Contribution of the α-gel phase to the stability of whippable emulsions

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STELLINGEN

1. De α-tending emulgator glycerollactopalmitaat (GLP) kan beneden de kristallisatietemperatuur een stabiele α-gelfase vormen in de aanwezigheid van water.
   Dit proefschrift.

2. De vergelijking, die Sebba tracht te maken tussen de fysische analogie van de structuur van een waterig schuim en die van levende cellen, is bijzonder hachelijk.
   F. Sebba, Foams and Biliquid Foams-Aphrons. Ed : Wiley and Sons, (1987).

3. Agglomeratie van vetbolletjes in toppings, die een relatief hoog gehalte aan GLP op vetbasis bevatten, hangt nauw samen met de vorming van een α-gelfase op het o/w-grensvlak van de deeltjes.
   Dit proefschrift.

4. Een emulgatormengsel dat beneden de kristallisatietemperatuur van de koolwaterstofketens een α-gelfase kan vormen met water kan dit onafhankelijk doen van het feit of dit mengsel boven de kristallisatietemperatuur mesomorfe fasen vormt met water.
   Dit proefschrift.

5. Hoewel men in de levensmiddelenindustrie graag zou beschikken over vetongevoelige eiwitschuimen, lijkt dit vanuit fundamenteel oogpunt, althans voorlopig, geen haalbare zaak.
   N.a.v. De 23e themadag georganiseerd door de NRLO : luchtige levensmiddelen, hun bereiding en eigenschappen, (1987).

6. De veronderstelling dat amorfe lactose bij bevochtiging met water beneden 93.5°C practisch alleen in α-lactose monohydraat overgaat is aan bedenkingen onderhevig.
   Zie bv. P. Morrissey, In : Developments in Dairy Chemistry-3. , Ed : P.F. Fox, Elsevier Applied Science Publishers, (1985).

7. Het aantreffen van troebelingen in bier kan ondermeer worden veroorzaakt door schuimvorming in de fles.

8. Op grond van resultaten bereikt met pulse NMR aan toppingpoeders mogen Barfod en Krog niet concluderen dat geadsorbeerde eiwitten de kristallisatie van het vet/emulgatormengsel in de gedispergeerde deeltjes onderdrukken.
   N.M. Barfod en N. Krog, J. Am. Oil. Chem. Soc. , 64, 112-119, (1987).

9 Eén en dezelfde emulgator kan zowel schuim stabiliserend als destabiliserend werken.

10. Om de eigenschappen van levensmiddelen, die bestaan uit complexen van biopolymeren, beter te kunnen begrijpen, verdient het de aanbeveling een integratie te bewerkstelligen tussen levensmiddelenfysica en -chemie.

11. Het succes van technologische vernieuwing staat of valt met de betrokkenheid van de werknemers.

12. Golf maakt een goede kans om uit te groeien tot een nationale sport, indien er geen haast gemaakt wordt met het oplossen van onze afvalproblematiek.

13. Uitgerekend op rekencentra lijkt men in de toekomst te zijn uitgerekend.

Stellingen behorende bij het proefschrift " Contribution of the α-gel phase to the stability of whippable emulsions " door J.M.M. Westerbeek, 24 februari 1989 te Wageningen.

J. M. M. Westerbeek

Contribution of the α-gel phase to the stability of whippable emulsions

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. H. C. van der Plas,
in het openbaar te verdedigen
op vrijdag 24 februari 1989
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ABSTRACT

Westerbeek, J.M.M. (1989). Contribution of the α-gel phase to the stability of whippable emulsions. Ph.D. thesis, Wageningen Agricultural University (209 pp, English and Dutch summaries).

Key words : α-tending emulsifiers, structure formation, whippable emulsions, α-gel phase.

The mechanism which explains extensive particle aggregation in topping emulsions, that contain a relatively large amount of the α-tending emulsifier glycerol lacto palmitate (GLP), was studied.

From x-ray and neutron diffraction and from differential scanning calorimetry it appeared that GLP forms an α-gel phase with water below the crystallization temperature of the emulsifier. From this phase study it was concluded that the process of particle aggregation in these emulsions is a result of the formation of this α-gel phase at the o/w-interface of the dispersed particles.

The results of both bulk and surface rheological experiments, performed with these emulsions, are discussed in relation to the physical properties of these systems. The results are interpreted by assuming that the physical properties of these whippable emulsions are determined by the formation of this α-gel phase at the interface of the fat particles.

VOORWOORD

Een proefschrift is nooit het resultaat van het werk van één persoon en zeker niet in dit geval. Ik realiseer mij bij de voltooiing van dit werkstuk dat ik aan velen dank verschuldigd ben.

