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on stability
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Abstract

Coalescence at rest and during flow was studied in emulsions of paraffin oil in water with several surfactants and with crystals of solid paraffin or tristearate in the oil phase. Solid fat in the oil phase was estimated by pulsed nuclear magnetic resonance. Without crystals, oil-in-water emulsions were mostly stable and flow hardly influenced coalescence, even of unstable emulsions. Emulsions with crystals in the dispersed oil phase were less stable if crystals appeared at the interface. The contact angle indicated that crystals could be oriented in the interface; if so, instability was promoted by creaming, Couette flow, turbulence or flow with Taylor vortices. Coalescence in such systems could be caused by crystals sticking through the interface and piercing the film between the globule and a second approaching globule. The effect of variables such as type of surfactant, type of crystal, amount of crystalline fat, globule size, volume fraction of fat and ionic strength fitted this view. Natural cream with part of the globular fat crystallised behaved to some degree like the model systems but there were deviations.

Free descriptors: coalescence; crystallisation; Couette flow; Taylor vortices; turbulence; cream; pulsed nuclear magnetic resonance; glycerol tristearate; solid paraffin; paraffin oil; contact angle.

Stellingen

1. Het coalescentiemechanisme van emulsies van olie in water met kristallen in de disperse fase verschilt van dat van echte emulsies.

   Dit proefschrift.

2. De schuimbrekende werking van emulsies met vaste deeltjes in de disperse fase is met hetzelfde mechanisme te verklaren als de coalescentie van dergelijke emulsiedruppels.

   Dit proefschrift.

3. De conclusie van Back dat de op elektronenfoto's waargenomen vervorming van melk-vetbolletjes veroorzaakt is door laminaire stroming, is gebaseerd op foutieve bereke-ningen. De vervorming kan veroorzaakt zijn door de prepareertechniek.

   W.D. Back, 1975. Dissertatie, Technische Universität, Hannover.

4. De 'nieuwe en nauwkeurige' methode ter bestudering van emulsiestabiliteit met behulp van pulse-NMR (kernspinresonantie), zoals ontwikkeld door Trumbetas et al., is weliswaar nieuw doch onjuist.

   J. Trumbetas, J.A. Fioriti & R.J. Sims, 1976. J. Am. Oil Chem. Soc. 53: 722-726.

5. Het beschrijven van reologische eigenschappen van materialen met behulp van mechanische modellen van veertjes en zuigertjes geeft geen wezenlijk inzicht in de fysische achtergrond van die eigenschappen.

   o.a. B.W. Barry, 1975. Adv. Colloid Interface Sci. 5: 37-75.

6. Volgens Fleming heeft het thermiseren van melk als hoofddoel het voorkomen van lipasewerking, terwijl een bijkomend voordeel zou zijn dat bacteriën gedood worden. Gezien de thermoresistentie van sommige bacteriële lipasen is het grootste voordeel juist het doden van bacteriën.

   M.G. Fleming, 1979. IDF report of Group A3-lipolysis, A-Document 43. p. 40-52.

7. Pectine blijkt een specifiek aandeel te hebben in de fysiologische werking van voedingsvezel. Veel bepalingsmethoden voor de samenstelling van voedingsvezel vertonen tekortkomingen bij de bepaling van pectine en dienen op dit punt verbeterd te worden.

M. Stasse-Wolthuis, 1980. Wld. Rev. Nutr. Diet (in druk).
D.A.T. Southgate, G.J. Hudson & H. Englyst, 1978. J. Sci. Food Agric. 29: 979-988.

8. In tegenstelling tot de hypothese van Chiba et al. dat enzymatische omzetting van aldehyden, ter verwijdering van de bonesmaak van soya-eiwit, ook plaatsvindt wanneer aldehyden gebonden zijn aan het eiwit, steunen hun experimenten veeleer de veronderstelling dat alleen vrije aldehyden worden omgezet.

H. Chiba, N. Takahashi, N. Kitabatake & R. Sasaki, 1979. Agric. Biol. Chem. 43: 1891-1897.

9. De suggestie van Kramer dat het beter benutten van afvalprodukten die vrijkomen bij het verwerken van landbouwprodukten, bijdraagt aan een oplossing van het wereldvoedselvraagstuk, is een treurig voorbeeld van een eenzijdige benadering van ontwikkelingsproblematiek.

A. Kramer, 1977. J. Food Quality 1: 279-289.

10. Het gebruik van extract van schapemest voor de kleuring van biologisch-dynamische Texelse schapekaas is vooral microbiologisch-dynamisch.

11. Voorstanders van de idee dat sport en politiek niets met elkaar van doen hebben, miskennen het sportieve element in de politiek.

Woord vooraf

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Curriculum vitae

De auteur werd geboren op 26 december 1951 te Veldhoven. Hij behaalde in 1970 het gymnasium-β-diploma aan Gymnasium 'Beekvliet' te Sint-Michielsgestel, en begon in hetzelfde jaar met de studie aan de Landbouwhogeschool te Wageningen. In januari 1974 werd het kandidaatsexamen Levensmiddelentechnologie (chemisch-biologische specialisatie) afgelegd, en in maart 1977 werd het doctoraaldiploma behaald met als hoofdvakken levensmiddelenchemie en colloïdchemie en als bijvak technische microbiologie. Van april 1977 tot april 1980 werkte de auteur als promotie-assistent bij de Landbouwhogeschool op het laboratorium voor Zuiveltechnologie en Melkkunde. Sinds juni 1980 is hij werkzaam bij de Keuringsdienst van Waren te Rotterdam.

Contents

List of symbols

a	activity	(1)
a_f	flocculation rate constant	$(m^3 \; s^{-1})$
A	Hamaker constant	(J)
A'	constant defined in Equation 34	(1)
$A(r^*)$	function defined in Equation 54	(1)
$b; \; b_i; \; b_j$	radius of a sphere; of sphere i; of sphere j	(m)
B	constant defined in Equation 34	$(mN \; m^{-1})$
B_1	shortest dimension of a deformed sphere	(m)
$B(r^*)$	function defined in Equation 54	(1)
c_s	relative standard deviation of the surface weighed distribution	(1)
$C(r^*)$	function defined in Equation 54	(1)
$d; \; d_{32}$	diameter of a sphere; volume-surface average diameter	(m)
D	relative deformation	(1)
D_i	diffusion coefficient of particle i	$(m^2 \; s^{-1})$
e	elementary charge	(C)
E	optical density (extinction)	(1)
E_m	energy level of a proton in a magnetic field	(J)
f	factor used in pulse NMR, Equation 27	(1)
F	mass fraction of fat in emulsions	(1)
$F_A; \; F_R; \; F_{int}$	attraction force; repulsive force; interaction force	(N)
g	acceleration due to gravity	$(m \; s^{-2})$
$G; \; G'$	shear rate; apparent shear rate	(s^{-1})
h	distance between the surfaces of two equal sized spheres: $h = r - 2b$	(m)
h_{cr}	thickness of a cream layer	(m)
H	height of cylinders of Couette and Taylor equipment	(m)
H_0	static magnetic field	(T)
H_1	pulse of radio frequency	(T)
$J; \; J_S$	capture frequency per particle; according to Smoluchowski	(s^{-1})
$J_0; \; J_1$	capture frequencies defined in Equations 67 and 68	(s^{-1})
k	Boltzmann's constant (1.38×10^{-23})	$(J \; K^{-1})$
$k_c; \; k_1; \; k_2; \; k_3$	coalescence rate; estimated by spectroturbidimetry at one wavelength; by Coulter Counter; by spectro-turbidimetry	(s^{-1})
l	thickness of a layer, Equation 9	(m)

l_s	characteristic length in Re, Equation 22	(m)
L; L^*	semi-axis of the boundary of the capture cross-section; dimensionless semi-axis (L/b)	(m; 1)
M	molecular weight	(kg kmol^{-1})
M_0	resultant magnetisation vector	(J T^{-1})
n_1; n_2	refractive index of medium 1; of medium 2	(1)
n_i	number of ions per unit volume	(m^{-3})
N; N_i; N_t	number of particles per unit volume; of particles i; at time t	(m^{-3})
N_0; N_1	number of particles in Equations 67 and 69, respectively	(m^{-3})
N_1; N_h	number of protons in lower and higher energy level (NMR), Equation 26	(1)
p	$2\pi h/\lambda$	(1)
Pe_t	translational Péclet number, Equation 58	(1)
q	viscosity ratio n_d/n_c	(1)
Q; Q^*; Q_i^*	light-scattering coefficient; corrected; of particles i	(1)
r; r^*	distance between centres of two spheres; dimensionless distance (r/b)	(m; 1)
R	molar gas constant (8.314)	(J K^{-1}mol^{-1})
R_o; R_i	radius of outer and inner cylinder of Couette and Taylor equipment	(m)
R_{ij}	'collision radius' of particles i and j $(b_i + b_j)$	(m)
Re; Re_p	Reynolds number, Equation 23; particle Reynolds number, Equation 59	(1)
s	gap width, $R_o - R_i$	(m)
S_F; S_{EM}	specific surface area of the fat; of the emulsion	(m^{-1})
S_n	the n-th moment of particle size distribution, Equation 1	(m^n)
$S(T)$; $S(T_m)$	NMR signals at temperature T; at temperature T_m	(1)
S_f	mass fraction of solid fat	(1)
$S_R(T)$; $S_R(T_m)$	NMR signals of reference oil at temperature T; at temperature T_m	(1)
S_b; S_∞	solubility of particle with radius b; of a particle with $b = \infty$, Equation 30	(1)
t; t^*	time; dimensionless time $(t\ G)$	(s; 1)
T; T_m	temperature; temperature of fusion of solid fat	(K)
T_1; T_2	longitudinal (NMR) relaxation time; transversal (NMR) relaxation time	(s)
T_c; T_f	final melting point; fusion temperature, Equation 29	(K)
Ta	critical Taylor number, Equation 24	(1)
u_o; u_i	circumferential velocity of outer cylinder; of inner cylinder	(m s^{-1})

Symbol	Description	Units
u_1; u_2; u_3	velocity components along x_1; x_2; x_3 axes	$(m\ s^{-1})$
V_A; V_R	attraction energy; repulsion energy	(J)
v	circumferential speed of a sphere rotating in Couette flow	$(m\ s^{-1})$
v_s	velocity of a sphere according to Stokes' law, Equation 48	$(m\ s^{-1})$
W_{ij}	rate of encounters of particles i and j in Brownian motion	$(m^{-3}\ s^{-1})$
We	Weber number, Equation 61	(1)
x_1; x_2; x_3	Cartesian coordinate axes; distance coordinates	(m)
x_s	mole fraction of solute, Equation 29	(1)
$Z(x_2)$; $Z^*(x_2^*)$	function describing boundary of the capture cross section; dimensionless $(Z(x_2)/b)$	$(m;\ 1)$
z	valency of ion	(1)
z	reduced turbidity, Equations 11 and 14	(1)
α; α_1	coalescence efficiency: fraction of encounters in Couette flow leading to coalescence; efficiency defined in Equation 68	(1)
α_o; α_p; α'	orthokinetic capture efficiency, Equation 52; perikinetic capture efficiency, Equation 45; fraction of encounters leading to $h < 30$ nm or $h < 25$ nm in Couette flow	(1)
γ; γ_{ow}	interfacial tension; oil-water interfacial tension	$(mN\ m^{-1})$
γ^0; γ^d	interfacial tension of the pure phase; dispersive contribution to the interfacial tension, Equation 35	$(mN\ m^{-1})$
γ_g	gyromagnetic ratio, Equation 25	$(s^{-1}\ T^{-1})$
Γ	surface excess, Equation 32	$(mol\ m^{-2})$
$\bar{\Delta}$	average displacement of a particle in Brownian motion, Equation 49	(m)
$\Delta\gamma$	interfacial-tension gradient	$(mN\ m^{-1})$
$\Delta_f H$	enthalpy of fusion	$(J\ mol^{-1})$
ζ	electrokinetic potential	(mV)
η; η_c; η_d	viscosity; of the continuous phase; of the disperse phase	$(N\ s\ m^{-2})$
θ	polar coordinate	(1)
θ_c	contact angle	(1)
κ	reciprocal double-layer thickness	(m^{-1})
λ	wavelength	(m)
μ	magnetic moment of a proton	$(J\ T^{-1})$
ν	kinematic viscosity	$(m^2\ s^{-1})$
ρ; ρ_{32}	size parameter in spectroturbidimetry, Equation 8; volume-surface average size parameter, Equation 13	(1)
σ_n	coefficient of variation of size distribution, Equation 3	(1)

σ_{cr}	pressure in a cream layer, Equation 47	$(N\ m^{-2})$
$\bar{\tau}$	average life time of a transient doublet in Couette flow, Equation 66	(s)
ϕ	polar coordinate	(1)
$\phi_v;\ \phi_{cr}$	volume fraction of fat; in a cream layer	(1)
ψ_d	stern potential	(mV)
ω	angular velocity	(s^{-1})
ω_L	Larmor frequency, Equation 25	(s^{-1})

1 Introduction

1.1 GENERAL INTRODUCTION

An emulsion is a dispersion of one liquid in another, the two being immiscible. Emulsions are used, for example, in foods, pharmaceutics, cosmetics and insecticides. In some uses, an emulsion must remain stable (e.g. during processing and storage of milk), in others instability is required (e.g. when making butter from cream). Research mainly deals with emulsification and stability (creaming, flocculation, coalescence).

Mostly, stability is studied in a quietly standing emulsion, in which only Brownian motion of the droplets would occur, but sometimes a flow field is applied ('mechanical stability'). Most studies are made on model systems and are of a fundamental nature and the results may then be difficult to apply to practical systems, which are much more complicated. On the other hand, many studies of practical interest are difficult to rationalise with a theoretical model. Consequently there is a gap between fundamental research and its practical application.

In practice, the oil phase may crystallise at a certain temperature. There is hardly any literature describing this effect and its consequences on the stability of the emulsion. Information as to the effect of crystals on stability of emulsions is effectively limited to the stabilisation by solid particles (Pickering stabilisation). Lucassen--Reynders (1962) studies stabilisation of water-in-oil emulsions by trisearate crystals as a model system for margarine. Some of the features she observed may also apply to oil-in-water emulsions with crystals in the oil phase, but on the whole conditions were far different. Skoda & Van den Tempel (1963) used oil-in-water emulsions with triglycerides in the oil phase to study crystallisation kinetics of triglycerides. These emulsions were observed to be rather unstable. Walstra & Van Beresteyn (1975) studied the crystallisation of milk fat in the emulsified state (oil-in-water emulsions) but again the interest was in kinetics of crystallisation. El-Difrawi & Ismail (1979) studied the stability, thermal dilatation and solidification properties of emulsions of partially hydrogenated cottonseed oil in skim milk. However, they did not properly measure the stability of the emulsion, nor did they pay any attention to the possible effect of crystallisation on stability.

Sideman et al. (1972) studied coalescence of droplets containing $Na_2SO_4 \cdot 10H_2O$ crystals in saturated Na_2SO_4 mother liquor, dispersed in kerosene or perchloroethylene. Experiments were made in agitated vessels and it appeared that droplets with crystals coalesced easier than droplets without crystals. These droplets were, however, several orders of magnitude larger than those normally observed in emulsions: droplets with crystals were 1-3 mm and droplets without crystals 0.1-0.3 mm.

Fukushima et al. (1976, 1977) observed that emulsions of cetyl alcohol in water

1

(stabilised by a polyoxyethylene surfactant) were unstable if the alcohol crystallised in a certain polymorphic form. A similar effect was found by Barry (1968), when adding cetyl alcohol to paraffin oil-in-water emulsions stabilised by sodium dodecylsulphate. Slight instability was accompanied by crystallisation of the alcohol.

Churning of cream to produce butter is impossible without crystals in the oil phase or when the fat is completely solidified (Mulder & Walstra, 1974). According to Berger & White (1971), fat crystals are necessary for clumping of fat globules ('churned fat') in ice-cream.

Addition of certain solids could enhance coalescence in emulsions (Mizrahi & Barnea, 1970). For example, Labuschagne (1963) noticed that addition of solid particles to cream could impair stability when cream was churned in the absence of air. The latter phenomena, however, are caused by addition of solids to emulsions, whereas this investigation is concerned with the possible effect of crystals on stability, the solid phase being a part of the emulsion droplet itself.

It appears from this superficial survey that crystals can influence the stability to coalescence, but it remains uncertain how and under what circumstances the effect can be explained. The aim of this study was to investigate the effect of fat crystals in the oil phase on stability of oil-in-water emulsions. Strictly speaking, these systems are not true emulsions but three-phase systems. Since, however, the fat crystals appear at a certain temperature in what originally are real emulsions, it is acceptable to refer to these systems as oil-in-water emulsions. The use of the terms 'oil' and 'fat' may be somewhat confusing because in the literature 'oil' is sometimes used to mean liquid oil and 'fat' a partially crystalline fat. Here the term 'oil' refers to the non-polar phase, thus liquid as well as solid fat.

1.2 STABILITY OF EMULSIONS

It is possible to distinguish between several types of stability or instability in emulsions: creaming, flocculation, coalescence and occasionally disruption. Stability may be defined as resistance to physical change by external factors (Mulder & Walstra, 1974). Thus the term stability refers to a characteristic time (e.g. a half-life) for a certain change to occur. Emulsions may have half-lives of minutes, days or years and may kinetically be stable, but in a thermodynamic sense they are always unstable. Free energy is accumulated in the interface due to the large interfacial area in emulsions. The system strives for the lowest possible free energy, which eventually means complete phase separation. Microemulsions, which are thermodynamically stable, are not considered here.

Instability to gravity creaming (or generally to sedimentation) is due to the density difference between the two phases. Amongst other factors, size of the emulsion droplets, density difference and viscosity of the continuous phase govern the extent of creaming (Walstra & Oortwijn, 1975). Creaming is not a reversible process, but the effect can easily be destroyed.

A second type of instability is flocculation which may be defined as the capture of particles to form aggregates, in which particles remain together for some time whilst the

2

individual particles still exist. The classical theory of colloid stability for hydro-
phobic sols applies to flocculation of emulsion droplets. This theory describes the de-
pendence of flocculation on the interaction energy between two particles as a function of
interparticle distance. The total interaction energy is the resultant of attraction and
repulsion. Attraction is usually caused by London-Van der Waals forces, whereas in emul-
sions, repulsion is mostly due to the presence of surfactants at the oil-water interface.
In the case of ionic surfactants the interaction can conveniently be described by the
theory of Deryagin-Landau-Verwey-Overbeek (DLVO theory) (Van den Tempel, 1953). For non-
ionics and macromolecular substances steric repulsion comes into play, and for polyelec-
trolytes a combination of electrostatic and steric repulsion is present (for example
Van Vliet, 1977). Figure 1 gives an example of the interaction energy between two glo-
bules. In principle, particles can flocculate in the primary minimum (A in Fig. 1) and
in the secondary minimum (B in Fig. 1). An energy barrier (maximum at point C) can pre-
vent the particles from flocculation in the primary minimum. But in the primary minimum
emulsion droplets are so close together that coalescence is inevitable. The location as
well as the depth of the secondary minimum depend on the actual interaction energy. When
the depth is less than about 1 kT no flocculation takes place, but only short time en-
counters. When this depth is more than a few times kT flocculation may occur. Floccula-
tion may be retarded because of viscous drag when the particles approach each other, the
more so when the interparticle distance becomes small. When flocculated in the secondary
minimum the particles are separated by a thin film of continuous phase with a thickness
ranging from about 10 to 100 nm.

Rupture of this thin film results in the flowing together of the droplets. This
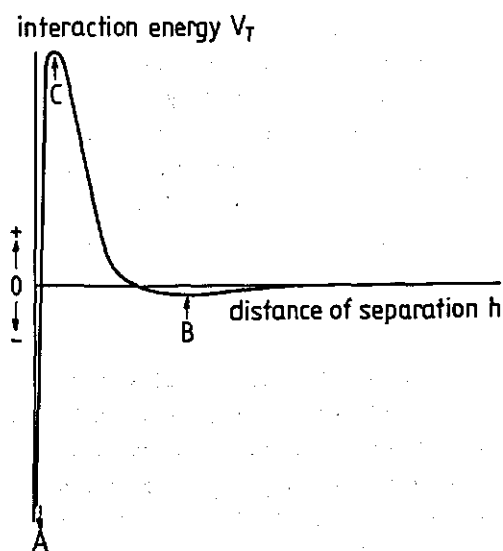process is called coalescence, a third cause of instability in emulsions. If the energy

Fig. 1. Schematic representation of the interaction energy (the energy needed to bring
particles from $h = \infty$ to h) as a function of the interparticle distance h. A refers to
the primary minimum, B to the secondary minimum and C to the maximum energy barrier.

barrier has been overcome, rupture will take place rapidly, because it will be accelerated by Van der Waals attraction. Rupture can occur, however, when there is still an energy barrier to overcome, perhaps when the globules have been flocculated for a longer time. Besides the repulsive interaction energy, other aspects are also involved. Interfacial phenomena like Gibbs-Marangoni effects tend to stabilise the thin film between droplets when disturbances arise in the film (Van den Tempel, 1960). Viscous resistance, experienced when liquid has to flow out of the film, can also have a stabilising effect. Finally rupture or desorption of surfactant must take place, and this requires some activation energy as well. The process of rupture of thin films is not yet fully understood. The theory developed to date (Vrij et al., 1970) attempts to correlate the probability of rupture with interaction energy and distance of separation. It is studied by examining whether small waves along the interface (surface ripples as a result of external disturbances) are damped, or grow until rupture occurs. This depends on the interaction energy as a function of interparticle distance and on the possible development of interfacial tension gradients. For most practical systems, however, theory predicts no rupture to occur, whereas in practice emulsions may be unstable.

Another phenomenon is Ostwald ripening, which is the growth of larger globules at the expense of the smaller ones. It depends strongly on the solubility of the disperse phase in the continuous phase. Its effect on emulsion stability was recently considered by Buscall et al. (1979). It is of minor importance for emulsions of paraffin oil in water (except maybe for very small droplets), because the solubility of paraffin oil in water is very low.

The last type of instability is disruption. This is not a spontaneous process: it requires input of energy, as for example in homogenisation. Disruption becomes easier when the globule size increases. It also depends strongly on the type of flow. Walstra (1980) gave a more extensive discussion of the parameters involved.

The phenomena mentioned above are found with true emulsions. When crystals are present in the oil phase the picture may be different in some respects. Coalescence may then be incomplete in the sense that droplets do not flow together completely, because crystal structures prevent this. Instead, clumps of irregular size are formed (Mulder & Walstra, 1974). Flocculation is probably not affected by the presence of crystals. Disruption on the other hand will be more difficult, the more so when more solid fat is present.

1.3 EFFECT OF FLOW FIELDS ON STABILITY OF EMULSIONS

As indicated in Section 1.2, droplets must approach each other before coalescence can occur. Encounters may be realized by Brownian motion (perikinetic aggregation) and the kinetics of this process were originally described by Smoluchowski (Overbeek, 1952) based on the assumption that every encounter leads to aggregation. Corrections for hydrodynamic and colloidal interaction have been made by Spielman (1970) and Honig et al. (1971). Encounters may also occur as a result of a velocity gradient (orthokinetic aggregation). The rate of aggregation of colloids in simple shear flow was again derived by Smoluchowski (Overbeek, 1952). Orthokinetic aggregation becomes far more important than

4

perikinetic aggregation for particles larger than 1 μm, because the rate of encounters is proportional to the cube of the particle radius (and to the shear rate). Recently, Van de Ven & Mason (1976a, 1977) applied corrections to the Smoluchowski equation by introducing hydrodynamic and colloidal interaction (see also Zeichner & Schowalter, 1977). Their analysis revealed that, depending on the interaction energy and shear rate, encounters can either lead to separating doublets (short-time encounters) or to permanent doublets; in the latter case, flocculation may be in the primary or in the secondary minimum.

Most experimental work on flocculation and/or coalescence pertains to perikinetic aggregation. Some experiments have been carried out on aggregation of lattices in simple shear flow (Stamberger, 1962; Swift & Friedlander, 1964; Curtis & Hocking, 1970; Warren, 1975; Utracki, 1973; Ives, 1978; Zeichner, 1978; Zeichner & Schowalter, 1979, and the work by Mason and coworkers, summarized by Mason, 1977). Flow was found to promote aggregation of particles. Most results were, at least qualitatively, in agreement with the theory of Van de Ven & Mason (1976a, 1977).

Studies on the effect of flow on stability of emulsions are scarce. Labuschagne (1963) studied the behaviour of natural cream in flow with Taylor vortices and cream was found to be very unstable in this type of flow. Swift & Friedlander (1964) carried out some experiments with emulsions in Couette flow. They observed that stable emulsions were also stable in shear flow (no coalescence). Back (1975) studied the stability of milk in Couette flow and he found instability only when the flow had changed from laminar to turbulent.

Besides aggregation of particles in shear flow, disruption of aggregates and even emulsion droplets may occur. Normal emulsion droplets in the micron size range are not disrupted in simple shear flow unless the shear rate is very high and the droplet very large. Moreover, fat crystals in the emulsion droplets make disruption more difficult. Other types of flow like turbulence or elongational flow (pure shear) are more effective in disruption (Walstra, 1980). Kao & Mason (1975) showed that disruption of aggregates (flocculated in the secondary minimum) was three times faster in elongational flow than simple shear flow of the same velocity gradient.

In conclusion, the stability of an emulsion to flocculation or disruption may be affected by flow. The effect must depend on properties of the emulsion (such as droplet size, interaction forces) and on the flow field applied. Very little is known about the effect of a flow field on coalescence stability.

1.4 OUTLINE OF THIS STUDY

The purpose of this study was to investigate influence of fat crystals in the oil phase on stability of oil-in-water emulsions. Most attention was directed to model systems, in which parameters could be varied independently, such as surfactants (anionic soaps, nonionics, polymers, oil-soluble surfactants), crystals (type and content), fat content and droplet size of the emulsions. The study was restricted to oil-in-water emulsions, but results may in some respects also apply to water-in-oil emulsions.

Stability against coalescence at rest (perikinetic) and in flow fields was studied

for emulsions with and without crystals. Most experiments were done in simple shear (Couette flow), since a theoretical analysis is available for this kind of flow. Furthermore, emulsions were subjected to flow with Taylor vortices and occasionally to turbulent flow. Finally, the behaviour of cream was compared with that of the model emulsions. Since air bubbles can destabilise an emulsion very effectively (Mulder & Walstra, 1974), care was taken to exclude air.

The results obtained show a striking difference in behaviour between true oil-in-water emulsions and emulsions with crystals in the oil phase. A mechanism is proposed by which the specific effects of fat crystals, together with the effects of flow, could be explained, thereby indicating one possible cause of coalescence in these systems.

Although practical systems are much more complicated than model systems, it is hoped that this work represents a useful compromise between the practical and fundamental approach.

2 Characterisation of materials

2.1 PARAFFIN

Paraffin oil was obtained from Lamers & Indemans, 's-Hertogenbosch, The Netherlands, Ph. Ned. VI, viscosity 6.8-8.1 x 10^{-2} Pa s. It had a density of about 860 kg m^{-3}. The oil contained, however, some traces of surface-active material, since the interfacial tension γ_{ow} of paraffin oil against water decreased with time. When an oil layer was placed upon a water layer and the interfacial tension measured with a Wilhelmy plate, γ_{ow} decreased in about one day from 50 mN m^{-1} to 20-30 mN m^{-1} (this final value varied for different paraffin samples). This very slow (diffusion determined) decrease indicated that only traces of contaminant were involved. Diffusion in an emulsion droplet will be very fast (e.g. 1 ms over 1 μm); the interfacial tension of emulsion droplets may there-fore be regarded as constant.

Solid paraffin was obtained from Merck A.G., Darmstadt, W-Germany. It had an apparent melting point of 52-54 ^{o}C and a density of about 880 kg m^{-3}.

2.2 TRIOLEIN

Triolein was supplied by K & K Laboratories Inc. USA. No further specifications were available.

2.3 TRISTEARATE

Tristearate was obtained from Pfaltz & Bauer Inc., Stanford, USA. It was recrystal-lised three times in acetone and washed with methanol to remove monoglycerides. Gaschro-matographic analysis revealed, however, that the tristearate was not pure. The fatty acid pattern showed 70% (w/w) stearic acid, 25% (w/w) palmitic acid and 5% (w/w) myristic acid. The distribution of these fatty acids over the triglyceride molecules was not de-termined.

Some experiments were also performed with very pure tristearate, kindly supplied by P. de Bruyne, Unilever Research, Vlaardingen, The Netherlands. In this triglyceride was 99.3% of the fatty acids stearic acid and the content of mono- and diglycerides was less than 0.5%.

2.4 WATER-SOLUBLE SURFACTANTS

Polyvinyl alcohol (PVA) is a nonionic water-soluble polymer, consisting of monomers of vinyl alcohol and esters of acetate and vinyl alcohol (Fig. 2). The percentage of
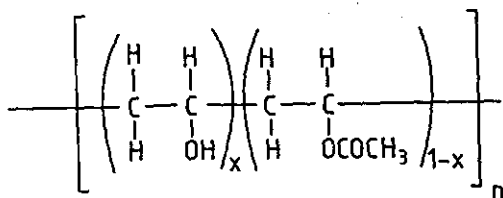
Fig. 2. Structural formula of polyvinyl alcohol. x = fraction hydrolysed, n = degree of polymerisation.

alcohol groups is indicated by the degree of hydrolysis. Following Lankveld (1970) the PVAs were coded by two numbers: the first indicates the viscosity of a 4% (w/v) aqueous solution at 20 ^{o}C and the second the degree of hydrolysis. The PVAs used were the same as those used by Lankveld (1970), Fleer (1971) and Koopal (1978). The molecular weights (viscosity average) of the polymers were determined by Koopal (1978) and turned out to be much higher than the values given by Lankveld (1970) (which were in fact the values stated by the manufacturer). Table 1 summarizes the different values. PVAs with a degree of hydrolysis of 88% were soluble at room temperature and became insoluble at about 70 ^{o}C. The PVAs with a degree of hydrolysis of 98% were easily soluble at about 80 ^{o}C and remained in solution upon cooling. PVA is completely insoluble in paraffin oil (Lankveld, 1970). Fleer (1971) pointed out that PVA can be regarded as a nonionic polymer.

