}. Emulsions of milk fat in CWP.

treatment	treatment temp (°C)	change in fatcontent (%)	relative change	change in d_{32} (µm)	relative change observed	relative change expected
turbulence	15	26.2→24.1	- 8%	3.2→3.4	+ 7%	0%
turbulence	15	26.2→2.7	-90%	3.2→1.0	-70%	-65%
creaming	20	27.7→12.4	-55%	14.8→9.2	-38%	-25%
creaming	7	27.7→4.0	-86%	14.8→5.7	-61%	-55%
creaming	2	27.7→3.3	-88%	14.8→5.2	-65%	-64%

a) on the basis of figure 6.5

the average droplet size, but a size distribution that hardly alters while fat content is reduced. This is also shown in fig. 6.4. During the first 20 minutes only fat content changed, after a longer time a gradual modification of the distribution occurred.

The relative decrease in d_{32} turned out to be directly rela-

ted to the relative reduction in fat content. This relation appeared to be independent of the original average diameter of the emulsion (see fig. 6.5).

The influence of the shape of the original size distribution was not investigated but is probably not large except for very broad size distributions. The influence of temperature during treatment was not systematically studied. A few experiments are summarized in table 6.3. They suggest that the influence on the way of coalescence is at most slight; if no crystals were present, no coalescence occurred, as is to be expected.

Only emulsions that were also unstable at temperatures in which all the fat crystals are melted, such as those that were acidified to a pH between 4 and 6 or those with too low a protein content, coalesced in a different manner. Because of the specific way in which coalescence in all other cases proceeded, sufficient information about the coalescence stability of an emulsion during a certain treatment is given by the relative change in fat content. To facilitate comparisons between emulsions, the relative change in fat content is used to characterize coalescence instability.

6.4 Coalescence stability

6.4.1 Stability during storage

All emulsions were stored in slowly rotating flasks to prevent creaming and subsequently coalescence. The emulsions remained stable for at least one week when stored in this way at 2°C, except in the following cases:

- The pH of the emulsions was between 4 and 6.
  An emulsion of pH = 5.6 stored for one day exhibited a significant increase in d_{32}, while fat content remained the same, and an emulsion with pH = 4.8 broke completely after one night's storage.
- The emulsion contained very large globules.
  Emulsions with $d_{32} > 10$ μm exhibited coalescence, resulting

Tabel 6.4 Partial coalescence of emulsions of clarified whey and milk fat during storage at rest.

storage temperature (°C)	fat content original emulsion (%)	fat content remaining emulsion (%)
storage time: 7 days, d_{32} = 14.8 µm		
2	27.7	3.3
7	27.7	4.0
20	27.7	12.4
storage time: 3 days, d_{32} = 5.5 µm		
2	27.9	27.0
14	27.9	27.4
20	27.9	26.8
storage time: 6 days, d_{32} = 4.3 µm		
2	28.7	25.7
7	28.7	27.3
20	28.7	28.7
storage time: 7 days, d_{32} = 3.7 µm		
2	27.9	27.0
14	27.9	27.4
20	27.9	26.8

in a decrease of fat content while globule size distribution remained the same.

- The estimated protein load was below 1 $mg.m^{-2}$
  Usually this type of emulsion brok within half an hour (see 6.2.1), but emulsions with small globules (< 1 µm) and protein loads just below 1 $mg.m^{-2}$ only after one night's stor-

age.
In all other cases no coalescence took place during storage.

6.4.2 Stability upon creaming

Emulsions of milk fat and clarified whey were fairly stable upon creaming, except in the cases outlined in the previous section. For the other emulsions studied, coalescence was at most 11% and larger as globule size was larger, storage time was longer and storage temperature was lower (see table 6.4).
Only if coalescence occurred in the cream layer a tough cream layer resulted; otherwise the cream layer remained fully liquid, unlike the cream layers on emulsions of skimmilk and milk fat.

6.4.3 Stability in a flow field with Taylor vortices

In these experiments treatment temperature, treatment time, fat content, globule size, protein/fat ratio, pH and pretreatment of the emulsion were varied.

At temperatures above the melting point of fat (40°C) emulsions of this type were stable in this flow field, provided that surface load was above 1 $mg.m^{-2}$ and pH was not between 4 and 5.5. At 25°C an emulsion with 30% fat and d_{32} = 3.2 μm gave after 20 minutes hardly any coalescence but at treatment temperatures between 5°C and 25°C more coalescence occurred if the temperature was lower (fig. 6.6).
Not only with regard to the course of coalescence but also with regard to the temperature at which coalescence stability was minimal in a flow field, this type of emulsions differed thus clearly from natural cream which is most unstable at temperatures around 20°C (Mulder & Walstra, 1974).
As coalescence was most pronounced at temperatures around 10°C, most experiments with Taylor vortices were carried out at 10°C.

Partial coalescence, expressed as the relative decrease in fat content, was almost proportional with treatment time (fig. 6.7).

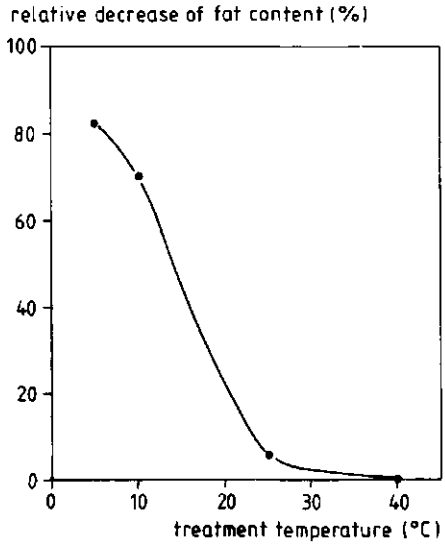

Fig. 6.6 The influence of treatment temperature on the extent of partial coalescence
Emulsion: milkfat in clarified whey, d_{32} = 3.2 µm, fat content: 28%
Treatment: flow with Taylor vortices, G = 550 s^{-1}, time: 20 min.

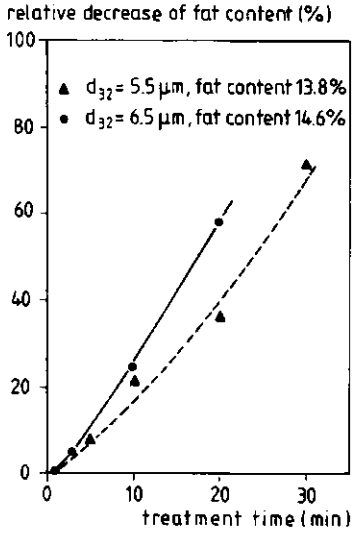

Fig. 6.7 The influence of treatment time on the extent of partial coalescence.
Emulsion: milk fat in clarified whey.
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C

Deviations from linearity may certainly occur near the end of the coalescence process, when most of the fat globules have already clumped. Yet it is obvious from these results and the almost fixed relation between the change in fat content and the change in globule size, that these emulsions do not suddenly break when the clump size has reached a critical value. The treatment time was arbitrarily set at 20 min in the other experiments. In some cases partial coalescence had proceeded to such an extent that the decrease in fat content was no longer linear with time.

The influence of fat content on coalescence stability was studied with emulsions of different globule size. Variations in fat content were obtained by diluting a concentrated emulsion (30% fat) with the same aqueous solution as that used for making the emulsion. In this way variation in surface load due to a modification of the fat/protein ratio or due to desorption of protein afterwards (which may occur if the emulsion is diluted in water) is minimal. So within one concentration series, surface load and globule size distribution were equal.

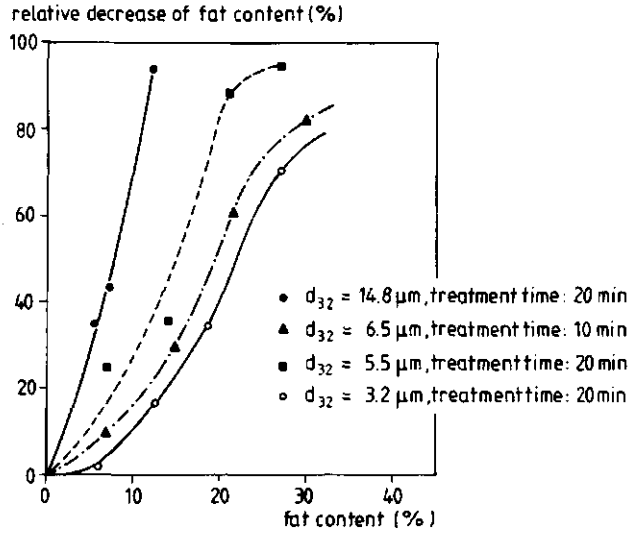

Fig. 6.8 The influence of the fat content on partial coalescence.
Emulsions: milkfat in clarified whey
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C

As the surface load of the globules not only depends on the fat/protein ratio but also on the diameter of the globules (see Eq. 6.4) and the fat/protein ratio was kept constant in this series of experiments (except for one case described below), surface load varied with globule size. Hence, emulsions with a different globule size also had a different surface load. In most cases coalescence rate was more than proportional to the fat content (see fig. 6.8), but emulsions made by diluting a 30% emulsion of milk fat and a solution of 30 $g.dm^{-3}$ C.W.P. (instead of 70 $g.dm^{-3}$) in demineralized water (instead of tap water) were unstable at fat contents just below 30% and stable at fat contents above 30% (fig. 6.9). Such anomalous behaviour, that we cannot explain yet was also observed in a few other experiments in which demineralized water was used.

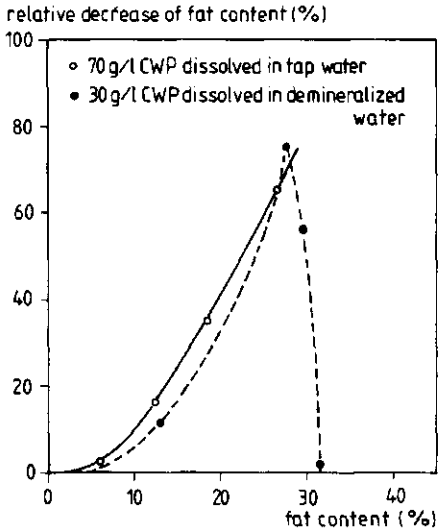

Fig. 6.9 The influence of fat content on partial coalescence.
Emulsions: milkfat in (diluted) clarified whey, d_{32} = 3.2 μm
Treatment: flow with Taylor Vortices, G = 550 s^{-1}, T = 10°C, time: 20 min

Using the results of fig. 6.8 and adding a few extra points results in fig. 6.10: the influence of d_{32} on coalescence stability. Despite the increase in surface load (see 6.2.1) emulsions

were less stable as globule size was larger. Below d_{32} = 1 μm no instability occurred under the applied conditions even if fat content was as high as 30%. Above about d_{32} = 1 μm instability increased roughly linearly with globule size. The slope of each line in this figure depends on the fat content.

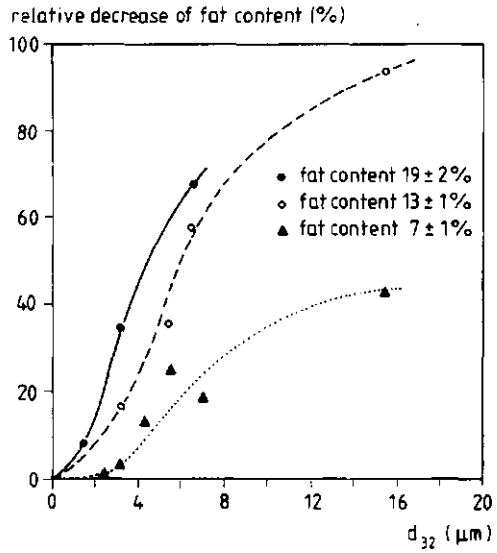

Fig. 6.10 The influence of the average globule diameter on partial coalescence.
Emulsions: milk fat in clarified whey
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min

The influence of the amount of C.W.P.-powder in the aqueous phase on the coalescence stability of the emulsion after homogenizing is depicted in fig. 6.11. The amount of C.W.P. powder is for constant fat content directly related to the surface load of the fat globules in the emulsion. In this series of experiments emulsions with 30% fat were made by homogenizing the various mixtures of fat and clarified whey under the same conditions (T = 50°C, homogenisation pressure = 410 kPa), which resulted in emulsions with exactly the same globule size distribution. This exemplifies that globule size is not influenced by the protein/fat ratio in this range. Emulsions with ca 14% fat were obtained by diluting the original emulsions.