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CONTENTS

1 INTRODUCTION.

1.1 GENERAL INTRODUCTION

Nowadays, emulsions are produced by the food industry, the cosmetic and pharmaceutical industry for the consumer market and by chemical industries for technical applications. Emulsions consist of two immiscible fluids in which one liquid is dispersed in the other. The fact that either the water phase or the oil phase is the continuous phase determines whether these systems are called oil-in-water emulsions or water-in-oil emulsions or briefly o/w-emulsions and w/o-emulsions.

Emulsions may contain an oil fraction which crystallizes partly or completely below a certain temperature. Consequently the question rises, whether such systems may still be referred to as emulsions. However, since these dispersions originate from real emulsions, we shall also call these systems o/w-emulsions or w/o-emulsions. In fact, oil means the non-polar phase of the system which can be in the liquid or in the solid state.

Usually emulsions need to have specific rheological properties which depend on their applications. Sometimes consumers want emulsions to have solid or semi-solid properties, like cosmetic creams or, in the case of foodstuffs, e.g. whipped cream or butter. Other products should behave like a liquid as in the case of for example body milk. The rheological properties of solid-like emulsions are closely related to the presence or absence of some kind of network structure in the product. Network formation may take place in the continuous phase on a molecular level, like in cosmetic or pharmaceutical creams (for example Barry, 1975). In food systems often some kind of aggregation mechanism of the dispersed particles occurs, as is the case with dairy whipping cream or with products, like ice-cream and whipped topping.

Whipped cream or whipped topping should always have solid-like properties, because the aerated product has to be stable against flow for a long period of time. Solid behaviour of a product may be obtained either by means of a yield stress or by means of a relatively high viscosity. An example of a semi-solid foodstuff which does not have a measurable yield stress but which has a very high matrix viscosity is, according to Luyten (1988) Gouda cheese. In the case of whipped products a yield stress, caused by the presence of a particle network is usually the way to prevent the product from flowing. Another way to obtain a yield stress in a whipped product is producing a foam having a high overrun in combination with small air bubbles (Princen, 1985). This is partly the explanation for the firmness of whipped egg white.

Food technologists have tried to imitate a product, like whipped cream, in the form of topping powders for several reasons. First of all they wanted to produce whippable emulsions with a low fat content, probably for economical as well as nutritional reasons. Secondly they strived for reproducible whipping properties. Thirdly they wanted to give such products a longer shelf life. Furthermore, the whipped product should be stable at temperatures below 0°C. Finally which is of minor importance, by the production of powders costs of transport could be lowered. In order to fulfil these requirements food technologists were obliged to add specific emulsifiers and stabilizers to the formulations of these topping emulsions.

Krog (1977) and Andreasen (1981) studied the physical properties of these newly-developed whippable products, but it can be stated that the origin of these properties is still poorly understood. This thesis will deal with the formation of network structures consisting of aggregated fat particles in topping emulsions. Since these dispersions always are o/w-emulsions, we will disregard w/o-emulsions. Especially the role of structure inducing emulsifiers is subject of this study. Therefore we will now go into further detail on the concept of the stability of an emulsion and the function of the added surfactants.

1.2 THE FUNCTION OF EMULSIFIERS IN WHIPPED EMULSIONS.

When speaking of emulsions distinction should be made between microemulsions and macroemulsions. Macroemulsions are always unstable systems from a thermodynamical point of view, whereas microemulsions are stable systems that are being formed spontaneously. Macroemulsions can only be obtained by the input of energy. During homogenization free energy is accumulated in the interfaces that are formed. Since every system strives for the lowest possible free energy, break-down of an o/w-emulsion through coalescence is energetically the most favourable condition. However, this destabilization process does not necessarily have to occur. It depends on the type and concentration of certain stabilizing agents present, whether an emulsion may have a life time, varying from a few seconds to several years. The emulsions that are dealt with in this thesis are macroemulsions.

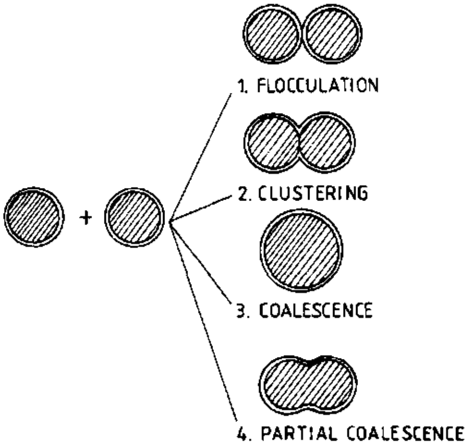

Figure 1.1 : Schematic representation of the major destabilization mechanisms for the dispersed phase of an emulsion.