Sodium Laurylsulphate (NaLS), also called sodium dodecylsulphate (SDS) was obtained from BDH chemicals, England. Its grade was specially pure. The critical micelle concentration (CMC) in water is 8 mmol/l at 20 ^{o}C and 1.5 mmol/l in 0.1 mol/l NaCl (Cockbain, 1952).

Two types of Tween were used: Tween 60 (polyoxyethylene sorbitan monostearate) and Tween 80 (polyoxyethylene sorbitan mono-oleate). They were obtained from Baker Chemicals, Deventer, The Netherlands.

Manoxol OT is the dioctylester of sodium sulfosuccinic acid (also called Aerosol OT). It is slightly soluble in oil. The manufacturer was BDH Chemicals, England. The critical micelle concentration (CMC) in water is about 4 mmol/l (Cockbain, 1952).

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

Table 1. Characterisation of polyvinyl alcohols (PVAs).

Type	Molecular weight (Lankveld, 1970)	Molecular weight (Koopal, 1978)	Manufacturer
4-88	22 000		Konam, The Netherlands
40-88	106 000	183 000	Wacker, Germany
8-98	35 000		Konam, The Netherlands
16-98	55 000	116 000	Konam, The Netherlands

2.5 OIL-SOLUBLE SURFACTANTS

Glycerolmono-oleate (GMO) was supplied by K & K Laboratories Inc., USA (KEK 11013). It was not pure, and consisted of about 50% (w/w) monoglycerides, 40% (w/w) diglycerides and 10% (w/w) triglycerides.

Span 80 is sorbitan mono-oleate and was obtained from Baker Chemicals, Deventer, The Netherlands.

2.6 NATURAL CREAM

Fresh cow's milk was used. Cream was obtained by centrifugation at about 35 $^{\circ}$C. The treatment was essentially the same as described by Labuschagne (1963). The cream was pasteurised at 70 $^{\circ}$C during 10 minutes, deaerated after cooling and subsequently kept overnight at 4 $^{\circ}$C. Crystallization in all fat globules has then taken place (Walstra & Van Beresteyn, 1975). When a sample was required, a portion was gradually warmed to room temperature during a period of about one hour. If necessary, sodium azide was added to prevent bacterial deterioration.

3 Methods

3.1 PREPARATION OF EMULSIONS

Weighed amounts of oil (+ fat crystals and in some cases oil-soluble surfactants) and water phase with a surfactant were heated to a temperature where the solid fat was melted. The sample was then premixed with a Vibromixer and finally homogenised at a temperature where the solid fat was still melted. Mostly, a Rannie 1-stage laboratory homogeniser with a LW value and a capacity of 100 l/h was used. Sometimes use was made of a Condi laboratory homogeniser (Foss Electric type 127-05). Occasionally an Ultra-Turrax was used with a device to exclude air during homogenisation. After homogenisation the emulsion was cooled to such a temperature that crystallisation in all globules was ensured. When it was essential to avoid creaming, the emulsions were stored in 50 or 100 ml jars, which were slowly rotated. These jars were carefully filled so that air was excluded.

The concentration of surfactant was such, that, at least in absence of crystals, stable emulsions were formed. In emulsions with a volume fraction $\phi_v = 0.2$, this amounted mostly to 5 g/l in the aqueous phase (exceptions: SDS: 4 g/l; sodium caseinate: 10 g/l; Manoxol OT: 2.5 g/l.

3.2 ESTIMATION OF FAT CONTENT OF EMULSIONS

The fat content of the emulsions was determined by the Gerber method (NEN, 1964). This method was developed for milk but can also be used for paraffin oil-in-water emulsions, when the density difference between paraffin oil and milk fat is taken into account. The volume fraction fat ϕ_v was obtained by multiplying the Gerber reading by 0.01125.

3.3 ESTIMATION OF GLOBULE SIZE DISTRIBUTIONS

3.3.1 Characterisation of size distributions

A particle size distribution can be characterised adequately by some average (diameter, volume), the width of the distribution and possibly some other parameter such as an upper size limit (Walstra, 1968; Walstra et al., 1969).

Consider spherical drops with diameter d. When the number per unit volume of drops with a diameter smaller than d is given by $F(d)$, then the number frequency is $f(d) = \partial F(d)/\partial d$ and the volume frequency $(1/6)\pi d^3 f(d)$. The n-th moment of the distribution is defined by:

$$S_n = {}_o\!\int^\infty d^n \, f(d) \, \partial d \tag{1}$$

and an average diameter by

$$d_{nm} = (\frac{S_n}{S_m})^{\frac{1}{n-m}} \tag{2}$$

The relative width is indicated by the variation coefficient of the distribution:

$$\sigma_n = (\frac{S_n \, S_{n+2}}{S_{n+1}} -1)^{\frac{1}{2}} \tag{3}$$

Now, the total number of droplets per unit volume is given by S_0, the number-average diameter by d_{10}, the volume-average diameter by $d_{30} = (S_3/S_0)^{1/3}$ and the volume-surface average diameter (the Sauter average) by $d_{32} = S_3/S_2$. The most suitable parameter is d_{32} (Walstra, 1965; Walstra et al., 1969). It can be considered as the arithmetic mean of the surface-weighted distribution. Then the width can be best expressed as the relative standard deviation of the surface-weighted distribution ($c_s = \sigma_2$ from Eqn 3):

$$c_s = (\frac{S_2 \, S_4}{S_3^2} -1)^{\frac{1}{2}} \tag{4}$$

d_{32} is a useful parameter because it relates the surface area of the fat to its volume:

$$d_{32} = \frac{\Sigma N_i \, d_i^3}{\Sigma N_i \, d_i^2} \tag{5}$$

with N_i and d_i the number and diameter of particles in size class i. The specific surface area of the emulsion is:

$$S_{EM} = \frac{6\phi_v}{d_{32}} \tag{6}$$

with ϕ_v the volume fraction of the fat phase. The specific surface area of the fat is:

$$S_F = \frac{6}{d_{32}} \tag{7}$$

Often, size distributions of emulsions are adequately described by a log normal function. Often some upper size limit is found, therefore, truncated log normal functions are frequently useful for describing globule size distributions in emulsions.

Spectroturbidimetry was among others developed by Walstra (1965, 1968) as a method for the determination of globule size distribution in milk. Walstra (1968), Lankveld (1970), Böhm (1974) and Van Vliet (1977) used the method for paraffin oil-in-water emulsions. Since these authors have described the method extensively, only a short description is given here (for further details see Walstra, 1965).

A dielectric sphere with diameter d and refractive index n_1 in a medium with refractive index n_2, illuminated by incident light of unit intensity (with wavelength λ in air), will scatter an amount of light equal to $(1/4)\pi\, d^2\, Q$. Q is the light scattering coefficient and is a function of the parameter ρ:

$$\rho = 2\pi\, d\, (n_1 - n_2)/\lambda \tag{8}$$

Now the optical density E of a layer l, containing N monodisperse particles per unit volume will be (using the law of Beer and Lambert):

$$E = \frac{1}{4}\pi\, d^2\, N\, Q\, l\, \log e \tag{9}$$

The attenuation is thus governed by $d^2\, Q$ and per unit suspended phase:

$$E/\phi_v = \frac{3\pi\ (n_1 - n_2)\ l\ Q\ \log e}{\rho\ \lambda} \tag{10}$$

By rearranging Equation 10 a relation is found between the theoretical quantities Q/ρ and the reduced turbidity Z, which can be determined experimentally:

$$Z = Q/\rho = \frac{0.2443 E\ \lambda}{l\ (n_1 - n_2)\ \phi_v} \tag{11}$$

Q has to be corrected for forward scattering leading to the corrected scattering coefficient Q^*. For polydisperse systems Q^*/ρ must be replaced by an average reduced turbidity $(\overline{Q^*}/\rho)$, where the average $\overline{Q^*}$ is given by:

$$\overline{Q^*} = \frac{\Sigma\ N_i\ d_i^2\ Q^*\ (\rho_i)}{\Sigma\ N_i\ d_i^2} \tag{12}$$

The average of ρ is then ρ_{32}:

$$\rho_{32} = 2\pi\ (n_1 - n_2)\ d_{32}/\lambda \tag{13}$$

Now Equation 11 can be transformed for polydisperse systems into:

$$Z = \overline{(Q^*/\rho)} = \frac{0.2443E\ \lambda}{l\ \phi_V(n_1-n_2)} \tag{14}$$

When the optical density of a strongly diluted emulsion (to avoid dependent scattering) is measured as a function of the wavelength λ, Z can be calculated using Equation 14. For $\overline{(Q^*/\rho)}$ theoretical curves can be calculated, assuming a size distribution function. A truncated log normal distribution was found to be the most suited to describe the emulsions used in this study. d_{32} and c_s can be found by matching the experimental and theoretical curves. The method can be used for emulsions having d_{32} between about 0.2 μm and 15 μm.

Apart from spectroturbidimetry, d_{32} can be estimated from the turbidity at one wavelength (Walstra, 1969). Q^* as a function of ρ is nearly constant for larger ρ. Walstra (1969) found that also $\overline{Q^*}$ was fairly constant for larger ρ_{32} ($\rho_{32} > 4$), considering globule size distributions that did not differ appreciably in shape from milk. From Equation 9 it can be shown that the turbidity expressed as optical density E is given by:

$$E \approx \text{constant}\ \Sigma\ N_i\ d_i^2\ Q_i^* \tag{15}$$

where Q_i^* is the effective light scattering coefficient of a particle in size class i. The weight fat percentage F is proportional to $\Sigma\ N_i\ d_i^3$. By expressing the optical density per weight fat percentage (E/F) and considering that for $\rho_{32} > 4$ Q^* is constant, it is found that:

$$E/F \approx \text{constant}\ \Sigma\ N_i\ d_i^2\ /\ \Sigma\ N_i\ d_i^3 = \text{constant}/d_{32} \tag{16}$$

The requirement $\rho_{32} > 4$ leads to the requirement that for, say, $\lambda = 400$ nm, d_{32} should be higher than 2 μm. If this requirement is fulfilled, a simple relationship is thus obtained between the turbidity at one wavelength (per weight fat percentage) and the average globule size. The relationship no longer applies when the shape of the distribution is appreciably altered.

The instrument used was a Zeiss spectrophotometer with an attachment for turbidity measurements and an angle of acceptance of 1.5°. Paraffin oil emulsions were diluted with a 0.1 g/l Brij 35 solution (polyoxyethylene laurylether). Milk samples were diluted with a solution of disodium ethylenediamine tetraacetate (EDTA) and polyoxyethylene sorbitan monolaurate in water. The necessary quantities of these components were given by Walstra (1965). The optical density was measured at the wavelengths 380, 420, 470, 530, 615, 725, 890, 1150 and 1700 nm. The refractive indices of water and paraffin oil were given by Walstra (1968). From time to time, the refractive indices were checked with an Abbe refractometer.

Coalescence of emulsion droplets with crystals does not necessarily result in new spherical particles, but instead clumps may be formed (Fig. 3). Methods for the estimation of globule size distribution are based upon spheres. Therefore, samples were heated prior to measuring the turbidity to melt fat crystals so that the clumps changed into
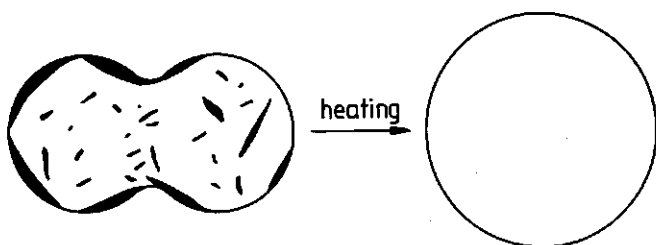
Fig. 3. Schematic drawing of a clump formed by coalescence of two globules containing fat crystals; upon heating the solid fat melts and a globule is formed.

spherical particles. The turbidity was measured at room temperature. It usually requires some time before the onset of crystallization after cooling but, especially in large globules, crystallisation may occur. According to Walstra (1965), a little crystallisation in the fat globules will not significantly alter the turbidity. Moreover, good agreement was found between spectroturbidimetry and Coulter Counter measurements (see below).

3.3.3 Coulter Counting

The Coulter Counter is a widely used instrument for the determination of size distributions, though it has some disadvantages. Walstra & Oortwijn (1969) gave an extensive discussion of the method. The method is based upon registration of voltage pulses, arising when particles, suspended in an electrolyte solution, pass through a narrow opening across which an electric field exists. The height of a pulse is proportional to the volume of particles passing through. By selecting levels above which pulses of a certain size are counted a cumulative size distribution can be obtained. From this distribution other data can be obtained such as d_{32}, c_s, volume number frequency, total number of particles (hence also fat content).

Use was made of a Coulter Counter model Z_B with an orifice tube of aperture of 50 μm. The lower limit of particle size that can be detected is 1 μm and the upper limit about 25 μm. The electrolyte used was 9.0 g/l NaCl, filtered through a 0.2 μm Millipore filter and boiled for a short time to remove air. Calibration was carried out with a milk sample, the size distribution of which was determined by spectroturbidimetry. The coincidence correction was taken as twice the value given in the instruction manual since Walstra & Oortwijn (1969) found this to be approximately half the real value.

Since the Coulter Counter was mainly used as a check for the turbidity measurements, no attempts were made to obtain very accurate results since then the method would have been very time consuming and many precautions have to be taken. The agreement between d_{32}, obtained by turbidity measurements and Coulter Counter, was reasonably good, certainly for emulsions with $d_{32} > 3$ μm. In accordance with Walstra & Oortwijn (1969) and Lankveld (1970) d_{32} from Coulter Counter measurements was somewhat higher than d_{32} from turbidity measurements (Table 2). Especially below $d_{32} \approx 3$ μm the Coulter Counter yielded higher diameters than spectroturbidimetry because of underestimation of small particles.

14

Table 2. Comparison of volume-surface average diameter (d_{32}) obtained by spectroturbidimetry and Coulter Counter.

d_{32} from spectroturbidimetry (μm)	d_{32} from Coulter Counter (μm)
1.75	2.41
2.88	3.08
3.31	3.41
3.89	3.90
5.13	5.24

3.4 ESTIMATION OF COALESCENCE RATE

To estimate the coalescence rate of an emulsion, the change in particle size or number with time must be followed. When particles coalesce immediately after floccula- tion, the latter process is rate determining and the decrease in number of particles fol- lows a second order reaction. If the particles stay together for a long time, coalescence is rate determining and the decrease in number follows a first order reac- tion. Van den Tempel (1953, 1957) showed that first order kinetics are often encountered in coalescence studies. Flocculation is rate determining only for dilute and unstable emulsions (fast coalescence). In the experiments of this study it is expected that coalescence will be rate determining, certainly in flow fields where the number of en- counters is very high. As a result of coalescence the number of globules decreases and their mean size increases. The relative width of the distribution can remain the same (if all globules coalesce at the same rate), it can increase (if larger globules coalesce faster), and it can decrease (if smaller globules coalesce faster). The flocculation rate will increase with polydispersity, as explained by Müller (Overbeek, 1952). It is not known whether polydispersity has an effect on coalescence. Swift & Friedlander (1964) claimed that the shape of a particle size distribution remains the same for coagu- lation in Brownian motion as well as in laminar shear flow. It will be seen later that this is not so for the systems dealt with in this study. The number of globules N per unit volume can be derived from the Coulter Counter method (provided that not too many small particles under the lower size limit are present). Spectroturbidimetry gives d_{32} and c_s, while turbidity at one wavelength gives E/F, which is related to d_{32} via Equation 16. When plotting the logarithm of N, E/F or d_{32} against coagulation time, a straight line was obtained. This indicated a first order reaction. The slope of the straight line was taken as the rate constant ($k_1 = -\mathrm{d}\ln(E/F)/\mathrm{d}t$, $k_2 = -\mathrm{d}\ln N/\mathrm{d}t$, $k_3 = \mathrm{d}\ln d_{32}/\mathrm{d}t$). With very unstable emulsions the linear relationship broke down after a certain time. The rate constant was then estimated from the first points only, when linearity was still observed.

Some typical results for coagulation (of cream in Couette flow) are given in Table 3. Similar results were obtained with other emulsions. Excellent agreement existed between all three rate constants, if c_s remained relatively constant. According to Equation 16 E/F is proportional to $(d_{32})^{-1}$, hence k_1 should be equal to $-k_3$. When c_s varied, the re- lation between E/F and d_{32} no longer held and k_1 was then no longer equal to k_3. In

15

Table 3. Comparison of coalescence rates as estimated by three methods (see text). Results for various creams in Couette flow.

$k_1 \times 10^5$ (s^{-1})	$k_2 \times 10^5$ (s^{-1})	$k_3 \times 10^5$ (s^{-1})	Change in σ_s
4.0	4.1	4.2	$0.45 \rightarrow 0.52$
4.2	4.2	3.8	$0.45 \rightarrow 0.61$
7.3	7.1	5.2	$0.45 \rightarrow 0.71$
8.3	8.5	4.3	$0.45 \rightarrow 0.83$
12.0	13.0	6.3	$0.45 \rightarrow 0.91$

fact, Q^* decreased somewhat with increasing ρ_{32} (Walstra, 1969) and this would lead to a more rapid increase in k_1 than in k_3.

The ratio k_2/k_3 varied between 1 and 2, depending on the change in the width of the distribution σ_s. The relation between mean diameter and particle number per unit volume depends on the kind of average used. For the volume-, surface-, or number-average diameter the relation is easy to describe, e.g. for d_{30} ($d_{30} = (S_3/S_0)^{1/3}$, Eqn 2, S_3 remains constant):

$$\frac{(d_{30})_t}{(d_{30})_0} = \frac{(S_0)_0^{1/3}}{(S_0)_t^{1/3}} = \left(\frac{N_0}{N_t}\right)^{\frac{1}{3}}$$

(17)

where the subscripts 0 and t indicate the time zero and t, respectively. Equation 17 indicates that the relative increase in volume-average particle diameter would be three times slower than the relative decrease in particle number. However, the volume-, surface- or number-average diameters are not very useful because they are very sensitive to the total number of particles S_0, which is usually uncertain.

Analogous to Equation 17 it follows that for d_{32}:

$$\frac{(d_{32})_t}{(d_{32})_0} = \frac{(S_2)_0}{(S_2)_t}$$

(18)

The relative change in d_{32} is thus directly related to the relative change in total globular surface area but a simple relationship between d_{32} and N was not found. Srivastava (1978) found experimentally that the relative change in number of globules was 1.47 times faster than that in specific surface area. This seems to be in accordance with the observation reported here that the ratio k_2/k_3 varied between 1 and 2. Since the relation between d_{32} and N is unknown, the reason why the ratio k_2/k_3 varied, depending on the change in σ_s, can neither be explained.

One may wonder whether k_2 is reliable, because the number of small droplets is underestimated by the Coulter Counter method. However, small globules did not coalesce in these systems and only the number of particles larger than 1 µm changed (Section 7.2.4.4). Hence, k_2 may directly be related to the change in number of particles. It should then also be possible to determine the relative increase in volume-average diame-

ter d_{30}. This was done in a few cases using the Coulter Counter method and the relation indicated by Equation 17 was approximated (the reciprocal of the exponent varied between 2 and 3).

An explanation was not found why k_1 and k_2 matched so closely. Since this was always so, k_1 was used throughout this study because of the ease of determining k_1. According to Table 3, k_1 may be directly related to the relative change in particle number. Only for emulsions with small globule size was k_3 necessarily used.

When coalescence was studied in a flow field, the coalescence rate was reproducible within 30%. Errors could arise due to the following:
- variation in sampling time
- uncertainty in shear rate
- irreproducible way of filling of the apparatus and drawing of samples (especially with rather unstable emulsions)
- errors upon dilution of the samples and estimation of particle size distribution.

3.5 FLOW FIELDS

3.5.1 Couette flow

Simple shear flow is a two-dimensional steady flow with velocity gradient G (see Fig. 4a). The velocity components along the x_i axes are $u_1 = 0$, $u_2 = 0$, $u_3 = G\,x_2$. There is also a rotational component about the vorticity axis x_1 with angular velocity $\frac{1}{2}G$. Simple shear flow was approached with a Couette equipment with the outer cylinder rotating (Fig. 4b). The apparatus was built in the workshop at the Laboratory of Food Science and Technology of the Agricultural University. A schematic representation is shown in Figure 5. The height of the outer cylinder $H = 87$ mm, the radius $R_o = 65$ mm, while two inner cylinders were available of radius $R_i = 60$ and $R_i = 63$ mm, giving an annular clearance $s = R_o - R_i$ of 5 and 2 mm, respectively. The inner cylinders were made of polished stainless steel, and the outer one of transparent Perspex. The outer cylinder could be
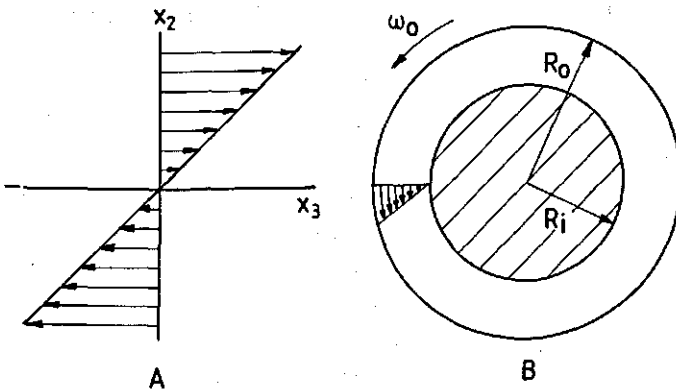

Fig. 4. Simple shear flow (A) and Couette flow (B). The symbols are explained in the text.
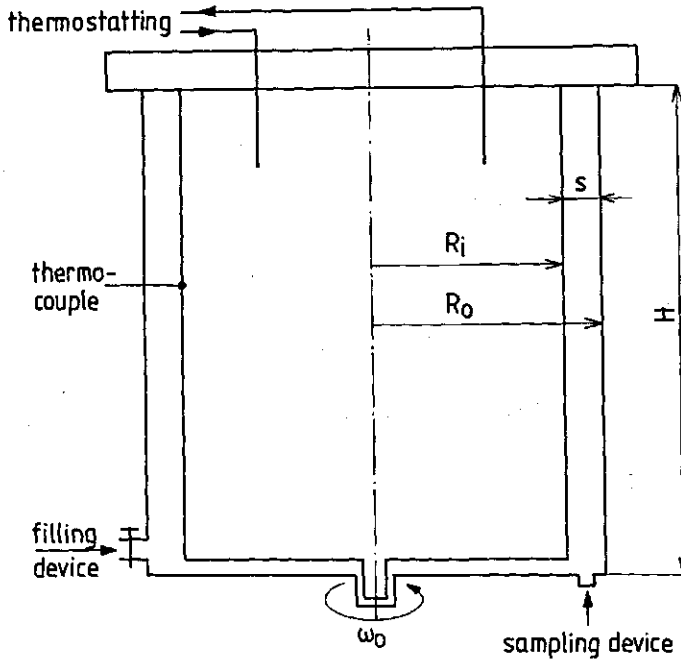
Fig. 5. Schematic representation of the Couette equipment (not to scale). The symbols are explained in the text.

rotated with an electric motor. The minimum rate of rotation was about 0.5 s^{-1} and maximum about 7.5 s^{-1}. In every experiment rotation rate was measured using a tachometer. The temperature of the samples was regulated with a thermostat, which controlled cooling of the inside of the inner cylinder. The temperature was measured with a thermocouple, immersed into the inner cylinder (to avoid disturbances of the flow it did not project into the gap between the cylinders). In all experiments the temperature was 22 $^{\circ}$C. The equipment was so filled that air was excluded.

When the gap width s is small compared to the outer cylinder radius R_o, the flow field established by rotating the outer cylinder and keeping the inner one fixed, is almost entirely equal to simple shear flow. The circumferential speed u_o of the outer cylinder is:

$$u_o = \omega_o R_o \tag{19}$$

where ω_o is the angular velocity of the outer cylinder. The shear rate G is constant throughout the gap:

$$G = \frac{2 \omega_o R_o R_i}{(R_o^2 - R_i^2)} \tag{20}$$

or if $s \ll R_i$

18

$$G = u_o/s \qquad\qquad (21)$$

Flow is, of course, not stable under all circumstances. The stability depends on the geometry of the equipment, the rate of rotation and the kinematic viscosity of the fluid. Laminar flow will change to turbulent at a critical Reynolds number Re. This is a measure of the relative contribution of hydrodynamic to inertial effects:

$$Re = u \, l_s/\nu \qquad\qquad (22)$$

u is the velocity of the flow, l_s is a characteristic length and ν is the kinematic viscosity of the fluid. The hydraulic diameter should be used for l_s, which for concentric cylinders is $2(R_o - R_i)$. Usually, however, $R_o - R_i$ is chosen for l_s (Back, 1975; Taylor, 1935; Labuschagne, 1963). To facilitate comparison with earlier work l_s will be chosen as $R_o - R_i$ in this work. Thus for Couette flow with rotating outer cylinder Re may be defined as:

$$Re = u_o \, s/\nu \qquad\qquad (23)$$

Back (1975) reviewed the influence of the ratios of outer and inner cylinder as a function of Re for the change of laminar to turbulent flow; for the systems studied here the change from laminar to turbulent flow would take place at Re = 2000 - 3000. End effects that may disturb the flow, can be neglected if $H/s > 40$ (Back, 1975). This is true for the inner cylinder with R_i = 63 mm but not for R_i = 60 mm. The smaller inner cylinder was therefore only used for small shear rates or for turbulent flow.

Influence of Couette flow on coalescence of emulsions was studied by drawing small samples out of the gap at certain points of time with a needle (care was taken to determine that this operation caused no instability). The first sample was taken immediately after filling, just before shearing started. The samples were diluted with Brij solution, and analysed for changes in globule size distribution.

3.5.2 Taylor vortices

The equipment for generating Taylor vortices was built in the workshop at the Laboratory of Food Science and Technology of the Agricultural University. It was basically the same as the one used by Labuschagne (1963). It consisted of two polished stainless steel coaxial cylinders, the inner one of which could rotate (Fig. 6). The dimensions of the apparatus were as follows: radius of the (fixed) outer cylinder R_o = 25.5 mm, radii of the inner cylinders R_i = 14.0; 18.0; 20.0; 21.5; 23.5 mm, height of the inner cylinder H = 90 mm. The outer cylinder consisted of a double wall, through which a cooling medium could be pumped. There were two Perspex observation windows in the outer cylinder. The bottom end of the inner cylinder rested on a steel ball bearing, whilst its upper end was connected to an electromotor. The apparatus was covered with a closure that could be screwed onto the outer cylinder. The top and bottom end clearances were 1-2 mm. The apparatus was filled in such a way as to prevent the ingress of air

thermostatting

thermocouple

ω_i

s

R_i

R_a

observation windows

thermo-statting

steelball

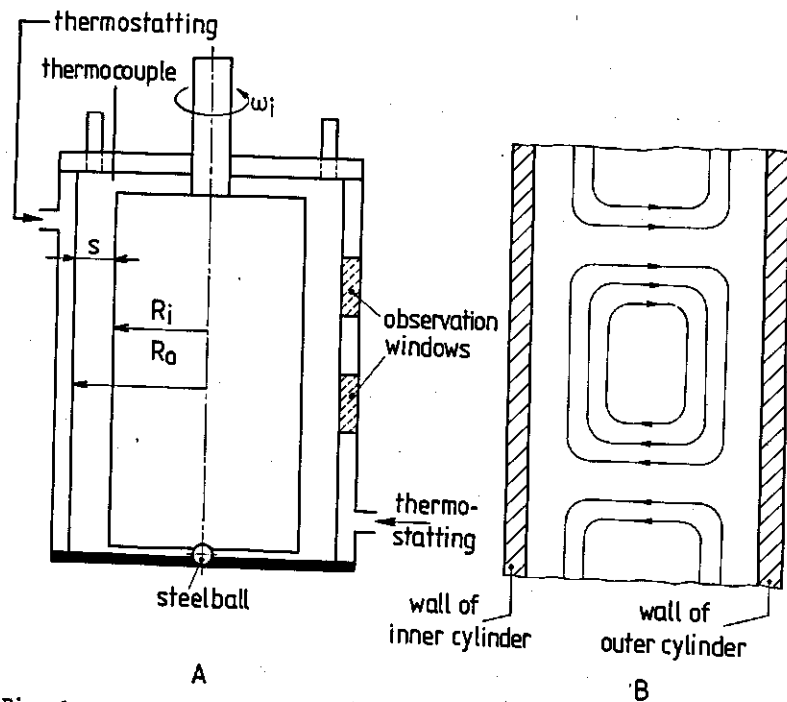wall of inner cylinder

wall of outer cylinder

A

B

Fig. 6. Schematic representation of the Taylor equipment (A) and of cellular vortices (B). Drawing is not to scale.

during an experiment. The speed of the inner cylinder could be varied by a transmission system. The minimum rate of rotation was 8 s^{-1} and the highest about 50 s^{-1}.

With the inner cylinder rotating a critical Reynolds number exists above which flow is no longer laminar and a flow field with cellular vortices is developed. These Taylor vortices are due to centrifugal instability. Taylor (1923) described them very thoroughly for viscous fluids, theoretically as well as experimentally. A schematic representation is given in Figure 6. The critical Reynolds number Re for Taylor vortices to appear is called the critical Taylor number Ta (Schlichting, 1968):

$$Ta = \frac{u_i s}{\nu} \left(\frac{s}{R_i} \right)^{\frac{1}{2}}$$

(24)

When $Ta \gg 41.3$ Taylor vortices appear. Ta was always larger than 41.3 for the apparatus and emulsions used in this study. The shape of the vortices is square at $Ta = 41.3$. At higher speeds the number and size of the vortices may change by wavy disturbances (Coles, 1965). Labuschagne (1963) also reported on the presence of these disturbances in his investigation on stability of cream in Taylor vortices. Since Taylor's work numerous authors have published work on the critical Taylor number and the effect of cylinder height and width of the gap between cylinders (Chandrasekhar, 1961; Cole, 1974). Other authors evaluated the behaviour of Taylor vortices beyond the critical Taylor number

where new kinds of instability occured (Davey, 1962, 1968; Stuart, 1958, 1960; Snyder & Lambert, 1966; Eagles, 1971). Apparently, the flow field is difficult to characterise in detail when Re is larger than the critical Taylor number. Besides, in the present work the presence of emulsion droplets may cause some disturbance as well. Flow with Taylor vortices is thus a complicated three dimensional flow, although the motion is still highly ordered compared to turbulent flow. There is an important difference from Couette flow since elongational flow occurs between the counter-rotating vortices. This implies a velocity gradient parallel to the flow direction, whereas in simple shear flow the velocity gradient is perpendicular to the flow direction. Elongational flow is especially effective in disruption (Walstra, 1980). Pennings et al. (1970) observed that crystallisation of polymers from solution started in particular at the elongational flow fields between counter rotating vortices.