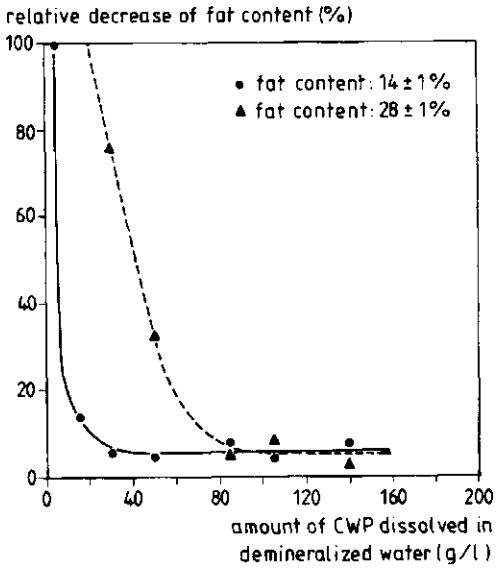

Fig. 6.11 The influence of protein content on partial coalescence.
Emulsions: milk fat in (diluted or concentrated) clarified whey, d_{32} = 3.1 μm.
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min

Both series of emulsions thus have the same protein load and globule size distribution at each C.W.P. concentration; differences in coalescence stability are therefore only a consequence of differences in fat content. In this series of experiments demineralized water was used in stead of tap water. Particularly at concentrations below 30 $g.dm^{-3}$ C.W.P.-powder, coalescence stability was less reproducible; this may be a consequence of surface active components occurring sometimes in demineralized water. Emulsions were unstable if the C.W.P. content was below 15 $g.dm^{-3}$, which for this emulsion corresponded to a surface load of about 1.2 $mg.m^{-2}$. Between 15 $g.dm^{-3}$, corresponding to about 1.2 $mg.m^{-2}$, and 85 $g.dm^{-3}$, corresponding to about 2.4 $mg.m^{-2}$, the emulsion with 14% fat was almost stable while the emulsion with 30% fat was still very unstable. Above 85 $g.dm^{-3}$ emulsions with a d_{32} = 3.1 μm always were stable under this treatment, irrespective of the fat content.

Table 6.5 The influence of the pH on the stability against partial coalescence.
Emulsion: milkfat in clarified (acidified) whey, amount of CWP: 30 g/l.
Treatment: flow with Taylor vortices, $G = 550\ s^{-1}$, T = 10°C, time: 20 min.

pH	d_{32}(μm)	fat content of original emulsion (%)	fat content of remaining emulsion (%)
3.2*	3.0	23.4	19.6
5.6	3.4	29.5	4.0
6.9	3.0	29.3	12.2
8.0	3.2	30.0	27.7
3.1*	3.0	9.3	8.5
5.8	3.2	12.1	11.3
6.9	3.0	13.1	12.3
8.6	3.2	11.7	8.3

* = acidified before emulsifying

The pH appeared to have a large influence on the coalescence stability of this type of emulsions in a flow field with Taylor vortices. In this series of experiments, summarized in table 6.5, the pH of the emulsion was adjusted after emulsifying, except for the emulsion at pH = 3 which was made by emulsifying milk fat in an acidified C.W.P. solution. After acidification none of the emulsions showed any macroscopic instability. The emulsion acidified to pH = 4.8 became more viscous; this emulsion broke immediately after it was diluted with water, so that it was impossible to measure the globule size distribution. A treatment in a flow with Taylor vortices led in this case to the formation of a butterlike substance, that separated into three layers upon heating above the melting point of milk fat, namely a yellowish, hazy layer consisting of milk fat; a white, opaque layer probably consisting of denatured protein and remaining fat globules and a clear layer consisting of water with the remainder of the protein. At pH's below 4 and above 5.5 emulsions could be made that were rather stable in a flow field with Taylor vortices, the more so when fat content and d_{32} were low. Similar results were found by de Wit et al (1976). They made emulsions of milk fat and normal whey and estimated the creaming according to Mol (1963), which they used as a measure for coa-

lescence, as a function of pH;. They found, that the coalescence stability of emulsions acidified after homogenisation was roughly the same as that of emulsions made from milk fat and acidified whey.

The coalescence stability of emulsions made of C.W.P. powder and milk fat was at moderate fat concentrations little affected by heat treatment, whether that was given before or after homogenisation of the mixture (tables 6.7 and 6.6); at higher fat content results were erratic and poorly reproducible, probably because in this series the emulsions were made with a relatively low concentration of C.W.P. powder dissolved in demineralized water instead of tap water, but a clear reduction in coalescence stability did not occur. In this respect our emulsions differed

Table 6.6 The influence of a heat treatment of CWP dissolved in demineralized water, before emulsifying the milk fat, on stability to partial coalescence.
Emulsion: d_{32} = 3.1 μm, amount of CWP in demineralized water: 30 g/l.
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min.

heat treatment	clustering	change in fatcontent (%) of	
		concentrated emulsion	diluted emulsion
none	-	29→12; 28→7	13→12
30 min 60°C	-	30→22	14→11
30 min 73°C	-	26→6	13→10
30 min 87°C	-	31→24	15→13

- = no clustering

Table 6.7 The influence of a heat treatment of milk fat in whey emulsions on the stability of these emulsions.
Emulsion: d_{32} = 3.1 μm, amount of CWP in demineralized water: 30 g/l.
Treatment: flow with Taylor vortices, G = 550 s^{-1}, T = 10°C, time: 20 min.

heat treatment	clustering	change in fatcontent (%) of	
		concentrated emulsion	diluted emulsion
none	-	29→12;28→7	13→12
30 min 60°C	-	27→7	13→10
30 min 73°C	-	28→27	14→12
30 min 87°C	-	28→24	

- = no clustering

from emulsions made of milk fat and natural whey, studied by de Wit (1976), that became unstable after a heat treatment. This difference may be a consequence of a difference in the behaviour of the aqueous phase: solutions of 30 $g.dm^{-3}$ C.W.P. powder, but also those of 70 $g.dm^{-3}$ (i.e. with the same dry matter content as in natural whey) heated for 30 minutes at 90°C remained clear and gave no deposit, while normal whey would become turbid and give some sediment. This is probably a consequence of the different calcium contents of normal and clarified whey as de Wit (1981) showed that the extent of whey protein aggregation upon heating does depend on the presence of calcium ions. The stability after heating is up till now the only case wherein an emulsion made of milk fat and C.W.P. powder behaves markedly different from an emulsion made of milk fat and normal whey.

6.4.4 Stability in a laminar flow field

In this series of experiments, carried out in the Couette apparatus, a treatment temperature of 10°C was chosen, since this type of emulsion proved to be most unstable at temperatures around 5 or 10°C; a treatment time of 20 min and a C.W.P. powder content of 70 $g.dm^{-3}$ were taken. Varied were the shear rate of the laminar flow, the fat content and the globule size of the emulsions. The influence of these variables on the coalescence rate is shown in fig. 6.12. Emulsions with a d_{32} up to 3 μm and a fat content up to 20% remained fairly stable at every shear rate applied (up to 1250 s^{-1}), but emulsions with larger globules became, irrespective of fat content, very unstable at shear rates above 600 s^{-1}. This decrease in stability was more pronounced if fat content was higher.

These results indicate that a flow with Taylor vortices at the same apparent shear rate is much more effective in breaking an emulsion than is laminar flow.

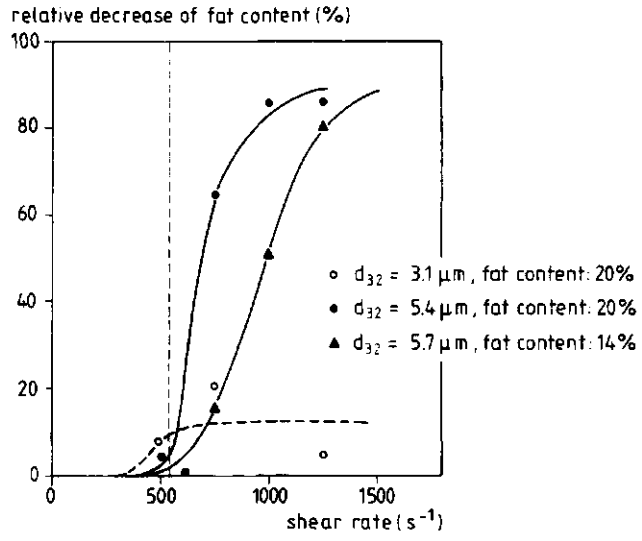

Fig. 6.12 Stability in laminar flow: influence of shear rate.
Emulsion: milkfat in clarified whey.
Treatment: laminar flow, T = 10°C, time: 20 min.
The vertical dashed line denotes the apparent shear rate applied when these emulsions were tested in a flow with Taylor vortices.

6.5 Discussion of the results

In this section various models, constructed to explain the results obtained with whey emulsions in flow fields, are proposed and discussed.

Models that describe the coalescence proces of milk fat-in-whey emulsions in a flow field should agree with the following observations:

1 The coalescence proces proceeds in a very particular way: During partial coalescence a gradual decrease in the average globule size (and not an increase), in combination with a decrease of fat content is observed. The shape of the size distribution remains fairly constant.
2 The decrease of the fat content is fairly linear with treatment time, and the emulsion does not suddenly break.
3 The globules have no crystals in the interface (L or M crystallisation habit). Many globules did not contain crystals

large enough to be seen under a microscope (O type of crystallisation habit), others did contain visible crystals, but these were inside the globules (N type of crystallisation habit). But the fat globules discernible in the clumps commonly had crystals at the boundary (L or M type).

Interpretation of these observations:
Only globules containing crystals oriented in the oil-water interface cause partial coalescence of emulsions that are stable at temperatures above the melting point of the disperse phase. Consequently, emulsions that are stable at temperatures above the melting point of the disperse phase, such as milk fat-in-whey emulsions above 40°C, are not made sensitive to partial coalescence upon cooling if the crystals are only formed inside the globules (van Boekel 1980). Observation 3 indicates that milk fat-in-whey emulsions probably do not contain reactive globules. As these emulsions do show partial coalescence, reactive globules must be created in one way or another during the treatment.

A shift of a crystal from the inside to the edge of a globule possibly can occur as a consequence of:

1 A deformation of the globule in a flow field.
Such a transition occurred with milk fat-in-skimmilk emulsions with very large globules (> 6 μm) that were deformed during microscopical examination by the pressure exerted on the diluted emulsion by the cover glass (3.2.1).

2 Collisions of two or more fat globules.
It was observed earlier with natural milk fat globules that partial coalescence of two unreactive globules leads to a reorientation of crystals towards the interface, resulting in the formation of very reactive doublets (Walstra 1967).
This observation also means that partial coalescence of such a doublet with a third globule results in the formation of a reactive triplet and so on.

If during the treatment of the emulsion a substantial part of the globules would form small clumps, d_{32} would increase and shape of size distribution would change, which is not accordance with observation 1. This observation indicates the presence or the formation of only a few though very reactive globules, that aggregate very rapidly to form large clumps that coalesce further to floating fat when the treated emulsion is heated.

Observation 2 indicates that the coalescence proces occurs at a fairly constant rate. If new reactive kernels (= globules or doublets) are made by deformation or by two or more-body collisions, others have to be removed from the emulsion in order to avoid an increase in the number of reactive kernels resulting in an acceleration of the coalescence proces. Reactive kernels can be removed via a removal of (still reactive) clumps caused by a centrifugal force occuring in Couette and Taylor apparatus. As these clumps are lighter than their surroundings they may be thrown against the inner cylinder, which is in agreement with the observation that the inner cylinder was covered with a butter layer before heating a treated unstable emulsion.

Based on these interpretations of the above described observations two models are made: In model 1 reactive globules are formed as a consequence of globule deformation; in model 2 reactive globules are formed by two-body collisions of non reactive globules. For both models the following assumptions apply:

1 The size distribution of the fat globules is so narrow that it is allowed to use an average diameter in the calculations.
   - This assumption is reasonable since the size distributions were fairly narrow. A consequence of this assumption is, however, that the model can never predict the gradual decline of d_{32} during the coalescence process.
2 During the process, the shape of the size distribution does not change; This implies that the fat globules that are partially coalesced, coalesce further to yield floating fat when the emulsion is heated to above the melting point of fat.

- This assumption is in accordance with our experimental results.

3 No reactive globules are initially present in the emulsion. These globules are formed in situ as a consequence of deformation (model 1) or two-body encounters (model 2).

4 Mutual coalescence of reactive kernels is negligible as the actual number of reactive globules and clumps remains very low during the experiment.

5 Shortly after the beginning of the treatment, the production of reactive globules by globule deformation or two-body collisions equals the removal of clumps by centrifugal forces. This implies that the number of reactive globules is a function of the actual fat content only and does not depend on the history of the emulsion. This situation can be considered as a kind of steady state.

With these assumptions equations for coalescence rate as a function of fat content, globule diameter and applied shear rate can be derived:

The production of reactive kernels may occur in several ways:

MODEL 1	MODEL 2
Cause is deformation of the globules in the applied flow field	Cause is a collision between two unreactive globules
$B'(t)_{\text{production}} = \frac{G\, d_f\, \eta_c\, n_e(t)\, R_1}{\gamma}$	$B'(t)_{\text{production}} = \frac{4}{3} d_f^3\, n_e^2(t)\, G\, R_2$
(Eq. 6.5a)	(Eq. 6.5b)

with:

B = number of reactive kernels (m^{-3}); d_f = original average globule diameter (m);

$n_e(t)$ = number of globules (m^{-3}); G = apparent shear rate (s^{-1})

R_1 = fraction of deformed globules that change into reactive kernels per unit time (s^{-1})

R_2 = fraction of collisions that leads to the formation of reactive kernels (-)

' = derivative, with respect to time.