In principle, emulsions are unstable, but this instability may manifest itself in different ways. Therefore it is important to define the term instability in a proper way. When the expression instability of an emulsion is used in this thesis, it is meant that the dispersed particles undergo a kind of aggregation process. The major possible destabilization processes of an emulsion have been visualized in figure 1.1 according to Mulder and Walstra (1974) :

- The droplets may flocculate. In this case the particles aggregate, but they keep their own identity. Usually this type of aggregates can be redispersed without great effort.
- The droplets may form clusters, meaning that the particles also keep their individual identity, but they share the same interfacial layer. It is more difficult to redisperse these aggregates.
- The droplets may undergo coalescence. This process leads to the formation of an emulsion with larger droplets and this process may eventually lead to complete phase separation.
- The droplets may form clumps as a result of partial coalescence. This process can only occur in emulsions which contain crystals in the dispersed phase. When these crystals are able to pierce the thin liquid film between two globules, coalescence is likely to occur. The presence or absence of a crystal network in the globules will determine, whether clumps will be formed or the droplets will coalesce. This mechanism has been studied by van Boekel (1980).

It is common knowledge that the stability of an emulsion against aggregation of the dispersed particles is determined by the presence of emulsifiers. These molecules have amphiphilic properties, meaning that they contain both hydrophilic and hydrophobic parts. An important distinction should be made between emulsifiers, according to the fact, whether they contain ionic groups or not. If these molecules contain an acid or basic group, they are called anionics or kationics, whereas neutral emulsifiers are called nonionics.

Emulsifiers have several important functions in emulsions.

They are able to lower the interfacial tension by means of adsorption. Ionic emulsifiers may stabilize an emulsion against aggregation by means of electrostatic repulsion and in the case of polymers steric repulsion may give an important additional effect. Nonionics can only stabilize an emulsion against particle aggregation by means of steric repulsion. Furthermore, the presence of adsorbed emulsifiers may enhance emulsion stability against coalescence by the occurrence of a surface tension gradient, when two dispersed particles closely meet each other.

In whipped toppings both proteins and nonionics of low-molecular weight are used as stabilizing agents. It is believed that these molecules play an important role in the formation process of a stable topping emulsion. However, nonionics have another, more important function. These additives have a large promoting influence on particle aggregation according to e.g. Krog (1977) or Andreasen (1981). Lipophilic, so-called α-tending emulsifiers, like propylene glycol monostearate (PGMS), acetylated monoglycerides (ACTM) or lactylated monoglycerides (GLP) are especially effective in promoting aggregation of fat globules. The α-tending emulsifiers are non-polymorphic and they can only exist in the α-crystalline form below their melting point (e.g. : Schuster, 1985 ; Andreasen, 1981 and Krog, 1975).

It is not understood what mechanism is responsible for this aggregation process. Krog (1977) suggested that proteins, which are usually present in whipped toppings, are loosely bound by hydrogen bonds to the polar head groups of the α-tending emulsifiers adsorbed at the o/w-interface. This protein film is therefore easily swept off during the whipping process, resulting in increased agglomeration of the fat globules. However, in our opinion this explanation is not very satisfactory, since toppings that contain comparable amounts of saturated monoglycerides are not sensitive to structure formation according to Andreasen (1981).

Some authors suggested that the α-tending properties of these emulsifiers may be closely related to foam stability. It is believed that these emulsifiers are able to form a rigid α-crystalline film at the interface of the fat globules (Wootton, 1967 and Andreasen, 1981). However, the fact that these molecules are able to form such interfacial films does not necessarily imply that these molecules should have structure promoting properties.

Recently, Buchheim and Krog (1985) suggested that clumping may well be the mechanism, which causes the occurrence of fat particle aggregation in topping emulsions. It is true indeed that crystallization phenomena play an important role in the formation of a particle network in whippable toppings. Like in whipped cream, the network probably consists of partly crystallized oil droplets. However, since toppings, which contain relatively large amounts of an α-tending emulsifier, do not churn during whipping, it seems likely that another mechanism is responsible for these kind of systems. Thus for a better understanding of the physical behaviour of these toppings it seems to be important to elucidate the micro structure of these whippable systems.

1.3 OUTLINE OF THIS THESIS

Since the occurrence of structure formation in a whippable emulsion is of great importance for its practical application, more knowledge on the mechanism that may explain fat particle aggregation induced by α-tending emulsifiers is necessary. In this thesis the physical behaviour of glycerol lacto palmitate (GLP), as an example of an α-tending emulsifier, is the central theme of study. Our aim has been to propose a satisfying mechanism for the structure formation in whippable emulsions containing an α-tending emulsifier.