In this study, flow with Taylor vortices was mainly used to compare the effect on emulsion stability with Couette flow. In view of the difficulty of characterising the flow field adequately, this was characterised by an apparent shear rate G' calculated from Equation 21. The stability of emulsions was determined by drawing small samples out of the apparatus at regular times. These samples were analysed for changes in size distribution. All experiments were performed at 22 $^{\text{o}}$C.

3.6 MICROSCOPE

A Zeiss WL polarising microscope was used, usually with a 40 x objective and a numerical aperture of 0.65. The total magnification was 400 x.

3.7 VISCOSITY

Emulsion viscosities were measured with a Haake Rotovisko at different shear rates (in the range of 14.1 - 1142.0 s^{-1}). Measurements were made at 22 $^{\text{o}}$C.

3.8 INTERFACIAL TENSION

The interfacial tension was measured by the static Wilhelmy Plate method, using a Prolabo tensiometer from Dognon Abribat. The length of the platinum plate used was 19.50 mm. The plate was first wetted by the aqueous phase and then brought into contact with the interface. Corrections were made for buoyancy. All measurements were performed at 22 $^{\text{o}}$C.

3.9 CONTACT ANGLE

Contact angle measurements were kindly performed by Dr. D. Darling, Unilever Research, Colworth House, England. The method used has not been reported (Darling, personal communication). A short description of the principles is given here. First, the fat crystals were melted and the ensuing liquid was placed upon an aqueous layer. A glass rod in a syringe needle was brought into the interface as depicted in Figure 7a.
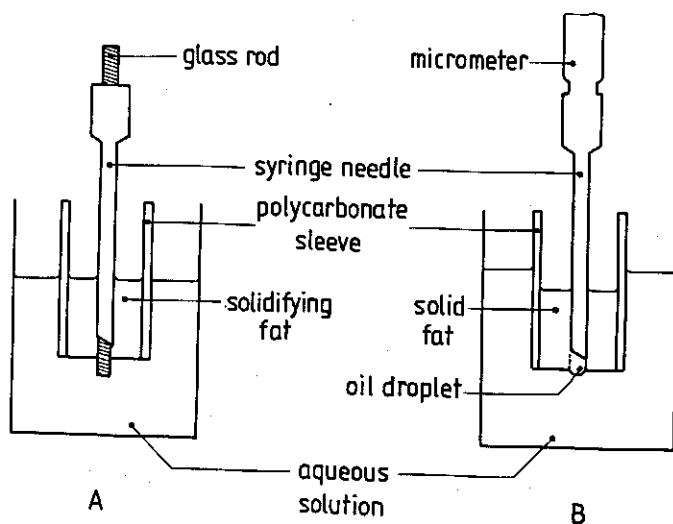
Fig. 7. Schematic representation of the equipment for measuring the contact angle.

Then the temperature was lowered to induce crystallisation. Afterwards the glass rod was removed and liquid oil put into the hole with a micrometer. In this way a drop of liquid oil formed at the interface crystal/water (Fig. 7b). The contact angle of this drop was measured with a goniometer.

The advantage of this method is that crystallisation takes place in the presence of the water phase (with or without surfactant). In this way the situation in emulsion droplets is approached, even though a difference in scale remains a problem.

4 Content of solid fat in emulsions

4.1 INTRODUCTION

Since the influence of fat crystals on the stability of emulsions was the object of the present study, a method was needed to measure the content of solid fat in emulsions. Dilatometry could be used, as, for example, applied to emulsions by Skoda & Van den Tempel (1961) and Walstra & Van Beresteyn (1975). This method is, however, rather tedious. Recently Van Putte & Van den Enden (1974) developed a pulse NMR (nuclear magnetic resonance) method, for the determination of the content of solid fat of fats and oils. Attempts have been made to apply this method to emulsions. Firstly, some of the general principles of NMR have to be considered. A basic treatment was for instance given by Farrar & Becker (1971).

NMR is a method that makes use of the magnetic properties of some atomic nuclei. Since the present work is concerned with lipids, the nuclei considered can be restricted to protons. Hydrogen nuclei have an angular momentum (spin) and are charged. Hence, the spinning generates a magnetic field along the axis of rotation. The hydrogen nuclei can therefore be looked upon as small magnets. When a sample containing hydrogen nuclei is placed between the poles of a strong magnet, the nuclei precess about their axis in the direction of the magnetic field H_0 with the so called Larmor frequency ω_L:

$$\omega_L = \gamma_g \, H_0 \tag{25}$$

Here γ_g is the gyromagnetic ratio, indicating the relation between the magnetic moment μ and the magnetic quantum number. Two energy levels are associated with this alignment for a hydrogen nucleus. When aligned parallel to H_0 the lowest energy level is obtained ($E_m = - \mu \, H_0$) and when aligned antiparallel to H_0 the highest energy level ($E_m = \mu \, H_0$). The energy diffence $\Delta E_m = 2 \, \mu \, H_0$ is very small so that because of thermal movement almost as many hydrogen nuclei are at the higher (less favourable) energy level as at the lower level. At thermal equilibrium there will be a net alignment in the direction of H_0, yielding a resultant magnetisation M_0. M_0 is proportional to the total number of hydrogen nuclei. The proportion of protons in the two energy levels at equilibrium is indicated by Boltzmann's distribution law:

$$N_1/N_h = \exp \left(\frac{-2 \, \mu \, H_0}{k \, T} \right) \tag{26}$$

Here N_1 and N_h are the number of protons in the lower and higher energy level, respectively, k is Boltzmann's constant and T is absolute temperature. By applying

electromagnetic radiation at the resonance frequency ω_L, nuclei can be switched from the lower to the higher energy level. This transition (or its consequences) can be measured using an NMR apparatus.

NMR measurements can be made in two ways. With continuous-wave NMR the frequency of electromagnetic radiation is slowly varied and at the Larmor frequency resonance occurs, which can be measured. Continuous-wave NMR can be further distinguished into wide-line NMR and high resolution NMR, but that is beyond our scope. The other NMR method is pulse NMR. Then a short intense pulse of electromagnetic radiation at the resonance frequency is given and the decay of the signal following the pulse is observed. From this decay, information can be obtained (among other things) about the content of solid fat.

Consider a reference frame, rotating at the Larmor frequency about the x_1 axis, as depicted in Figure 8a. In the static magnetic field H_0 the net magnetisation M_0 is directed parallel to H_0. Since the receiver coil is along the x_3 axis a signal will be detected only when there is some magnetisation in the x_2x_3 plane. In the static state no signal will be detected, because the effective magnetisation in the x_2x_3 plane is zero. By applying a pulse of radiofrequency H_1 along the x_2 axis the magnetisation M_0 can be shifted away from the x_1 axis. When M_0 is shifted 90° from the x_1 axis so that a compo- nent can be detected along the x_3 axis, this is called a 90° pulse (Fig. 8b). Immediate- ly after a 90° pulse the signal induced in the receiver coil is proportional to M_0 and M_0 is proportional to the number of hydrogen nuclei. After the pulse the system relaxes back to the equilibrium state and consequently the signal decays.

There are two processes causing the signal to decay. The first process is the so called longitudinal or spin-lattice relaxation, characterised by the relaxation time T_1. The energy taken up is given back to the 'lattice' (other molecules, H_0). T_1 indicates the time it takes before the equilibrium state, described by Boltzmann's law (Eqn 26), is obtained. The second process is caused by loss of phase coherence of spins. Imme- diately after the pulse the nuclei rotate at the same frequency about H_0: they rotate in phase. However, the nuclei may begin to rotate at a slightly different frequency due to the small magnetic fields exerted by neighbouring molecules. This reduces the net mag-
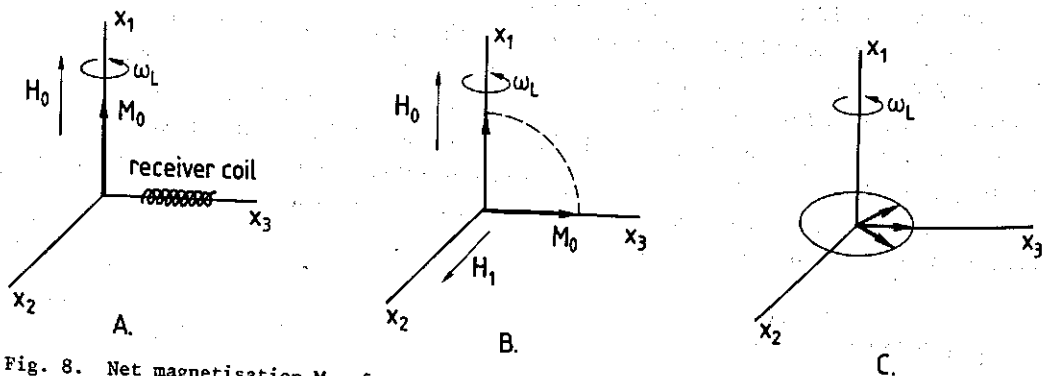

Fig. 8. Net magnetisation M_0 of nuclei in a static magnetic field H_0 (A). Net magnetisation M_0 directly after a 90° pulse H_1 (B). Dephasing of nuclei in the x_2-x_3 plane directly after a 90° pulse (C). The reference frame rotates at the Larmor frequency ω_L.

netisation along the x_3 axis (Fig. 8c), though M_0 is still in the x_2x_3 plane. This process is called transverse or spin-spin relaxation, characterised by the relaxation time T_2. Since $T_2 \leqslant T_1$ the loss of signal after a 90^0 pulse is always governed by T_2. However, T_1 has also an influence since the system has to return back to its equilibrium value before a new pulse can be given. If this is not so, there will be loss of signal and hence an underestimation of the number of hydrogen nuclei. This process is called saturation. To avoid saturation, the time between pulses should be about five times longer than T_1. The relaxation times T_1 and T_2 are strongly related to the mobility of nuclei and hence the physical state of the nuclei. T_2 increases with mobility. In solids the mobility is small so that neighbouring nuclei exert a small magnetic field that does not change so fast as in liquids. T_2 of solids is about 10 μs and T_2 of liquids about 100 - 1000 ms. This very large difference offers the possibility of measuring separately the contribution of the protons in the solid and liquid state and hence the solid-liquid ratio.

4.2 EQUIPMENT FOR PULSED NUCLEAR MAGNETIC RESONANCE

The pulse NMR apparatus used was a Bruker Minispec p20, with an operating frequency of 20 MHz and several methods for determination of the relaxation times T_1 and T_2. In this study only the 90^0 pulse method was used. The instrument was equiped with an oscilloscope and the sample holder could be thermostatted if required. The magnet temperature was constant at 33 ^{0}C. If a measurement is carried out within, say, 15 seconds, thermostatting is not necessary. Phase sensitive detection was used throughout.

The sample holder was placed in such a way that the bottom of the sample tubes was inside the receiver coil. Sample tubes had a diameter of 10 mm and were $\pm$ 10 cm long. They were filled for about 1 - 1.5 cm, so that the samples were within the receiver coil.

4.3 EVALUATION OF METHODS WITH PULSED NUCLEAR MAGNETIC RESONANCE FOR ESTIMATION OF CONTENT OF SOLID FAT IN FATS AND OILS

The signal decay after a 90^0 pulse contains information about the proportion of liquid and solid protons (Van Putte & Van den Enden, 1974). Consider the signal decay of a partially crystalline fat as depicted in Figure 9. Immediately after the pulse the decay begins, but the signal cannot be measured then due to electronic problems (the so called dead time of the receiver). At about 10 μs after the pulse (s' in Fig. 9) the signal can be measured. At that point the signal of 'solid protons' has already decayed somewhat because of the very small T_2. To obtain M_0 the signal immediately after the pulse (s in Fig. 9) is calculated by multiplying s' by a factor f. The signal of 'solid' hydrogen nuclei has disappeared after 30 - 40 μs after the pulse. The signal of hydrogen nuclei in the liquid state on the other hand does not decay significantly within a period of some 100 μs. When measuring 90 μs after the pulse (1 in Fig. 9) only the signal of 'liquid' hydrogen nuclei is measured, which is virtually the same as immediately after the 90^0 pulse. The fraction of solid fat S_f can thus be calculated as:
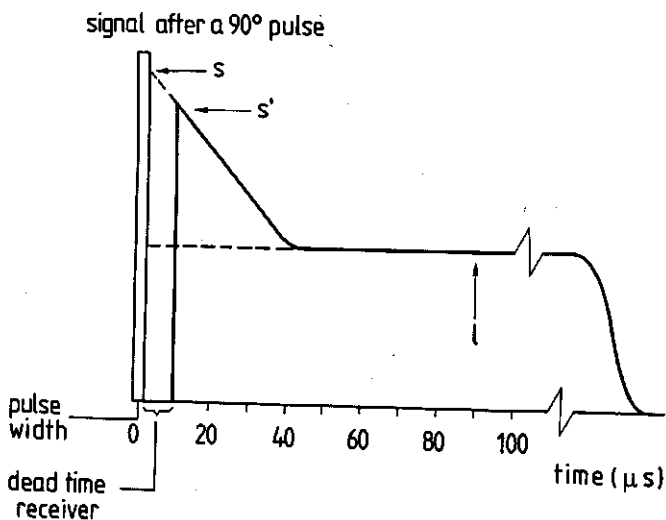
signal after a 90° pulse

pulse width

dead time receiver

0 20 40 60 80 100 time (μs)

Fig. 9. Schematic representation of signal decay after a 90° pulse for a partially crystalline fat, s is the signal directly after the plane, s' 10 μs after the pulse and 1 90 μs after the pulse.

$$S_f = \frac{fs'}{fs' + 1} \tag{27}$$

It must be assumed that the actual value of the f-factor depends on the mobility of the hydrogen nuclei and hence on temperature, composition of the solid, polymorphic forms, mixed crystals, imperfection of crystals etc. The f-factor depends, of course, also on adjustment of the equipment. There are some ways to determine the f-factor. One way is to take into account the liquid signal only (1 in Fig. 9) and measure also at a temperature at which all the fat is liquid. The increase in signal at the higher temperature is due to solids. This method is called the indirect method (Van Putte & Van den Enden, 1974) and can be used to determine the actual f-factor. A correction has to be made for influence of temperature upon magnetisation and detection. This is done with a reference oil, which is liquid at both temperatures. With the following formula the proportion of solid fat can be calculated:

$$S_f = \frac{\dfrac{S_R(T)\ S(T_m)}{S_R(T_m)} - S(T)}{S_R(T)\ S(T_M)/S_R(T_M)} \tag{28}$$

$S_R(T)$ and $S_R(T_M)$ is the 'liquid signal' of the reference oil at temperature T and T_M (where all the fat is liquid), respectively. $S(T)$ and $S(T_M)$ are the 'liquid signals' of the fat at temperature T and T_M. Olive oil is frequently used as the reference oil. For the samples of this study paraffin oil and triolein can be used. The indirect method

26

gives reliable results. A disadvantage is that measurements must be made at two tempera-
tures and that a reference oil is needed. Moreover, the sample tubes must be filled in
such a way that the sample remains inside the receiver coil at the higher temperature,
because solid fat expands upon melting. Van Putte & Van den Enden (1974) used this
method to determine the f-factor for several edible oils. They concluded that the use of
a mean f-factor gives correct results.

Another way to determine the f-factor is by comparing pulse NMR results with other
methods like dilatometry or wide-line NMR (Van Putte et al., 1975; Van den Enden et al.,
1978). Another possibility would be to extrapolate the 'solid' signal to time zero (s in
Fig. 9) by plotting the logarithm of signal against time, as was done by Templeman et al.
(1977). However, the shape of the signal after a pulse is unknown so that this method is
not reliable.

In this study the f-factor was evaluated by performing experiments with pure
tristearate in oil. This is possible because the solubility of tristearate in paraffin
oil or triolein is known and can be described by the following Equation (Hannewijk,
1964):

$$\ln x_s = \frac{\Delta_f H}{R} \left(\frac{1}{T_f} - \frac{1}{T_c} \right)$$

(29)

Here x_s is the mole fraction of the solute, $\Delta_f H$ is the enthalpy of fusion per mole, R the
gas constant, T_f the fusion temperature and T_c the final melting point of a mixture with
composition x_s. Equation 29 is valid for a perfect solution (no mixed crystals). The
crystal modification affects the solubility. Presumably crystallisation starts in the
α-modification, but this form will be rapidly transformed into the β' or β form (Skoda &
Van den Tempel, 1963). The solubility of tristearate in paraffin oil and triolein was
calculated from Equation 29 for the three polymorphic forms α, β' and β. The (average)
molecular weight of paraffin oil (a mixture of alkanes) was unknown. Skoda &
Van den Tempel (1963) determined it by cryoscopy and found $M = 440$. This value was also
used here. The results are presented in Table 4. The solubility of tristearate in
paraffin oil as well as in triolein is thus negligible at room temperature, even if the
α-modification is present.

Experiments were performed with tristearate in paraffin oil and triolein. The
tristearate used was very pure (Section 2.3). Known (weighed) amounts of tristearate in
oil were analysed by pulse NMR using a 90° pulse. The repetition rate between pulses was
such that no saturation occurred (5 s). Measurements were made within 15 seconds so that
temperature control was not necessary. All samples were situated within the receiver
coil. The samples were treated in three different ways. Firstly (Treatment I), tristea-
rate was just added to the oil and measured. Secondly (Treatment II), tristearate was
added to the oil and the temperature raised until the tristearate was melted and there-
after it was crystallised during 24 hours at 65° - $60\ ^\circ C$ and then cooled very slowly to
room temperature and measured. In Treatment III the samples were melted, quickly cooled
to $0\ ^\circ C$ and kept at that temperature during a few hours, slowly warmed to room tempera-

Table 4. Solubility of tristearate in paraffin oil and in triolein as calculated from Equation 29.

Temperature (°C)	Solubility of α-form[1] in		Solubility of β'-form[2] in		Solubility of β-form[3] in	
	paraffin oil (% w/w)	triolein (% w/w)	paraffin oil (% w/w)	triolein (% w/w)	paraffin oil (% w/w)	triolein (% w/w)
55	100.0	100.0	34.4	20.8	4.9	2.5
45	31.5	18.7	6.3	3.3	0.5	0.2
35	6.1	3.1	0.9	0.5	0.04	0.02
30	2.4	1.2	0.3	0.2	–	–
25	0.9	0.5	0.1	0.05	–	–
20	0.3	0.2	0.04	0.02	–	–

1. $\Delta_f H = 1.46 \times 10^5$ J/mol, $T_f = 328$ K

2. $\Delta_f H = 1.61 \times 10^5$ J/mol, $T_f = 337$ K

3. $\Delta_f H = 2.05 \times 10^5$ J/mol, $T_f = 345$ K

ture and measured. Since the solubility of tristearate may be neglected at 22 °C, the f-factor could be calculated from the known mass fraction of tristearate and the measured signals (s' and 1 in Figure 9). The f-factor depended on the way of cooling (Table 5). This was presumably due to differences in crystal modifications or imperfect crystals. The more stable a polymorphic form is, the lower T_2 will be; the T_2 of α tristearate is about two times larger than that of β tristearate (Chapman et al., 1960). The lower T_2 is, the higher the f-factor will be. The tristearate in the rapidly cooled samples is thus, at least partially, in a less stable polymorphic form, as would be expected. The difference in f-factor between tristearate in triolein and paraffin oil was due to the higher proton content of paraffin oil. Van Putte & Van den Enden (1974) found a mean f-value of about 1.40 for margarine fats. This was also found by Jönsson & Andersson (1976) for butterfat. The results of Table 5 show a higher f-factor, which moreover depended on the way of cooling. Hence, the value of the f-factor must be determined for every type of fat. A mean f-factor may be useful only for samples with roughly the same composition and with the same temperature history. For the purpose of this study (determination of content of solid fat in emulsions) the use of the f-factor did ¬not prove to be successful.

Table 5. Dependence of the f-factor on several temperature treatments (see text). f_{calc} is the f-factor calculated from the known content of tristearate. Measurements were made at 22 °C.

	f_{calc} for paraffin oil with an amount of tristearate of			f_{calc} for triolein with an amount of tristearate of		
	10.4%	25.4%	39.7%	12.4%	20.9%	33.0%
Treatment I	2.18	2.35	2.34	1.85	1.91	1.90
Treatment II	2.30	2.37	2.30	1.82	1.98	1.95
Treatment III	2.02	2.00	1.93	1.47	1.45	1.42

To overcome this difficulty another method was developed for estimation of the content of solid fat from the signal after a 90^0 pulse taking into account the liquid signal (1 in Fig. 9). A reference sample (liquid oil) was needed. The samples were situated within the receiver coil and were weighed. From the reference sample (paraffin oil or triolein) the signal per unit weight of liquid phase was calculated. The 'liquid' signal of a partially crystalline fat could in turn be converted to weight of liquid oil. Since the total weight of the sample was known, the proportion of solid fat could be calculated. This method (called the weight-method) was checked by comparing the results with the known (added) mass fraction of tristearate. The indirect method could also be used in the case of triolein (not with tristearate in paraffin oil because of the difference in proton content). The results of this method are given in Table 6. The same temperature treatments were given as in Table 5. The weight-method gave correct results, compared with the known mass fractions and with the results of the indirect method. Moreover, the weight-method gave results independent of the way of cooling. The advantages are that the method does not depend on the signal of solid fat (and hence factors like polymorphism) and that a measurement at one temperature is sufficient. The major disadvantages are that a reference sample is needed and that the samples must be weighed.

4.4 ESTIMATION OF CONTENT OF SOLID FAT IN EMULSIONS

A complication in the measurement in emulsions was the presence of water protons contributing to the signal. The relaxation time of water is somewhat higher than that of oil, but not enough to distinguish the oil and water signal on that basis. In the literature some methods can be found to exclude the water signal (Shanbag et al., 1971; Conway, 1971). One method is to saturate the water signal by selecting a very short repetition time between the pulses. To lower the water signal significantly, however, the oil signal becomes somewhat saturated too (incidentally, the 'solid' signal is saturated to the same degree as that of water). Another method is to change the relaxation times of water by adding paramagnetic ions (Cu^{2+}, Mn^{2+}). The relaxation time of water becomes so small then that the oil and water signal can be distinguished on that basis. However, for at least some emulsions, addition of ions will cause instability. Another method was therefore examined which involved deducing the oil signal from the measured signal by subtracting the water signal. Trumbetas et al. (1976, 1977, 1978) did this also, but they did not check the method. Moreover, they used such a high repetition rate that the oil signal must have been saturated too. Since the fat and water content of the emulsion and the weight of the sample were known, the water signal could in principle be calculated when the signal of the water phase was known. Water appeared to have a large disturbing effect on the detection (loss of signal) when the sample height was above the receiver coil. It was therefore necessary that the samples were placed within the receiver coil. The samples were also weighed so that the weight-method could be applied. An investigation was conducted to determine whether the oil and water signals could indeed by subtracted from each other. The signals of oil-in-water emulsions of varying fat content were measured (no crystals in the oil phase). If the oil

Table 6. Results obtained by the weight-method and the indirect method for tristearate samples in oil with different temperature treatments (see text).

|	10.4% in paraffin oil	25.4% in paraffin oil	39.7% in paraffin oil	12.4% in triolein		20.9% in triolein		33.0% in triolein	
	weight method	weight method	weight method	weight method	indirect method	weight method	indirect method	weight method	indirect method
Treatment I	10.1	25.5	39.8	12.0	11.4	20.4	21.0	32.4	33.5
Treatment II	10.5	25.0	39.2	12.2	12.2	20.9	20.8	32.6	33.5
Treatment III	10.0	25.3	39.4	12.8	12.8	21.2	21.6	33.7	34.4

30
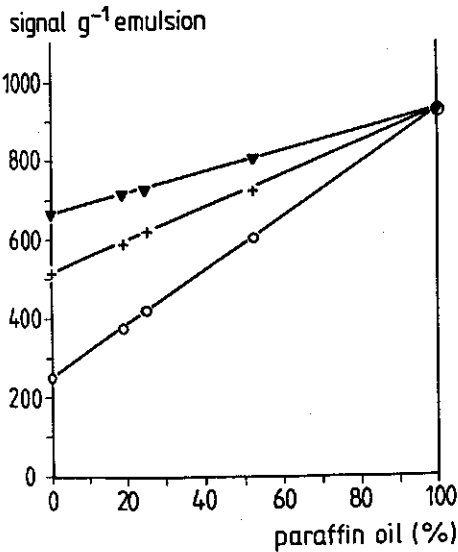
signal g^{-1} emulsion

Fig. 10. NMR signals of oil-in-water emulsions as a function of the fat content. The surfactant was NaLS and measurements were made at 22 $^{\circ}$C. The repetition rate was varied: 1 s (0); 3 s (+); 6 s (▼).

and water phases give independent signals, the measured signals per unit weight of emulsion should lie on a straight line when plotting them against the fat content. Measurements were made at different temperatures, different repetition rates and with different (water soluble) stabilisers. Some results are shown in Figure 10. The straight lines indicated that the separate signals can indeed be added, independent of the repetition rate. It was also independent of temperature (not shown). The same results were obtained when measuring oil and water phases together in one tube in the unemulsified state. This supports the idea that the signals of the oil and water phases do not depend on the interfacial area between the phases. An exception was shown by sodium caseinate emulsions: no straight lines were obtained at repetition times higher than 3 s. This phenomenon is probably related to interaction of caseinate with water and/or oil. Another complication was found when water was dissolved in oil into micelles by monoglycerides, as observed with triolein. In that case higher signals than expected were found. These phenomena are the subject of another paper (Van Boekel, 1980). In most of the systems studied these complications were unimportant.

Determination of the content of solid fat in emulsions could possibly be affected by the size of crystals, which in turn depends on globule size. In larger droplets larger crystals are formed, and in smaller droplets smaller crystals (as could be seen under the microscope). The solubility of very small crystals may be increased compared to large crystals, as indicated by Kelvin's rule:

$$R \, T \, \ln\frac{S_b}{S_\infty} = \frac{2 \, \gamma \, M}{\rho b} \tag{30}$$

31

Here, R is the gas constant, T absolute temperature, S_b the solubility of a crystal with radius b, S_∞ the solubility of a very large crystal, γ the interfacial tension crystal/ oil (γ = 10 mN m^{-1}, according to Skoda & Van den Tempel, 1963), M is the molecular weight and ρ the density of the crystals. When 30% tristearate in paraffin oil would consist of crystals with radius b = 10 nm, there would be some 0.6% α-tristearate soluble, 0.08% β'- -tristearate and 0.0005% β-tristearate. Hence, this effect was negligible.

It is also conceivable that very small crystals give a different NMR signal because of the large interfacial area crystal/oil. Therefore, the relaxation time T_2 was esti- mated for tristearate crystals in the emulsified state, in paraffin oil (bulk) and in pure tristearate. T_2 was determined by evaluating the signal of the solid phase with a transient recorder (i.e. an instrument that stores a signal in its memory and this signal can afterwards be plotted, for example, by a recorder). By plotting the logarithm of the signal after a 90° pulse against time, the relaxation T_2 was estimated from the slope of the straight line. Because of the very low T_2 and the inaccuracy of the transient re- corder used, the results were not very accurate. T_2 turned out to be about 7 µs and no systematic difference came out for tristearate in the emulsified state. The 'solid sig- nal' is therefore probably not affected by small crystals. Another possibility is that triglyceride molecules at the interface crystal/oil are more mobile than in the crystal and behave therefore more or less like liquid molecules; when this effect plays a role, it strongly depends on crystal size. Consider an emulsion droplet with diameter 1 µm consisting of 70% liquid oil and 30% tristearate. The solid phase could, for example, consist of 150 crystals with a length of 200 nm, width 100 nm and thickness 50 nm. This leads to a specific surface area of 7 x 10^7 m^{-1}. This is larger than in bulk (where no artefacts were found, Section 4.3): Knoester et al. (1968) found for 25% tristearate in paraffin oil (bulk) a specific surface area of 1 x 10^6 m^{-1} and 1.5 x 10^7 m^{-1} when crys- tallised at 50 $^\circ$C and 20 $^\circ$C, respectively. Therefore, the surface area in emulsion drop- lets may be a factor 10 higher than in the bulk. The triglyceride molecules are oriented in the crystal in the way depicted in Figure 11 (Skoda et al., 1967). The molecules in the lateral faces are assumed to contribute to the liquid signal. The lateral faces take
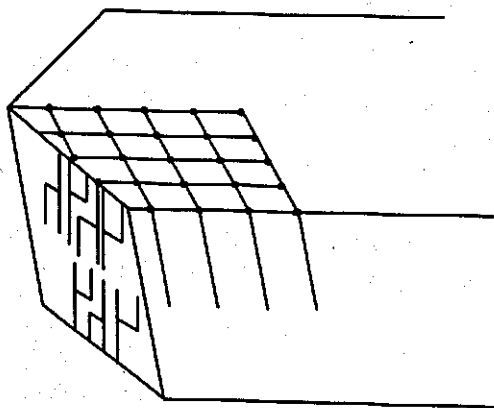

Fig. 11. Schematic drawing of the arrangement of tristearate molecules in a crystal (not to scale). After Skoda et al. (1967).

Table 7. Content of solid fat in the oil phase of NaLS emulsions
containing pure tristearate as determined by the pulse NMR weight-method.
Total fat content was 45% and mean droplet size 1 μm. Measurements were
made at 22 °C.