η_c = viscosity continuous phase (Pas)

γ = interfacial tension fat plasma (Nm^{-1})

(Application of a formula derived by Torza et al. (1972) that approximates to

$$D_r = \frac{Gd_f\eta_c}{\gamma}$$

with D_r = relative deformation (-)).

(Application of Smoluchowski's formula for collisions of two globules in a laminar flow field)

These reactive kernels collide with other globules and a fraction of these collisions causes partial coalescence. Since every globule that partially coalesces with a reactive kernel will ultimately be removed from the emulsion, the number of effective collisions can be related to the decline in fat content.

$$J(t) = -n'(t) = -\frac{6}{\pi d_f^3} \cdot \phi'(t) \qquad \text{(Eq. 6.6)}$$

with: J(t) = number of effective collisions per unit time ($m^{-3}s^{-1}$)

$\phi(t)$ = volume fraction of fat (-)

The number of removed clumps equals the number of effective collisions divided by the number of fat globules in a clump just before this clump is removed from the emulsion. In formula:

$$-B'(t)_{\text{removal}} = \frac{J(t)}{N_{cl,m}} \qquad \text{(Eq. 6.7)}$$

$N_{cl,m}$ = the number of fat globules in a clump just before this clump is removed from the emulsion.

Since $N_{cl,m}$ is still dependent on the size distribution of the original emulsion, it has to be replaced by a parameter that is virtually independent of this emulsion property. Such a parameter is $V_{cl,m}$, the volume of a clump just before it is removed from the emulsion.

$$V_{cl,m} = 2\frac{\pi}{6}d_f^3 N_{cl,m} \qquad \text{(Eq. 6.8)}$$

As the fat globules are not completely fused, the clumps contain also enclosed plasma. Therefore, their volume is assumed to be about twice the sum of volumes of the containing fat globules.

As soon as a steady state is reached, the number of reaction kernels remains constant, which means that the production of reactive globules or doublets equals the removal of clumps. In models 1 and 2 it is assumed that this steady state situation is arrived at instantaneously after starting the experiment.
In formula:

$$-B'(t)_{removal} = B'(t)_{production} \qquad \text{(Eq. 6.9)}$$

Substitution of Eq. 6.8, Eq. 6.7 and Eq. 6.5 in Eq. 6.9, substitution of J(t) by the right hand side of Eq. 6.6 and substitution of $n_e(t)$ by $6\phi(t)/\pi\ d_f^3$, results in a differential equation in $\phi(t)$

$$\phi'(t) = -\frac{3\ V_{cl,m}\ \eta_c\ R_1\ G\ \phi(t)}{\pi\ d_f^2\ \gamma} \qquad \text{(Eq. 6.10a)}$$

hence

$$\phi(t) = \phi(o)\ \text{Exp}-\left[\frac{3V_{cl,m}\ \eta_c\ R_1\ G\ t}{\pi\ d_f^2\ \gamma}\right] \qquad \text{(Eq. 6.11a)}$$

$$\phi'(t) = -\ 24\pi^{-2}\ V_{cl,m} d_f^{-3}\ R_2\ G\ \phi^2(t) \qquad \text{(Eq. 6.10b)}$$

hence

$$\phi(t) = \frac{\phi(o)}{1+24\pi^{-2}\ V_{cl,m} d_f^{-3} R_2\ G\ \phi(o)\ t} \qquad \text{(Eq. 6.11b)}$$

The only unknown variables are R_1 and $V_{cl,m}$ or R_2 and $V_{cl,m}$.

Moreover these variables are interchangeable in either model, so that it is impossible to obtain the separate values by applying the models to more than one experimental result, only their product can be derived:

MODEL 1

$$R_1V_{cl,m} = \frac{\pi\, d_f^2\, \gamma}{3\eta_c Gt} \ln \frac{\phi(o)}{\phi(t)} \qquad \text{(Eq. 6.12a)}$$

MODEL 2

$$R_2V_{cl,m} = \frac{\pi^2 d_f^3}{24Gt} \left\{ \frac{1}{\phi(t)} - \frac{1}{\phi(o)} \right\} \qquad \text{(Eq. 6.12b)}$$

All the parameters on the right hand side can be determined.

From the experimental results $R_1V_{cl,m}$ and $R_2V_{cl,m}$ were calculated (see tables 6.8a, b, c and 6.9).

Table 6.8 Calculation of $R_1V_{cl,m}$ and $R_2V_{cl,m}$ from the experimental results.
Treatment: Taylor vortices, T=10°C, G = 550s^{-1}

a) The influence of initial fat content

treatment time (min)	d_{32} (μm)	$\phi(0)$ (-)	$\phi(t)$ (-)	$10^{16}R_1V_{cl,m}$ (model 1)	$10^{22}R_2V_{cl,m}$ (model 2)
20	3.2	0.266	0.076	1.0	1.9
		0.184	0.119	0.35	0.6
		0.127	0.105	0.15	0.3
		0.061	0.059	0.03	0.1
20	5.5	0.275	0.026	5.7	36.1
		0.211	0.033	4.5	26.5
		0.138	0.089	1.1	4.1
		0.069	0.052	0.7	4.9
10	6.5	0.300	0.056	11.3	49.7
		0.214	0.083	6.4	25.2
		0.146	0.108	2.0	8.2
		0.070	0.062	0.8	6.3

b) The influence of the surface average diameter
(t = 20 min)

d_{32} (μm)	$\phi(0)$ (-)	$\phi(20)$ (-)	$10^{16} R_1 V_{cl,m}$ (model 1)	$10^{22} R_2 V_{cl,m}$ (model 2)
3.2	0.061	0.059	0.03	0.1
	0.127	0.105	0.15	0.3
4.3	0.070	0.061	0.2	1.0
5.5	0.069	0.052	0.7	4.9
	0.138	0.089	1.0	4.1
6.5	0.070	0.058	0.6	5.0
	0.146	0.062	2.9	15.9
14.8	0.070	0.040	9.7	216.4
	0.123	0.007	49.8	2731.3

c) The influence of treatment time

treatment time (min)	d_{32} (μm)	$\phi(0)$ (-)	$\phi(0)$ (-)	$10^{16} R_1 V_{cl,m}$ (model 1)	$10^{22} R_2 V_{cl,m}$ (model 2)
5	5.5	0.138	0.127	0.8	2.6
10			0.108	1.2	4.2
20			0.089	1.1	4.1
30			0.039	2.0	12.7
3	6.5	0.146	0.139	1.1	3.9
10			0.108	2.0	8.3
20			0.062	2.9	15.9

Table 6.9 Calculation of $R_1 V_{cl,m}$ and $R_2 V_{cl,m}$ from the experimental results.

Treatment: Laminar flow, T = 10°C, time: 20 min.
Influence of shearrate.

d_{32} (μm)	shear rate G (s^{-1})	$\phi(0)$ (-)	$\phi(20)$ (-)	$10^{16} R_1 V_{cl,m}$ (model 1)	$10^{22} R_2 V_{cl,m}$ (model 2)
5.4	500	0.20	0.19	0.1	0.3
	750		0.07	1.8	6.7
	1000		0.03	2.4	15.3
	1250		0.03	1.9	12.2
5.7	750	0.142	0.119	0.3	1.2
	1000		0.069	1.0	4.7
	1250		0.028	1.8	14.6

Discussion of results:

Model 1: Table 6.8a: The product $R_1V_{cl,m}$ increases steeply with the fat content. Since the number of collisions with a given kernel increases with fat content, a clump that is large enough to be moved to the inner cilinder under the influence of centrifugal forces should have grown larger as fat content is higher before it would actually reache the inner cilinder. Consequently, an increase of $V_{cl,m}$ is possible. An increase of the product $R_1V_{cl,m}$ is also possible since the deformation calculated with the formula of Torza, using the viscosity of the continuous phase without taking into account possible effects of surrounding fat globules increasingly underestimates the real deformation for a higher fat content, resulting in an overestimation of $R_1V_{cl,m}$. However, if this effect is accounted for by replacing the viscosity of the continuous phase by the viscosity of the emulsion (calculated with the formula of Phipps (1969)), the increase of the newly calculated $R_1V_{cl,m}$ is still far more than proportional (see table 6.10).

Table 6.10

treatment time (min)	d_{32} (μm)	$\phi(0)$ (-)	$\phi(t)$ (-)	$10^{16}R_1V_{cl,m}$ 1)	$10^{16}R_1V_{cl,m}$ 2)
20	3.2	0.266	0.076	1.0	0.31
		0.184	0.119	0.35	0.17
		0.127	0.105	0.15	0.09
		0.061	0.059	0.03	0.03

1) calculated using the viscosity of the continuous phase
2) calculated using the viscosity of the emulsion

Table 6.8b: The product $R_1V_{cl,m}$ increases very steeply with the volume surface average diameter. As d_{32} has hardly any influence on $V_{cl,m}$, R_1 must increase very steeply with d_{32}. If model 1 is correct, it means that the possibility of a shift of a crystal from the inside of a globule to the edge during a given deformation within a given time increases strongly with

the diameter of the globule.

Table 6.8c: The product $R_1V_{cl,m}$ increases somewhat with treatment time. The fat content of an emulsion decreases during treatment since, according to this model, clumps are thrown against the inner cilinder. If the interpretation of table a is correct, it means that $V_{cl,m}$ must decrease with treatment time. Also R_1 would decrease rather than increase because the diameter of the remaining fat globules decreases (see fig. 6.5 and the interpretation of table 6.8b). Consequently, the product should decrease rather than increase.

Table 6.9: Below $G = 500\ s^{-1}$ $R_1V_{cl,m}$ is zero, above $G = 500\ s^{-1}$ $R_1V_{cl,m}$ increases with the shear rate. Because the centrifugal forces increase with the shear rate, $V_{cl,m}$ will decline; consequently, R_1 has to increase more to cancel this effect.

If model 1 is correct the results imply that a transition from N or O crystal habit to L or M crystal habit can only occur if a certain deformation is exceeded.

Conclusion: In order to establish the validity of this model, which seems to give conflicting results (compare table 6.8c with 6.8a and 6.8b), the relation between the deformation of a globule and the probability that a shift of crystals occurs as well as the value of $V_{cl,m}$ as a function of fat content and angular velocity should be determined. Until these relations have been established and this model is checked, it has no practical predictive value as each measurement gives its own value of $R_1V_{cl,m}$.

Model 2: Table 6.8a: $R_2V_{cl,m}$ increases steeply with initial fat content. $V_{cl,m}$ may increase for the same reasons as mentioned under model 1. If two-body collisions are enough to make reactive doublets, as is assumed in this model, R_2 has to remain constant.

Table 6.8b: $R_2V_{cl,m}$ increases very steeply with the average diameter. An increase of d_{32} with a factor 5 results in an increase of $R_2V_{cl,m}$ with a factor 9000. Since $V_{cl,m}$ is indepen-

dent of globule size, it is R_2 that increases with d_{32}.
An emulsion with all the crystals inside the globules would behave just like an emulsion without any crystals, as long as these crystals are not transferred to the interface (van Boekel 1980). The results summarized in table b thus suggest that in emulsions without crystals a very slight increase of d_{32} would be sufficient to change an emulsion that is almost stable in laminar flow or in a flow with Taylor vortices into a completely unstable one. A result that has, to the authors knowledge, never been observed. Therefore the influence of d_{32} on $R_2V_{cl,m}$ cannot be explained within this hypothesis.

Table 6.8c: $R_2V_{cl,m}$ increases with the treatment time.
For the same reasons as mentioned under model 1 these results are in conflict with those obtained in table a and b.

Table 6.9: $R_2V_{cl,m}$ increases steeply with shear rate. Since $V_{cl,m}$ decreases rather than increases, R_2 has to increase even more steeply. So R_2 has to increase by a factor 50 or more if G is increased from 500 s^{-1} to 1000 s^{-1}. Van Boekel (1981) used the term coalescence efficiency to define the fraction of the collisions that results in coalescence. This coalescence frequency equals R_2. He found that in emulsions stabilized with surfactants coalescence efficiency decreased steeply with shear rate while in natural cream coalescence efficiency remained more or less constant. So in none of the emulsions studied coalescence efficiency increased strongly with shear rate. The influence of the shear rate on the value of $R_2V_{cl,m}$ is thus difficult to explain.
Conclusion: It is very unlikely that model 2 gives a correct description of the partial coalescence proces.