The structure formation itself has been investigated with microscopical methods. Since phase behaviour of emulsifiers is often an important parameter in the stability of emulsions and since this effect is always linked with crystallization phenomena of both the oil phase and the emulsifier itself, diffraction techniques and differential scanning calorimetry have been used to elucidate the microstructure of the fat particle network. Furthermore it has been tried to relate the physical properties of this network structure to the bulk and surface rheological behaviour of these structured systems.

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2 MATERIALS AND METHODS

2.1 CHARACTERIZATION OF MATERIALS.

2.1.1 Glycerol lacto palmitate (GLP)

Glycerol lacto palmitate (GLP) was purchased from Grindsted, Denmark. The sample is a complex mixture of mono-, di- and triglycerides. Glycerol molecules are esterified both with palmitic acid and lactic acid. According to the supplier the product contains about 15% lactic acid. Its crystallization and melting properties are represented in chapter 5.

2.1.2 Acetylated monoglycerides (ACTM)

Acetylated monoglycerides were also obtained from Grindsted products, Denmark. This sample consists of a complex mixture of mono- di- and triglycerides of palmitic acid and acetic acid. Its melting properties are represented in chapter 5.

2.1.3 Sodium caseinate (Nacas)

Sodium caseinate was obtained from DMV Campina, Veghel, The Netherlands. This sample is a spray-dried milk protein powder containing 94.5% protein (N x 6.38) on moisture free basis, 5.2% moisture, 4.1% ash and 0.8% fat. The pH of a 10% solution at 20°C is 6.7.

2.1.4 Hardened coconut oil (HCNO)

The sample was purchased from Vandemoortele, Oudenbosch, The Netherlands. The average relative fatty acid composition of coconut fat is : C_8 = 8% , C_{10} = 6% , C_{12} = 47% , C_{14} = 18% ,

C_{16} = 9% and C_{18} = 12%. The melting point of the fat is about 32°C. The crystallization curve is shown in chapter 5.

2.1.5 Soybean oil (SBO)

Soybean oil (Reddy^{r}) was purchased from Vandemoortele, Oudenbosch, The Netherlands. According to the supplier it is a product of 100% vegetable origin, containing about 54-64% multiple, unsaturated fatty acids.

2.1.6 Medium chain length triglycerides (MCTO)

MCT-oil was purchased from Cargill bv, The Netherlands. The crystallization temperature is lower than -20°C. With GLC the fatty acid composition was determined to be : C_8 = 57.9% , C_{10} = 41.6% and C_{12} = 0.5%.

2.1.7 Hardened Palm Kernel oil (HPO)

HPO was purchased from Friwessa, Wormerveer, The Netherlands. With DSC it was found that the fat melts between 55°C and 70°C. The fatty acid composition was determined with GLC, giving the following results : C_{12} = 0.3% , C_{14} = 1.1% , C_{16} = 41.0% , $C_{18:0}$ = 49.7% , $C_{18:1}$ = 7.0% , $C_{18:2}$ = 0.3% and C_{20} = 0.6%.

2.1.8 Tripalmitin (GTP)

GTP was purchased from Fluka. The sample had a GLC purity of 95%. The crystallization curve is shown in chapter 5.

2.1.9 Glucose syrup

Glucose syrup was obtained from Cerestar, The Netherlands. It is a combined acid/enzymatic hydrolysed corn starch of which the mean DE = 35%.

2.1.10 Demineralized water

Unless mentioned otherwise, all experiments have been performed with demineralized water.

2.2 METHODS

2.2.1 Sample preparation

2.2.1.1 Preparation of emulsions and gels

O/w-emulsions (usually 1000 grams) were prepared as follows. In the case of emulsifier dispersions the desired amount of emulsifier was added in the melted state to an aqueous solution of sodium caseinate at 70°C under stirring conditions. In the case of emulsions the emulsifier/fat mixture was melted and was added to the hot protein solution. Some samples were prepared in 2.0 mMol phosphate buffers instead of using sodium caseinate. When high concentrations of caseinate were applied, say more than 3% (w/w), the dry protein powder was dispersed directly in the melted emulsifier sample. This protein/emulsifier mixture was added to the water phase in the homogenization vessel.

The sample was pre-emulsified by stirring with a vibrating perforated plate during 7 minutes and subsequently this mixture was homogenized at a constant pressure of 100 atmosphere at 70°C in a high-pressure homogenizer (Rannie, 100 l/hr). First, the working volume of the apparatus was prewashed with an emulsion having the same composition as the sample to be prepared. To obtain a small size distribution of the emulsion droplets, the emulsion was continuously recycled during homogenization over a period of 20 minutes (Melsen, 1987). Evaporation of water was prevented as good as possible by performing emulsification in an almost completely closed homogenizing apparatus. After preparation of the emulsions, the samples were collected and weighed. The weight of the samples was always larger than 990 grams. Small losses of water, caused by evaporation, could not be prevented completely.