	Content of solid fat (% w/w)
10% tristearate added	10.7 ± 0.9
30% tristearate added	29.9 ± 0.5
50% tristearate added	49.6 ± 0.9

about 45% of the surface of a crystal with length : width : thickness = 4 : 2 : 1. The
unit cell of β-tristearate has the dimensions 1.197×10^{-9} m, 0.545×10^{-9} m, 4.59×10^{-9}
m (Skoda et al., 1967). The triglyceride molecules in the lateral faces of a crystal
with dimensions 200, 100 and 50 nm would then represent 1.6% of the volume of the crys-
tal. The effect is thus seen to be small and may be insignificant.

Emulsions were made with the pure tristearate in paraffin oil. The surfactant was
NaLS and the mean droplet size was about 1 μm. The fat content was 45%. The emulsions
were cooled sufficiently to ensure crystallisation in all globules; measurements were
made at room temperature. The oil signals were obtained by subtracting the calculated
water signals, as described above. The content of solid fat was then determined by the
pulse NMR weight-method. The results are given in Table 7. The amounts determined were
in agreement with the amounts added. Since the droplet size was fairly small, crystals
must have been small too. Apparently, the determination of the content of solid fat is
not affected by small crystals. Determination of the content of solid fat in emulsions
is thus possible, when disturbing effects like water dissolved in oil and/or the beha-
viour of emulsifiers such as sodium caseinate can be excluded.

4.5 RESULTS

The content of solid fat in emulsions depends on the actual solubility of the fat
crystals in the oil phase. Therefore, the solubilities of tristearate and solid paraffin
crystals in paraffin oil, used in this study, were determined with the pulse NMR weight-
-method. The tristearate (PB tristearate) used for the stability studies, proved to be
impure (Section 2.3). It turned out that the solubility characteristics differed from
those of pure tristearate when first dissolved and then recrystallised. When the
tristearate was added to the oil and measured without melting it first, nothing appeared
to dissolve. Slowly crystallising at 55 °C during 24 hours resulted in a solubility of
about 3% at 22 °C (additional cooling did not alter the solubility). Quick crystallising
at 0 °C resulted in a solubility of about 1.5%. These effects were explained by consid-
ering that some triglycerides (containing other fatty acids) remained in solution when
crystallisation was slow, whereas they were incorporated in the crystals on rapid cool-
ing. In the latter case mixed crystals may have been formed.

The solubility of solid paraffin is not precisely known. It is a mixture of several
alkanes. As a model a single alkane was chosen with a melting point close to solid
paraffin: pentacosane (n-$C_{25}H_{52}$) with molecular weight $M = 352$, a melting point of 51 °C

33

Table 8. Solubility of pentacosane in paraffin oil, calculated from Equation 29, and solubility of solid paraffin in paraffin oil, as determined by the pulse NMR weight-method.

Temperature (°C)	Solubility of pentacosane in paraffin oil (% w/w)	Solubility of solid paraffin in paraffin oil (% w/w)
40	36.0	
35	25.0	30.0
30	17.0	21.0
25	11.0	15.0
20	8.0	9.5
15	5.0	8.0
10	3.0	6.0
5	2.0	5.0
0	1.5	3.0
		2.5

and enthalpy of fusion $\Delta_f H$ = 5.77 x 10^4 J/mol. Assuming a molecular weight of 440 for paraffin oil (Skoda & Van den Tempel, 1963) the solubility of pentacosane in paraffin oil was calculated from Equation 29. The results are presented in Table 8, together with the solubility of solid paraffin in paraffin oil, as estimated by the pulse NMR weight method. The agreement between the calculated and experimental solubilities was good despite the complicated composition of paraffins. It follows from Table 8 that above 0 °C a certain quantity of solid paraffin will dissolve.

Crystallisation in emulsion droplets requires supercooling. This is about 20 - 25 °C below the final melting point of the α modification (Skoda & Van den Tempel, 1963) for tristearate and it is about 10 °C below the final melting point of the β modification for solid paraffin (Phipps, 1964). To ensure complete crystallisation in emulsions, even in the smallest droplets, the emulsions must therefore be fully cooled to low temperature. This was done in all the experiments. The content of solid fat in emulsions with the impure tristearate (PB tristearate) in the oil phase was lower than the amount added: 2 - 3% appeared to dissolve in NaLS emulsions with $d_{32} \approx 1$ μm. As described above, the solubility of PB tristearate depended on the way of cooling, and comparison was therefore difficult, but the solubility in emulsions seemed to be in accordance with the solubility in bulk.

The content of solid fat in emulsions containing solid paraffin is indicated in Table 9. The solubility of solid paraffin in emulsion droplets was in reasonable agreement with that in the bulk (Table 8), independent of globule size, and hence of crystal size.

Table 9. Content of solid fat (% w/w) of emulsions with solid paraffin, as determined by the pulse NMR weight-method.

	25% solid paraffin added		50% solid paraffin added	
	T = 22 °C	T = 5 °C	T = 22 °C	T = 5 °C
d_{32} = 1 μm	16.9	21.6	42.0	46.4
d_{32} = 3 μm	16.2	21.3	41.0	45.7

It may be concluded that the content of solid fat in emulsions with tristearate and solid paraffin crystals, as used for the stability studies, does not differ appreciably from the content of solid fat of the same crystals in the bulk.

4.6 CONCLUSION

In this chapter some pulse NMR methods were evaluated for measuring the content of solid fat in fats and emulsions. A method was developed, independent of the NMR signal from the solid phase, with which correct results were obtained for bulk fats. Good results were also obtained with emulsions, provided that the surfactant used caused no disturbance. The NMR method seemed to be independent of crystal size. The tristearate and solid paraffin crystals used in the stability studies appeared to dissolve at least to some extent.

5 Crystal habit in emulsion droplets

5.1 INTRODUCTION

The literature on the behaviour of crystals in oil droplets is rather scarce, even though crystals may often be present in practical systems at a certain temperature. Skoda & Van den Tempel (1963) observed that some emulsifiers could promote nucleation at the oil-water interface when the molecular structure of the crystal resembled that of the emulsifier.

Walstra (1967) studied extensively the crystal habit of fat globules in milk and butter. He distinguished four types of crystallisation, from the appearance of globules in the microscope under polarised light (Fig. 12). In the O type crystals are absent or too small to be visible. The N type (needle-type) consists of small or large fat crystal needles inside the droplet. The L type (layer-type) is made up of tangentially oriented needles: the crystals in the outermost layer are probably oriented in the oil-water interface. Then finally the M type (mixed type), which is a mixture of the L and N type. The globules may, to some extent, be distorted from spherical because of crystallisation, especially with large needle N types.

The L type has the same kind of appearance under the microscope as the birefringence caused by liquid crystalline layers around droplets (for instance, Friberg, 1971; Krog, 1977). These layers are built up by association of the emulsifier, oil and water. They enhance the stability of emulsions to coalescence, because such a cohesive layer is unlikely to rupture. The L and M types in this work, however, are caused by the presence of fat crystals and not by liquid crystalline layers. Moreover, in contrast to the stabilising effect of liquid crystalline layers, the L and M types were frequently asso-

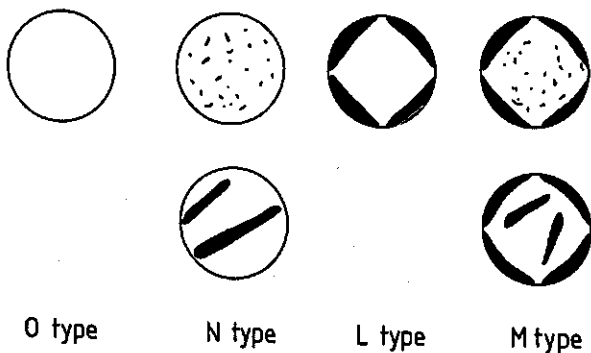O type   N type   L type   M type

Fig. 12. Crystallisation types in emulsion droplets containing fat crystals, as observed under the microscope with polarised light. The different types are explained in the text.

36

ciated with gross instability.

In the L and M types, some of the crystals are most probably oriented in the oil-water interface, whereas in the O and N types all crystals are inside the droplet. The crystals will tend to orient in such a way, that the interfacial free energy is at minimum. The equilibrium situation is determined by the contact angle. The crystallisation type of the globules may therefore depend on this. Usually the contact angle is measured in the phase with the highest density (hence water for oil-in-water emulsions). A contact angle of 180° means that a crystal is completely wetted by the oil phase, an angle of 90° means that a crystal is equally wetted by the oil and water phase, and with an angle of 0° the crystal is completely wetted by the water phase. The value of the contact angle θ_c is determined by the three interfacial tensions through Young's Equation:

$$\cos\theta_c = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} \qquad (31)$$

Here γ is the interfacial tension and the subscripts o, w and s denote oil, water and solid, respectively. Surfactants may thus influence the contact angle, because they affect γ. Bargeman & Van Voorst Vader (1973) and Van Voorst Vader (1977) studied this effect in more detail, based upon earlier work of Lucassen-Reynders (1962). By combination of Gibb's law:

$$\qquad (32)$$

$$d\gamma = -R\ T\ \Gamma\ \ln a$$

(Γ is surface excess and a the activity of the surfactant) and Young's Equation 31 it is found that:

$$\frac{d(\gamma_{ow} - \gamma_{sw})}{d\gamma_{ow}} = \frac{d(\gamma_{ow}\cos\theta_c)}{d\gamma_{ow}} = \frac{\Gamma_{so} - \Gamma_{sw}}{\Gamma_{ow}} \qquad (33)$$

A graph of $\gamma_{ow}\cos\theta_c$ against γ_{ow} appeared to yield a straight line with the general Equation:

$$\qquad (34)$$

$$\gamma_{ow}\cos\theta_c = A'\ \gamma_{ow} + B$$

The constant A' is about -1 for adsorption of surfactants from aqueous solutions on non-polar solids, as follows from Equation 33: if $\Gamma_{so} = 0$ and $\Gamma_{ow} = \Gamma_{sw}$ (as will be valid for water-soluble surfactants, insoluble in oil), then $A' = -1$. The constant B is quite large for systems air/water/solids, say $B = 40 - 50$ mN m^{-1}, and this results in a large dependence of θ_c on surfactant concentration. For systems oil/water/solids, however, B is very small, say $0 - 1$ mN m^{-1}, indicating a small dependence of θ_c on surfactant concentration. When $A' = -1$, B can be related to the London - Van der Waals force which is the only force acting with non-polar solids and oil. The interfacial tension for pure phases, interacting by London - Van der Waals forces only can be described by Fowkes re-

lation (Fowkes, 1964). With the aid of this relation, Bargeman & Van Voorst Vader (1973) showed that:

$$B = 2 \{ (\gamma_o^0)^{\frac{1}{2}} - (\gamma_s^d)^{\frac{1}{2}} \} \{ (\gamma_o^0)^{\frac{1}{2}} - (\gamma_w^d)^{\frac{1}{2}} \} \tag{35}$$

(γ^0 denotes the interfacial tension of the pure phase, and γ^d the dispersive contribution to the interfacial tension). In those cases where γ^d values were known, good agreement was found between the experimental contact angles and the angles calculated from Equation 34. Of course, some deviations may occur from the theoretical relationship, especially when γ_{ow} is smaller than 10 mN m^{-1} and when A' is not -1. On the whole a satisfactory explanation was found for the rather small influence of surfactants on the contact angle as observed by Lucassen-Reynders (1962) and Bargeman & Van Voorst Vader (1973).

It can be shown from the work of these authors that the contact angle of fat crystals is always such that the crystals can orient in the oil-water interface ($90° < \theta_c < 180°$). This does not mean, however, that they are indeed oriented in the interface. Tristearate crystals in groundnut oil or paraffin oil may be flocculated in a network of considerable strength (Van den Tempel, 1961). This network prevents the crystals from reaching the interface. Attraction energy between the crystals in the network is reduced by addition of oil-soluble surfactants so that they can reach the interface (Lucassen-Reynders, 1962). In normal milk fat globules crystals are hardly ever seen in the interface, that is to say type 0 or N is commonly observed. Walstra (1967) suggested that some barrier at the interface (the nature of which is not understood) prevents the crystals from reaching the interface. In butter on the other hand, many L and M types are found. Possibly, the energy barrier has been overcome during churning. Walstra (1967) also observed that many water-soluble substances could induce the formation of L and M types, even when the fat crystallisation was already complete. It is still not clear how the effect of these substances may be explained. They have no effect on the oil-water interfacial tension. The only single common factor was the reduction of the water concentration in the aqueous phase. The same observations were made for oil-in-water emulsions of tristearate crystals in paraffin oil, stabilised by caseinate.

This investigation was concerned with the effect of fat crystals on stability. No attention was paid to such crystallisation phenomena as kinetics or surface nucleation. The investigation on stability started after crystallisation had stopped.

5.2 RESULTS

In this section results on the crystal habit in the emulsions investigated are presented. The parameters which were varied were the (water-soluble) type of surfactant and kind of crystal (solid paraffin or tristearate). Here, no attention was paid to the amount of crystals or the concentration of surfactant. The influence of the amount of crystals is dealt with elsewhere and the concentration of surfactant was such that, at least in the absence of crystals, stable emulsions were obtained.

Observations were made on the crystallisation type occurring in the various

emulsions. From the interfacial tension γ_{ow} contact angles were calculated (the trace of surface active material present in paraffin oil (Section 2.1) had hardly any effect on γ_{ow} when surfactant was present). According to Bargeman & Van Voorst Vader (1973) the theoretical equation for paraffin oil/tristearate/aqueous solution is:

$$\gamma_{ow} \cos\theta_c = -\gamma_{ow} + 0.6 \tag{36}$$

The term 0.6 was calculated from Equation 35. The experimental equation (determined by contact angle measurements) was (Bargeman & Van Voorst Vader, 1973):

$$\gamma_{ow} \cos\theta_c = -0.98\,\gamma_{ow} + 0.2 \tag{37}$$

No experimental data are available for the system paraffin oil/solid paraffin/aqueous solution, but the following theoretical relationship could be derived from Bargeman & Van Voorst Vader (1973) and Fowkes (1964):

$$\gamma_{ow} \cos\theta_c = -\gamma_{ow} + 1 \tag{38}$$

The contact angles calculated and the crystallisation type in the emulsion droplets are given in Table 10. In addition to Table 10 it should be noted that the proportion of L and M types to N types could vary. It depended on surfactant type, cooling rate and may be globule size. For most emulsions, containing L and M types, the proportion of L and M types to N types varied from 15 to 30%. This variation could have an influence on stability and a detrimental effect on reproducibility. Attempts were made to standardise the rate of cooling after preparation of the emulsion.

The contact angles calculated show (Table 10) that the crystals can indeed be oriented in the interface. This is, in most cases, confirmed by the appearance of L and M types. There were, however, four exceptions. Sodium caseinate with tristearate and cream showed no L or M types, probably because the crystals were flocculated in a network or because some energy barrier prevented the crystals from reaching the interface. But L and M types could be induced in these two emulsions, for example by addition of glycerol (Walstra, 1967). Also PVA 16-98 and PVA 8-98 with solid paraffin showed no L type, although the contact angle indicated that it was possible. Addition of glycerol did not change the crystallisation type in these cases.

Obviously, the calculated contact angles reflect only the order of magnitude of θ_c. The actual value of θ_c can only be obtained by measurements (though then also artefacts may arise). Some measurements were performed using an alternative method of measuring contact angles (Section 3.9). Results for some systems are given in Table 11. Comparison with Table 10 shows that the contact angles measured were lower than those calculated. The contact angles calculated were probably somewhat in error, but the measured ones may also be incorrect, due to irregularity of the interface. Unfortunately, the contact angles against water were difficult to interpret, because the oil-water interfacial tension was not constant (Section 2.1). Then only values for two systems remain and a close

39

Table 10. Calculated contact angles and crystallization types in various emulsions.

	γ_{ow} (mN m^{-1})	Kind of crystal	Crystallization type	Θ_c (Eqn 36) (degrees)	Θ_c (Eqn 37) (degrees)	Θ_c (Eqn 38) (degrees)
PVA 40-88	14.1	solid paraffin	N,M,L			158
PVA 4-88	14.0	solid paraffin	N,M,L			158
PVA 16-98	22.7	solid paraffin	N			164
PVA 16-98	22.7	tristearate	L,M,N	166	166	163
PVA 8-98	21.7	solid paraffin	N			153
NaLS	9.4	solid paraffin	N,M,L			
NaLS	9.4	tristearate	N,M,L	159	163	158
sodium caseinate	14.2	solid paraffin	N,M,L			
sodium caseinate	14.2	tristearate	N	163	165	
Tween 60	4.7	solid paraffin	N,M,L			142[1]
Tween 80	3.2	solid paraffin	N,M,L			133[1]
Cream	5[2]	milkfat	N			

1. Equation 38 is not valid below γ_{ow} = 10 mN m^{-1}.
2. Mulder & Walstra, 1974.

Table 11. Contact angles of crystals with paraffin oil and aqueous solutions.

	Water	0.5 g/l PVA 16-98	0.5 g/l NaLS
Solid paraffin[1]	$132^{\circ} \pm 3$	$120^{\circ} \pm 5$	$116^{\circ} \pm 2$
Solid paraffin[2]		$114^{\circ} \pm 2$	$108^{\circ} \pm 3$
Tristearate[1]	$158^{\circ} \pm 2$	$141^{\circ} \pm 4$	$88^{\circ} \pm 3$
Tristearate[2]		$118^{\circ} \pm 3$	$96^{\circ} \pm 4$

1. Crystallisation against water, surfactant added afterwards.
2. Crystallisation against surfactant solution.

comparison of these results with the theoretical equations is not so feasible. Neverthe-less, it is clear that the influence of surfactants on the present systems is larger than was found by Bargeman & Van Voorst Vader (1973) or Lucassen-Reynders (1962). The only difference is that, using the method due to Darling (Section 3.9), crystallisation takes place in the presence of an oil-water interface, whereas this was not so in the methods used by the former authors. This suggests that the interface exerts some influence, per-haps via surface nucleation. The question is whether this also occurs in emulsions. Skoda & Van den Tempel (1961) have shown that surface nucleation takes place only when the molecular structure of the surfactant resembles that of the crystallising substance. It is therefore unlikely to occur in the systems used in the present study.

However, these contact angles could not explain the difference in crystallisation type for PVA 16-98 (and PVA 8-98) emulsions with solid paraffin and tristearate. Possi-bly some barrier prevents paraffin crystals from reaching the interface, a barrier which can be overcome by tristearate crystals. There is also evidence of anomalous behaviour of the contact angle for tristearate and PVA 16-98 when crystallised in the presence or absence of emulsifier. This effect was much smaller for the other systems.

Finally it is noted that the influence of surfactants on the contact angle was larger for tristearate than for solid paraffin. This is also in contrast with the theoretical Equations 36 and 38. No explanation can currently be offered, though possibly it is a consequence of the fact that the tristearate used was impure.

5.3 CONCLUSION

In this chapter some factors were investigated that may influence the crystal habit in emulsion droplets. The equilibrium position for fat crystals is in the oil-water in-terface, as indicated by the contact angle. This was theoretically predicted and experi-mentally confirmed. The influence of surfactant on the contact angle was, however, larger than that predicted theoretically. Although the contact angle is such that fat crystals should always orient in the oil-water interface, this was not always the case. The crystal habit is ultimately determined by type of surfactant and type of solid fat. Flocculation of fat crystals in a network or some energy barrier at the interface (the nature of which is not understood) can prevent the crystals from reaching the interface.

6 Stability of emulsions at rest

6.1 INTRODUCTION

Coalescence of emulsion droplets must be preceded by flocculation. When the emulsion itself is at rest, this can be brought about by Brownian motion. The flocculation rate of spherical particles in Brownian motion (perikinetic flocculation) was originally described by Smoluchowski (see for a detailed discussion Overbeek, 1952). The equation for the 'collision' frequency W_{ij} between particles with radius b_i and b_j and concentration N_i and N_j is:

$$W_{ij} = 4\pi \, R_{ij} \, D_{ij} \, N_i \, N_j \tag{39}$$

with:

$$R_{ij} \, D_{ij} = (b_i + b_j)(D_i + D_j) \tag{40}$$

and the diffusion coefficient:

$$D_i = \frac{k \, T}{6\pi \, \eta \, b_i} \tag{41}$$

k is Boltzmann's constant, T absolute temperature, η viscosity. Assuming that every encounter leads to coalescence and that the particles are monodisperse, it can be shown that the total number of particles at time t (N_t) is governed by the equation:

$$\frac{dN_t}{dt} = - \, 8\pi \, D \, b \, N_t^2 \tag{42}$$

Integrating this expression leads to (N_0 is the number of particles at time zero):

$$N_t = \frac{N_0}{1 + \alpha_f \, N_0 \, t} \tag{43a}$$

or:

$$\frac{1}{N_t} = \frac{1}{N_0} + \alpha_f t \tag{43b}$$

$$a_f = 8\pi \, D \, b \qquad\qquad\qquad\qquad\qquad\qquad (44)$$

Equation 43 describes the so called rapid flocculation, because every encounter would lead to flocculation (actually coalescence). The number of particles decreases according to a second order reaction. Smoluchowski neglected hydrodynamic and colloidal interactions between particles, though these are always present. Fuchs took the potential energy between particles into account by introducing a stability factor α_p into the equations:

$$\frac{1}{N_t} = \frac{1}{N_0} + \alpha_p \, a_f \, t \qquad\qquad\qquad\qquad\qquad (45)$$

α_p can be related to the actual colloidal interaction between particles, as e.g. described by DLVO theory. Whenever $\alpha_p < 1$ the process is called slow flocculation because not every encounter leads to flocculation. If the energy barrier is high, α_p can be very low, thus providing complete stabilization against flocculation. Hydrodynamic interaction has to be taken into account as well as colloidal interaction. This was done by Spielman (1970) and Honig et al. (1971). They pointed out that because of viscous resistance flocculation would not be possible, unless a net attraction force (like Van der Waals) would exist at small separation. Smoluchowski assumed the particles to move independently ($D_{ij} = D_i + D_j$). By incorporating the hydrodynamic interaction into D_{ij}, Spielman (1970) and Honig et al. (1971) were able to combine both hydrodynamic and colloidal interaction into the Smoluchowski equation. Another improvement to the Smoluchowski equation is the introduction of the effect of polydispersity, a phenomenon always encountered in emulsions. This effect leads to a higher flocculation rate, which is described as the Müller effect (Overbeek, 1952). The smaller particles disappear more rapidly than the larger ones. A detailed treatment was given by Swift & Friedlander (1964), Suzuki et al. (1969) and Bernstein et al. (1972).

The repulsion between particles is so high for the emulsions used in this study that flocculation in the primary minimum will never occur ($\alpha_p = 0$). However, flocculation in the secondary minimum can occur and then only Van der Waals attraction comes into play, and hydrodynamic resistance on approach of two particles is often roughly compensated by the increasing attraction when there is no repulsive force (Spielman, 1978). The Smoluchowski equations may thus be applied to flocculation of emulsion droplets in the secondary minimum. Polydispersity may still enhance flocculation.

It should be emphasised that the stability of an emulsion is determined experimentally from the change in the particle size distribution which is a result of coalescence only. Van den Tempel (1953, 1957) analysed under what conditions either flocculation or coalescence would be the rate determining step. According to his analysis coalescence is a first order reaction:

$$N_t = N_0 \, \exp(-k_c t) \qquad\qquad\qquad\qquad\qquad (46)$$

and flocculation is a second order reaction, as described by Smoluchowski (Eqn 43a).

The ratio of flocculation to coalescence rate is given by $a_f N_0/k_c$. Whenever $a_f N_0/k_c$ >> 1, flocculation is the fastest step and coalescence is rate determining (hence a first order reaction is measured). When $a_f N_0/k_c$ << 1 coalescence is the fastest step and flocculation is rate determining (hence a second order reaction). The theoretical value of a_f is about 10^{-17} m^3 s^{-1}. Van den Tempel (1953) found experimental values for a_f ranging from 10^{-18} to 3×10^{-16} m^3 s^{-1} for fast flocculation in emulsions (realised by adding salts). For stable emulsions, say $k_c = 10^{-7}$ s^{-1}, the ratio $a_f N_0/k_c$ is always much larger than 1 and then a first order reaction is to be expected. For unstable emulsions, say $k_c = 10^{-3}$ s^{-1}, the ratio $a_f N_0/k_c$ will still be larger than 1, if the number of droplets is not too small (say $N_0 > 10^{16}$ m^{-3}). Only for very dilute and unstable emulsions a second order reaction is to be expected.

6.2 RESULTS

6.2.1 Emulsions without crystals in the oil phase

Several 'true' emulsions, that is with only a liquid oil phase, were investigated regarding their stability to coalescence, in order to facilitate comparison between the same emulsions with and without crystals in the oil phase.

Emulsions stabilised by PVA 40-88, PVA 16-98, PVA 4-88, sodium caseinate, sodium laurylsulphate (NaLS), Tweens, with a d_{32} ranging from 2-4 µm, were found to be stable. The observed stability for these emulsions is in accordance with the literature. Lankveld (1970) found no instability for his PVA emulsions over 2½ years. Rowe (1965) observed that NaLS emulsions were stable for at least two years when the concentration of surfactant was near or above the CMC. Also Van den Tempel (1957) found no instability for a NaLS emulsion (using a concentration of NaLS that was just above the CMC). This stability is to be expected when it is considered that the globules should stay together for some time for coalescence to be possible. The potential energy diagram shows no secondary minimum for the emulsions mentioned and a very large repulsion at short distance. Then only short time encounters occur and coalescence becomes unlikely. Addition of NaCl to a NaLS emulsion can induce flocculation. Even then the coalescence rate was very low: Van den Tempel (1957) found for a NaLS emulsion with 0.1 mol/l NaCl a coalescence rate of 2.7×10^{-7} s^{-1}.

An emulsion stabilised by Manoxol OT was rather unstable. Addition of salt could break this emulsion within a day. A Manoxol OT emulsion was mixed with a salt solution to give a concentration of 0.04 mol/l NaCl, 0.0056 mol/l Manoxol OT, $\phi_v = 0.2$, $d_{32} = 3.40$ µm ($N_0 \approx 10^{17}$ m^{-3}). The emulsion was rotated slowly under exclusion of air to prevent creaming. The coalescence rate was found to be $3.4 \pm 0.4 \times 10^{-5}$ s^{-1}. Van den Tempel (1953) found for about the same electrolyte concentration 1×10^{-4} s^{-1}, but the Manoxol OT concentration was lower. This author also found that a lower coalescence rate was obtained with a higher Manoxol OT concentration, presumably because some soap was precipitated by salt, so that the 'rigidity' of the interfacial film was increased. This could also explain the present observation that the coalescence rate with 0.08 mol/l NaCl was about the same as with 0.04 mol/l NaCl. Comparison with literature

data may also be hampered by the possible influence of globule size on coalescence rate. Sometimes the coalescence rate increased with increasing globule size, but the results were too scarce to draw conclusions. Such an effect may be expected because the film area between droplets increases with increasing droplet size, and hence the probability of coalescence. Further research on this subject is needed. No further attention was paid to these phenomena, since the main object was to get an impression of the coalescence rate of emulsions without crystals.

In conclusion, most stabilisers used in this study produced stable emulsions when the oil phase was liquid. This is not a very sensational conclusion, but the significance of it becomes clear in Section 6.2.2.

6.2.2 Emulsions with crystals in the oil phase

When the same emulsions, described in Section 6.2.1, contained crystals in the oil phase, the stability could be influenced in a negative way. In some cases, instability was observed at the very moment that crystallisation started. Coalescence of two globules with crystals does not result in a new globule, but instead clumps are formed (Fig. 3; upon heating (melting of the fat crystals) complete coalescence is achieved). Visible clumps could eventually be seen in unstable emulsions. Creaming was found to enhance possible instability and should therefore be prevented for a real measure of instability of emulsions at rest. Nevertheless, the stability at rest when creaming was not eliminated gave a first indication of the factors involved. The time after cooling when visible clumps were seen was taken as a measure of instability. This was, of course, not a very quantitative measure, but the differences were quite clear.

Table 12 shows the results. The presence of fat crystals could have a pronounced effect on the stability, since all these emulsions were stable without crystals. A mechanism has to be considered first, by which this effect can be explained. Since coalescence is an interfacial phenomenon, crystals may have an effect only when they act via the interface. Table 12 indicates that instability was always accompanied by the appearance of L and M types. The behaviour of cream is revealing in this respect. Normal milk-fat globules with N crystallisation types were stable, but when L and M types were induced the stability decreased considerably. This dependence on crystallisation type rules out that coalescence is caused by the action of surface active components, which could be present as contaminants of the solid phase.

It may be assumed that in L and M types some of the fat crystals are oriented in the interface of the droplet. This is allowed by the contact angle (Chapter 5). The free energy is at minimum in the equilibrium situation, which is in this respect the same as a minimum surface free energy (Lucassen-Reynders, 1962). A crystal will be wetted for a part by the water phase if that lowers the surface energy. Whether this occurs or not depends, of course, on the contact angle, but also on the size and geometry of the crystal. The change in surface free energy can be calculated when a crystal would move from the oil phase to the oil-water interface. The calculation is easy for simple geometries such as a cube or a sphere. The surface free energy is for a cube always minimum when one face is in the oil-water interface and nothing sticks out into the water phase.

Table 12. Stability of emulsions with crystals in the oil phase when the emulsions were at rest and creaming was not prevented.