In models 1 and 2 it was assumed that the rate of partial coalescence is fully determined by the rate of reactive kernel (= globule or doublet) production. Once the reactive kernel is formed, its reactivity is considered to be very high, so that clumps can be formed within a very short period of time. The production of these reactive kernels was an unknown parameter

that had to be determined from experimental results. In a following model (model 3), it is the reactivity of the reactive kernels that is considered to be an important parameter that has to be calculated from the results. In order to avoid unwieldy calculations it is assumed that a certain fraction of the globules is reactive or becomes reactive immediately after starting the experiment.

In model 3 the coalescence rate of emulsions in a flow field is calculated starting from Smoluchowski's equation for collisions in laminar flow. Only the observation that coalescence of milk fat-in-whey emulsions causes a decline in fat content and not an increase of d_{32} is used explicitly in the derivation of the ultimate equation. According to this model, clump growth is gradual and the assumption of a decline in fat content thus has to be justified afterwards. Also the other observations have to be discussed in connexion with this model.

For model 3 the following assumptions apply (these assumptions are to a large extent similar to those of models 1 and 2):

1) The size distribution of the fat globules is so narrow that it is allowed to use an average diameter in the calculations.
   - This assumption has the same consequences for model 3 as it has for models 1 and 2.
2) During the process the shape of the size distribution does not change; this implies that the fat globules that are partially coalesced, coalesce further to form floating fat when the emulsion is heated to above the melting point of fat.
   - This assumption is in accordance with our experimental results. It has to be verified afterwards whether in model 3 such an assumption is justifiable.
3) A small part of the fat globules is reactive or becomes reactive immediately after starting the experiment; during the treatment no more reactive globules are made.
4) Mutual aggregation of reactive kernels is negligible since the actual number of reactive globules and clumps is low.

This assumption requires some explanation:

The ratio Q(t) of collisions between fat globules and reactive kernels and collisions between reactive kernels mutually is given in a laminar flow by:

$$Q(t) = \frac{n_e(t)}{B} \cdot \frac{(d_f + d_{cl}(t))^3}{(2d_{cl}(t))^3} \qquad \text{(Eq. 6.13)}$$

at t=0 $\quad d_{cl}(t) = d_f \quad$ consequently: $Q(o) = \frac{n_e(o)}{B}$

at t=∞ $\quad d_{cl}(t) >> d_f \quad$ consequently: $Q(\infty) = \frac{n_e(\infty)}{8B}$

therefore: $\quad \frac{n_e(t)}{8B} < Q(t) < \frac{n_e(t)}{B}$

If $B << n_e(0)$, $Q(0) >> 1$ and the assumption is valid at the beginning of the experiment. However, since the number of reactive kernels remains constant in this model, while the number of fat globules decreases, there will be a moment whereupon Q approximates 1.

Moreover the fraction of collisions between two clumps that result in partial coalescence probably is higher than that of clumps and globules; this would be due to inertial forces, which are negligible for colliding globules but not for colliding large clumps. Consequently, assumption 4 can only be valid at the beginning of the coalescence proces. However, since clumps consisting of smaller clumps are easier to disrupt by viscous stresses, than clumps consisting of single globules, disruption of these "composite" clumps may actually take place, especially in a flow with Taylor vortices. Consequently, an equilibrium state may develop between clumps solely build up of single globules and composite clumps. Also the influence of mutual interactions between clumps (hence a decrease in the number of clumps) on the number of collisions between clumps and fat globules will diminish as the size of the clumps formed out of single globules increases. This can be shown by the following

calculation:
The number of collisions between a globule and a clump ($J_1(t)$) is:

$$J_1(t) = \frac{1}{6} (d_f + d_{cl}(t))^3 \, n_e(t) BG \qquad \text{(Eq. 6.14)}$$

(for an explanation of the symbols see page 101).
Suppose that all clumps aggregate into one large clump: the volume of this clump would be $Bd^3_{cl}(t)\frac{\pi}{6}$ and its diameter $d_{cl}(t)\sqrt[3]{B}$. The number of collisions between this clump and the globules ($J_2(t)$) is:

$$J_2(t) = \frac{1}{6} (d_f + d_{cl}(t) \sqrt[3]{B})^3 \, n_e(t) . \frac{B}{B} . G \qquad \text{(Eq. 6.14b)}$$

For $d_{cl}(t) >> d_f$ $(d_f + d_{cl}(t))^3 \rightarrow d^3_{cl}(t)$, $(d_f + d_{cl}(t).\sqrt[3]{B})^3 \rightarrow B\, d^3_{cl}(t)$

and $J_1(t) = J_2(t)$.

This implies that composite clump formation does not disturb the course of the coalescence process provided that the clumps are large with respect to the original fat globules. Thus, although assumption 4 gradually loses its validity, the consequences for the accuracy of the calculations will remain limited.

5) A constant fraction of the collisions between reactive and non reactive globules leads to the formation of clumps; these have the same reactivity as the original reactive globules. The clumps are not removed from the emulsion by centrifugal forces.
6) The actual shear rates occurring in a flow with Taylor vortices are replaced by one shear rate: the apparent shear rate. Also the number of collisions in a flow with Taylor vortices is approximated by a collision rate in laminar flow.

The final assumption (6) is only required if the model is used to describe partial coalescence of emulsions in a flow with Taylor vortices and requires some explanation:

A flow field with Taylor vortices is a complicated three-dimensional flow with locally different velocity gradients resulting in various shear rates in each vortex and elongational flow between vortices (see 2.3.2). A model that takes these local differences into account will require very complicated calculations that cannot be easily verified, since only overall coalescence rates can be measured. The actual shear rates occuring in this type of flow are therefore replaced by one apparent shear rate, that is the shear rate that would exist if the flow were laminar. Owing to this complicated three-dimensional flow, the collision rates also are locally different. For the same reasons as outlined above, these different collision frequencies are replaced by one average number calculated with Smoluchowski's formula using the apparent shear rate. Although this formula is derived for laminar flow and the real average collision frequency in a flow with Taylor vortices is higher, it nevertheless will be proportional to the calculated frequency.
The most important difference between a flow with Taylor vortices and laminar flow remains the velocity gradient in the direction of the flow which occurs between two vortices, since such an elongational flow is known to be effective in the disruption of aggregates (Walstra 1980).

The calculations leading to the ultimate formula are outlined below:

$$J(t) = \frac{1}{6} (d_f + d_{cl}(t))^3 \, n_e(t) \, BGR_3 \qquad \text{(Eq. 6.15)}$$

$J(t)$ = number of effective collisions per unit time ($m^{-3}s^{-1}$)
d_f = initial average diameter of fat globules (m)
d_{cl} = average diameter of clumps (m)
$n_e(t)$= number of globules (m^{-3})
B = number of reactive kernels (globules and clumps) (m^{-3})
G = apparent shear rate (s^{-1})
R_3 = fraction of collisions leading to partial coalescence (-)

Eq. 6.14 is an application of Smoluchowski's equation for collisions of reactive kernels with fat globules in a flow field.

$$n_e(t) = \frac{6\phi(t)}{\pi d_f^3} \qquad \text{(Eq. 6.16)}$$

$\phi(t)$ = fat content emulsion after heating and removal of coalesced fat (-). Eq. 6.16 is based on assumptions 1 and 2.

$$B = c.\ n_e(o) = c\ \frac{6\phi(o)}{\pi d_f^3} \qquad \text{(Eq. 6.17)}$$

c = the fraction of fat globules that is reactive or becomes reactive immediately after starting the experiment (-).
Eq. 6.17 is based on assumption 3.

$$J(t) = -\ \frac{6}{\pi d_f^3}\ \phi'(t) \qquad \text{(Eq. 6.6)}$$

$\phi'(t)$ = the time derivative of the fat volume fraction.
Eq. 6.6 is based on assumption 2: every globule that coalesces into a clump is considered to be withdrawn from the emulsion.

$$d_{ci}^3\ (t) = 2d_f^3\ N_{cl}(t) \qquad \text{(Eq. 6.18)}$$

$N_{cl}(t)$ = the number of fat globules in a clump.
Because the fat globules are not completely fused, the clumps also contain enclosed plasma. Therefore, their volume is about twice as high as the sum of volumes of the containing fat globules.

$$N_{cl}(t) = 1 + \frac{\pi d_f^3 \int_o^t J(t)\ dt}{6\ c\ \phi(o)} \qquad \text{(Eq. 6.19)}$$

Eq. 6.19 in words: The average number of globules in a clump equals the total number of effective collisions divided by the number of reactive kernels plus one, namely the reactive globule itself.

Combination of the above equations gives:

$$\phi'(t) = -\frac{1}{\pi} cR_3 G\ \phi(o)\ \phi(t)\ \left(\left(\frac{2(\phi(o)-\phi(t))}{c\ \phi(o)} + 2\right)^{1/3} + 1\right)^3 \qquad \text{(Eq. 6.20)}$$

This differential equation, that cannot be simplified without causing anomalies, can only be solved numerically for preestablished values of c and R_3.

Table 6.11 Comparison between experimental results and results obtained with the optimized values of the two parameters occuring in model 3: c and R_3.

a) Influence of initial fatcontent
Treatment: Taylor vortices, T = 10°C, G = 550 s^{-1}

d_{32} = 3.2 µm $t \triangleq$ 20 min			d_{32} = 5.5 µm $t \triangleq$ 20 min			d_{32} = 6.5 µm $t \triangleq$ 10 min			d_{32} = 14.8 µm $t \triangleq$ 20 min		
	$c = 5x10^{-3}$ $R_3 = 2.5x10^{-5}$			$c = 5x10^{-3}$ $R_3 = 3.2x10^{-5}$			$c = 5x10^{-3}$ $R_3 = 5.3x10^{-5}$			$c=5x10^{-3}$ $R_3 = 7.5x10^{-5}$	
$\phi(0)$	$\phi(20)$ (Exp.)	$\phi(20)$ (Calc)	$\phi(0)$	$\phi(20)$ (Exp)	$\phi(20)$ (Calc)	$\phi(0)$	$\phi(10)$ (Exp)	$\phi(10)$ (Calc)	$\phi(0)$	$\phi(20)$ (Exp)	$\phi(20)$ (Calc)
0.266	0.076	0.075	0.275	0.026	0.026	0.300	0.056	0.044			
0.184	0.119	0.112	0.211	0.033	0.057	0.214	0.083	0.091			
0.127	0.105	0.105	0.138	0.089	0.089	0.146	0.108	0.106	0.123	0.007	0.010
0.061	0.060	0.059	0.069	0.052	0.063	0.070	0.062	0.066	0.070	0.040	0.035

b) Influence of treatment time
Treatment: Taylor vortices, T = 10°C, G = 550s^{-1}

d_{32} = 5.5 µm $\phi(0)$ = 0.138			d_{32} = 6.5 µm $\phi(0)$ = 0.146			
time (min)	$\phi(t)$ exp	$c=5x10^{-3}$ $R_3=3.2x10^{-5}$	time (min)	$\phi(t)$ exp	$c=5x10^{-3}$ $R_3=3.9x10^{-5}$	$c=5x10^{-3}$ $R_3=5.3x10^{-5}$
0	0.138	0.138	0	0.146	0.146	0.146
5	0.127	0.135	3	0.139	0.144	0.143
10	0.108	0.128	10	0.108	0.125	0.106
20	0.089	0.088	20	0.062	0.062	0.025
30	0.039	0.040				

The optimized values of these parameters and the calculated fat contents are given in tables 6.11a and b. To facilitate comparison, the experimental values are also given.

Table 6.12 Influence of d_{32} on the best fit of R_3

Treatment: Taylor vortices, G = 550 s^{-1}
Temperature: 10°C
Time: 20 min.
Initial fatcontent: about 13%

d_{32}	$10^5 R_3$
3.2	2.5
4.3	2.9
5.5	3.2
6.5	3.9
14.8	7.5

In spite of the fact that c and R_3 are not interchangeable in formula Eq. 6.20, it was found that all the experimental results obtained in a flow with Taylor vortices at 10°C could be fitted in this model, taking only one value for c namely $5x10^{-3}.R_3$ appeared to be independent of initial fat content, almost independent of the treatment time and to vary in a linear way with the volume-surface average diameter (table 6.12). It is also remarkable that the reactivity of the reactive globules, calculated with this model, lies between $2.5x10^{-5}$ and $7.5x10^{-5}$ while van Boekel (1980) derived for his emulsions a value of $7x10^{-5}$, which is clearly of the same order of magnitude.

In table 6.13 the relation between the reactivity R_3 and the shear rate G, determined for emulsions in laminar flow, is given. As the number of experiments was too small to establish properly the values of c and R_3, the value of c was set equal to that found in the experiments with Taylor vortices ($c = 5x10^{-3}$). R_3 appeared to depend on shear rate. Below 500 s^{-1}, R_3 was found to be zero, above 500 s^{-1}, R_3 increased steeply with shear rate until, for emulsions with d_{32} = ca 5.5 μm, a value of about $2.3x10^{-5}$ is reached. Such a result is not in disagreement with the calculations of van Boekel (1980). He found that the minimum distance of approach is decreased if the shear rate is increased. This implies that crystals that do not stick out far enough to pierce a film between two colliding globules, which is required

Table 6.13 Comparison between experimental results and results obtained with the most appropriate value of R_3. (For c a value of 5.10^{-3} is taken).