If necessary, the samples were diluted to a desired dispersed phase concentration. Unless mentioned otherwise, the emulsions were subsequently cooled down to room temperature. Dependent on the dispersed phase level the samples would remain in the liquid state or would turn into gels as a result of particle aggregation.

2.2.1.2 Preparation of topping powders.

The emulsions were prepared as described above, though the samples were more concentrated. The emulsions contained 30% dispersed phase (w/w), 5% sodium caseinate, 15% glucose syrup and 50% demineralized water. The emulsions were spray-dried with an A/S NIRO Atomizer, comparable to the procedure described by Barfod and Krog (1987). Then the powders were stored at room temperature for DSC experiments or for diffraction studies. These powders appeared to be very stable against polymorphic transitions of the crystallized α-tending emulsifiers.

2.2.1.3 Preparation of a freeze-dried GLP powder.

Melted GLP was mixed with demineralized water at a temperature of about 60°C with a Sorvall mixing apparatus. During this mixing procedure the sample was gradually cooled down to a temperature below the crystallization point of the emulsifier mixture. Then the obtained GLP gel was freeze-dried and stored at room temperature.

2.2.2 Light Microscopy

Structure formation in dispersions was investigated with a Zeiss Axiomat microscope by using both ordinary light and polarization microscopy. With the latter technique information about the orientation of crystals in globules can be obtained (Walstra, 1967). Normally, a magnification of 1000x was used and at this magnification a drop of paraffin oil was brought between object and objective.

Some experiments have been performed with a Jena Peraval interphako microscope, equipped with a special heating-cooling stage, thermostatted to an accuracy of ± 0.5°C (See section 5.2.2).

2.2.3 Scanning electron microscopy (SEM)

The samples were investigated with the cryo-SEM technique partly developed at TFDL, Wageningen, The Netherlands. Some samples were cryo-protected, with glycerol in the water phase. Formation of ice crystals could be minimized by applying a fast freezing technique ($V_T > 10.000$ K/s). Therefore these samples were not cryo-protected.

A gel sample was brought into a small sample cup (inside diameter = 2 mm) with a sample height of about 4mm. The sample was frozen in nitrogen slush at a vacuum of 10^{-3} Pa. Then the sample was transferred under vacuum condition to the freeze etch chamber of the microtome. The sample was fractured with a cold knife and freeze etched for 5 minutes at a temperature of 173 K in order to sublimate some water from the fractured surface of the sample. Then a gold layer was sputtered upon the surface of the sample and it was transferred to the scanning electron microscope under vacuum condition. SEM observations were performed with a Jeol 35C Scanning Electron Microscope.

2.2.4 X-ray diffraction

X-ray diffraction has been performed both on spray-dried powder samples and gels, containing α-tending emulsifiers. The powder samples were dispersed in demineralized water the day before the x-ray diffraction experiments. The time between preparation of the gel samples and x-ray diffraction varied from a few days up to several weeks. These samples were stored in a refrigerator at a temperature of 4°C. Furthermore, 100 ppm thiomersal were added to the emulsion as a preservative directly after sample preparation. From the experiments performed the GLP gels appeared to be stable over a longer period of time (1-2 months) both from microbial and physical point of view.

Three different x-ray diffraction apparatuses have been used for the measurements of the short and long spacings. Wide angle and small angle x-ray diffraction will frequently be abbreviated as WAXD and SAXD. Most WAXD and SAXD experiments were performed at room temperature with a Kiessig camera (Ni-filtered CuKα-radiation of wavelength λ = 1.5418Å) using photographic detection. The gels were put into small glass capillaries (ϕ_{inside} = 1.0 mm) with a wall thickness of about 0.01 mm. Experimentally, it has been proved that no Bragg reflections could be detected, caused by scattering from this capillary. When this type of detection technique was used, relatively long measuring times (about 24 hours) were necessary in order to obtain strong signals for the long spacings of the samples. When WAXD experiments were performed, the samples were exposed to radiation only during a period of 1 - 4 hours. In the case of WAXD experiments a sample/photo distance of 100 mm was used and in the case of SAXD experiments a distance of 400 mm was chosen. The diffraction angles were measured by hand. The intensities of the photographic detected reflections are expressed according to the following terms : VS = very strong, S = strong, M = medium, W = weak, VW = very weak and EW = extremely weak.

Temperature dependent SAXD measurements were performed with a Kratky camera, manufactured by A. Paar, equipped with a Braun one-dimensional position sensitive detector which was connected to a Braun multi-channel analyzer. The radiation source was a PW-1729 x-ray generator, producing Ni-filtered CuKα-rays, its wavelength being 0.154 nm. Each channel of the multi-channel analyzer corresponded to a certain diffraction angle.