	Content (% w/w) and kind of crystals	d_{32} (μm)	Crystalli-zation type	Time after cooling for visible clumps to appear
PVA 4-88	17% solid paraffin	2.5	N,M,L	> 1 week
PVA 4-88	42% solid paraffin	2.5	N,M,L	> 1 week
PVA 4-88	42% solid paraffin	4.0	N,M,L	1 day
PVA 40-88	42% solid paraffin	3.0	N,M,L	1 day
PVA 40-88[1]	42% solid paraffin	3.0	N,M,L	> 1 week
PVA 40-88[1]	42% solid paraffin	5.0	N,M,L	> 1 week
PVA 40-88[1]	42% solid paraffin + 0.2% GMO	3.0	N,M,L	1 day
PVA 16-98	42% solid paraffin	3.0	N	> 1 week
PVA 16-98	20% tristearate	3.0	N,M,L	< 1 hour
sodium caseinate	22% solid paraffin	2.5	N,M,L	> 1 week
sodium caseinate	25% tristearate	2.5	N	> 1 week
Tween 60	22% solid paraffin	2.0	N,M,L	> 1 week
Tween 80	22% solid paraffin	2.0	N,M,L	< 1 hour
Tween 80	22% solid paraffin + 0.2% Span 80	2.0	N,M,L	> 1 week
NaLS	17% solid paraffin	2.5	N,M,L	> 1 week
NaLS	17% solid paraffin	5.0	N,M,L	1 day
NaLS	42% solid paraffin	1.0	[2]	> 1 week
NaLS	42% solid paraffin	3.0	N,M,L	1 day
NaLS	20% tristearate	3.0	N,M,L	< 1 hour
Manoxol OT	17% solid paraffin	3.0	N,M,L	< 1 hour
Cream	20% solid milkfat	3.0	N	> 1 week
Cream[3]	20% solid milkfat	3.0	N,M,L	1 day

1. Creaming was prevented during the first 24 hours after preparation.
2. Droplets were too small to observe different crystallization types.
3. L and M types were induced by addition of glycerol; afterwards glycerol was removed by dialysis.

The surface free energy for a sphere is on the other hand at minimum, when the solid is partially wetted by the water phase (Fig. 13). When the contact angle is 120°, a sphere would stick out over a distance of half the radius of the sphere. Now, it may be possible that a fat crystal, being wetted for the larger part by the oil, sticks also somewhat out into the water phase. Of course, a crystal will neither be a cube nor a sphere, but more like a platelet. Furthermore, the oil-water interface is curved in the case of an emulsion droplet. The larger part of the crystal will probably not stick out of the droplet, but the curved interface and the typical geometry of fat crystals can possibly lead to a situation where an edge sticks out of the globule, as shown in Figure 13c. The geometry of a fat crystal, as depicted in Figure 13c, is in accordance with reality (Skoda et al., 1967), though it is a two-dimensional picture. This situation may occur in at least some globules depending on geometry, crystal size and contact angle and a protruding crystal may stick out some 20-30 nm.

The effect of such a protruding crystal on the coalescence process could be explained as follows. When two globules are close to each other, the protruding crystal could pierce the thin film between the globules. When the crystal touches the oil phase of the other globule, coalescence is inevitable, because the contact angle will strive for its
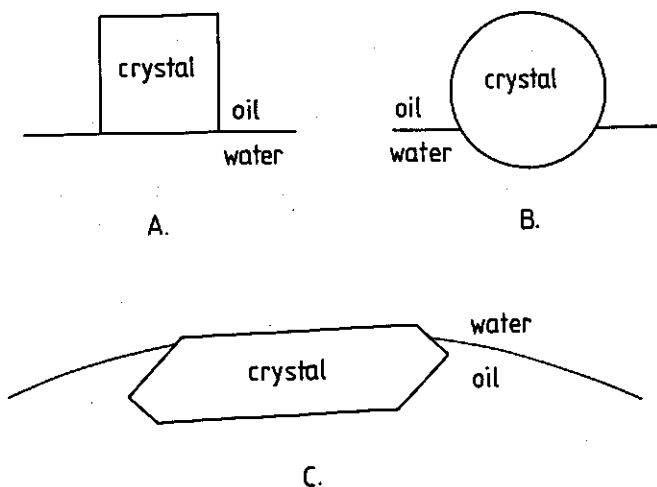
Fig. 13. Possible orientation of fat crystals at the oil-water interface. Orientation of a cube for $90° < \Theta_c < 180°$ (A); of a sphere with $\Theta_c = 120°$ (B); of a fat crystal at the interface of an oil droplet (C). The drawing is to scale in case C for a droplet with diameter 3 µm and a crystal with length 450 nm and width 150 nm.

equilibrium value. Figure 14 illustrates this.

A similar mechanism for film rupture has been proposed for a very different system by Anfruns & Kitchener (1977), who observed that flotation of angular quartz particles, which were rough on a microscopic scale, was faster than of spherical, more or less smooth, particles. The authors suggested that the film between a particle and a bubble ruptured quite easily at edges and corners of the rough particles, whereas the film between a bubble and a spherical particle had to thin further before rupture occured and thinning was opposed by viscous drag. Blake & Kitchener (1972) investigated stability of aqueous films on hydrophobic silica and assumed that surface roughness of the silica could be a cause of film rupture. Also Garret (1979) postulated this as a part of the mechanism for the antifoaming behaviour of polytetrafluorethylene particles. Protruding fat crystals could destabilise the film formed between approaching globules in a similar way at a relatively large film thickness.

Several phenomena of Table 12 were explained by this mechanism. The influence of the content of solid fat may be explained by considering that the number of droplets with protruding crystals increased with increasing content of solid fat or that crystals stick
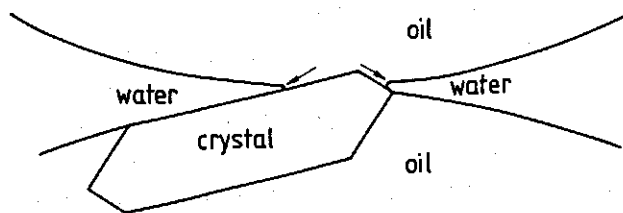

Fig. 14. Schematic drawing of the coalescence process caused by a crystal. The arrows indicate the flow direction of oil established by the non-equilibrium contact angle.

47

out further when globules contain more crystals. The difference between solid paraffin and tristearate may be due to the difference in contact angle (Section 5.2). The contact angle was smaller for surfactants with tristearate than with solid paraffin, hence an increased probability on protruding crystals, which may stick out further too. The effect of droplet size on stability may also be reduced to an effect of crystals. In larger globules crystals may grow larger so that they stick out further, thereby increasing the probability of coalescence. Another effect is that the contact area between droplets increases with increasing droplet size.

Surfactants have an influence on stability via the repulsion they bring about when globules approach each other. The forces on globules in a cream layer should be considered in this respect. The pressure at the top of the cream layer was approximated by:

$$\sigma_{cr} = \phi_{cr}(\rho_c - \rho_d) \, g \, h_{cr} \tag{47}$$

with ϕ_{cr} the volume fraction of fat in the cream layer, ρ_c and ρ_d the density of the continuous phase and disperse phase, respectively, g the acceleration due to gravity, h_{cr} the thickness of the cream layer. Assuming that $h_{cr} = 1 \times 10^{-2}$ m and $\phi_{cr} = 0.5$ it is found that $\sigma_{cr} = 8$ N m^{-2}. The area that is taken in by a globule with diameter 3 μm is about 10^{-11} m^2. The force on a globule is then 8×10^{-11} N. Of course, this is only an order of magnitude, because, for example, the pressure on the globules decreases from top to bottom. This force must be compared with the interaction force between globules. The interaction between globules stabilised by NaLS is taken as an example. This interaction can be described by DLVO theory and is treated in more detail in Sections 7.2.2 and 7.2.4.1. The total interaction force (resultant of attractive and repulsive forces) between two globules with diameter 3 μm is 7×10^{-11} N at $h = 16$ nm and 1×10^{-11} N at $h = 17$ nm. Hence, globules ($d = 3$ μm) in a cream layer where a force of 8×10^{-11} N acts would be pressed together to a distance of about 16 nm. Without such a force the globules cannot approach each other closer than about 32 nm. Creaming could enhance instability in this way, when other parameters (globule size, amount and type of crystals) favour coalescence.

The overall picture is that the stability depends on the magnitude of the repulsion and if repulsion can be overcome to some extent, protruding crystals can accomplish coalescence. In general, steric repulsion (by PVAs, sodium caseinate, Tweens, the membrane of milk fat globules) is stronger than electrostatic repulsion (NaLS, Manoxol OT, and also somewhat by sodium caseinate and the membrane of milk fat globules) and is effective over a longer distance. Still, there are some peculiarities seen in Table 12. PVA 40-88 gave only stable emulsions when creaming was avoided during the first 24 hours. Probably, the polymer reconformed after emulsification and this takes some time (Lankveld, 1970). Apparently, the reconformed polymer gave rise to stronger steric repulsion. The difference in stability between PVA 4-88 and PVA 40-88 emulsions must be due to difference in molecular weight. PVA 40-88 had a higher molecular weight which causes stronger repulsion (Van Vliet, 1977). Addition of glycerolmono-oleate (GMO) to PVA 40-88 emulsions led to a less stable emulsion. The polymer may partly be expelled from the interface by GMO (Ogden, 1973). GMO may also affect the crystal habit and size

of crystals. GMO can also affect the contact angle so that crystals can stick out further. The difference in stability of PVA 16-98 stabilised emulsions with tristearate and solid paraffin, or actually the difference in crystallisation type, is difficult to explain (PVA 16-98 with tristearate showed also anomalous behaviour in contact angle measurements, Section 5.2).

Finally the behaviour of Tween 80 with Span 80 is worth noting. Without Span 80 the emulsion was quite unstable, but the stability was strongly increased when Span 80 was added to the oil phase. This must have been due to the association at the interface of the two emulsifiers, giving a very cohesive interfacial layer and hence a good stability to coalescence (Boyd et al., 1972). A reason why Tween 60 gave stable emulsions and Tween 80 did not was not found. The difference between the two is that Tween 80 is more hydrophobic.

Since creaming influenced the stability, the stability at rest was also investigated when creaming was prevented. This was achieved by rotating the emulsions slowly (about 6 rpm) in a jar under exclusion of air. Although the formation of a cream layer was prevented in this way, there was some movement of the globules due to creaming. The velocity can approximately be calculated from Stokes' law:

$$v_s = \frac{g \ (\rho_c - \rho_d) \ d^2}{18 \eta_c} \tag{48}$$

with g the gravity acceleration, ρ_c and ρ_d the densities of the continuous and disperse phase respectively, d the diameter, and η_c the viscosity of the continuous phase. A globule of $d = 3$ μm would move about 0.2 μm in one second. This has to be compared with the displacement of two globules relative to each other because of Brownian motion, as projected on a plane perpendicular to the creaming motion. This is $(4/3)^{\frac{1}{2}} \bar{\Delta}$ (Walstra & Oortwijn, 1975) and $\bar{\Delta}$ is:

$$\bar{\Delta} = \left(\frac{2k \ T \ t}{3 \pi \ \eta_c \ d} \right)^{\frac{1}{2}} \tag{49}$$

This displacement is about 0.5 μm per second for a globule of 3 μm. The motion due to gravity may therefore not be totally negligible and the rate of encounters may be somewhat enhanced compared to normal Brownian motion.

Some of the emulsions described in Table 12 were investigated under avoidance of creaming. The very unstable emulsions PVA 16-98 and NaLS with tristearate could not be investigated in this way, because the slightest movement (e.g. when drawing a sample) caused already instability. The emulsions investigated and some results are presented in Table 13. The emulsions that were unstable in 1 day when creamed, were mostly stable when creaming was avoided. This demonstrates that some repulsion must be overcome in order to achieve instability. Only the NaLS emulsion with $d_{32} = 5.05$ μm was somewhat unstable. The coalescence rate was about 6×10^{-8} s^{-1}. The efficiency $\alpha_n = 4 \times 10^{-6}$ as calculated from the rate of coalescence and the rate of encounters (Eqn 43), in other words, roughly only four encounters in a million lead to coalescence. The coalescence

Table 13. Stability at rest of emulsions with crystals in the oil phase when creaming was prevented.

	Solid paraffin (% w/w)	ϕ_v	d_{32} at t_0 (μm)	d_{32} after
PVA 4-88	42	0.2	2.48	23 days: d_{32} = 2.50
PVA 40-88	42	0.2	3.31	15 days: d_{32} = 3.31
PVA 40-88 + 0.2% GMO	42	0.2	4.22	23 days: d_{32} = 4.25
NaLS	17	0.2	2.00	10 days: d_{32} = 2.00
NaLS + NaCl (0.1 mol/l)	17	0.2	2.00	10 days: d_{32} = 2.00
NaLS	17	0.2	5.05	1 day : d_{32} = 5.07
				2 days: d_{32} = 5.13
				5 days: d_{32} = 5.19
NaLS + NaCl (0.1 mol/l)	17	0.2	5.05	(visible clumps after 1 day)

rate was less than 10^{-10} s^{-1} for the other emulsions. Compared to the rate of encounters, it follows that $\alpha_p < 10^{-9}$, or even less, because it was reasoned above that the rate of encounters was somewhat higher under slow rotation than in normal Brownian motion. Table 13 shows also that addition of NaCl caused no additional instability when d_{32} = 2 μm. The double layer repulsion decreases by addition of NaCl, the globules can approach each other closer and they flocculate in the secondary minimum at a distance of about 8 nm. Yet, no instability was found. It may be argued that the globules, once flocculated, do not move (or very little) relative to each other and when the number of globules with protruding crystals is small, a situation is reached in which protruding crystals cannot be effective anymore. Nevertheless, addition of NaCl to the NaLS emulsion with d_{32} = 5.05 μm had a drastic effect. The number of 'reactive' globules may be larger when the droplet size increases and crystals may stick out further, but the inevitable mixing of the emulsion with the salt solution could also be a cause. In Chapter 7 the rather drastic influence of flow on these systems will be treated.

The hypothesis of protruding crystals as the cause of coalescence was not contradicted by the present results. Factors that influenced the distance of approach between globules and the probability of protrusion of crystals influenced the stability. In addition, some force was necessary (like in a creamed layer) which was able to overcome some repulsion, otherwise the emulsions were stable.

6.2.3 Effect of crystals on aqueous films in oil

In Section 6.2.2 it was suggested that crystals, sticking out of emulsion droplets, were able to pierce the film between globules and thus cause coalescence. Attempts were made to simulate such an effect in a macroscopic way with aqueous films in oil with crystals. These experiments served merely as an indication, because factors such as film thickness and crystal size were unknown but certainly different from emulsions. Films were made with a platinum wire of 0.1 mm thick. The frames were heated in a flame to remove dirt and grease before any experiment. The films were drawn in two ways:
(a) with a circular frame (diameter 0.5 cm) in such a way that the films were horizontal and isolated in the oil (Fig. 15a),
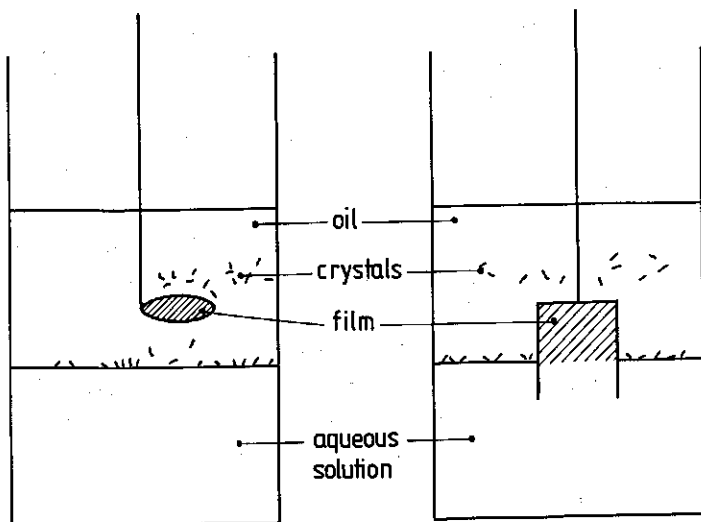(b) with a rectangular frame of width 0.5 cm that was drawn out of the aqueous phase for

Fig. 15. Schematic drawing of aqueous films drawn in an oil phase containing crystals.

about 0.5 cm in such a way that the films were vertical and remained in contact with the aqueous phase (Fig. 15b).

The films drawn in these ways were rather stable (say at least one day) when there were no crystals in the oil phase. When crystals were allowed to settle slowly on the films formed, the films remained stable. In fact, the crystals did not come into the interface of the film, because they could be removed after one day by rotating the circular frame. However, when the films were drawn in the presence of crystals in the oil phase, films of some surfactant solutions were found to be unstable: they collapsed within 10 seconds or could not even be drawn. This was so with solutions of NaLS, Tween 80 and Manoxol OT. As seen in Table 12, emulsions of these surfactants with crystals in the oil phase were very unstable. Films could be drawn in the presence of crystals in the oil phase (and remained stable) with PVAs and sodium caseinate. There is thus a striking agreement between the stability of films in an oil phase, drawn in the presence of crystals and the stability of emulsions with crystals in the oil phase. There was, however, one exception: a PVA 16-98 emulsion with tristearate was very unstable, but a film of PVA 16-98 solution could be drawn in the presence of tristearate crystals. Once again, no explanation could be found for the behaviour of PVA 16-98 with tristearate.

Although these film experiments were only of a tentative nature, some resemblance with the stability of emulsions was found. It illustrated that fat crystals indeed had an effect on the stability of aqueous films, when they penetrated in the interface in some way.

6.3 CONCLUSION

In this chapter the stability at rest of emulsions with and without crystals in the oil phase was investigated. The emulsions without crystals were, with one exception, all very stable. The same emulsions with crystals in the oil phase could, however, be unsta-

ble, dependent on several factors. Instability was always accompanied by the crystal habit in which some crystals are probably oriented in the oil-water interface. The suggestion was made that coalescence is caused by this presence of crystals, which may stick out somewhat in the water phase. When droplets can approach each other close enough, these protruding crystals may pierce the film between approaching droplets. The surfactant adsorbed is one of the factors that determine how close globules approach each other. Most emulsions were stable when creaming was avoided, but instability could arise when creaming was not avoided. The conclusion was that the pressure in a cream layer pushed the droplets more close to each other, thereby increasing the probability that protruding crystals induce coalescence. The influence of factors such as globule size and type and amount of solid fat was explained by their influence on the probability of protruding crystals. Additional evidence for the hypothesis proposed was obtained from experiments with aqueous films, drawn in an oil phase containing crystals.

7 Stability of emulsions in flow fields

7.1 INTRODUCTION

A flow field may affect the stability of emulsions by increasing the frequency of encounters. Experiments have been reported on the instability of latices in flow (Stamberger, 1962; Swift & Friedlander, 1964; Curtis & Hocking, 1970; Utracki, 1973; Warren, 1975; Van de Ven & Mason, 1977; Ives, 1978; Zeichner, 1978; Zeichner & Schowalter, 1979). Flow can promote aggregation as well as de-aggregation of particles, depending on the strength and nature of the flow. In addition, the process of coalescence is important in emulsions. Little is known how coalescence is affected by a flow field. Swift & Friedlander (1964) showed that emulsions, which were stable at rest could not be made unstable in Couette flow.

The stability of emulsions was investigated in the present study in three different types of flow, namely Couette flow, flow with Taylor vortices and turbulent flow. Emphasis was laid on Couette flow, since a theoretical analysis was available for interactions of spheres in this type of flow.

7.2 STABILITY OF EMULSIONS IN COUETTE FLOW

Simple shear was approached with Couette flow, as described in Section 3.5.1. Recently, Van de Ven & Mason (1976a, 1977) have presented a theory, which describes encounters of particles in simple shear, taking into account hydrodynamic as well as colloidal interaction. This theory may be useful for an explanation of the effect of Couette flow on the stability of emulsion droplets and is treated in more detail in Section 7.2.1.

7.2.1 Trajectories of spheres in simple shear flow

Consider N neutrally buoyant spheres of equal radius b per unit volume in simple shear flow with velocity gradient G. Brownian motion is neglected. The rate of encounters, J_S, of spheres with a reference sphere (Fig. 16) was calculated by Smoluchowski (Overbeek, 1952) and given by:

$$J_S = \frac{32}{3} N G b^3 \tag{50}$$

Smoluchowski assumed that the spheres moved along rectilinear trajectories (no hydrodynamic effects) and that interaction forces were absent until the spheres touched.
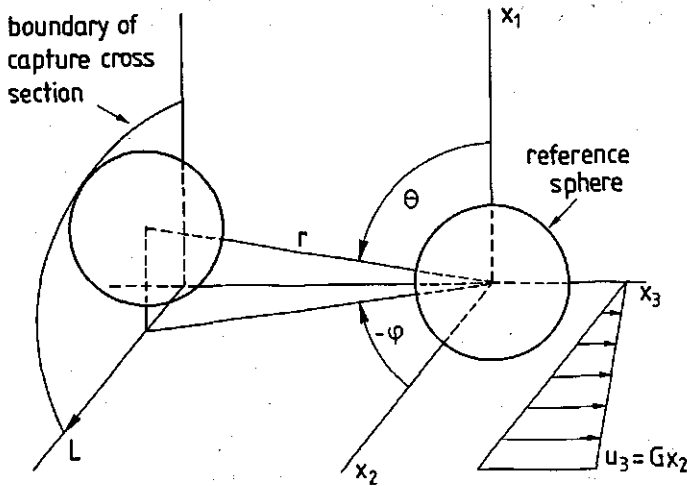
53

Fig. 16. An encounter between two spheres in simple shear flow. The reference sphere is at the origin of the coordinate system (r, θ and φ are spherical coordinates) and the other sphere enters the capture cross section so that a permanent doublet is formed (after Van de Ven & Mason, 1976a, 1977).

Assuming that every encounter leads to coalescence, that only two-body encounters take place and that no de-aggregation occurs, the following relationship can be derived (Swift & Friedlander, 1964; Zeichner & Schowalter, 1979):

$$\frac{dN}{dt} = \frac{4\ G\ \phi_V\ N}{\pi} \tag{51}$$

where ϕ_V is the volume fraction of the spheres. Hence, the change in number of (initially monodisperse) particles follows a first order reaction.

In the absence of interparticle forces, however, most of the spheres never touch but separate after an encounter because of hydrodynamic interaction (Arp & Mason, 1976). When interparticle forces act between spheres, these may either capture each other on an encounter (permanent doublet formation), or separate after a short time encounter (separating doublets). Two kinds of permanent doublets can be formed; primary doublets (flocculated in the primary minimum) in which the spheres touch and secondary doublets in which the spheres do not touch but orbit around each other at a certain (small) distance in the secondary minimum. Van de Ven & Mason (1976a, 1977) showed that Equation 50 can readily be adjusted for permanent doublet formation or the so called capture frequency J by:

$$J = \frac{32}{3}\ \alpha_0\ N\ G\ b^3 \tag{52}$$

with the orthokinetic capture frequency $\alpha_0 = J/J_S$. The same authors showed that α_0 can be calculated when the trajectories of spheres relative to the reference sphere are known. The trajectory equations are:

54

$$\frac{dr^*}{dt^*} = A(r^*) \sin^2\theta \ \sin2\phi + \frac{C(r^*) \ F_{int}(r)}{3\pi \ \eta \ G \ b^2} \tag{53}$$

$$\frac{d\theta}{dt^*} = \tfrac{1}{4}B(r^*) \sin2\theta \ \sin2\phi \tag{53}$$

$$\frac{d\phi}{dt^*} = \tfrac{1}{2} \ \{ \ 1 + B(r^*) \ \cos2\phi \ \} \tag{54}$$

where $r^* = r/b$, r being the distance between the particle centers, the dimensionless time $t^* = t \ G$, η the viscosity of the suspending fluid, and r, θ and ϕ are spherical coordinates (Fig. 16). $A(r^*)$, $B(r^*)$ and $C(r^*)$ take the hydrodynamic interaction for two equal sized spheres into account and are dimensionless functions of r^*. They are available in tabular form (Lin et al., 1972; Batchelor & Green, 1972; Zeichner & Schowalter, 1977 and Arp & Mason, 1977). Kao et al. (1977) and Arp & Mason (1977) gave approximation formulas for $A(r^*)$ and $B(r^*)$, while Honig et al. (1971) gave an approximation formula for $C(r^*)$. The formulas are:

$$A(r^*) = 0.5 \times 8.15 \ (r^* - 2) \ \{1 + 0.9 \ (r^* - 2) \ \ln(\frac{r^* - 2}{23.62})\} \quad \text{when } r^* < 2.09$$

$$A(r^*) = \tfrac{1}{2}r^* - \frac{2.5}{r^{*2}} + \frac{4}{r^{*4}} - \frac{12.5}{r^{*5}} \qquad\qquad \text{when } r^* > 2.09$$

$$B(r^*) = \{r^* - 0.8118 - \frac{1.9178}{\ln(r^* - 2)} - \frac{2.25}{\ln^2(r^* - 2)} \ \} \ /r^* \qquad \text{when } r^* < 2.09 \tag{54}$$

$$B(r^*) = 1 - \frac{16}{3r^{*5}} + \frac{10}{3r^{*8}} \qquad\qquad\qquad \text{when } r^* > 2.09$$

$$C(r^*) = \frac{6(r^* - 2)^2 + 4(r^* - 2)}{6(r^* - 2)^2 + 13(r^* - 2) + 2} \qquad\qquad \text{for all } r^*$$

and were used in the calculations in this study. $F_{int}(r)$ is the interaction force as a function of distance between the spheres and is usually composed of a repulsive force, F_R, and the Van der Waals attraction force, F_A. When F_{int} is known the trajectory Equations 53 can be solved and α_o determined as follows.

Consider particles that will flocculate with the reference sphere; the number of particles, dJ, passing through one quadrant of the 'capture cross section' between x_2 and $x_2 + dx_2$ per unit time (Fig. 16) is then:

$$\tag{55}$$

$$dJ = N \ G \ x_2 \ Z(x_2) \ dx_2$$

$G \ x_2$ represents the particle velocity (equal to the fluid velocity) and $Z(x_2)$ is some function describing the boundary of the 'capture cross section'. This boundary can be

calculated from the trajectory equations. If L is the semi-axis of the 'capture cross section', then the total number of particles passing through this per unit time is:

$$dJ = 4N \ G \int_0^L x_2 \ Z(x_2) \ dx_2 = 4N \ G \ b^3 \int_0^L x_2^* \ Z^*(x_2^*) \ dx_2^* \qquad (56)$$

Hence $x_2^* = x_2/b$, $Z^*(x_2^*) = Z(x_2)/b$ and $L^* = L/b$. Combining Equations 56 and 52 yields:

$$\alpha_o = \frac{3}{8} \int_0^{L^*} x_2^* \ Z^*(x_2^*) \ dx_2^* \qquad (57)$$

Van de Ven & Mason (1977) found that in the absence of repulsion the rate of doublet formation is not proportional to G, as would follow from the original Smoluchowski Equation 50 but to $G^{0.82}$. If repulsion forces predominate at all interparticle distances, no permanent doublets can be formed, hence $\alpha_o = 0$. Otherwise α_o depends on the actual interaction energy and the shear rate. At very high shear rates, primary doublets may be formed, at low shear rates secondary doublets, while at intermediate shear rates no permanent doublets may be formed. In other words, a suspension can be unstable at low and high shear rates, and stable at intermediate rates.

7.2.2 Application of trajectory analysis to emulsion droplets in Couette flow

The trajectory analysis, as described in Section 7.2.1, was used in discussing the results for the behaviour of emulsions in Couette flow. The application of the trajectory analysis involves several assumptions, some of which need justification.

Brownian encounters should be negligible. When the so called translational Péclet number, Pe_t, is much greater than unity, Brownian encounters can be ignored (Van de Ven & Mason, 1976a):

$$Pe_t = \frac{G \ b^2}{D_i} \qquad (58)$$

where D_i is the translational diffusion coefficient of a particle i. For the lowest shear rate used ($G \approx 50 \ s^{-1}$) and the smallest (mean) particle radius ($b = 0.5 \ \mu m$) with $D_i = 4.4 \times 10^{-13} \ m^2 \ s^{-1}$, $Pe_t = 25$ and the condition was fulfilled.

There is an absence of inertial effects. The Reynolds number for the particles, Re_p, should be much less than unity to avoid inertial effects:

$$Re_p = \frac{G \ b^2}{\nu} \qquad (59)$$

Taking extreme conditions of $G = 1500 \ s^{-1}$ (about the highest shear rate used), the kinematic viscosity $\nu = 10^{-6} \ m^2 \ s^{-1}$ and $b = 5 \ \mu m$ (the mean particle radius was mostly 1 - 2 μm) $Re_p = 0.038$.

56

The trajectory analysis is based upon hard non-deformable spheres. According to Torza et al. (1972), the maximum deformation of fluid spheres in simple shear flow is given by:

$$D = \frac{5(19q + 16)}{4(1 + q) \{(19q)^2 + (20/We)^2\}^{\frac{1}{2}}} \qquad (60)$$

where $D = (L_1 - B_1)/(L_1 + B_1)$ with L_1 and B_1 being the largest and smallest dimensions of the deformed droplet, respectively, q is the ratio of the viscosity of the disperse phase to that of the continuous phase and We is the Weber number given by:

$$We = \frac{G \, b \, \eta_c}{\gamma} \qquad (61)$$

For a shear rate $G = 1500 \, s^{-1}$, interfacial tension $\gamma_{ow} = 10 \, mN \, m^{-1}$, droplet radius $b = 1.5 \, \mu m$, $D \approx 10^{-4}$. The deformation is thus seen to be small. Furthermore, internal circulation inside emulsion droplets is inhibited by surfactants, because the tangential stress is compensated for by an interfacial tension gradient. In this respect, deformation of the emulsion droplets is also reduced.

The generated change in interfacial tension, $\Delta\gamma$, is very small, as calculated from the tangential shear force (Goldsmith & Mason, 1967):

$$\Delta\gamma = \frac{5}{2} \, \eta_c \, G \, b \qquad (62)$$

For $G = 1000 \, s^{-1}$ and $b = 1.5 \, \mu m$, $\Delta\gamma = 4 \times 10^{-6} \, N \, m^{-1}$, indeed a very small change.