Influence of shear rate
Treatment: Laminar flow, T = 10°C, time: 20 min.

d_{32} = 5.4 μm, $\phi(0)$ = 0.20 c = $5x10^{-3}$				d_{32}= 5.7 μm, $\phi(0)$=0.142 c=$5x10^{-3}$			
G (s^{-1})	$\phi(20)$ Experimental	$\phi(20)$ acc. to model 3	10^5R_3	G (s^{-1})	$\phi(20)$ Experimental	$\phi(20)$ acc. to model 3	10^5R_3
500	0.19	0.19	1				
750	0.07	0.07	2.3	750	0.119	0.118	1.6
1000	0.03	0.03	2.3	1000	0.069	0.066	2.1
1250	0.03	0.01	2.3	1250	0.028	0.028	2.3

for partial coalescence to occur, can suddenly start to do so if this film is thinner as a consequence of an increased shear rate.

Model 3 describes a gradual growth of a small part of the globules during an experiment. This seems to be in disagreement with the observation of a decline of the fat content instead of an increase of d_{32}, but if the coalescence proces described by this model is studied more accurately, calculated results and experimental observations may agree better:
Shortly after starting the experiment each reactive fat globule has partially coalesced with a few non-reactive ones to form small clumps. As these clumps still are very small, they contain a very small fraction of the fat. If this fraction is so small that the turbidity spectrum is not changed markedly, the size distribution is considered unchanged. After a longer time, the clumps have grown larger and now contain a substantial fraction of the fat. If these clumps are now so large that they immediately cream out of the emulsion and coalesce further to floating fat upon heating the emulsion in the apparatus, coalescence is considered to cause a decrease in fat content and not an increase in d_{32}. The clumps formed would thus be either so small that they do not materially affect the globule size distribution

of the emulsion or so large that they would immediately cream and coalesce after the apparatus is stopped, thus only affecting the value of the fat content. This implies an abrupt change in clump size which we will discuss on the basis of an example.

A milk fat-in-whey emulsion with d_{32} = 5.5 μm coalesced in a flow with Taylor vortices resulting already within 5 minutes in a slight decrease of the fat content ($\phi(0)$ = 0.138; $\phi(5)$ = 0.127). For all emulsions the fraction of reactive globules in a flow with Taylor vortices at 10°C was calculated to be 5.10^{-3}. Since the model was derived for an emulsion with a narrow size distribution it is allowed to replace d_{32} by d_f. The number of fat globules equals approximately:

$$n_e(0) = 0.138x6/\pi\ d_f^3 = 1.6x10^{15}\ m^{-3}$$

The number of reactive kernels equals: B = $5x10^{-3}$ x $1.6x10^{15}$ = $7.9x10^{12}m^{-3}$. After 5 minutes these clumps contain 0.011 m^3 fat which is per clump 1400 μm^3. With a swelling factor of 2 the volume of such a clump is 2800 μm^3 corresponding to a diameter of 17.5 μm.

Although such clumps certainly will coalesce, once creamed (see table 6.4), they are too small to reach the cream layer within the time that is required to heat the emulsion from 10°C to 40°C since they would cream in this period over only some 0.5 cm, applying Stokes' equation. Apparently some additional aggregation of clumps has to occur:

In the example given the number of clump-clump encounters is calculated to be about 2 per clump per sec immediately after starting the experiment and 60 per clump per sec after 5 minutes. The total number of clump-clump encounters in the first 5 minutes is then about 10.000 per clump. In order to cream rapidly enough to reach the cream layer within the required heating time, about 10 min, these composite clumps should contain about 100 small clumps, which can only occur if the average reactivity of a clump (R_{cl}) is at least 10^{-2}, which is about 350 times as

high as R_3. The required reactivity R_{cl} is even higher if disruption would occur. Consequently, the rapid creaming of the clumps can only be explained by assuming a high fraction of effective clump-clump encounters (=R_{cl}).

Model 3 predicts that after a very short treatment partial coalescence will result in small clumps that would remain stable upon creaming and heating. In order to remain stable upon creaming the clumpsize has to lie below 10 μm (see 6.4.2).
In our example the number of reactive kernels was 7.9×10^{12} m^{-3} containing now 0.002 fat which is only 1.5% of the total amount of fat. As this amount of fat is in relatively large clumps, this fraction will hardly change the turbidity spectrum of the emulsion and the size distribution will be considered unchanged. The observed course of coalescence thus need not be in disagreement with this model.

Assumption 3 of model 3 states that a small fraction of the fat globules is reactive or becomes reactive soon after starting the experiment. This assumption looks at first glance in disagreement with the observation that the crystallization habit of all globules was N or O, globules that are known to be unreactive (van Boekel 1980). The calculations, based on model 3, however, show that the fraction of reactive globules would only be about 0.5%. So the number of globules with a M or L crystallization habit would be very small. Moreover a fast transition of globules with an O or N crystallisation habit into globules with an L or M crystallisation habit as a consequence of deformation is not excluded by this model. Consequently, this observation need not be at variance with model 3 either.
Table 6.11b shows that it is possible to approximate the change of the fat content with treatment time with eq. 6.20. Thus also the observed relation between partial coalescence and treament time need not be in disagreement with model 3.

The observation, that the inner cylinder can be covered with a butterlike layer after an experiment but before heating the treated emulsion, can only be explained by assuming composite clump formation. The formation of composite clumps thus appears

to be essential in explaining several observations and measurements and, although it was shown that the influence of this interaction of the calculated values of R_3 and c is limited, it will certainly introduce errors if it is already extensive when the clumps are still small. The maximum error introduced by omitting composite clump formation is a factor 8 in the calculated value of R_3, which would occur if the reactive globules react mutually to one clump before they coalesce with the other globules. Probably the real error is much lower.

Probably, a combination of model 3 with calculations according for composite clump formation would provide a good description of the partial coalescence process of these emulsions in a flow field.

7 STABILITY AND APPLICABILITY OF RECOMBINED EMULSIONS

7.1 Characterization of instability

In chapter 1 we described several changes that may occur to the fat globules in oil-in-water emulsions: creaming, flocculation, clustering, partial coalescence, (normal) coalescence and disruption. In the emulsions studied all these changes could occur. Take, for example, emulsions made of milk fat and skimmilk.
During storage creaming occurs, sometimes followed by a kind of flocculation, sometimes by partial coalescence, depending on the globule size. Partial coalescence occurs in a turbulent flow field with very high shear rates or after inclusion of air. Clustering (heat coagulation) occurs during an indirect ultra-high temperature treatment and disruption during a direct ultra high temperature treatment. The type of treatment influences thus for a large part which type of aggregation occurs. But two different emulsions may react very differently on the same treatment. A milk fat-in-skimmilk emulsion with very large globules coalesces completely within an hour when left at rest i.e. to cream at temperatures around 20°C. The same emulsion remains perfectly stable in a laminar flow field. An emulsion, consisting of milk fat with phospholipids dissolved and skimmilk, with small fat globules reacted the other way around. It only creams but gives no coalescence when left at rest at temperatures around 20°C, but coalesces almost completely in a flow with Taylor vortices (and probably also in laminar flow). Also fat content, surface load and droplet size appear to have a large influence on one or more types of instability. It is therefore the combination of emulsion type, emulsion characteristics and the applied treatment, including pretreatments, which is decisive as to whether, of which type and at what rate aggregation takes place. Comparisons between various systems are difficult and results obtained with model emulsions give useful information about general principles, but no direct information about the behaviour of recombined emulsions. If treatment and kind of aggregation are specified, however, more general conclusions can

be obtained.

For instance: An emulsion of clarified whey and milk fat is less stable to coalescence in a flow field at 10°C if globule size is larger, surface load is lower and fat content is higher.

We studied stability by comparing emulsions before and after a certain well defined treatment: e.g. coalescence stability, which was the major part of the study, was determined by measuring differences in fat content and globule size distribution before and after a certain treatment. The microscope was used to control whether flocculation or clustering had occurred. This method is laborious but the results obtained were mostly reproducible and easy to interpret.

Several other ways to estimate the stability of emulsions have been proposed. Some authors used a creaming or centrifuge test to determine emulsion stability. An example is the test of Acton and Saffle: an emulsion is kept at a prescribed temperature in a cylindrical glass. After one day the water content of the lower part of the emulsion is compared with the original water content (Halling 1981). A similar centrifuge test is described by Mol (1963). These types of test are a measure for the stability against creaming which is possibly enhanced by flocculation or coalescence of fat globules. In fact no distinction is made between the various forms of instability. If emulsions are compared before and after a wel defined treatment and a microscope is used, these tests do give information about stability against coalescence, flocculation or clustering but this information is only qualitative since there is no clear correlation between these types of instability and an enhanced creaming. Moreover the method is almost as laborious as the one we used.

Another approach is to correlate the stability of the emulsion with some characteristic parameter. Often the so called free fat content is used (Fink and Kessler 1985). Apart from the, in the authors opinion, misconception about the designation

of the method (the interface between fat and an aqueous protein solution is within, say, 10^{-3} s covered with protein, so the conception of minuscule "bare" fat droplets is incorrect) the results depend greatly on slight variations in the method in an unknown way; consequently, the results are very difficult to interpret.
Also other characteristics such as the activity of certain enzymes (Stelzer 1973) or the concentration of free fatty acids (Puhan 1983) are difficult to correlate to the stability of the emulsion during various treatments. Moreover these characteristics are particular to natural and homogenized cream and not transferable to other emulsion types.

7.2 Ways in which partial coalescence may proceed

In chapter 6 it was shown that there are situations where partial coalescence proceeds in a way wholly different from normal coalescence. However, in other systems such as those described by Van Boekel (1980), partial coalescence had the same consequences as has normal coalescence, namely an increase in average globule size while fat content remains the same until a critical size is reached above which coalescence is accelerated and the emulsion breaks. Labuschagne discerned in natural cream various ways in which partial coalescence may proceed. His results, summarized and compared with our own results in chapter 4, show that for natural cream, treatment temperature determines to a large extent whether the shape of the globule size distribution, the average globule size, the fat content or a combination of these is changed. Emulsions of milk fat-in-skimmilk are very stable but if - under extreme conditions - coalescene occurs, it may proceed in various ways, in some cases resulting in a lower fat content, in others in an increase of the average globule size. The same was found for emulsions made of skimmilk and milk fat with lecithin dissolved in the milk fat.
Consequently, the course of a coalescence process seems to vary between (1) a decline of the fat content in combination with a

gradual decline of d_{32} and (2) a constant value of the fat content in combination with a gradual increase of d_{32} with (3) all combinations in between.

Model 3, worked out in section 6.5, describing a coalescence process in monodisperse emulsions resulting in a decline of the fat content, gradually changes to a model that describes a coalescence proces in originally monodisperse emulsions resulting in an increase of the average globule size, if the fraction of reactive globules passes from less than 0.5% (milk fat in whey emulsions) to 20% or more (emulsions described by van Boekel (1980)). The type of coalescence seems thus to be determined by the proportion of reactive kernels while the rate of coalescence seems to be determined by (1) the proportion of reactive kernels (= c), (2) their reactivity i.e. the fraction of collisions that leads to partial coalescence (=R_3) and (3) the total number of collisions.
The proportion of reactive kernels depends on such emulsion properties as nature of continuous and disperse phase, surface load and average globule size, and those treatment conditions that determine size and number of crystals in a fat globule (for instance, treatment temperature and temperature history) but not on the fat content and those treatment conditions that determine the nature of a collision. The reactivity depends on the same emulsion properties and on those treatment conditions that determine the nature of a collision such as the presence or absence of a flow field, the kind of flow field and the shear rate.

The nature of a collision (or better encounter) would comprise:

1) <u>The lifetime of an encounter (τ)</u>

   If the emulsion is kept at rest and creaming is prevented only the Brownian motion of the globules causes encounters, and these have a lifetime of 4.10^{-5} s (Overbeek 1977). In flow fields the lifetime depends on the (apparent) shear rate and the type of encounter. Mason and van der Ven discerned in

laminar flow four types of encounters (1976a, b):

- Transient encounters: the globules meet eachother and separate immediately $\tau = 5\pi/6G$ (Arp & Mason, 1976)
- Separating doublets: The globules meet eachother, orbit a few times around eachother and separate.
- Primary permanent doublets: The globules meet eachother and flocculate in the primary minimum. $\tau = \infty$
- Secundary permanent doublets: The globules meet eachother and remain orbiting around eachother in the secondary minimum. $\tau = \infty$.

The encounter type depends on the globule interaction, which is the sum of electrostatic repulsion, steric repulsion and van der Waals attraction, as function of the distance of their interfacial layers.