Calibration of the apparatus was carried out with lead stearate. Measurements were usually performed in 30 minutes. Corrections were made for background noise and the curves were subsequently desmeared with a program based on the theory of Lake (1967).

Some WAXD experiments on dry powder samples were performed with a Philips powder diffractometer (PW-1730) equipped with a proportional detector.

2.2.5 Differential Scanning Calorimetry (DSC)

The measurements were performed with a Mettler TA-3000 system. In the DSC-cup the sample amount varied between 10 and 20 mg, depending on the concentration of potentially crystallizing matter present in the sample. Some measurements were performed by cooling a droplet of water in contact with a droplet of an emulsifier/oil sample. The heating and cooling curves in chapter 5 which are shown together in one figure, were not corrected for differences in the amount of sample in the DSC-cup. Therefore the peak areas below the curves may not be interpreted as being representative of the heat values per unit amount of sample.

2.2.6 Capillary viscosimetry

Information on the particle shape was obtained from capillary viscosimetry. For these experiments we made use of ubbelohdes. The applied ubbelohdes, coded 0 or 0A, had capillary diameters of 0.36 mm and 0.53 mm, respectively. Emulsified samples, consisting of hot emulsifier dispersions containing 1% emulsifier (w/w), were diluted to the desired emulsifier concentration. This was performed with a 2 mMol phosphate buffer (pH = 6.9) or with a 0.1% sodium caseinate solution subject to the composition of the continuous phase of the dispersions. Dilution was performed one hour before the actual rheological experiment and the samples were stored in a thermostatted water bath at the desired temperature. Dilution has been performed with solutions having an average temperature of about 50°C.

The viscosity measurements were performed in a temperature controlled waterbath thermostatted to an accuracy of 0.005°C. It was checked both visually and by microscopy whether shear-induced flocculation occurred during the experiment. The ubbelohdes were calibrated with distilled water both at the start and at the end of each experimental series.

2.2.7 **Rheological methods**

2.2.7.1 Adam's consistometer test

The emulsions as described in section 2.2.1 were poured into perspex rings of following dimensions ($H = 4.1$ cm, $\phi = 6.2$ cm) of which the bottoms were sealed with pieces of parafilm. The top sections were also sealed in the same way and the samples were stored in a thermostatted cell overnight.

The next day the samples were placed upon a plate of glass, the parafilm was removed and the cylinders were carefully lifted by hand. This would cause the samples either to flow or to deform slightly, the effect depending on the value of the yield stress of the sample. After 30 seconds the new diameter of the samples was measured and it was used as an indication of the rheological properties of the system.

2.2.7.2 Compression experiments

The gels for the uniaxial compression measurements were prepared in the way described in the section dealing with sample preparation (2.2.1). The hot emulsions were poured into perspex cylinders having the following dimensions : $\phi = 34$ mm and $H = 50$ mm. The gels did not stick to the inner wall of the perspex cylinders. Before filling the cylinders the bottom of each cylinder was sealed with a piece of parafilm. After cooling down to room temperature and cutting off the top layer of the gels with a thin iron wire, the samples were sealed with parafilm. The gels were stored at 20°C during the night.

The compression measurements were performed with a tensile and compression testing apparatus (type : Overload Dynamics, table model S 100), equipped with a 200 N or a 2000 N load cell. The former load cell was always calibrated with a weight of 500 grams, the latter by means of an internal testing method. The apparatus consists of a fixed bottom plate and an up and downward movable bar, containing the load cell. The cylindrical compression plate was fixed to this load cell. For our experiments we always used a compression plate made of perspex, whereas the bottom plate consisted of metal. The compression device was placed in a temperature controllable box. All the experiments were performed at 20°C.

At the time of measurement the gels were carefully pushed out of the cylinders and the rough top sections were cut off with an iron wire (ϕ = 0.5 mm) in order to obtain smooth and parallel sample surfaces. During this procedure, deformation of the gel itself was carefully prevented. The sample height, generally amounting to a value of about 45 mm, was measured with a linear gauge with an accuracy of 0.05 mm. The uniaxial compression measurements were performed at different compression rates, ranging from 0.2 mm/min to 200 mm/min.

Cyclic compression experiments were performed in the following way. A sample was compressed at some constant compression rate up to a certain strain. Then the plunger was moved upwards at the same rate. After four minutes the sample was compressed once more at the same rate to the same sample strain. This means that in the case of permanent deformation the position of the plunger had to be adjusted before each new compression cycle. These cycles were repeated four or five times for each sample.