The globules in a doublet may independently rotate and then a velocity profile may develop as depicted in Figure 17; this could also generate an interfacial tension gradient. When the globules rotate as free spheres in simple shear flow, the pheripheral velocity v of a globule is:
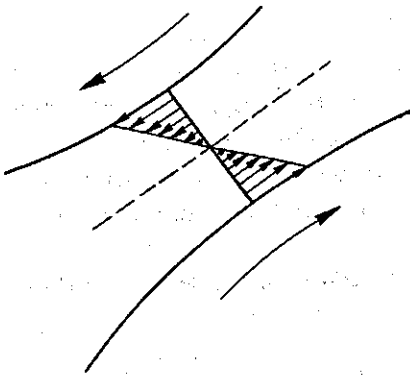

Fig. 17. Flow pattern in the film between two globules rotating in a doublet in Couette flow.

$$v = \tfrac{1}{2} G\, b \tag{63}$$

The velocity gradient in the film with thickness h is then $(\tfrac{1}{2}G\,b)/(\tfrac{1}{2}h)$, and this leads to a stress of $n_c\, G\, b/h$, which is 50 N m^{-2} for $b = 1.5 \times 10^{-6}$ m, $n_c = 10^{-3}$ Pa s, $G = 10^3$ s^{-1} and $h = 3 \times 10^{-8}$ m. This in turn leads to a change in interfacial tension $\Delta \gamma = 7.5 \times 10^{-5}$ N m^{-1}. It is believed that these changes in interfacial tension are too low to cause any appreciable disturbance in the flow.

The spheres must be neutrally buoyant, but this is rarely true in emulsions. However, creaming of the droplets during an experiment will, to a large extent, be prevented by the streaming of the fluid (Walstra & Oortwijn, 1975). However, the density difference may have some influence on the trajectories of emulsion droplets in Couette flow (Goldsmith & Mason, 1967).

A serious defect which cannot be taken into account is the heterodispersity of emulsions, since the analysis is given for monodisperse spheres. Van de Ven & Mason (1976a, 1977) emphasised that the analysis is valid only for two sphere encounters, hence for strongly diluted suspensions (say $\phi_V < 0.01$). Interactions between more than two droplets take place at higher volume fractions, resulting in a different behaviour. For example, a permanent doublet in the secondary minimum can be transformed into a permanent doublet in the primary minimum by collision with a third sphere. More important perhaps is that the trajectories of the spheres, in concentrated dispersed systems, are disturbed (Goldsmith & Mason, 1967).

Hence, it is unlikely that the measured and calculated stability factors will be the same. Therefore, the trajectory analysis cannot give a quantitative explanation but it can give information about the interplay between hydrodynamic and colloidal forces acting between emulsion droplets in Couette flow.

The colloidal interaction between emulsion droplets depends upon the type of emulsifier. The interaction force F_{int} in Equation 53 is composed of a repulsive force F_R and an attractive force F_A. With ionic emulsifiers the DLVO theory is applicable for which a useful approximation formula (when $\kappa\, h > 1$) is (Verwey & Overbeek, 1948):

$$F_R = \frac{64\pi\, n_i\, b\, k\, T}{\kappa}\ \tanh^2\!\left(\frac{z\, e\, \psi_d}{4k\, T}\right) \exp(-\kappa\, h) \tag{64}$$

where n_i is the number of ions with valency z per unit volume, b the radius of the spheres, k Boltzmann's constant, T absolute temperature, κ is the reciprocal double layer thickness, ψ_d the electric potential of the Stern layer, e the elementary charge, h the distance between the spheres ($h = r - 2b$). The question whether the constant potential or constant charge model should be used for F_R is not of interest here, since $\kappa\, h > 1$ (Frens & Overbeek, 1972).

The formulas given by Schenkel & Kitchener (1960) were taken for the Van der Waals attraction:

$$F_A = \frac{A \cdot b}{12h^2} \left(\frac{1 + 3.54p}{(1 + 1.77p)^2} \right) \qquad \text{when } p < 1$$

(65)

$$F_A = \frac{A \cdot b}{12h^2} \left(\frac{0.98}{p} - \frac{0.434}{p^2} + \frac{0.0674}{p^3} \right) \qquad \text{when } p > 1$$

where A is the Hamaker constant and $p = 2\pi h/\lambda$ with λ being the characteristic wavelength of the dispersion interaction. The value for λ is not precisely known but is usually chosen to be 100 nm. The formulas of Schenkel & Kitchener (1960) differ from the ones given by Vincent (1972) but give essentially the same results when $b > 0.5$ μm. For $b < 0.5$ μm the formulas given by Vincent (1972) are in fact better.

Often, steric repulsion is important in the stabilisation of emulsion droplets, for example, with polymers and nonionic surfactants. There is, however, not a simple formula that can adequately describe steric repulsion. Therefore, some experimental data were taken from the literature, when steric repulsion came into play (Section 7.2.4.1).

The trajectory Equations 53 were solved numerically using a DEC 10 computer of the Agricultural University. Use was made of the CSMP language (continuous system modelling program). Numerical integration was performed by a fourth order Runge-Kutta method with variable step size.

7.2.3 Stability of emulsions without crystals in the oil phase

The stability of emulsions without crystals in the oil phase in Couette flow was investigated to compare their behaviour with similar emulsions containing crystals in the oil phase. Real oil-in-water emulsions, stabilised by Tweens, sodium caseinate, PVAs, NaLS, which were stable at rest for several weeks, were subjected to Couette flow at various shear rates. The volume fraction ϕ_v was 0.2 and $d_{32} = 2 - 3$ μm and no signs of instability were found in any case. Also addition of NaCl (0.1 mol/l) to a NaLS emulsion did not cause measurable instability during the time span of an experiment (0.5 - 1 hour). It was concluded that emulsions which were stable at rest, were also stable in Couette flow, a conclusion also arrived at by Swift & Friedlander (1964).

A Manoxol OT emulsion which was unstable at rest upon addition of NaCl, was also subjected to Couette flow. The volume fraction of oil was $\phi_v = 0.2$, $d_{32} = 3.40$ μm, the concentration of Manoxol OT 0.0056 M, and the salt concentration 0.04 mol/l NaCl. This emulsion was subjected to various shear rates. The coalescence rate was determined from the change in particle size distribution with time (Section 3.4) and the results are given in Figure 18a, together with the coalescence rate of the emulsion at rest. It is apparent that the coalescence rate is not drastically affected by Couette flow. An impression of the 'collision efficiency', α, the fraction of encounters leading to coalescence, was calculated as k_1/k_{theor}, where k_1 is the measured coalescence rate and k_{theor} is derived from Equation 51 for Couette flow and Equation 43 for Brownian motion. In Figure 18b $\log \alpha$ is given as a function of the shear rate and although α will only be an approximation since k_{theor} is derived for a monodisperse and dilute emulsion, it is clear that the efficiency α decreased appreciably in Couette flow as compared to Brown-
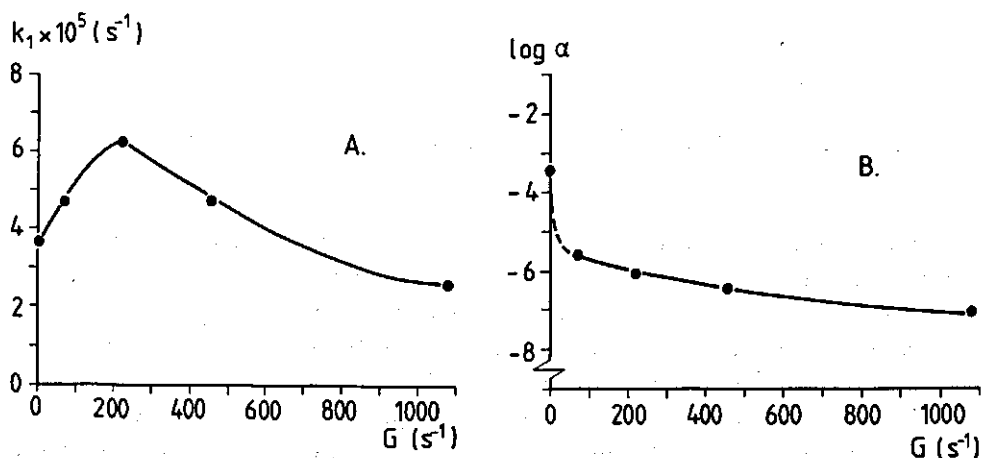
59

Fig. 18. Coalescence rate k_1 (A) and coalescence efficiency α (B) in Couette flow of a Manoxol OT emulsion (ϕ_v = 0.20, d_{32} = 3.40 μm, 0.04 mol/l NaCl).

ian motion. This is because the rate of encounters increases considerably, whereas the coalescence rate was not significantly affected by the flow. It is not a consequence of disruption because the droplet size and the shear rate were not large enough (Walstra, 1980). In this sense, Couette flow can be said to have a stabilising effect, which, to the author's knowledge, has not been mentioned before.

Trajectories of emulsion droplets stabilised by Manoxol OT in Couette flow were considered for an explanation of the above observations. It was assumed that the inter-action can be described by the DLVO theory, hence Equations 64 and 65 are applicable. The surface potential ψ_d approximated the zeta potential, which is about 100 mV for a Manoxol OT emulsion droplet in 0.04 mol/l NaCl (Van den Tempel, 1953; Sherman, 1968) and the Hamaker constant A for paraffin oil is 1.7×10^{-20} J (Visser, 1972). Because of the high zeta potential, a very high energy barrier exists at distances smaller than about 10 nm, while a weak secondary minimum is present at about 12 nm. The trajectory calcula-tions showed that permanent secondary doublets could be formed up to a certain shear rate, above which no permanent doublets were formed. The minimum distance of approach was about 11 nm, which was not largely affected by the shear rate (10 nm at G = 1000 s^{-1}).

The calculated α_o for permanent (secondary) doublet formation is illustrated in Figure 19. The calculated α_o was much higher than the experimental α for coalescence, in other words, coalescence was much slower than flocculation. The observed decrease in co-alescence rate above G = 210 s^{-1} (Fig. 18) is in qualitative agreement with the traject-ory calculations, which show that above G = 120 s^{-1} no permanent doublet formation was possible. The maximum in coalescence rate (Fig. 18) was reproducible for this particular emulsion, but not for another Manoxol OT emulsion having a larger particle size. The co-alescence rate increased then somewhat with increasing shear rate.

Nevertheless, independent of globule size the experimental α was found to decrease with increasing shear rate as depicted in Figure 18b. An explanation for this may be that, when no permanent doublets are formed, only short time encounters take place and
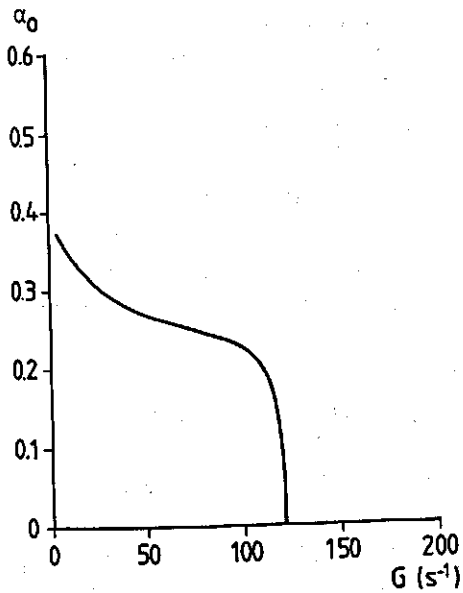
Fig. 19. Calculated capture efficiency α_0 for permanent doublet formation in Couette flow of Manoxol OT stabilised emulsion droplets (d_{32} = 3.40 μm, 0.04 mol/l NaCl).

the life time of an encounter may become important. The average life time $\bar{\tau}$ of a transient doublet is (Arp & Mason, 1976):

$$\bar{\tau} = \frac{5\pi}{6G} \tag{66}$$

hence, the life time decreases as shear rate increases.

It may be concluded that the coalescence process is not drastically affected by Couette flow. The fact that two globules stay together for some time is probably more important than that they meet each other frequently.

7.2.4 Stability of emulsions with crystals in the oil phase

Several factors influenced the stability at rest of emulsions containing crystals in the oil phase (Section 6.2.2). These factors may also influence the stability in Couette flow. Therefore, the influence of several parameters such as the type of surfactant, globule size, density difference between oil and water phase, fat content of the emulsions, amount and type of crystals, and ionic strength in case of emulsions with ionic stabilisers, was investigated.

7.2.4.1 Influence of surfactant type

The influence of surfactant type on stability was investigated as a first parameter. Three representative surfactant types were selected from the emulsion systems with crys-

61

tals in the oil phase, as characterised in the Chapters 5 and 6. These were NaLS, PVAs and sodium caseinate (NaCas). As described in Section 7.2.3, 'true' emulsions (without crystals) stabilised by these surfactants were stable in Couette flow. These emulsions with crystals in the oil phase were also fairly stable at rest (Section 6.2.2).

The effect of crystals on emulsion stability in Couette flow is indicated in Table 14 together with the crystal habit in the unclumped and clumped droplets. The presence of L and M types in the original droplets caused instability. In one case, L and M types were originally absent but appeared in the clumps formed from unstable droplets (NaCas with tristearate) suggesting that N types may be transformed into L and M types. The question arises whether the possible transformation of N to L types took place before, during or after coalescence. If N types persisted, no instability was found (PVA 16-98 with solid paraffin). In the latter case, raising of the content of solid fat did not affect the stability. A tentative conclusion is that for instability to occur some crystals must be somehow in the interface as was concluded for unstable (creamed) emulsions (Section 6.2.2).

The same mechanism for coalescence is proposed as for creamed emulsions is operative, namely some fat crystals at the oil-water interface can be oriented in such a way that they stick out into the water phase (Fig. 14). Such a protruding crystal could pierce the thin film between two globules thereby inducing coalescence. The emulsions of Table 14 were, however, stable at rest when creaming was not prevented (confer Table 12). The destabilising effect of Couette flow has therefore to be considered in more detail.

For a more quantitative understanding the instability was further characterised by determination of the coalescence rate. It was found convenient to indicate instability by the efficiency α, defined as the measured coalescence rate divided by the theoretical rate of encounters (derived from Eqn 51). The reproducibility was usually within 30%. The reasons for this rather poor reproducibility have already been discussed in Section 3.4.4.

The effect of surfactant type on stability under Couette flow is depicted in Figure 20 for three systems, though type of surfactant was not the only variable. An increase in content of solid fat and in globule size decreased stability. PVA emulsions were more stable than NaLS emulsions; in fact, PVA emulsions containing 17% solid paraffin were completely stable. The variation in the volume fraction of fat, ϕ_v, as seen in Figure 20, had no effect on the results (Section 7.2.4.3).

The results of Figure 20 show that the effect of Couette flow on stability is large

Table 14. Stability of some emulsions with crystals in the oil phase in Couette flow in relation to their crystal habit.

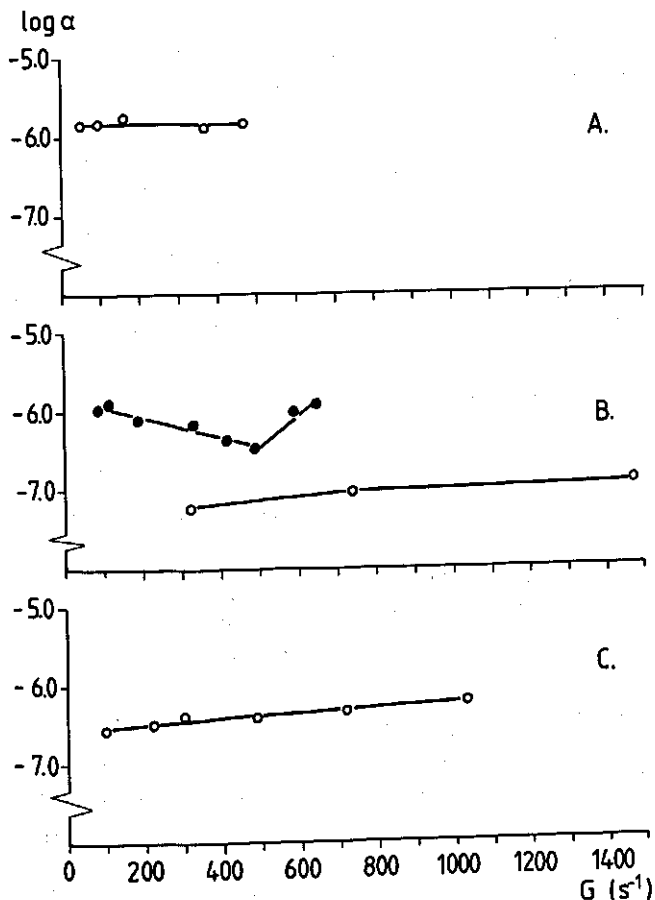|	Crystals	Crystal habit in unclumped droplets	Instability?	Crystal habit in clumps
NaLS	solid paraffin	N,M,L	yes	M,L,N
PVA 4-88	solid paraffin	N,M,L	yes	M,L,N
PVA 40-88	solid paraffin	N,M,L	yes	M,L,N
PVA 16-98	solid paraffin	N	no	
Sodium caseinate	tristearate	N	yes	M,L,N

Fig. 20. Coalescence efficiency α in Couette flow:
A of a NaLS emulsion, $\phi_v = 0.20$, $d_{32} = 2.55$ μm, 17% (w/w) solid paraffin in the oil phase;
B of a PVA 4-88 emulsion (●), $\phi_v = 0.16$, $d_{32} = 2.20$ μm, 42% (w/w) solid paraffin in the oil phase; of a PVA 40-88 emulsion (O), $\phi_v = 0.20$, $d_{32} = 3.16$ μm, 42% (w/w) solid paraffin in the oil phase;
C of a sodium caseinate emulsion, $\phi_v = 0.19$, $d_{32} = 2.95$ μm, 20% (w/w) tristearate in the oil phase.

since α will be about 10^{-10} under quiescent conditions ($G = 0$ s^{-1}, Section 6.2.2). Compared to Brownian motion, Couette flow can affect the stability of emulsions in several ways. The globules may be deformed, but this effect is very small (Section 7.2.2); moreover, the presence of crystals will hamper deformation. Alternatively, only the slightest deformation may be enough to rearrange the orientation of crystals inside the droplet.

As discussed in Section 7.2.2, a very small interfacial tension gradient at the oil-water interface may develop in Couette flow. Apparently, this gradient did not affect the stability of true emulsions in Couette flow (Section 7.2.3) and it will therefore probably also not affect the stability of emulsions containing crystals. Perhaps oil-soluble surface active contaminants from crystals could have an effect, but this is not

very likely since the stability of emulsions with solid paraffin depended on crystallisation type (Table 14). It can, however, not completely be ruled out for tristearate.

Once again, the hypothesis of protruding crystals was considered as the cause of instability. The destabilising effect of Couette flow may then be explained by considering the way in which globules encounter each other. During an encounter a 'contact area' may be defined (though the globules are still separated by a thin film of continuous phase). This area does not change during an encounter in Brownian motion or during the life time of a doublet, rotating as a rigid dumbbell in Couette flow. Mostly, however, there may be some relative rotation of globules in a permanent (non-touching) or separating doublet (Arp & Mason, 1977a, 1977b; Van de Van & Mason, 1976b). This rotational movement depends in a complicated way on the orientation of the spheres towards each other. A more quantitative treatment is therefore not feasible, but qualitatively it is clear that the 'contact area' may be increased in Couette flow. The average life time of an encounter is also much longer in Couette flow (5 x 10^{-2} s at G = 50 s^{-1} and 2.5 x 10^{-3} s at G = 1000 s^{-1}, as calculated from Eqn 66); in Brownian motion it is about 4 x 10^{-5} s (Overbeek, 1977).

Globules can approach each other closer in Couette flow than in Brownian motion. This effect depends on the strength of the flow and the interaction between the globules, hence on the surfactant. The trajectory analysis, as treated in Section 7.2.1, may be helpful in this respect.

First, emulsion droplets stabilised by NaLS are considered, the interaction of which can be described by the DLVO theory, hence by Equations 64 and 65. The zeta potential was taken as a measure for ψ_d and was taken from literature. Values were found ranging from -90 to -110 mV (Anderson, 1959; Haydon, 1960; Groot, 1965). The interaction energy is not sensitive to its exact value for this range of ψ_d and a value of -100 mV was selected. For the Hamaker constant the value for paraffin oil was chosen: 1.7 x 10^{-20} J (Visser, 1972). The Hamaker constants for solid paraffin and tristearate lie in the same order of magnitude (Srivastava & Haydon, 1964, and Van den Tempel, 1961, respectively). The potential energy diagram of two droplets with radius 1.5 μm shows a weak secondary minimum (1 kT) at h = 32 nm and very strong repulsion at shorter distances (several thousands kT). The trajectory analysis showed that permanent doublet formation was not possible for 50 < G < 1000, hence α_0 = 0. Only short time encounters occured, during which coalescence must have taken place.

The minimum distance of approach varied from 32 nm at G = 0 s^{-1} till 21 nm at G = 500 s^{-1}. Assuming a crystal to stick out some 20 - 30 nm (Section 6.2.2), Couette flow could thus accomplish coalescence. The fraction of encounters α', which would lead to an encounter with a minimum distance h less than either 30 nm or less than 25 nm, was calculated (Fig. 21a). The shear rate had an effect on α' when h < 25 nm but not when h < 30 nm. Experimentally, the shear rate appeared to have little effect on α in case of the NaLS emulsion containing 17% solid paraffin (indicating that the coalescence rate was directly proportional to the rate of encounters). Figure 21a shows that below G = 100 s^{-1} no encounter with h < 25 nm would occur, but Figure 20a shows that the NaLS emulsion was unstable below G = 100 s^{-1}. This would mean that protruding crystals were sticking out over a distance of more than 25 nm in this particular emulsion.
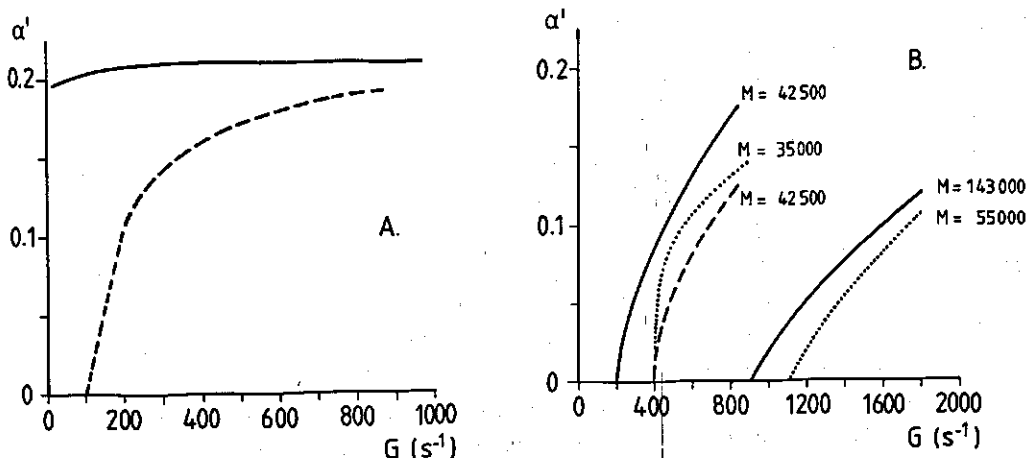
Fig. 21. Calculated fraction of encounters α' in Couette flow for which either $h < 30$ nm
(———) or $h < 25$ nm (----):
A for NaLS emulsion droplets with $d = 3$ μm;
B for PVA emulsion droplets with $d = 3$ μm, results of Sonntag et al. (1979) (·····) only
for $h < 30$ nm.

The value of α' is much higher than the experimental α, but this can be explained as
follows. Assume that, on average, one crystal per globule sticks out far enough to
pierce the film between two globules. Consider a sphere of diameter 3 μm with such a
protruding crystal (cf. Fig. 13). The area over which the crystal can cause coalescence
may to a first approximation be taken as the cross section of a circle with a radius of
25 nm. This means that instead of the whole spherical surface only 7×10^{-5} part of it
is 'reactive'. The probability that an encounter results in coalescence, is then $7 \times$
10^{-5}. However, only 15 - 30% of the globules is of the L and M type and consequently
'reactive'. Combining this with the fraction of encounters that could in principle lead
to coalescence (at most 0.2, Fig. 21a), the value of α' reduces to 4.2×10^{-6}. In this
way the experimental α is approached. This reasoning is, of course, an oversimplifica-
tion of the actual situation, but it explains qualitatively the observed effects. In ad-
dition, polydispersity may also have an influence. According to Arp & Mason (1977a), the
distance of separation increases for an encounter between unequal spheres compared to
equal sized spheres.

Qualitatively, the same reasoning may apply to emulsions, stabilised by surfactants
other than NaLS. The type of surfactant could possibly influence the orientation of fat
crystals via the contact angle, but the differences between PVA 40-88 and 4-88 and NaLS
will be small. The effect must therefore be explained by the influence of the surfactant
on the distance over which the globules can approach each other. Analysing trajectories
of droplets stabilised by PVA involved finding an equation that adequately described the
steric repulsion term. Such an equation is not yet available and therefore some
experimental results were adapted from the literature. Van Vliet (1977) and Lyklema &
Van Vliet (1978) measured the thickness of free PVA films and concluded that tails of the
adsorbed polymer play an important role in steric repulsion. They also found a strong

65

dependence of steric repulsion on molecular weight of the polymer. Recently, Sonntag et al. (1979) also published results on steric repulsion by PVA in aqueous films between an apolar fluid phase. The repulsion increased with decreasing film thickness more than was found by Lyklema & Van Vliet (1978), and no effect of the molecular weight on steric repulsion was found with one exception. This effect was ascribed to penetration of PVA in the apolar phase, but in the author's opinion it may also have been a consequence of poorly defined PVAs, since Koopal (1978) showed that large differences could exist between the molecular weights as stated by the manufacturer and the true values. The different results of Lyklema & Van Vliet (1978) may also have been a consequence of a different experimental technique, since Sonntag et al. (1979) applied pressures that were ten times higher and consequently measured much smaller film thicknesses.

Both results of Lyklema & Van Vliet (1978) and Sonntag et al. (1979) have been made use of for the trajectory analysis. These authors observed a linear relationship between the steric repulsion force and h^{-2}, so that their results can be extrapolated to other distances than experimentally determined. It is realised that this approach will introduce errors, but it may at least serve as an indication of the effect of shear on the distance of separation. This method probably underestimates the actual repulsion at larger distances using the results of Sonntag et al. (1979) and at shorter distances using the results of Lyklema & Van Vliet (1978). From the latter authors the results for PVA with molecular weight M = 42 500 and M = 143 000 were taken, and from the former authors PVA with M = 35 000 (the exception with less repulsion than all other PVAs) and M = 55 000. All these PVAs had the same degree of hydrolysis (88%). The data were rearranged for interaction between two spheres by a method given by Derjaguin (1934). The possible effect of the adsorbed PVA layers on the Van der Waals attraction was neglected, because the polymers are strongly expanded and the Hamaker constant of the adsorbed layer is then close to that of water. Equation 65 was used to describe Van der Waals attraction.

The results of the calculations showed that only short time encounters were possible, but that flow could overcome steric repulsion to some extent. This seems not unrealistic when steric repulsion is dominated by tails (at larger distances). The fraction of encounters α', leading to encounters with h < 30 nm, is shown in Figure 21b as a function of shear rate. Also shown is α' for encounters with h < 25 nm for PVA with M = 42 500 (h < 25 nm was not reached for the PVAs with M = 55 000 and M = 143 000). Again α' was much higher than the experimental α, which may be explained by the same arguments as given previously. The minimum distance of approach depended strongly on molecular weight of the polymer and on the shear rate. This could explain the difference in α between PVA 4-88 and 40-88 emulsions, as shown in Figure 20b. Figure 21b indicates that encounters can be more effective when the shear rate increases, because the particles approach each other closer. This is reflected in the increase of α for PVA 40-88 and for PVA 4-88, when G > 500 s^{-1}. However, α' depended more on the shear rate than α, suggesting that some crystals stick out further than 30 nm. The rate of coalescence of the PVA 4-88 emulsion remained constant for 100 < G < 500, so that α decreased in that region (Fig. 20b). An explanation for this behaviour was not found.

The results for the sodium caseinate emulsion with tristearate are given to show the

effect of tristearate. This emulsion was the only one with tristearate studied, which was stable at rest. The efficiency α was in between that of the emulsions stabilised by the two PVAs with different molecular weight. The repulsion by sodium caseinate will also largely be of a steric nature (as well as some electrostatic repulsion), which could explain the increase in α with increasing shear rate; the globules can approach each other closer at higher shear rates so that encounters can be more effective.

As indicated in Table 14, a change in crystallisation type occured from N types in unclumped droplets to L and M types in clumps. Assuming the hypothesis of protruding crystals and assuming that in N types crystals do not stick outside, L and M types should be formed before coalescence can occur. They could possibly be formed because of deformation of globules in shear flow, which can be calculated from Equation 60 and lies in between 10^{-5} and 10^{-4} for $100 < G < 1000$. A network of 25% tristearate crystals in paraffin oil breaks down at a deformation in between 10^{-4} and 10^{-3} according to Nederveen (1963) and Van den Tempel (1961), and the required stress for this breakdown is about 100 $N\,m^{-2}$. However, the stress on a globule is only 5 $N\,m^{-2}$ at $G = 1000\ s^{-1}$, suggesting that the crystal network in a globule would not be broken down in Couette flow. L types could not be detected in unclumped globules during an experiment, but the possibility remains that they coalesced very rapidly after they had been formed. The low value of α may indicate that L types were formed rarely.

In conclusion, the present results do not contradict the hypothesis that coalescence of oil droplets with fat crystals is caused by protruding fat crystals, piercing the thin film between approaching globules. The destabilising effect of Couette flow compared to Brownian motion may be explained by:
- the relative motion of the globules about each other during an encounter;
- the relatively long life time of an encounter;
- the decrease in interparticle distance because flow can overcome some repulsion.

Although it is clear that the type of surfactant determines the extent of stability, there are other interfering parameters. Their influence was investigated in more detail and is described in the Sections 7.2.4.2 - 7.2.4.7.

7.2.4.2 Influence of mass density of the oil phase

Unfortunately, there was a density difference between the water phase and the paraffin oil used in this study. This could possibly have an effect on the stability of emulsions with crystals in the oil phase in Couette flow and may then hinder interpretation.

Oil with a density equal to water was made by bromating salad oil (addition of bromine to unsaturated fatty acids in glycerides). The salad oil was first purified by column chromatography (for removal of mono- and diglycerides) as described by Walstra & Van Beresteyn (1975). After shaking some bromine with salad oil and removal of excess bromine by evaporation, the density was made equal to the water phase by mixing oils of different densities, and an emulsion was then made in the normal way.