2) The minimum distance between the globules during an encounter

The minimum distance is determined by the globule interaction and the hydrodynamic forces acting on the globules. These effects are elaborated for laminar flow by van der Ven and Mason (1976a), resulting in equations for the trajectories of globules relative to a reference globule. If the interaction function of the globules is known or assessable, the minimum distance between the globules can be calculated with these equations (van der Ven & Mason 1976a, van Boekel 1980). The minimum distance in an encounter due to Brownian motion is greater than in an encounter due to laminar flow.

3) The position of the two globules with regard to eachother during an encounter

In an encounter due to Brownian motion the relative position of the globules remains the same, which means that during that encounter the contact area is fixed on one spot of both globules.

In this respect two types of encounters can exist in laminar flow, namely encounters resulting in transient doublets or primary permanent doublets in which the contact area is fixed during the encounter and encounters resulting in separating doublets or secondary permanent doublets in which the glo-

bules orbit around eachother thus changing the contact area continuously. If the contact area changes continuously, the probability that a protruding crystal pierces the aqueous layer between the fat globules, resulting in partial coalescence, steeply increases.

The reactivities, R_3, determined by fitting the parameters to the experimental results are in fact average values; model 3 does not discriminate between the reactivity of a reactive globule and that of a (small) clump.

The description of the partial coalescence proces may further be complicated by collisions of two clumps resulting in the formation of composite clumps, by the centrifugal forces occurring in a flow between two concentric cylinders causing removal of clumps and by locally occuring elongational flow in a flow with Taylor vortices causing disruption of clumps (Labuschagne 1963).

The coalescence process in a cream layer can not be described by either of the models considered. The buoyancy forces exerted on the globules in combination with the interaction function of the globules and number, size and shape of protruding crystals determine whether enough globules can approach eachother so closely that the protruding crystals can pierce the aqueous layer and partial coalescence is obtained. If the first clumps are formed partial coalescence may be accelerated since it is likely that these become reactive due to a reorientation of the crystals (Walstra 1967).

7.3 Differences between homogenized and recombined creams

One should be careful in making general statements about differences in properties of recombined emulsions and homogenized creams, since many types of recombined emulsions can be made. However, the product obtained by homogenizing natural cream differs in four fundamental respects from recombined cream.

1) The composition of the disperse phase of homogenized creams

is fixed as it is not possible to dissolve oil soluble components via an aqueous continuous phase in the disperse phase. The composition of the disperse phase of recombined emulsions can be influenced by dissolving oil soluble components in the fat before homogenization or by using higher or lower melting fat fractions obtained via fractionated crystallisation of anhydrous milkfat.

2) Only the new interface between the fat globules and plasma created during homogenizing is covered with material (mostly proteins) adsorbed from the plasma. Consequently, the composition of the surface layer can only partly be influenced by adding substances to the cream before homogenizing. Moreover, one is limited in applying surface active materials, since it is impossible to dissolve oil soluble components in the disperse phase. For instance, the relative amount of adsorbed whey protein can be raised by adding whey, but even large additions of sweet cream buttermilk do not lead to an appreciable adsorption of phospholipids onto the interface. The composition of the (remnants of the) original membrane will probably hardly be influenced by this kind of additions. Although at the commonly applied homogenisation pressures the major part of the interface consists of adsorbed components, the original membrane would still cover 5-30% of the interface, continuing to influence stability properties. Even a repeated homogenisation probably does not lead to an important modification of membrane material (see 4.2).
   Synthetic fat droplets in recombined emulsions contain only adsorbed compounds in their interface. The composition of this interface can be varied more easily e.g. by changing the aqueous milk fraction or by adding components such as lecithins, to the fat.

3) In natural cream the individual globules show considerable differences in fat composition (e.g. Walstra & Borggreve, 1966). When these globules are disrupted in a homogenizer, smaller globules are obtained of which the fat composition is still different. Since recombined cream is made from a mix-

ture of homogeneous fat and an aqueous milk fraction, all synthetic globules in one emulsion will contain fat of the same composition. This difference has consequences for the crystallisation behaviour of the fat globules in homogenized and recombined emulsions. Natural cream and homogenized cream contain globules both with a higher and a lower melting fat. Consequently, the proportion of droplets with crystals inside shows in a homogenized cream a wider range with temperature than it does in a recombined emulsion. (Mulder & Walstra 1974). However the supercooling needed to obtain crystallisation within a prescribed time primarily depends on globule size: as sizes are smaller, deeper cooling is needed to induce the first crystallisation since the number of catalytic impurities per globule is reduced (Walstra & van Beresteyn 1975). Only emulsions with the same size distribution can therefore be compared: if these distributions are equal, the cooling needed to induce the first crystallisation in the globules of a recombined emulsion is somewhat deeper than it is for a homogenized emulsion, which means that if all other differences are left out of consideration, a homogenized emulsion would be slightly less stable to coalescence for a given treatment, at a given temperature and temperature history.

4) The largest average droplet size to be obtained in homogenized creams is of course that of natural cream (3 - 4 μm). Via repeated homogenisation at very low pressures of mixtures of milk fat and aqueous milk fractions, emulsions with average droplet sizes larger than 4 μm can be obtained without any fat present in very large, rapidly creaming globules.

Because of these features it is easier to vary stability properties by recombination of various mixtures than by adding components to natural cream before homogenisation.

As to overall composition, homogenized cream can best be compared with milk fat-in-buttermilk emulsions. Recombined and homogenized emulsions obtained after homogenizing at high pressures behave similar: both are very stable to coalescence and

hardly cream during storage. Differences increase as homogenisation pressure is reduced: Recombined emulsions with droplet sizes up to 5 μm and fat contents up to 30% remain completely stable in a flow field and give upon creaming the tough cream layer described in 3.1.1.1; Homogenized natural creams with average droplet sizes over 2 μm are very unstable in a flow field and give upon creaming a liquid cream layer that is sensitive to rebodying thus leading to the formation of a cream plug if temperature fluctuations occur.

Other differences between homogenized natural cream and recombined emulsions are summarized by Mulder & Walstra (1974). These fall outside the scope of this study.

7.4 Possible applications of recombined emulsions

In this final section the (presumed) reaction of the studied recombined emulsions on four treatments is discussed.

- Churning: The emulsion is agitated, often while beating in air, in order to obtain butter. This will only result in the formation of butter granules if the globules clump readily and if these clumps aggregate further to visible butter grains. A recombined butter can, indeed, also be made by fast cooling and agitating a mixture of skimmilk or buttermilk and liquid milk fat, but the consistency of the product obtained will differ from conventional butter. Both types are water-in-(solidified) fat emulsions, but the continuous phase of conventional butter contains also many fat globules, fragments of fat globules and remnants of globule membranes (Mulder 1947), whereas the continuous phase of the recombined type only consists of solidified milk fat. This difference in structure causes a difference in the consistency of the two butter types: at a given temperature, temperature history and intensity of softening, butter obtained by churning a (recombined) cream is and remains softer and more spreadable than recombined butter (Mulder & Walstra 1974).

- Whipping: Air is beaten into an emulsion in order to obtain a stable foam containing the entire emulsion. Such a foam can only be arrived at if the globules adhere to the beaten in air bubbles and clump with other fat globules when these air bubbles collide or collapse, or clump as a consequence of the agitation of the emulsion, to give ultimately a network of air bubbles and attaching fat clumps, that confers rigidity to the foam and entraps the remainder of the emulsion.
- Sterilisation: a heat treatment is given to the emulsion in order to obtain longlife sterile products. Application: sterilized milk, coffee cream etc. Acceptable products are only obtainable if the emulsions are heat stable, giving no clustering nor fat separation upon the heat treatment. Moreover, creaming should be very slight, since these products are often stored for several weeks or even months.
- Drying: The emulsion is dried in order to obtain a powder. Heat stability and stability to aggregation upon concentrating are essential properties of the emulsions; otherwise the powder will not give a stable emulsion upon dispersion in water.

Other operations, such as freezing, concentrating, renneting, fermentation and possible new operations are not considered here.

Pure milk fat-in-skimmilk emulsions are not suitable for most of the above described treatments:

- Churning without air never leads to clumping, since this recombined emulsion is very stable against partial coalescence. Yet minor modifications can make these emulsions less stable to partial coalescence:

If the emulsion has been made at a low homogenisation pressure, addition of a few percent of natural cream is enough to start clumping during agitation; probably air inclusion is now also effective.

Dissolving a sufficient quantity of phospholipids in the milk fat before emulsifying the mixture results emulsions that clump

upon churning.

- Severe heat treatments are not endured by these emulsions. Upon sterilisation by the normally used indirect U.H.T. heating, considerable clustering occurs. However, a few experiments showed that emulsions sterilized via the less common direct U.H.T. treatment do not contain clusters, since any aggregates formed are disrupted again into single globules during evaporative cooling. The occurrence of clusters can also be prevented by homogenizing the mixture after sterilisation, but the storability of these products remains poor, since tough cream layers are formed that are only redispersable if the product is heated to above 40°C. Only if the mixture is emulsified at high homogenisation pressures, creaming resulting in the formation of tough cream layers is largely prevented .

It has not been studied wether emulsions with very small droplet sizes also remain stable during a direct U.H.T. treatment.

- Free-flowing non-sticky cream powders that give stable, unclustered emulsions upon dispersion in water can not be obtained from these emulsions. If emulsions with small droplet sizes were dried, the powders gave upon dispersion in water strongly clustered emulsions and if emulsions with larger droplet sizes were dried, the powders were sticky and gave upon dissolution emulsions with floating fat. The circumstances under which a stable powder, giving a stable and unclustered emulsion upon dissolution, can be obtained from a milk fat-in-skimmilk emulsion have not yet been determined. Presumably, the protein to fat ratio is crucial.

The use of buttermilk instead of skimmilk does not materially influence the (in)stability to partial coalescence of the emulsion. Milk fat-in-buttermilk emulsions are thus equally unsuitable for churning and whipping as are milk fat-in-skimmilk emulsions.

Since the addition of buttermilk to natural cream before homogenizing (Koops 1967) or of food grade lecithin to concentrated milk before homogenizing (Hardy et al, 1985) both lead to an increase of the heat stability, the same may be expected if

emulsions made of buttermilk and milkfat are used instead of emulsions made of skimmilk and milk fat, thus making them more suitable for products that require sterilisation.

Emulsions made of milk fat and clarified may be preferable for some applications. By varying globule size, protein to fat ratio and fat content, stability to partial coalescence can be modified as desired, making them suitable for churning and whipping. The heat stability is also much better than that of the other emulsions, provided that the surface load is sufficient (Oortwijn & Walstra, 1982), so that sterilized products can be obtained in various ways. Rientjes (1985) showed that drying of these emulsions leads to powders that give stable and unclustered emulsions upon dissolution.

Emulsions made of milk fat and natural whey instead of milk fat and clarified whey are equally stable to partial coalescence, but less heat stable. Moreover powders obtained from these emulsions yield upon dispersion emulsions with clustered fat globules (Rientjes 1985). Consequently, emulsions made of milk fat and clarified whey are more suitable for products that require sterilisation or drying than emulsions made of milk fat and untreated whey. Despite the obvious advantage of clarified whey with regard to untreated whey, the clarification proces is not (yet) economic since the proces is expensive (longe time, large sediment tanks) and losses of 20% occur.

Since the above mentioned differences are probably related to the calcium and magnesium contents, it may be commercially attractive to remove these ions in a cheaper way, for instance via an ion exchanger.

REFERENCES

Anderson, M., G.C. Cheeseman, D.J. Knight & W.F. Shipe, 1972. The effect of ageing cooked milk on the composition of the fat globule membrane. J. Dairy Res. 39:95.

Arp, P.A. & S.G. Mason, 1976. Orthokinetic collisions of hard spheres in simple shear flow. Can. J. Chem. 54:3769-3774.

Back, W.D., 1975. Veränderungen des systems Milch durch Strömungsvorgänge. Thesis, Technical University Hannover, W-Germany, 173 p.

Boekel, M.A.J.S. van, 1980. Influence of fat crystals in the oil phase on stability of oil-in-water emulsions. Thesis, Agricultural University Wageningen, The Netherlands, 94 p.

Böhm, J.T.C. & J. Lyklema, 1976. The adsorption Behaviour of Polyelectrolytes at Liquid-Liquid Interfaces and the Properties of Polyelectrolyte-Stabilized Emulsions.
In: A.L. Smith (Ed.), Theory and Practice of Emulsion Technology, Academic Press, London, Chapter 2.

Bull, H.B., 1947. Spread monolayers of protein. Adv. Protein Chem. 3:95-121.

Buma, T.J., 1971. Free fat in spray dried whole milk. Neth. Milk & Dairy J. 25:33-140.

Dobers, H.J., 1969. Uber die Abhängigkeit der Peroxid- und Epoxidzahl vom Phosphatidgehalt von heissgehaltenem Milchfett. Milchwissenschaft 24:198-207.