The force/time curves of the compression tests were recorded and the real stress and strain values were recalculated from these curves with the same formulae that were used by Peleg (1977) and (1984) and Luyten (1988) for their compression experiments. The

Hencky strain ϵ_h (-) was calculated with the following formula :

$$\epsilon_h = \ln \frac{H_t}{H_0} \qquad (\ 2.1\ )$$

where H_t is the sample height after a certain deformation and H_0 is the initial height of the gel sample.

The sample stress σ (N/m^2) was calculated according to equation 2.2 :

$$\sigma = \frac{F}{A_t} \qquad (\ 2.2\ )$$

where A_t is equal to :

$$A_t = \frac{H_0\ A_0}{H_t} \qquad (\ 2.3\ )$$

For the calculation of the relative deformation rate the Hencky strain rate $\dot{\epsilon}_h$ (s^{-1}) was used, since fracture measurements were always performed at large deformations :

$$\dot{\epsilon}_h = \frac{V_{def}}{H_t} \qquad (\ 2.4\ )$$

The Young modulus was calculated from the initial slope of the stress strain curve.

$$E = \left(\frac{d\sigma}{d\epsilon} \right) \ (\epsilon \longrightarrow 0) \qquad (\ 2.5\ )$$

2.2.8 Surface rheology

A special interfacial trough was manufactured for this research project. The apparatus was originally designed at the

Royal Shell Laboratories Amsterdam (KSLA), The Netherlands, but we have altered this design at a number of points. Figure 2.1 shows our interfacial trough filled both with oil and water in this specific case. The apparatus consists of three major parts, namely a system which controls the motion of the barriers, the interfacial trough itself and equipment dealing with data sampling and data treatment. These three parts will now be discussed subsequently.

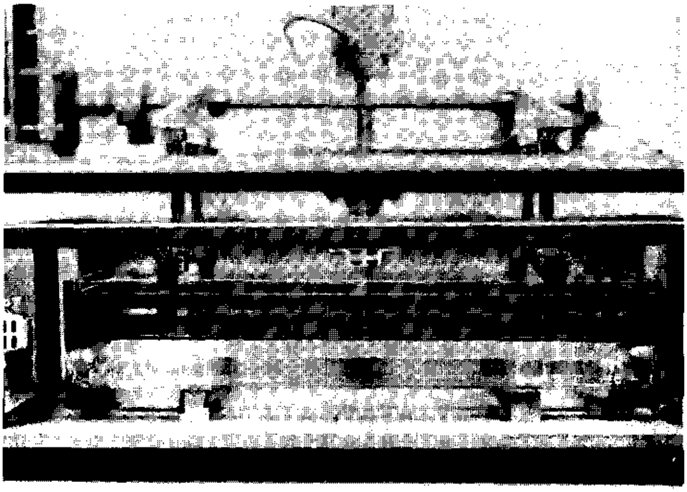

Figure 2.1 : A picture of the interfacial trough used for dynamic surface tension measurements at the a/w- or o/w-interface.

2.2.8.1 Barrier motion

We have chosen for the construction of an apparatus, where two barriers move in opposite direction (see figure 2.1 and 2.2). To this end a threaded spindle (THK, 2 MBF 1402 Go+450 LC3) having opposite pitch for the two barriers, in combination with two corresponding nuts, was purchased from van Gelder Company bv, Rotterdam, The Netherlands (see number 6). This spindle was driven by a DC-motor (Mattke, type : MAM 24 V, 50 W) which was fed by an amplifier also made by Mattke (type : MANR 24V).

The sinusoidal signal was obtained from a signal generator (Farnell, type DSG2-b) providing sine waves over a frequency range from 0.1 mHz to 110 kHz. A gear box was fixed between the motor shaft and the spindle. This construction provided sinusoidal movement of the barriers at very small amplitudes (0.1 mm - 10 mm) in the frequency range from 0.001 to 0.5 Hz. The tolerance-free gearbox was made of two adjustable decelerations of 1 to 5 or 1 to 500. The motion of the motor shaft was controlled both by means of a tacho-generator and a potentiometer.