Two emulsions were made: one containing 12% (w/w) solid paraffin in the oil phase and one without crystals (both stabilised by NaLS). The emulsions were perfectly stable at

rest. They were also subjected to Couette flow. The emulsion without crystals remained as stable as at rest. The one with crystals could be made unstable in Couette flow and the crystallisation type in the original globules was N, M and L. The efficiency α did not depend on the shear rate and amounted 5.0×10^{-7}, somewhat lower than of the NaLS emulsion of Figure 20a, but this was attributed to a smaller globule size ($d_{32} = 1.60$ μm) and a lower content of solid fat. The point is that the instability, as observed for emulsions with crystals in the oil phase in Couette flow, is not caused by the density difference between the oil and water phase.

7.2.4.3 Influence of volume fraction of fat

On first consideration one would expect a direct proportionality between the coalescence rate and the volume fraction of fat, ϕ_v, since the rate of encounters is proportional to ϕ_v (Eqn 51). However, other factors play a role as well. Encounters between more than two droplets (n-body interactions, with n > 2) occur when the volume fraction ϕ_v exceeds 0.02 (Goldsmith & Mason, 1967). This results in unsymmetrical encounters and displacements in other directions than the flow direction. Van de Ven & Mason (1976a) emphasised that the trajectories of spheres are influenced by n-body interactions. Moreover, the Couette flow will be disturbed at a certain volume fraction, probably at $\phi_v = 0.25 - 0.30$, and partial plug flow may develop (Karnis et al., 1966), leading to a larger velocity gradient at the inner wall and a smaller velocity gradient inside the annulus.
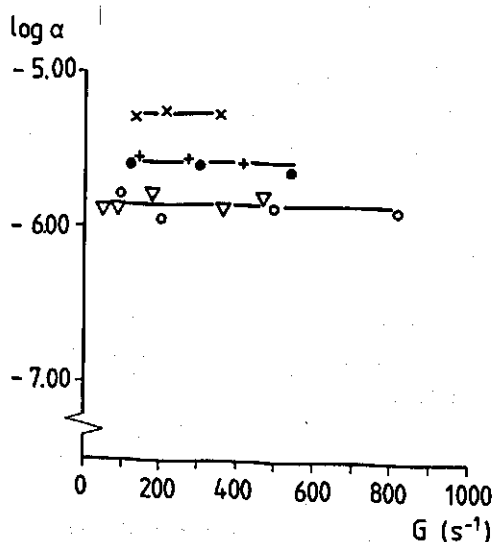
Fig. 22. Influence of the volume fraction of fat ϕ_v on the coalescence efficiency α of NaLS emulsions containing 17% (w/w) solid paraffin in the oil phase in Couette flow:
∇ $\phi_v = 0.20$, $d_{32} = 2.55$ μm
○ $\phi_v = 0.11$, $d_{32} = 2.50$ μm
● $\phi_v = 0.18$, $d_{32} = 3.00$ μm
+ $\phi_v = 0.08$, $d_{32} = 3.00$ μm
x $\phi_v = 0.33$, $d_{32} = 3.00$ μm

In view of these points, the influence of the volume fraction of fat on stability of emulsions in Couette flow was investigated. The results are again presented as the efficiency α: the measured coalescence rate divided by the theoretical rate of encounters. Since the theoretical rate of encounters is proportional to the volume fraction ϕ_v, differences in α would indicate that the coalescence rate is not proportional to the volume fraction. The results, given in Figure 22, show no difference in α for $\phi_v = 0.11$ and 0.21, and $\phi_v = 0.08$ and 0.18. The α for $\phi_v = 0.33$ was, however, higher, indicating that the coalescence rate was more than proportional to ϕ_v and this may be caused by disturbance of the Couette flow. Incidentally, in all cases α was independent of the shear rate, indicating that the coalescence rate was directly proportional to the rate of encounters. It seems justified to conclude from these results that the volume fraction of fat only had an effect on the rate of encounters for these systems and caused no extra disturbances when $\phi_v < 0.21$. It means that the instability was not largely affected by n-body interactions. This may seem somewhat surprising, but is probably a consequence of the fact that the number of encounters resulting in coalescence was very low.

7.2.4.4 Influence of globule size

Little is known about the effect of particle size on the coalescence stability of emulsions. Polydispersity is considerable in emulsions and is known to enhance flocculation (Overbeek, 1952). The shape of the particle size distribution of an unstable emulsion would remain the same both in Brownian motion and in Couette flow according to Swift & Friedlander (1964) ('self preserving size distribution'). Back (1975) noted, however, that larger milk fat globules (> 2 μm) coalesced easier in Couette flow than the smaller ones (< 2 μm). Also Labuschagne (1964) observed in his investigation on stability of cream in Taylor vortices that smaller globules were more stable than larger ones. Some results have already been presented, in which an influence of particle size has been observed (Sections 7.2.4.1 and 7.2.4.3).

Experiments were performed with emulsions, which differed only in particle size. A NaLS emulsion with d_{32} = 0.9 μm and 17% (w/w) solid paraffin in the oil phase was subjected to Couette flow. No changes in particle size distribution could be detected, even when the solid fat content was raised to 42% (w/w): the emulsion remained stable. The emulsions became unstable, however, with increasing particle size (Fig. 23). When d_{32} > 3 μm, NaLS emulsions containing 17% (w/w) solid paraffin became rather unstable and difficult to handle. For the emulsion with d_{32} = 4.80 μm the volume fraction of fat had to be lowered to 0.01 to be able to measure the coalescence rate. This emulsion was also somewhat unstable at rest, as indicated in Figure 23. This dependence of the stability on particle size was also found for a PVA 40-88 emulsion with 42% (w/w) solid paraffin in the oil phase, though the measure of instability was lower than for NaLS (Fig. 24). No explanation was found for the dependence of α on the shear rate for the NaLS emulsion with d_{32} = 4.80 μm (Fig. 23) and for the PVA 40-88 emulsion with d_{32} = 4 μm (Fig. 24).

An emulsion was made unstable in Couette flow until visible clumps appeared. The size distribution was measured before the experiment and also of the emulsion that remained after removal of the visible clumps (Table 15). The mean size decreased, indicat-
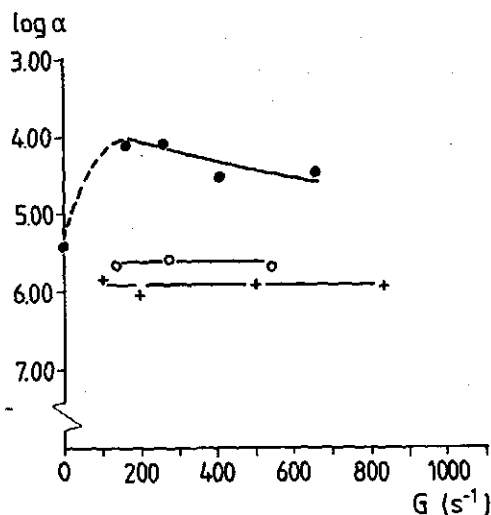
Fig. 23. Influence of droplet size on the coalescence efficiency α of NaLS emulsions containing 17% (w/w) solid paraffin in the oil phase in Couette flow:
+ d_{32} = 2.50 μm, ϕ_v = 0.11
0 d_{32} = 3.00 μm, ϕ_v = 0.18
● d_{32} = 4.80 μm, ϕ_v = 0.01

ing that the smaller globules were more stable and the relative width increased somewhat, indicating that some larger globules were present too but not large enough to be removed with the visible clumps.

This large dependence on globule size was not necessarily a consequence of the droplet size but probably of the crystals inside the droplet. By slowly cooling a PVA 40-88 emulsion with 42% solid paraffin in the oil phase, practically only N crystallisa-
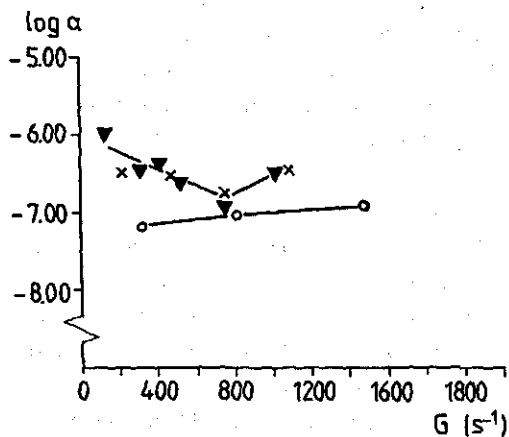

Fig. 24. Influence of droplet size on the coalescence efficiency α of PVA 40-88 emulsions containing 42% (w/w) solid paraffin in the oil phase in Couette flow:
▼ d_{32} = 3.80 μm, ϕ_v = 0.17
x d_{32} = 4.06 μm, ϕ_v = 0.14
0 d_{32} = 3.16 μm, ϕ_v = 0.20

Table 15. Changes in size distribution parameters when clumps were formed in Couette flow. The parameters 'after experiment' were determined after removal of clumps. Results were obtained with a NaLS emulsion with 17% (w/w) solid paraffin in the oil phase.

	$G = 130\ s^{-1}$		$G = 280\ s^{-1}$		$G = 540\ s^{-1}$	
	before experiment	after experiment	before experiment	after experiment	before experiment	after experiment
d_{32}	3.00	2.72	3.00	2.57	3.00	2.16
c_s	0.52	0.63	0.52	0.63	0.52	0.62
ϕ_v	0.18	0.15	0.18	0.11	0.18	0.09

tion types were obtained (the dependence of crystallisation types on cooling rate was discussed in Section 5.2). d_{32} was 5.20 µm, but in spite of this the emulsion was stable in Couette flow and further it illustrates that droplets with N types were stable. Therefore, the influence of particle size on stability must be due to an effect of crystals inside these droplets.

There is little effect of droplet size on the hydrodynamic and colloidal interaction for this relatively small increase in particle size. The large difference in α could not be explained by trajectory analysis. A possible explanation for the influence of globule size could be that the deformation increases somewhat with increasing droplet size. However, it raises from 6×10^{-5} for $G = 100\ s^{-1}$ and $d_{32} = 3$ µm to 1×10^{-4} for $G = 100\ s^{-1}$ and $d_{32} = 5$ µm, so this effect is probably not very important.

An explanation that remains is the effect of droplet size on crystal size, since crystals can grow larger in larger globules. The probability that crystals stick out must depend on size and geometry of the crystals (Section 6.2.2) and larger crystals may stick out further. Larger crystals would also mean fewer crystals, but this effect is considered negligible since only few crystals will stick out. Therefore, the result of larger droplet size may be that more droplets contain protruding crystals, and/or that encounters are more effective because crystals stick out further and because the contact area between droplets is proportional to droplet size.

7.2.4.5 Influence of content of solid fat and of glycerol mono-oleate

When the presence of fat crystals has an effect on stability it is to be expected that the amount of solid fat will also have an influence. Emulsions without crystals are usually very stable, and 'emulsions' with completely solidified fat globules cannot coalesce and a maximum instability may be found in between 0% and 100% solid fat. The measure of instability is governed by the surfactant present and the possible effect of solid fat content must therefore also depend on the type of surfactant.

The following results were obtained for PVA stabilised emulsions. PVA 16-98 with solid paraffin was very stable in flow (only N types were found), and variation in the content of solid fat had no effect at all. Addition of the oil-soluble surfactant glycerol mono-oleate (GMO) to a concentration of 2 g/l in the oil phase was unsuccessful because emulsification was not possible: the emulsion broke down immediately after prepara-

tion. Probably, GMO prevented adsorption of (the rather hydrophilic) PVA 16-98.

PVA 4-88 emulsions were unstable in flow with a content of solid fat of 42% (w/w) solid paraffin in the oil phase, but no instability was found at an amount of 17%. The same held for PVA 40-88 emulsions, although the instability was less than for PVA 4-88. Addition of GMO (2 g/l in the oil phase) did not alter the stability at rest as long as creaming was avoided (Section 6.2.2). The stability in Couette flow, however, was less when GMO was present. Figure 25 compares the results for PVA 40-88 emulsions with and without GMO.

The effect of GMO can be twofold. First, crystallisation can be affected by it and the tendency of crystals to flocculate will be less (Lucassen-Reynders, 1962), so that crystals can reach the interface. This would then lead to more globules with protruding crystals, and hence an increase in α. GMO can also affect the contact angle and cause the crystal needles to stick further into the water phase. Secondly, GMO may influence the adsorption of PVA 40-88. Ogden (1973) obtained evidence that mono-oleate in paraffin oil pushed to some extent PVA 16-88 out of the interface. The rather strong increase in α with increasing shear rate of the emulsion with GMO might have been a consequence of the latter effect; flow could then overcome more easily the steric repulsion. This leads to a shorter interparticle distance, hence to an increased probability of coalescence.

NaLS emulsions were very sensitive to the content of solid fat. This is reflected in Figure 26 where the efficiency α is expressed as a function of the shear rate for emulsions which differed in solid fat content. It is recalled that a NaLS emulsion with 42% solid paraffin was unstable when creamed and this emulsion was too unstable to measure in Couette flow. The results of Figure 26 show quite clearly the large effect of the content of solid fat in these emulsions.

An explanation of the influence of the fraction of solid fat could be that more globules contain protruding crystals, while crystals may stick out further too, when there are more crystals in the oil droplet, or when crystals grow larger. Attempts to
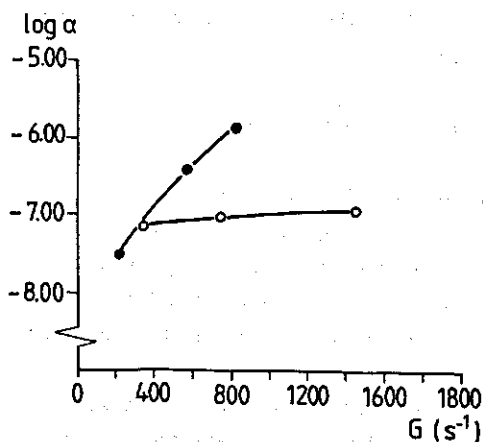
Fig. 25. Influence of glycerolmono-oleate (GMO) on the coalescence efficiency α of PVA 40-88 emulsions containing 42% (w/w) solid paraffin in the oil phase in Couette flow:
O   no GMO, d_{32} = 3.16, ϕ_v = 0.20
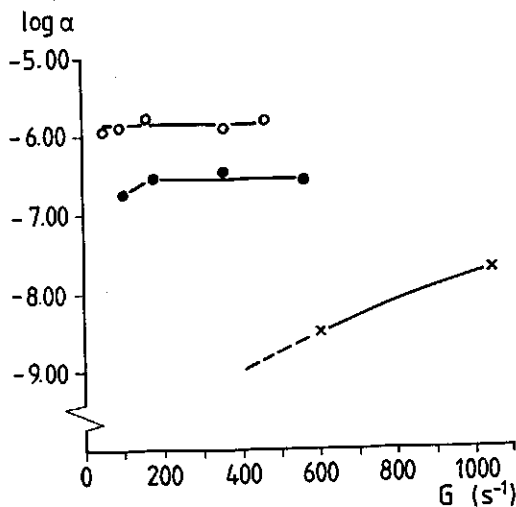●   2 g/l GMO in the oil phase, d_{32} = 3.20, ϕ_v = 0.20

72

Fig. 26. Influence of content of solid fat in the oil phase on the coalescence efficiency α of NaLS emulsions in Couette flow:
x   6% (w/w) solid paraffin, d_{32} = 2.60 μm, ϕ_v = 0.20
●   10% (w/w) solid paraffin, d_{32} = 2.66 μm, ϕ_v = 0.20
0   17% (w/w) solid paraffin, d_{32} = 2.55 μm, ϕ_v = 0.20

obtain small crystals in the droplets by cooling the emulsion very quickly in ice-water were unsuccessful. The crystals had the same appearance under the microscope as when cooled in the normal way. Moreover, some stirring was inevitable for cooling larger amounts of emulsion quickly and this caused instability.

7.2.4.6 Influence of ionic strength

NaLS is an ionic surfactant and the interaction between droplets stabilised by NaLS depends on ionic strength, as described by DLVO theory. Droplets containing fat crystals and stabilised by NaLS could be susceptible to NaCl. Addition of 0.1 mol/l NaCl to a NaLS emulsion without crystals did not cause measurable instability in Couette flow (Section 7.2.3). Furthermore, addition of NaCl to a NaLS emulsion containing solid paraffin had no effect on the stability at rest, when the droplet size was about 2 - 3 μm.

No changes in particle size distribution could be detected when a NaLS emulsion with d_{32} = 0.9 μm and 42% (w/w) solid paraffin and with 0.1 mol/l NaCl was subjected to Couette flow. But for NaLS emulsions with a higher d_{32} the stability was influenced by NaCl (Fig. 27). The effect was most pronounced at the lower shear rates. The increase in α due to the addition of NaCl was about three times (at the lower shear rates) for the emulsion with 10% (w/w) solid paraffin and about twice for the emulsion with 17% (w/w) solid paraffin.

The trajectory analysis was helpful for an explanation of the effect of NaCl, because the effect of NaCl can be accounted for in the DLVO theory (via Eqn 64). The potential energy diagram shows a secondary minimum for two NaLS emulsion droplets (d = 3 μm) in 0.1

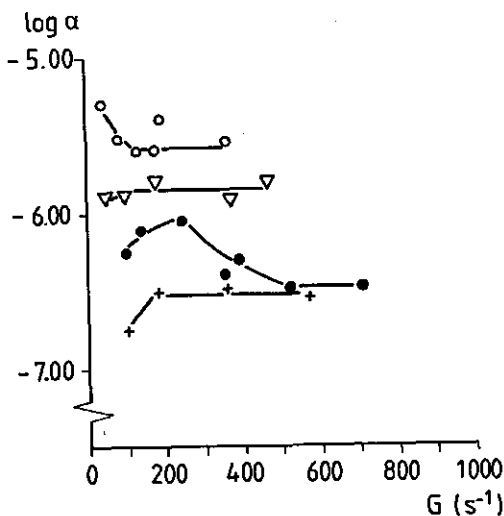Fig. 27. Influence of NaCl on the coalescence efficiency α of NaLS emulsions in Couette flow:

∇ no NaCl added,   17% (w/w) solid paraffin in the oil phase, d_{32} = 2.55 µm, ϕ_v = 0.20
o   0.1 mol/l NaCl, 17% (w/w) solid paraffin in the oil phase, d_{32} = 2.60 µm, ϕ_v = 0.19
+   no NaCl added,   10% (w/w) solid paraffin in the oil phase, d_{32} = 2.66 µm, ϕ_v = 0.20
●   0.1 mol/l NaCl, 10% (w/w) solid paraffin in the oil phase, d_{32} = 2.66 µm, ϕ_v = 0.20

mol/l NaCl at about 8 nm but still a large repulsion at shorter distances. The traject-
ory analysis revealed that at the lower shear rates permanent, secondary, doublets were
formed. The orthokinetic capture efficiency α_0 (for permanent doublet formation) was
calculated for d = 1 µm and d = 3 µm (Fig. 28) and for d = 1 µm permanent doublets were
formed over a wide range of shear rates. Experimentally, no instability was found for
d = 1 µm and therefore flocculation had no effect when coalescence was not possible,
probably because the crystals were too small to be effective. Permanent doublets were
formed for d = 3 µm up to a shear rate of 450 s^{-1}, which seems to correspond with the
experimental result for NaLS with 10% solid paraffin (Fig. 27), because the α for the
emulsion with 0.1 mol/l NaCl approached that of the one without NaCl when G > 400 s^{-1}.
Unfortunately, no experiments were carried out for the emulsion containing 17% solid
paraffin when G > 400 s^{-1}.

These results indicate that flocculation in shear flow had a negative influence on
stability when coalescence was possible. There is probably some relative motion of the
spheres in a permanent doublet and a protruding crystal will then have more chance to be
effective. Furthermore, addition of NaCl results in a closer approach of the particles,
say 8 - 10 nm (Van den Tempel, 1958). The fraction of encounters with h < 10 nm was the
same as the orthokinetic capture efficiency α_0 for G < 450 s^{-1} (Fig. 28). The fraction
of encounters with h < 10 nm was for G > 450 s^{-1} about the same as the fraction of en-
counters for which h < 30 nm for NaLS droplets without NaCl (Fig. 21a). The effect of a
smaller interparticle distance would be that crystals that protrude only to a small ex-
tent (say between 10 and 20 nm) can be effective as well, that is the fraction of 'reac-
tive' globules would increase. This is, however, not in accordance with the behaviour of
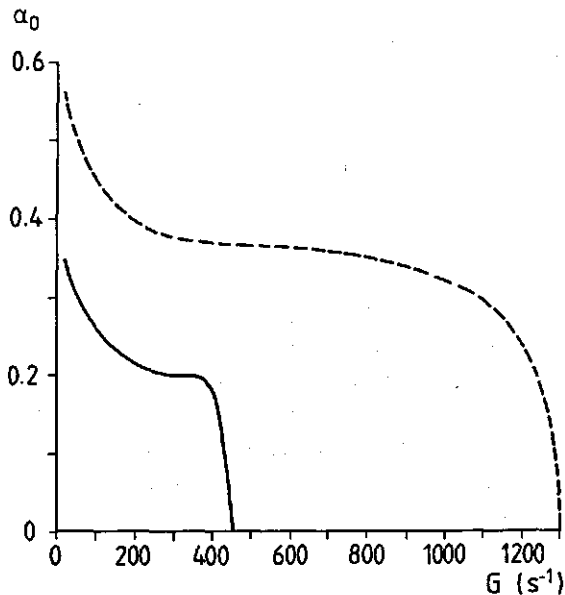
74

Fig. 28. Calculated capture efficiency α_0 for permanent doublet formation in Couette flow of NaLS stabilised emulsion droplets in 0.1 mol/l NaCl with $d = 3$ μm (——) or $d = 1$ μm (·—––).

the emulsion with 10% solid paraffin for which above $G = 400$ s^{-1} the α with and without NaCl became about the same. A tentative conclusion is that only crystals that stick out some 20 - 30 nm can induce coalescence. However, more experiments are needed to justify this conclusion. The most important effect of NaCl would thus be the capture of globules into doublets where they can orbit around each other, thereby increasing the probability of coalescence. The difference between the emulsion with 10% and 17% solid paraffin was explained by assuming that a higher content of solid fat gave rise to a higher number of 'reactive' globules, or to more effective crystals.

7.2.4.7 Influence of emulsion droplets containing crystals on stability of emulsion droplets without crystals

It has been shown that most emulsions without crystals were stable in Couette flow. With the picture of protruding crystals in mind it would be interesting to observe whether emulsion droplets without crystals would coalesce with emulsion droplets containing crystals, when subjected to Couette flow. In principle the following encounters are possible:
(a) between droplets with crystals;
(b) between a droplet with and one without crystals;
(c) between droplets without crystals.
It has been shown (Section 7.2) that in case (a) coalescence can occur, but not in case (c). It is to be determined whether case (b) leads to coalescence.
   When emulsions with crystals and without crystals in the droplets are mixed with each

other, the number of 'reactive' globules changes and this must lead to a change in kinetics of coalescence in Couette flow. This change can be expressed in the rate of encounters leading to coalescence (cf. Eqn 51, with $\phi_v = 4/3 \pi N b^3$):

$$J_0 = \frac{16}{3}\alpha N_0^2 G b^3 \tag{67}$$

$$J_1 = \frac{16}{3}\alpha_1 N_0^2 G b^3 \tag{68}$$

where N_0 is the total number of emulsion droplets, J_0 the rate of encounters leading to coalescence with efficiency α for emulsion droplets containing crystals, and J_1 the rate of encounters leading to coalescence with efficiency α_1 for emulsion droplets with and without crystals. If the total number of droplets, N_0, is kept constant and the number of droplets containing crystals is varied, the change in J_1/J_0 can be determined from the experimental change in α_1/α. The change in J_1/J_0 can also be calculated when the number of 'reactive' globules, N_1, changes according to case (a) or case (a) and (b) by replacing N_0 in Equation 67 by N_1. It then follows that:

$$\frac{J_1}{J_0} = \frac{N_1^2}{N_0^2} = \frac{\alpha_1}{\alpha} \tag{69}$$

Mixing experiments were performed with a NaLS emulsion without crystals and one with 12% (w/w) solid paraffin ($d_{32} = 2.72$, $\phi_v = 0.22$); and also with a PVA 40-88 emulsion without crystals and one with 42% (w/w) solid paraffin ($\phi_v = 0.2$, $d_{32} = 3.90$ μm). Mixed emulsions were subjected to Couette flow while the shear rate was kept constant (300 and 500 s^{-1} for the NaLS and PVA 40-88 emulsion, respectively). The results are presented in Table 16. The experimental ratio α_1/α is close to the theoretical ratio J_1/J_0 for case (a) + (b). This is strong evidence for the picture of a protruding crystal piercing the thin film between two globules and it does not matter whether the second globule contains crystals or not.

Table 16. Coalescence efficiencies in Couette flow of emulsions with different proportion of droplets with and without crystals.

Fraction of emulsion droplets containing crystals	J_1/J_0[1]	J_1/J_0[2]	α_1/α[3]
0.52	0.27	0.77	0.84
0.50	0.25	0.75	0.69
0.40	0.16	0.64	0.66
0.37	0.14	0.60	0.53
0.22	0.05	0.39	0.34
0.20	0.04	0.36	0.21

1. Calculated from Equation 69 on assumption that only encounters between droplets with crystals were effective.
2. Calculated from Equation 69 on assumption that encounters between droplets with and without crystals were effective.
3. Calculated from the experimentally determined efficiencies.

7.2.4.8 Behaviour of natural cream

The behaviour of model emulsions was compared with that of natural cream in Couette
flow. Mulder & Walstra (1974) gave a survey of the complicated structure and composition
of milk fat. When stored long enough at low temperature (2 - 4 ^{O}C), milk fat globules
contain crystals. Apart from bacterial deterioration and cold agglutination, milk fat
globules are quite stable at rest. Flow can, however, destabilise the milk fat globules,
as is necessary, for instance, in buttermaking and whipping of cream, and it is known
that the presence of crystals is necessary for these processes to occur (Mulder &
Walstra, 1974). Labuschagne (1963) studied the stability of cream in flow with Taylor
vortices and found that this type of flow could destabilise the cream. Back (1975) in-
vestigated the behaviour of milk (with 3.5% fat) in a Couette apparatus and found insta-
bility only at rates of revolution that caused turbulent flow.

In this section, experiments are described on cream with different fat contents in
Couette flow. The cream was pasteurised and cooled long enough to ensure crystallisa-
tion in all globules. Before an experiment, the cream was gradually warmed to room
temperature (22 ^{O}C), where the content of solid fat in the fat phase was about 15% (w/w)
as estimated by pulse NMR. More details about estimation of content of solid fat in
cream are described in another paper (Van Boekel, 1980).

Coalescence of milk fat globules was more complicated than that of model emulsions,
since milk fat globules coalesced somewhat in absence of crystals at 40 ^{O}C (Walstra &
Van Boekel, 1980). Even so, coalescence was faster in presence of crystals. The results
on coalescence of cream containing crystals in Couette flow at different volume fractions
are given in Figure 29. The crystallisation habit in milk fat globules was of the N and
O type. However, L types were frequently seen in the clumps formed by coalescence.
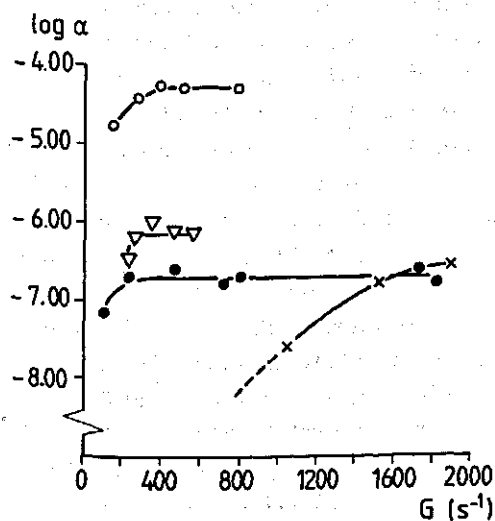These observations were the same as for sodium caseinate with tristearate (Section

Fig. 29. Coalescence efficiency α of natural cream in Couette flow, d_{32} = 3.30 μm,
T = 22 ^{O}C: ϕ_{V} = 0.10 (x); ϕ_{V} = 0.20 (●); ϕ_{V} = 0.32 (∇); ϕ_{V} = 0.43 (O).

7.2.4.1). The explanation given there could also apply to milk fat globules. It is not certain whether the L types were formed before, during or after coalescence, but from the results of the model emulsions one would conclude that L types are necessary for coalescence. If the latter, they should be formed before coalescence. The transformation of N types to L types is, however, unlikely, because the stress on a globule is probably not sufficient to break the crystal network in the globule. Alternatively, the efficiency α was very low and this may be explained by the small probability of L or M type formation.

Incidentally, Buchheim & Precht (1979) stated that L types would be very stable against coalescence. They concluded this from electron micrographs and the fact that many globules with L types can be seen in butter and they suggested that these globules could resist the mechanical treatment during churning. The results of the present work indicate that the opposite is true.

Several phenomena are reflected in Figure 29. The measure of instability strongly depended on the volume fraction of fat. The behaviour at $\phi_v > 0.30$ was in accordance with the behaviour of model emulsions (Section 7.2.4.3). Probably, the Couette flow field was disturbed at these volume fractions and these disturbances had apparently a destabilising effect. The behaviour at the lower volume fractions was, however, not in accordance with model emulsions, where α was the same for $\phi_v = 0.1$ and 0.2. The exception shown by cream, may be related to the occurence of N types. When it is assumed that in some globules L types were formed before coalescence occured, the volume fraction of fat could have an influence on the formation of L types because of encounters between more than two droplets. The increase in α with increasing shear rate may be explained by the increasing deformation caused by the flow, even though this deformation is small. The dependence of α on volume fraction is in line with the observation of Back (1975) that milk with 3.5% fat was stable in Couette flow.