Fink, A. & H.G. Kessler, 1985. The effect of heating on the storage stability of unhomogenized cream. Milchwissenschaft 40(6):326-328.

Fink, A. & H.G. Kessler, 1985. The effect of heating on the state of the emulsion in homogenized cream. Milchwissenschaft 40(7):394-397.

Fox P.F. & P.A. Morrisey, 1977. Reviews of the progress of Dairy Science: The heatstability of milk. J. Dairy Res. 44:627-646.

Griswold, B.L., F.L. Humoller & A.R. McIntyre, 1951. Inorganic phosphates and phosphate esters in tissue extracts. Analytical Chemistry 23(1):192-194.

Halling, P.J., 1981. Protein stabilized foams and emulsions. CRC 15:155-203.

Hardy, E.E., A.W.M. Sweetsur, I.G. West & D.D. Muïr, 1985. Heatstability of concentrated milk: enhancement of initial heatstability by incorporation of food grade lecithin. *J. Food Technology* 20:97-105.

Jensen, G.K. & P. Nielsen, 1982. Reviews of the progress of Dairy Science: Milk powder and recombination of milk and milk products. J. Dairy Res. 49:515-544.

Koops J, 1967. Preparation and properties of sterilized coffee cream. Neth. Milk Dairy J. 21:29-49.

Korver, O. & H. Meder, 1974. The influence of lysolecithin on the complex formation between β-lactoglobulin and K-casein. J. Dairy Res. 41:9-17.

Labuschagne, J.H., 1963. Churning in the absence of air. Thesis, Agricultural University Wageningen, The Netherlands. 77p.

Lankveld, J.M.G. & J. Lyklema, 1972. Adsorption of polyvinyl alcohol on the paraffin-water interface. J. Colloïd Interfase Sci. 41:454-483.

Laver, S., 1968. RNA and DNA determination in tobacco pith issue. Analytical Biochemistry 26:369-380.

Lyster, R.L.J., 1972. Chemistry of milk proteins. J. Dairy Res. 39:275-318.

MacRitchie, F., 1978. Proteins at interfaces. Advances in Protein Chemistry 32:283-326.

Mol, J.J., 1963. De beoordeling van de werking van homogenisatoren. Off. Org. FNZ 55:529.

Mulder, H., 1941. Over den invloed van het zouten op de stevigheid en vochtverdeling van boter. Verslagen Landbouwkundig

Onderzoek 47(11) c 1941 blz. 919.

Mulder, H., 1947. De samenstelling en de dispersiteit van het vet van de karnemelk. Zuivelonderzoek.

Mulder, H. & P. Walstra, 1974. The Milk Fat Globule; Emulsion Science as applied to milk products and comparable foods. CAB, Farnham Royal and PUDOC, Wageningen, 296 p.

NEN, 1964. Voorschrift nr. 962. Nederlands Normalisatie Instituut.

Ogden, L.V., 1973. Homogenization-induced clustering of fat globules in cream and model systems. Ph.D. Thesis, University of Minnesota, U.S.A. 217 p.

Ogden, L.V., P. Walstra & H.A. Morris, 1976. Homogenization induced clustering of fat globules in cream and model systems. J. Dairy Sci. 59:1727-1737.

Oortwijn, H., P. Walstra & H. Mulder, 1977. The membranes of recombined fat globules:1. Electron microscopy. Neth. Milk & Dairy J. 31:134-147.

Oortwijn, H. & P. Walstra, 1979. The membranes of recombined fat globules: 2. Composition. Neth. Milk & Dairy J. 33:134-154.

Overbeek, J.Th.G., 1977. Recent developments in the understanding of colloid stability. J. Colloid interface Sci. 58:408-422.

Oortwijn, H. & P. Walstra, 1982. The membranes of recombined fat globules:4. Effects on properties of the recombined milks. Neth. Milk & Dairy J. 36:279-290.

Pruthi, T.D., 1979. Phospholipid content of ghee prepared at higher temperatures.
Indian J. Dairy Sci 30:265-267.

Puhan, Z., 1983. Bedeutung und Erfassung der Fettschädigung im Rohstoff Milch. Deutsche Molkerei Zeitung 104 (4): 106-109.

Rientjes, G.J., 1985. Personal communication.

Rouse, H., 1959. Advanced Mechanics of Fluids. J. wiley & Sons

Inc., New York.

Schmidt, D.G., 1980. Colloidal aspects of casein. Neth. Milk & Dairy J. 34:42-64.

Shimuzu, M., T. Kamiya & K. Yamanchi, 1981. The adsorption of whey proteins on the surface of emulsified fat. Agricultural Biological Chemistry 45:2491-2496.

Solms zu Baruch, 1975. Lecture given at the annual meeting of the German Society of Process Engineering at Karlsruhe.

Stege, H.J. van der & P. Walstra, 1987. Atomizing disk for producing spray dried powders very low in vacuoles. To be published.

Stelzer, E., 1973. Unerwünschte Strukturänderung bei Lebenmitteln durch hohe Schergeschwindigkeiten beim Rühren. Chem. Ing. Techn. 45:502-505.

Sweetsur, A.W.M. & D.D. Muir, 1982. Natural variation in heat-stability of concentrated milk before and after homogenisation. J. Soc. Dairy Tech 35(4):120-126.

Sweetsur, A.W.M. & D.D. Muir, 1983. Influence of sulphydryl group interactions on the heatstability of homogenized concentrated milk. J. Dairy Res. 50:301-308.

Tempel, M. van den, 1953. Stability of oil-in-water emulsions. Thesis, Communication Rubber Stichting no. 225, Delft, The Netherlands, 78p.

Tempel, M. van den, 1957. Coagulation of oil-in-water emulsions. Proc. Second Int. Congr. Surf. Activity, Londen. I. p. 439-446.

Torza, S., R.G. Cox & S.G. Mason, 1972. Particle motions in sheared suspension. XXVII Transient and steady deformation and burst of liquid drops. J. Colloid Interface Sci 38:395-411.

Timmen, H., 1967. Phosphatidgehalt und Haltbarkeit von Milchfettsorten. Milchwissenschaft 22(1):45.

Vand, V., 1948. Viscosity of solutions and suspensions II. J. Phys. Coll. Chem. 52:300-314.

Ven, T.G.M. van de & S.G. Mason, 1976a. The microrheology of colloidal dispersions. IV Pairs of interacting spheres in shear flow. J. Colloid Interface Sci. 57:505-516.

Ven, T.G.M. van de & S.G. Mason, 1976b. The microrheology of colloidal dispersions. V. Primary and secondary doublets in shear flow. J. Colloid Interface Sci. 57:517-534.

Visser, F.M.W., 1977. Contribution of enzymes from rennet, starter bacteria and milk to proteolysis and flavour development in Gouda cheese. Thesis, Agricultural University Wageningen The Netherlands.

Walstra, P. & J.J. de Graaf, 1962. Note on the determination of the phospholipid content of milk products. Neth. Milk & Dairy J. 16:283-287.

Walstra, P., 1965a. Light scattering by milk fat globules. Neth. Milk & Dairy J. 19:93-109.

Walstra, P., 1965b. Discussion of errors in turbidimetry. Brittish J. Applied Physics 16:1187-1192.

Walstra, P. & G.J. Borggreve, 1966. Note on the refractive index of individual milk fat globules. Neth. Milk & Dairy J. 20:140-143.

Walstra, P., 1967. On the crystallization habit in fat globules. Neth. Milk & Dairy J. 21:166-191.

Walstra, P., 1968. Estimating globule-size distribution of oil-in-water emulsions by spectroturbidimetry. J. Colloid Interface Sci. 27:493-500.

Walstra, P., 1969. Studies on milk fat dispersion IV. A simple turbidimetric method for the determination of globule size and surface area in milk. Neth. Milk & Dairy J. 23:238-244.

Walstra, P. & L.V. Ogden, 1970. Unpublished results.

Walstra, P. & E.C.H. van Beresteyn, 1975a. Crystallization of

milk fat in the emulsified state. Neth. Milk & Dairy J. 29:35-65.

Walstra, P., 1975b. Homogenization and fat globule size distribution in milk. Neth. Milk & Dairy J. 29:279-294.

Walstra, P., 1980. Formation of emulsions. In: P. Becher (Ed.), Encyclopedia of Emulsion Technology, Vol I. Marcel Dekker inc, New York and Basel.

Walstra, P. & H. Oortwijn, 1982. The membranes of recombined fat globules: 3. Mode of formation. Neth. Milk & Dairy J. 36:103-115.

Walstra, P & R. Jennes, 1984. Dairy Chemistry and Physics. J. Wiley & Sons, Inc. New York.

Wit, J.N. de, G. Klarenbeek & G.A.M. Swinkels, 1976. De emulgerende eigenschappen van eiwit concentraten uit wei. Zuivelzicht 19:442-445.

Wit, J.N. de, G. Klarenbeek & R. de Boer, 1978. A simple method for the clarification of whey. Proc. 20th Int. Dairy Congr. (Paris): 919-920.

Wit, J.N. de, 1981. Structure and functional behaviour of whey proteins. Neth. Milk & Dairy J. 35:47-64.

SUMMARY

The subject of this study is the stability of the fat globules in recombined milk products against creaming, flocculation, clustering, partial coalescence and coalescence. Recombined milk products are oil-in-water emulsions made of anhydrous milk fat and an aqueous milk fraction such as skimmilk, buttermilk or whey.

In chapter 1 the advantages of recombined emulsions are mentioned and a description is given of the various aggregation types.

In chapter 2 the materials used, the preparation of the emulsion, the test conditions and the characterization of instability are described. In order to obtain measurable instability, recombined cream rather than milk was made. Emulsions with a narrow globule size distribution with average diameters from 0,5 μm to 15 μm were obtained in a reproducible way by homogenizing mixtures of milk fat and an aqueous milk fraction under continuous recycling at a defined temperature and homogenisation pressure. The stability of these emulsions was tested in several flow fields, at rest under admittance of creaming or slowly rotating to prevent creaming, and in some cases also after a heat treatment and after spray drying. Coalescence rate and course were characterized by determining changes in the globule size distribution and fat content. Clustering was examined microscopically and by means of the apparent viscosity.

Stability to aggregation of emulsions made of milk fat and skimmilk is described in chapter 3. This type of emulsion was very stable to partial coalescence certainly if globule size was small; only in strongly turbulent flow fairly rapid partial coalescence may occur, sometimes resulting in a decrease of fat content while the globule size distribution remains almost the same, sometimes resulting in an increase of the average diameter while fat content remains the same. If these emulsions were left to cream, tough and hardly dispersable cream layers were formed, not as a result of partial coalescence but of clustering; this

can be explained with the existing ideas about the structure of casein micelles.
Emulsions of milk fat and skimmilk may be unstable if heat treated: a direct ultra-high temperature treatment causes disruption of globules and an indirect ultra-high temperature treatment causes clustering. Whereas the first treatment has no macroscopic effects on the cream, the second results in the formation of a paste-like product.
Spray drying results, dependant on the average diameter of the spray dried emulsion, in powders that give upon redispersion in water clustered emulsions or emulsions with fat floating on top.

Stability of natural cream and mixtures of natural cream and milk fat-in-skimmilk emulsions are described in chapter 4. Natural cream is far less stable against partial coalescence than milk fat-in-skimmilk emulsions with the same average globule diameter. Also for these emulsions an influence of the treatment conditions on the type of coalescence was found.
If natural cream is "homogenized" with continuous recycling at such a low pressure that no disruption of globules occurs, the stability of the cream is not increased, indicating that during homogenisation, natural membrane proteins are hardly replaced by plasma proteins. Mixtures of natural cream and milk fat-in-skimmilk emulsions show considerable partial coalescence, provided that the average diameter of the recombined globules is not too low.

The influence of phospholipids on the stability of recombined emulsions is treated in chapter 5. Replacement of skimmilk by buttermilk did not change the stability to partial coalescence of the recombined emulsions. With depletion experiments it was shown that phospholipids present in buttermilk do not adsorb onto the fat-plasma interface during or after homogenisation, if enough plasma proteins are present to cover the created surface. However, if sufficient lecithins are added to the fat before homogenizing, very unstable emulsions result.
We did not succeed in obtaining an anhydrous milkfat from natural cream that contained sufficient milk phospholipids to give

unstable milk fat-in-skimmilk emulsions.

The stability of milk fat-in-clarified whey emulsions is treated in chapter 6. Partial coalescence of these emulsions resulted in the studied cases always in a decrease of the fat-content while the average globule diameter remained nearly the same for small reductions of the fat content and gradually decreased for reductions in fat content by more than 30%. A relation between the relative decrease in d_{32} and the relative reduction in fat content was found that appeared independant of the original average diameter of the globules, the fatcontent of the emulsion, the surface load of the globules and the pretreatment of the clarified whey and only slightly dependant on the treatment temperature.