The dependence of α on shear rate, especially at the lower shear rates, might also have been due to the fact that the interparticle distance was too large for coalescence to occur. The trajectory analysis should give more information, but the interaction between milk fat globules cannot be described in a quantitative way. Factors involved are Van der Waals attraction, electrostatic repulsion and steric repulsion. The zeta potential of milk fat globules is only -11 mV (Mulder & Walstra, 1974) but the influence of steric repulsion is unknown. The absorbed layer (mainly protein) is about 10 nm thick (Mulder & Walstra, 1974) but tails may stick out further. Because the membrane is fairly thick and not so strongly expanded, it also influences the Van der Waals attraction. As will be shown in another paper (Walstra & Van Boekel, 1980), the interaction between milk fat globules cannot adequately be described by DLVO theory because then always a considerable secondary minimum is found. Milk fat globules, however, do not flocculate (apart from cold agglutination) and, steric repulsion must be taken into account. The presence of at least a few tails must be assumed, which should stick out over a distance of some 10 - 15 nm from the outer surface of the adsorbed layer to prevent flocculation in the secondary minimum. Flow may overcome the relatively weak steric repulsion by tails to some extent, as with PVA stabilised emulsion droplets (Section 7.2.4.1).

In conclusion, the stability of milk fat globules in Couette flow is not fully understood. Although milk fat globules coalesced also in absence of crystals, the effect

of Couette flow on milk fat globules containing crystals may, at least partially, be explained by the same mechanism as was assumed for model emulsions containing crystals in the oil phase. Some uncertainty remains about the transformation of N to L and M types, while the interpretation of the effect of Couette flow is hindered by the uncertainty about the interaction between milk fat globules.

7.3 STABILITY OF EMULSIONS IN TURBULENT FLOW

A flow field is called turbulent when the motion of the fluid is random. The fluid velocity components vary in a chaotic way in direction and time. Eddies develop which transfer their kinetic energy to successively smaller eddies and eventually the energy is dissipated by viscous friction. The bulk flow may be taken as anisotropic, but on the scale of the smallest eddies the flow may locally be isotropic. In the case of isotropic turbulence, equations can be derived to describe turbulent motion and particle encounters in turbulent flow (for instance, Spielman, 1978). For isotropic turbulence to occur the Reynolds number (Eqn 23) must be very high ($Re > 40\ 000$). Strong shearing and elongational streaming occurs in turbulent flow and emulsion droplets can be deformed to a large extent and disruption is possible (turbulent flow is effective in homogenisation, Walstra, 1980). Coalescence is also possible as a result of particle encounters and inertial effects may well play a role.

Turbulent flow was achieved with the Couette equipment in the present investigation. Instabilities which normally arise in the flow, are no longer damped at a certain Re but reinforce and develop into turbulence. Laminar flow will change into turbulent flow at $Re = 2000 - 3000$ with the Couette equipment of the present study (well below the isotropic turbulence region).

The effect of turbulence on the stability of emulsions with crystals in the oil phase was studied with a model emulsion and with natural cream. Re could be varied without changing the shear rate by using different gap widths and results were expressed in coalescence rates as function of the shear rate and Re. The results for a PVA 40-88 emulsion with 42% (w/w) solid paraffin are given in Figure 30, where for comparison the coalescence rate in laminar flow is also given. The results for cream are given in Figure 31. The coalescence rate increased rather steeply at $Re \simeq 2000$ in both cases. Unfortunately, the results could not be analysed in a more quantitative way, because theoretical equations are only valid for isotropic turbulence. Qualitatively, the following considerations may apply. Inertial forces can overcome repulsion forces, so that droplets can approach each other closer than in laminar flow. Deformation of globules can also have an effect, especially on milk fat globules as N types may be transformed in L and M types, which may coalesce easier. The results for cream are to some extent in accordance with the observation of Back (1975) that milk (3.5% fat) was unstable in turbulent, but not in laminar flow.

Although a more quantitative analysis of the present results was not possible, it is clear that emulsions with crystals in the oil phase were very sensitive to flow and also type of flow, in accordance with the picture obtained so far of the factors that influence the stability of these systems.
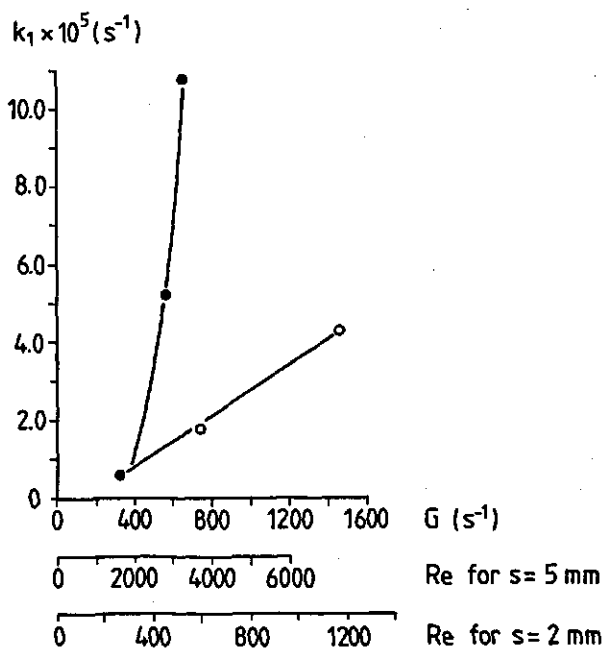
Fig. 30. Influence of Reynolds number Re on the coalescence rate k_1 of a PVA 40-88 emulsion in Couette flow, ϕ_v = 0.20, d_{32} = 3.16 μm, 42% (w/w) solid paraffin in the oil phase: s = 2 mm (O); s = 5 mm (●).

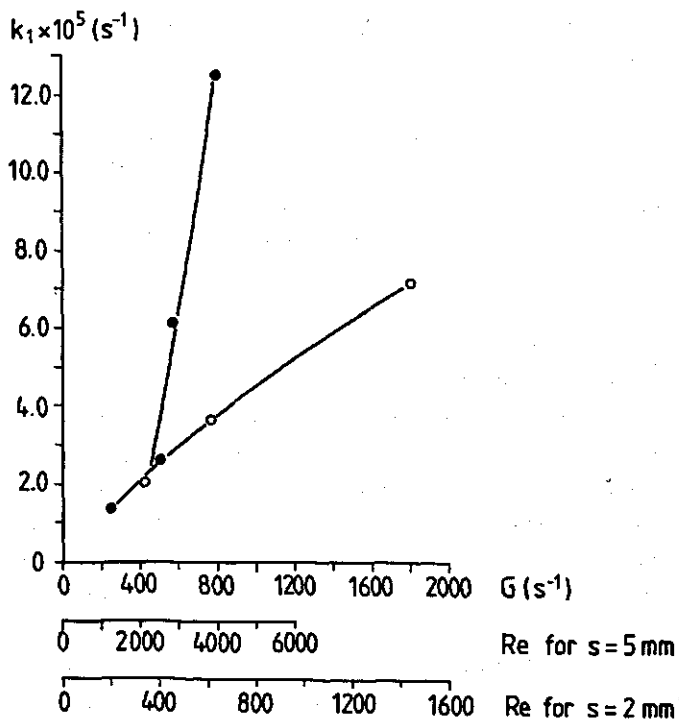

Fig. 31. Influence of Reynolds number Re on the coalescence rate k_1 of natural cream in Couette flow, ϕ_v = 0.20, d_{32} = 3.30 μm, T = 22 °C: s = 2 mm (O); s = 5 mm (●).

Laminar flow between two concentric cylinders can be achieved by rotating the inner or the outer cylinder. When the inner cylinder rotates, however, Taylor vortices arise at a relatively low Re due to centrifugal instability. They were described in more detail in Section 3.5.2. The flow field that develops is a complicated three dimensional motion of both shear flow and elongational flow present between counterrotating vortices. Elongational flow may particularly influence the stability of emulsions. It can be effective in disruption (Walstra, 1980), but the situation will be more complicated for emulsions with crystals in the oil phase, because the presence of crystals will hinder deformation. Labuschagne (1963) studied the stability of cream in flow with Taylor vortices and found that this type of flow could make the milk fat emulsion quite unstable.

Firstly, the effect of Taylor vortices was determined for emulsions without crystals in the oil phase. Emulsions which were stable at rest could not be made unstable in flow with Taylor vortices. A Manoxol OT emulsion, which could be made unstable at rest upon addition of NaCl was subjected to flow with Taylor vortices. The flow was characterised by an apparent shear rate, calculated as if it were normal Couette flow in order to enable comparisons with Couette flow. The coalescence rate is presented in Figure 32 as a function of the apparent shear rate and, for comparison, the result for Couette flow is also given. The coalescence rate decreased with increasing apparent shear rate and it was lower than in Couette flow. As for Couette flow, the explanation may be that globules do not stay long enough together for coalescence to occur. Disruption of globules
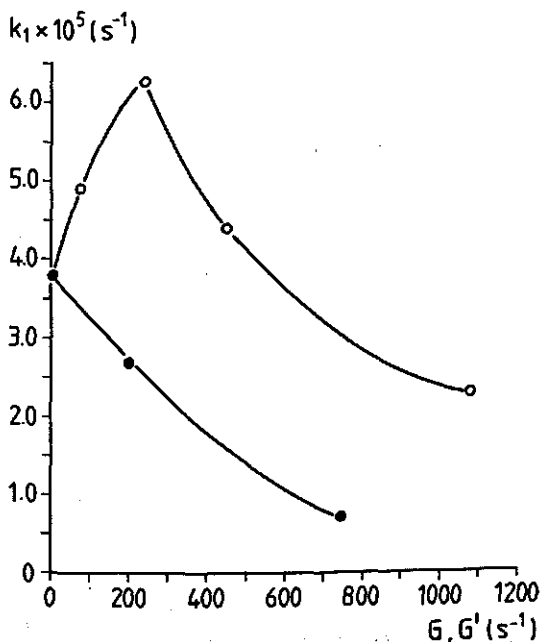

Fig. 32. Coalescence rate k_1 of a Manoxol OT emulsion in flow with Taylor vortices (●) and Couette flow (O), $\phi_v = 0.20$, $d_{32} = 3.40$ μm, 0.04 mol/l NaCl, no crystals.

81

was unlikely because the droplets were too small. The conclusion is that the coalescence process in 'true' emulsions is not promoted by this type of flow.

A PVA 16-98 emulsion with 42% (w/w) solid paraffin in the oil phase remained as stable in flow with Taylor vortices as at rest or Couette flow and only N types were found in this emulsion. Model emulsions containing solid paraffin (L and M types) and a Na caseinate emulsion containing 20% (w/w) tristearate (only N types) showed in flow with Taylor vortices a different behaviour from that in Couette flow. In the latter case, the coalescence rate could fairly well be determined before visible clumps eventually appeared. In flow with Taylor vortices, however, some visible clumps were often seen after a few minutes, and yet the coalescence rate measured was not much different from that in Couette flow and sometimes even lower. Some representative results are given in Figures 33 and 34, and the results for Couette flow are also given for comparison, even though the conditions were not completely the same. Re was higher (ranging from 4000 - 10 000) in flow with Taylor vortices while in Couette flow Re was below 2000. Analysis of the results was not feasible, because on the one hand the flow is of a complicated nature and on the other hand visible clumps were formed too quickly. This latter observation suggests that coalescence was quite rapid in the beginning of the experiment. The fact that the coalescence rate constant was about the same as in Couette flow or even smaller suggests that disruption of clumps, formed in the beginning, interfered with the coalescence rate as estimated in this study. The coalescence rate estimated would then not only reflect the disappearance of globules, but also the formation of droplets formed by disruption of clumps.

The fact that visible clumps appeared indicates that flow with Taylor vortices can destabilise emulsions with crystals in the oil phase and it can be explained by the same
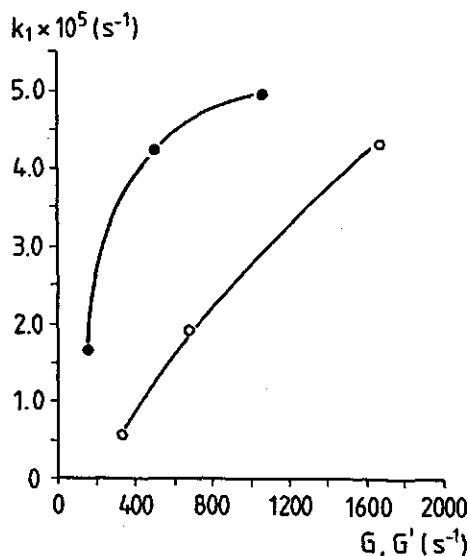

Fig. 33. Coalescence rate k_1 of a NaLS emulsion in flow with Taylor vortices (●) and in Couette flow (O), $\phi_v = 0.18$, $d_{32} = 3.00$ μm, 17% (w/w) solid paraffin in the oil phase.
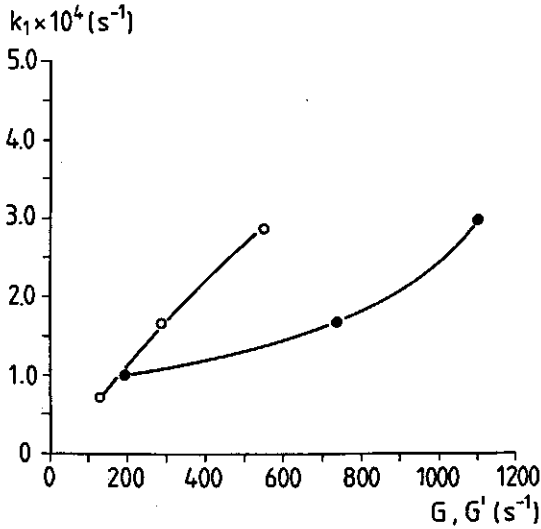
Fig. 34. Coalescence rate k_1 of a PVA 40-88 emulsion in flow with Taylor vortices (●) and in Couette flow (O), ϕ_v = 0.20, d_{32} = 3.16 μm, 42% (w/w) solid paraffin in the oil phase.

mechanism as in the case of Couette flow. An explanation about what happened after the rapid formation of clumps is not so easy, but appears to be due to some disruption in the elongational flow fields between counter-rotating Taylor vortices.

In contrast to the behaviour of model emulsions with crystals in the oil phase, cream was found to be much more unstable in flow with Taylor vortices than in Couette flow. Visible clump formation was much more regular than in model emulsions and the coalescence
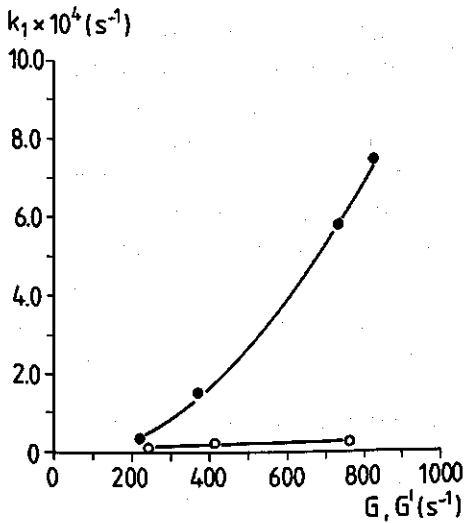

Fig. 35. Coalescence rate k_1 of cream in flow with Taylor vortices (●) and in Couette flow (O), ϕ_v = 0.20, d_{32} = 3.30 μm, T = 22 °C.
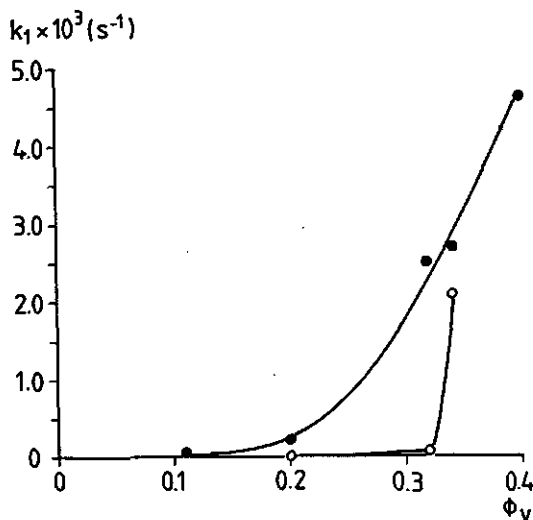
Fig. 36. Coalescence rate k_1 of cream (d_{32} = 3.30 μm) with different volume fraction of fat in flow with Taylor vortices, G' = 370 s^{-1} (●) and in Couette flow, G = 370 s^{-1} (O).

rate could be determined before visible clumps appeared. The coalescence rate in Taylor vortices was much higher than in Couette flow (Figs. 35 and 36), but Re was higher in flow with Taylor vortices (Re = 2000 - 4000) than in Couette flow (Re < 2000).

The enormous effect of Taylor vortices on milk fat globules could be due to the effect on crystallisation type. The deformation of globules in Taylor vortices will be greater than in Couette flow, and this could mean that N types are more rapidly transformed into L types, thereby increasing the probability of coalescence. The influence of the volume fraction of fat (Fig. 36) could then be explained by considering that the coalescence rate is proportional to the number of globules than can change in crystallisation type and that the rate of encounters was proportional to the fat content. The possible influence on the formation of L and M types should also be valid for the Na caseinate emulsion with tristearate, but visible clumps rapidly formed with this emulsion in Taylor vortices, whereas the coalescence rate was not much different from that in Couette flow. An explanation could not be found for the different behaviour of cream. Apparently, disruption of clumps formed by milk fat globules does not take place, perhaps because milk fat crystals form a stronger network than solid paraffin or tristearate crystals.

7.5 CONCLUSION

In this chapter the effect of flow on stability of emulsions with and without crystals in the oil phase was investigated. Emulsions without crystals that were stable at rest, were also stable in a flow field. An emulsion being unstable at rest in the flocculated state, was not more unstable in Couette flow and even less unstable in flow with Taylor vortices. This was explained by considering that for coalescence to occur

84

the globules should stay together for some time and this is mostly not realised in flow.

In contrast, emulsions containing crystals in the oil phase were in general very sensitive to flow, indicating that the mechanism of coalescence is different from that of true emulsions. As at rest, the instability was always accompanied by the crystal habit in which some crystals are probably oriented in the oil-water interface, either in the unclumped globules or in the clumps formed by coalescence. The hypothesis of protruding crystals, piercing the film between approaching globules, was used to explain the mechanism of coalescence. The influence of flow was explained by making use of a theory that describes trajectories of spheres in simple shear flow. The destabilising effect of flow as compared to Brownian motion was explained by:

- the smaller distance of approach between globules because flow can overcome some repulsion;
- the rolling motion of spheres about each other during an encounter;
- the longer life time of an encounter.

The (very small) deformation of droplets in flow, possibly changing the orientation of crystals in the droplets, could also have an effect.

The kinetics of the coalescence process indicated that the surface area of a protruding crystal must be very small compared to the surface of the whole globule and that only a small number of globules would contain protruding crystals. The influence of several parameters like surfactant type, content of solid fat, droplet size, fat content and ionic strength, was explained by their influence on the distance of approach and their possible effect on protruding crystals. The fact that emulsion droplets containing crystals coalesced also with emulsion droplets without crystals was in agreement with the hypothesis of protruding crystals.

The behaviour of cream differed in some respects from model emulsions and it may be explained by the difference in crystal habit. With reference to the hypothesis of protruding crystals, it was reasoned that crystals had to reorient in such a way that they could come into the interface and then cause coalescence. However, coalescence of milk fat globules was not fully understood.

Finally, some experiments have been described with turbulent flow and flow with Taylor vortices. Turbulent flow had a large destabilising effect, probably because repulsion was more easily overcome and deformation greater.

Clumps were formed with model emulsions in Taylor vortices and these clumps were probably to some extent disrupted again by the elongational flow between counter-rotating vortices. Cream behaved differently from model emulsions, as it was much more unstable than in Couette flow. It fitted in the hypothesis that crystals have to orient in the interface, since the deformation in Taylor vortices with elongational flow will be larger, hence the probability of protruding crystals might have been increased.

Summary

Properties of oil-in-water emulsions with fat crystals in the oil phase were investigated. These systems may serve as a model for many foods, pharmaceutics, cosmetics and insecticides. For many purposes the emulsion should be stable, but for some purposes unstable. Factors, which influence the stability to coalescence of these emulsions, at rest and in flow, were investigated.

Chapter 1 reviews literature on crystallization in emulsions. It examines stability of emulsions in general and the influence of flow on it. Little proved to be known about the effect of crystals on stability and the effect of flow.

The materials used are described in Chapter 2 and the methods in Chapter 3. Most experiments were performed with model emulsions of paraffin oil in water containing solid paraffin or tristearate crystals. The stability of natural cream was investigated too. Spectroturbidimetry and Coulter counting were used to study coalescence.

Chapter 4 deals with crystallization of solid paraffin and tristearate in paraffin oil, in bulk or in emulsion droplets. Content of solid fat was measured by nuclear magnetic resonance (pulse NMR). The method was independent of properties of crystals (such as polymorphism). It could also be applied to emulsions, provided that the surfactant did not interfere.

Chapter 5 is devoted to the crystal habit in emulsion droplets. The principal parameter was the contact angle, which depended on the kind of crystal and surfactant used. Contact angle measurements showed that the influence of surfactants on the contact angle was larger than predicted.

Stability to coalescence of emulsions at rest is treated in Chapter 6. Most surfactants used yielded emulsions that were stable in absence of fat crystals. The same emulsions could, however, be unstable if fat crystals were present in the oil droplets. The difference in coalescence rate could, for instance, be six orders of magnitude. Globules of an unstable emulsion contained crystals that were most probably partly in the interface of the droplet. Coalescence could be caused by crystals sticking out of a globule and piercing the thin film between that globule and a second approaching globule. The influence of factors like globule size, kind of crystal, surfactant and the destabilizing effect of creaming could be explained by this hypothesis. Most emulsions with crystals appeared to be stable when creaming was avoided. Additional evidence for the hypothesis was obtained from experiments in which aqueous films were drawn in oil in the presence of fat crystals.

Chapter 7 deals with the influence of flow (Couette flow, turbulence, flow with Taylor vortices) on stability of emulsions. True emulsions (without crystals) that were stable at rest, were also stable when flowing. The coalescence rate of a true emulsion, unstable at rest, was hardly affected by Couette flow. The 'efficiency' (the proportion

of encounters leading to coalescence) decreased sharply with Couette flow, as compared to Brownian motion.

Flow could destabilize emulsions with crystals in the oil phase, if crystals were oriented in the oil-water interface. The efficiency increased by a factor 10^3 to 10^5. In explaining the destabilizing effect of Couette flow, a theory was used that describes the trajectories of spheres in simple shear flow by taking into account hydrodynamic and colloidal interaction. Compared to Brownian motion, the destabilizing effect of Couette flow could be explained by considering that the droplets:
- approach each other closer
- roll about each other during an encounter
- stay longer together in a transient doublet.

The influence of parameters like fat content, droplet size, content of solid fat and ionic strength on stability in Couette flow fitted in the hypothesis that protruding crystals induce coalescence. The fact that emulsion droplets with crystals coalesced with droplets without crystals favoured the hypothesis. According to the kinetics of coalescence, only a few globules need contain crystals protruding sufficiently far to achieve coalescence.

Stability of cream in Couette flow largely corresponded to that of model emulsions, although there were some deviations.

Emulsions with crystals were very sensitive to turbulent flow: the coalescence rate increased strongly over that with laminar flow, probably because the droplets approach each other closer.

Furthermore, flow with Taylor vortices could destabilize emulsions with crystals in the oil phase, but the coalescence rate did not differ much from that in Couette flow. Possibly clumps formed by coalescence were disrupted again in the elongational flow field between Taylor vortices. Cream, however, was less stable in flow with Taylor vortices than in Couette flow. This might have been caused by the difference in crystal habit between cream and model emulsions.

Samenvatting

In dit proefschrift zijn emulsies van olie in water met vetkristallen in de disperse fase onderzocht. Deze systemen komen vaak voor als levensmiddelen, farmaceutische en cosmetische produkten en als bestrijdingsmiddelen. Afhankelijk van de toepassing wil men graag dat emulsies stabiel, dan wel instabiel, zijn. Onderzocht is welke factoren invloed hebben op de coalescentiestabiliteit van deze emulsies, zowel in rust als in stromingsvelden.

In hoofdstuk 1 is enige literatuur over kristallisatie in emulsies besproken. Ook is enige aandacht besteed aan de stabiliteit van emulsies en de invloed van stromingsvelden daarop. Over het effect van kristallen alsmede van stroming is weinig literatuur beschikbaar.

De gebruikte materialen zijn beschreven in hoofdstuk 2 en de gevolgde methoden in hoofdstuk 3. De meeste experimenten zijn verricht met modelemulsies van paraffine-olie in water met vaste paraffine of tristearaat als kristallen. Daarnaast zijn ook enige experimenten met room verricht. Het coalescentieproces in de emulsies werd gevolgd met behulp van spectroturbidimetrie en Coulter Counter.

De kristallisatie van vaste paraffine en tristearaat in paraffine-olie, zowel in bulk als in emulsiedruppels, is beschreven in hoofdstuk 4. Een pulse-NMR methode (kernspinresonantie) werd ontwikkeld, waarmee het vast-vetgehalte gemeten kon worden, onafhankelijk van eigenschappen van kristallen (modificatie, mengkristallen e.d.). Ook voor emulsies bleek deze methode toepasbaar, mits de gebruikte grensvlakactieve stof geen verstoring veroorzaakte.

In hoofdstuk 5 is beschreven welke factoren de plaats van kristallen in emulsiedruppels beïnvloeden. De voornaamste parameter is daarbij de randhoek, die afhangt van het soort kristal en de grensvlakactieve stof. Uit randhoekmetingen bleek dat de invloed van grensvlakactieve stoffen groter was dan theoretisch voorspeld. In de evenwichtssituatie bevinden vetkristallen zich altijd in het grensvlak van olie en water. Toch was dat niet altijd de plaats waar ze zich bevonden, bijvoorbeeld omdat de kristallen vastgehouden werden in een kristalnetwerk of omdat een (onbekende) barrière verhinderde dat ze in het grensvlak kwamen.

De coalescentiestabiliteit van emulsies die in rust verkeerden, is behandeld in hoofdstuk 6. Met bijna alle in dit onderzoek gebruikte grensvlakactieve stoffen werden zeer stabiele emulsies verkregen, wanneer geen kristallen aanwezig waren. Dezelfde emulsies konden echter zeer instabiel worden wanneer kristallen aanwezig waren in de druppeltjes. De coalescentiesnelheid werd dan b.v. 10^6 maal zo groot. Daarbij werd steeds het kristallisatietype waargenomen waarbij (zeer waarschijnlijk) enige kristallen in het grensvlak van het druppeltje aanwezig zijn. De hypothese werd opgesteld dat coalescentie veroorzaakt wordt door kristallen die gedeeltelijk uit het bolletje steken en bij

nadering van een tweede bolletje het dunne waterfilmpje tussen de bolletjes 'doorprikken'. De invloed van factoren zoals druppelgrootte, soort kristal en de grensvlakactieve stof, kon met deze hypothese verklaard worden, evenals het feit dat oproming de instabiliteit sterk bevorderde. Wanneer oproming vermeden werd, bleken de meeste emulsies vrij stabiel. De genoemde hypothese werd verder bevestigd door filmexperimenten, waarbij met draadraampjes dunne waterige vliesjes getrokken werden in olie in aanwezigheid van kristallen.

In hoofdstuk 7 is de invloed van stroming (Couette-stroming, turbulentie, stroming met Taylor-wervels) op de stabiliteit van emulsies beschreven. Emulsies zonder kristallen die in rust stabiel waren, bleken ook in een stromingsveld stabiel. Een in rust instabiele emulsie zonder kristallen bleek in Couette stroming niet veel instabieler te worden. Betrokken op het aantal ontmoetingen per tijdseenheid, betekende dit, dat de 'efficiëntie' (de fractie van het aantal ontmoetingen dat tot coalescentie leidt) in Couette-stroming sterk afnam ten opzichte van de situatie in rust.

Stroming bleek een sterk destabiliserende werking te hebben op emulsies met kristallen in de oliefase, wanneer het kristallisatietype werd bereikt, waarbij (waarschijnlijk) kristallen uit het druppeltje steken. De 'efficiëntie' nam toe met een factor 10^3 tot 10^5. Ter verklaring van het effect van Couette-stroming werd gebruik gemaakt van een theorie die de banen van bolletjes in eenvoudige afschuiving beschrijft met inachtneming van hydrodynamische en colloïdale wisselwerking. Het destabiliserende effect van Couette stroming ten opzichte van Brown beweging kon verklaard worden doordat de bolletjes:
- dichter tegen elkaar worden aangedrukt
- over elkaar heen schuiven tijdens een ontmoeting
- langer bij elkaar blijven in een tijdelijk doublet.
De invloed van factoren, zoals vetgehalte, druppelgrootte, hoeveelheid kristallen en ionensterkte paste in de hypothese dat kristallen die uit bolletjes steken, coalescentie veroorzaken. Ook het gegeven, dat emulsiedruppeltjes met kristallen kunnen coalesceren met emulsiedruppeltjes zonder kristallen paste in de hypothese. Uit de coalescentiekinetiek werd afgeleid, dat slechts weinig bolletjes voldoende ver uitstekende kristallen bevatten.

Het gedrag van room in Couette stroming kwam in grote lijnen overeen met dat van modelemulsies, hoewel ook enige afwijkingen optraden.

Emulsies met kristallen in de oliefase bleken erg gevoelig voor turbulente stroming: de coalescentiesnelheid nam sterk toe, waarschijnlijk omdat de druppeltjes elkaar veel dichter konden naderen.

Ook in stroming met Taylor-wervels bleken emulsies met kristallen in de oliefase vrij instabiel, maar de coalescentiesnelheid verschilde niet veel van die in Couette-stroming. Mogelijk trad enige disruptie op van door coalescentie gevormde kluitjes in de rekstroming tussen Taylor-wervels. Room bleek evenwel in stroming met Taylor-wervels instabieler dan in Couette-stroming. Mogelijk werd dit veroorzaakt door het kristallisatietype, dat anders was dan in modelemulsies.

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90

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