Instability of these emulsions to partial coalescence in a flow field with Taylor vortices was maximal at treatment temperatures around 10°C and increased with fat content and globule size. Instability was less as the surface load of the globules was higher. Similar instabilities were only found in laminar flows with shear rates higher than the apparent shear rate with which a flow with Taylor vortices is characterized. The emulsions were stable at temperatures where all the fat is liquid.

To explain the experimental results, several models are elaborated and discussed. Two models start with the formation of reactive globules after which these globules react infinitely fast with other globules to clumps so large as to be thrown out of the emulsion by centrifugal forces. In model 1 the formation of reactive globules is a consequence of globule deformation. The unknown parameters to be determined from the experiments are the fraction of deformed globules that change per unit time into reactive ones and the volume of a clump that is removed from the emulsion by centrifugal forces. In model 2 the formation of reactive globules is a consequence of globule collisions. The unknown parameters to be determined are the fraction of collisions that leads to the formation of reactive globules and the volume of a clump that is removed from the emulsion.

The third model assumes the existence of a small fraction of reactive globules that gradually grow into clumps during the treatment. In this model the unknown parameters are the fraction of reactive globules and the reactivity of these globules. Although the results obtained with milk fat-in-whey emulsions are best described with the third model, further refinements, such as a description of possible interactions between the growing clumps and the introduction of a globule size distribution instead of an average globule size, are required to explain all observations. These aspects are only discussed qualitatively.

In chapter 7 the partial coalescence processes observed for the other emulsions studied are qualitatively discussed: if the proportion of reactive globules (or of globules that become reactive during the treatment) is very low while composite clump formation (formation of large clumps as a consequence of clump-clump collisions) is easy, partial coalescence probably will result in the formation of a few very large clumps that coalesce, upon melting the fat, to a floating fat layer on top of the emulsion, thus causing a decrease of the fat content of the remaining emulsion. If the fraction of reactive globules is high while composite clump formation is more difficult, partial coalescence probably will result in the formation of many small clumps, that coalesce to fairly large globules when the fat is melted, thus causing an increase of the average diameter of the emulsion.

This chapter concludes with an enumeration of the possible applications of the studied recombined emulsions.

DE STABILITEIT VAN GERECOMBINEERDE MELKVETBOLLETJES

SAMENVATTING

Dit onderzoek betreft de stabiliteit van gerecombineerde zuivelproducten tegen oproming, vlokking, trosvorming, partiële coalescentie en coalescentie van de vetbolletjes. De hier bestudeerde gerecombineerde zuivelproducten zijn olie-in-water emulsies gemaakt van watervrij melkvet en een of andere vetvrije melkfractie zoals ondermelk, karnemelk of wei.

In hoofdstuk 1 worden een aantal voordelen van deze producten gegeven. Tevens wordt er een beschrijving gegeven van de verschillende manieren waarop vetbolletjes kunnen aggregeren.

In hoofdstuk 2 wordt een beschrijving gegeven van de gebruikte materialen, de bereiding van de emulsie, de omstandigheden waaronder de emulsie werd getest en de manier waarop de verschillende vormen van instabiliteit werden gekarakteriseerd en bepaald. Om een merkbare instabiliteit te krijgen werd meestal gebruik gemaakt van emulsies met een tamelijk hoog vetgehalte (30%).

Door mengsels van melkvet en een vetvrije melkfractie bij een bepaalde temperatuur en druk gedurende een langere tijd continu te homogeniseren werden op een reproduceerbare wijze emulsies met gemiddelde druppeldiameters van 0.5 μm tot meer dan 10 μm en een nauwe druppelgrootteverdeling verkregen. De stabiliteit van een aantal gerecombineerde emulsies werd bepaald onder invloed van oproming, in verschillende stromingsvelden en tijdens opslag in roterende cilinders. In sommige gevallen werd ook de invloed van een hittebehandeling of van sproeidrogen onderzocht.

De snelheid en het verloop van partiële coalescentie werden bepaald door vetgehalte en druppelgrootteverdeling van behandelde en onbehandelde emulsies te vergelijken. Trosvorming werd gevolgd onder een microscoop en door bepaling van de (schijnbare) viscositeit.

Hoofdstuk 3 gaat over de stabiliteit van melkvet-in-ondermelk emulsies. Dit type emulsie gaf, zeker als de gemiddelde druppel-

grootte klein was, nauwelijks partiële coalescentie. Alleen in een krachtig turbulent stromingsveld kon bij emulsies met een hoog vetgehalte en een tamelijk grote gemiddelde diameter duidelijke partiële coalescentie optreden, die in sommige gevallen resulteerde in een vermindering van het vetgehalte bij een nagenoeg gelijkblijvende druppelgrootteverdeling en in andere gevallen in een toename van de gemiddelde diameter terwijl het vetgehalte onveranderd bleef. Als deze emulsies oproomden, werd er een roomlaag gevormd die taai en slecht te redispergeren was. Deze taaiheid werd veroorzaakt door trosvorming van de vetbolletjes in de roomlaag, hetgeen met de bestaande ideeën over de structuur van caseïnemicellen kan worden verklaard. Melkvet-in-ondermelk emulsies kunnen een hittebehandeling vaak slecht verdragen: een directe UHT-verhitting veroorzaakte een versplintering van vetbolletjes, een indirecte UHT behandeling veroorzaakte trosvorming. Terwijl een versplintering nauwelijks merkbare effecten op de emulsie heeft, veroorzaakt trosvorming de vorming van een pasta-achtig produkt. Sproeidrogen van melkvet-in-ondermelk emulsies met een tamelijk grote gemiddelde diameter (2 μm) leverde een plakkerig poeder op dat na dispergeren in water een emulsie gaf waarop vet dreef. Emulsies met een kleinere gemiddelde diameter gaven een poeder dat na dispergeren een getroste emulsie vormde.

De stabiliteit van natuurlijke room en mengsels van natuurlijke room en melkvet-in-ondermelk emulsies wordt beschreven in hoofdstuk 4. Natuurlijke room was in een stromingsveld veel minder stabiel dan melkvet-in-ondermelk emulsies die dezelfde gemiddelde diameter hadden. Ook bij deze emulsies beinvloedden de testomstandigheden naast de snelheid ook het verloop van het coalescentie proces. De stabiliteit van natuurlijke room die gedurende een langere tijd continu werd gehomogeniseerd bij een druk die zo laag was dat er geen versplintering van de vetbolletjes kon optreden, bleek nauwelijks veranderd te zijn. Blijkbaar wordt het natuurlijke membraan tijdens het homogeniseren niet of nauwelijks vervangen door plasma eiwitten. Mengsels van natuurlijke room en melkvet-in-ondermelk emulsies

vertoonden in stroming een aanzienlijke partiële coalescentie, mits de gemiddelde diameter van de gerecombineerde vetbolletjes niet te laag was.

De invloed van fosfolipiden op de stabiliteit van gerecombineerde emulsies wordt behandeld in hoofdstuk 5. Het vervangen van ondermelk door karnemelk had geen invloed op de stabiliteit met betrekking tot partiële coalescentie van de gerecombineerde emulsies. Met depletie proeven werd aangetoond dat de fosfolipiden in de karnemelk tijdens of na het emulgeren van melkvet niet op het vet-plasma grensvlak adsorberen, tenminste zolang er voldoende plasma-eiwitten zijn om het nieuw gevormde grensvlak te bedekken. Als er echter in het vet voldoende lecithine werd gedispergeerd voordat het vet-ondermelk mengsel werd gehomogeniseerd, waren de gevormde emulsies zeer instabiel. We slaagden er niet in uit natuurlijke room een watervrij melkvet te verkrijgen dat zoveel fosfolipide bevatte dat de melkvet-in-ondermelk emulsies die daar mee gemaakt werden instabiel waren.

De stabiliteit van melkvet-in-geklaarde-wei emulsies wordt behandeld in hoofdstuk 6. Partiële coalescentie had in de bestudeerde gevallen altijd een afname van het vetgehalte tot gevolg terwijl de gemiddelde druppeldiameter voor geringe verminderingen van het vetgehalte gelijk bleef en geleidelijk afnam wanneer het vetgehalte met meer dan 30% verminderde. Het verband tussen de relatieve afname in de gemiddelde diameter en de relatieve afname in het vetgehalte bleek onafhankelijk van de gemiddelde vetboldiameter in de onbehandelde emulsie, van het vetgehalte van de emulsie, van de belading van de vetbolletjes en van de voorbehandeling van de geklaarde wei. De behandelingstemperatuur leek wel, zij het een geringe, invloed op dit verband te hebben. In een stromingsveld met Taylor-wervels gaf dit type emulsies de sterkste partiële coalescentie bij een temperatuur van 10°C, een hoog vetgehalte en grote vetbolletjes. Een verhoging van de belading resulteerde in een stabielere emulsie. In een laminaire stroming kwam partiële coalescentie alleen voor bij afschuifsnelheden die hoger waren dan de schijnbare afschuifsnelheid die behoort bij het stromingsveld met Taylor-

wervels.
Bij temperaturen waarbij het vet geheel vloeibaar is waren deze emulsies stabiel.
Om de experimentele resultaten te kunnen beschrijven en verklaren werden een aantal modellen uitgewerkt en bediscussieerd. Twee modellen gaan uit van de vorming van reactieve vetbolletjes die, eenmaal gevormd, oneindig snel doorreageren met andere vetbolletjes tot de klompjes die gevormd worden zo groot zijn dat ze uit de emulsie worden gedreven door de middelpuntvliedende kracht. In model 1 wordt de vorming van reactieve deeltjes veroorzaakt door vervorming van vetbolletjes. De parameters die in dit model berekend moeten worden uit de experimentele gegevens zijn: de fractie vervormde vetbolletjes die verandert in reactieve vetbolletjes en het volume van de klompjes die uit de emulsie verdreven worden door de middelpunt-vliedende kracht. In model 2 wordt de vorming van reactieve deeltjes veroorzaakt door botsingen tussen twee niet reactieve deeltjes. De onbekende parameters zijn nu: Het gedeelte van de botsingen dat leidt tot de vorming van reactieve deeltjes en het volume van de klompjes die uit de emulsie verdreven worden. In het derde model wordt aangenomen dat een klein deel van de vetbolletjes al reactief is vanaf het begin en dat deze reactieve vetbolletjes geleidelijk uitgroeien tot klompjes die tot het eind van het experiment in de emulsie actief blijven. In dit model zijn de onbekende parameters de fractie reactieve vetbolletjes en de reactiviteit van deze vetbolletjes. Ofschoon de resultaten verkregen met de melkvet-in-wei emulsies redelijk goed beschreven kunnen worden met het derde model, blijven verdere verfijningen zoals een beschrijving van de mogelijk wisselwerkingen tussen de groeiende klompjes en het gebruiken van druppelgrootteverdelingen in plaats van een gemiddelde druppeldiameter vereist om alle waarnemingen afdoende te verklaren. Deze aspecten zijn alleen kwalitatief besproken. Berekeningen met de modellen 1 en 2 bleken slecht met de waarnemingen overeen te komen.

In hoofdstuk 7 wordt uitgegaan van de juistheid van het derde model bij de bespreking van het partiële coalescentieproces bij

de overige bestudeerde emulsies: Als de fractie reactieve vetbolletjes erg laag is terwijl de vorming van samengestelde klompjes als gevolg van botsingen tussen klompjes onderling gemakkelijk verloopt, zal partiële coalescentie waarschijnlijk de vorming van een paar zeer grote klompjes tot gevolg hebben die, wanneer het melkvet geheel gesmolten wordt, doorcoalesceren tot een laag drijvend vet, waardoor het vetgehalte in de overblijvende emulsie verminderd wordt. Als de fractie reactieve vetbolletjes hoog is terwijl de vorming van samengestelde klompjes moeizamer verloopt, zal partiële coalescentie waarschijnlijk de vorming van grote aantallen kleine klompjes tot gevolg hebben die, wanneer het melkvet geheel gesmolten wordt, slechts doorcoalesceren tot grotere vetbolletjes waardoor de gemiddelde druppeldiameter van de emulsie toeneemt.

Het hoofdstuk wordt afgesloten met een opsomming van de mogelijke toepassingen van deze gerecombineerde emulsies.

CURRICULUM VITAE

De auteur werd op 24 december 1954 in Lent geboren. In juni 1973 behaalde hij het gymnasium-β diploma aan het Canisius College te Nijmegen. In datzelfde jaar werd begonnen met de studie aan de Landbouwhogeschool te Wageningen. In 1978 werd het kandidaatsexamen Moleculaire Wetenschappen (chemische specialisatie) afgelegd en in september 1981 volgde het doctoraaldiploma met als hoofdvakken kolloïdchemie, wiskunde en fytopathologie. Van oktober 1981 tot juli 1985 werkte de auteur als promotie-assistent op de vakgroep Zuivel en Levensmiddelennatuurkunde aan de Landbouwhogeschool. Sinds september 1985 is hij werkzaam bij de firma Quaker Chemical te Uithoorn bij de afdeling koelsmeermiddelen voor de metaalbewerking.