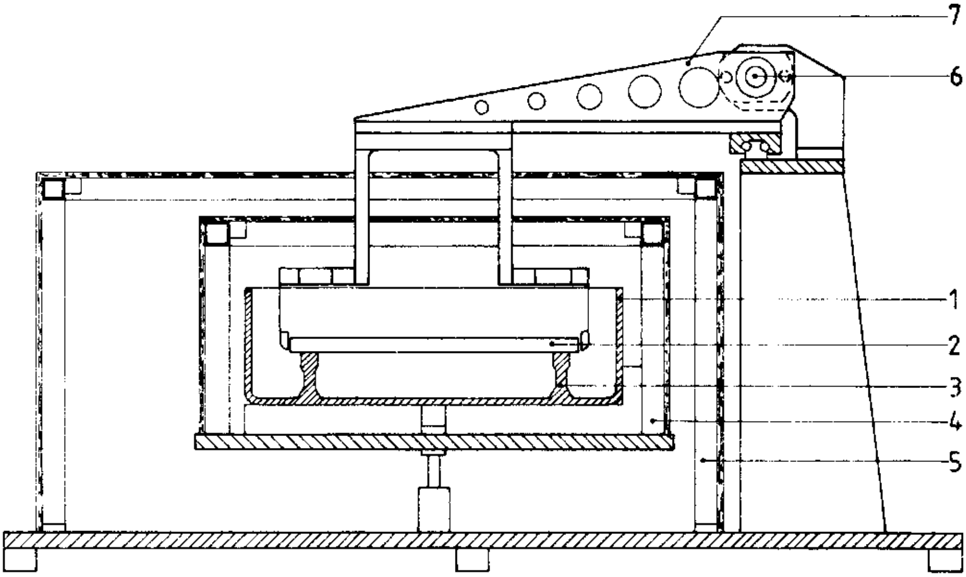

Figure 2.2 : Schematic representation of the interfacial trough which has been designed for this study (side view).

1 : Interfacial glass trough
2 : Glass barrier
3 : Support for glass slide
4 : Inner perspex box
5 : Outer perspex box
6 : Spindle with nuts
7 : Barrier suspension

2.2.8.2 The interfacial trough

The design of Mingins (private communication) for an interfacial trough was our starting point. In figure 2.3 the design for both trough and barriers is shown. Its construction may be described as follows. Two Pyrex glass strips (350 mm x 15 mm x 10 mm) were fused parallel to a trough of glass, the distance between the strips being 150 mm (figure 2.3.a). These strips were roughened co-planar and polished mechanically. The top sides of the two barriers (184 mm x 20 mm x 10 mm) were also roughened and polished (figure 2.3.d). On both sides of the barriers two hemispherical holes ($\phi = 4$ mm) were milled, which were necessary for the suspension of the barriers (figure 2.3.c).

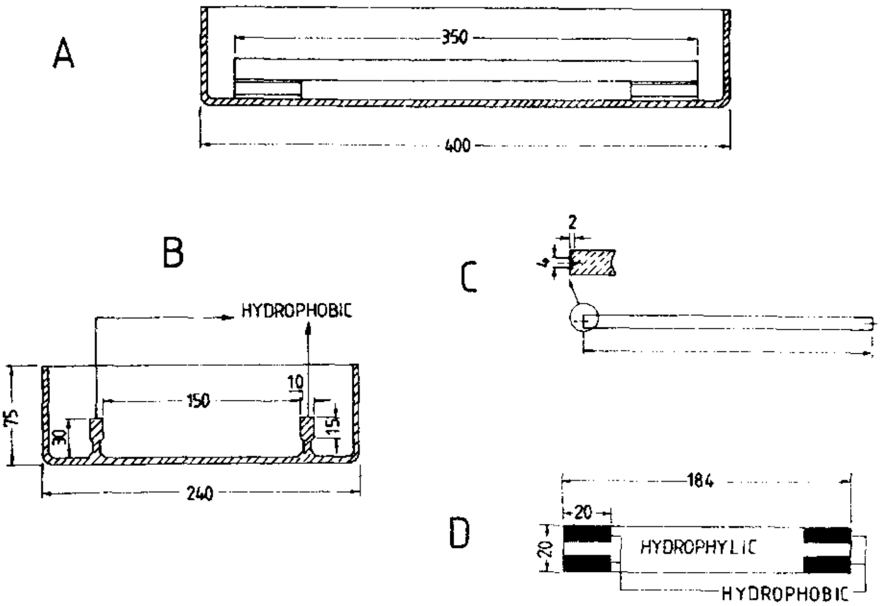

Figure 2.3 : Schematic representation of the interfacial glass trough and the glass strips. The relevant hydrophobic and hydrophilic parts have been indicated.

The wetting properties of the pretreated glass parts were altered according to the following procedure. The trough and barriers were washed with a 2% SDS solution, rinsed with water and distilled water and finally they were cleaned with hexane. Then the trough, with the barriers placed on the bottom of it, was filled with a 10% KOH solution in ethanol. After about 18 hours this alkaline solution was removed and the trough was washed with distilled water. Then, after drying the trough, the roughened parts were treated with a solution of 2% HF with a pencil to obtain hydrophilic glass properties. Subsequently the trough and barriers were cleaned with distilled water and they were dried in an oven at a temperature of 150°C. After 20 hours the top sides of the glass strips and the edges of the barriers were carefully hydrophobized with a solution of 2% dimethyl-dichlorosilane (DCMS) in trichloroethane with a pencil as indicated in figure 2.3.b and 2.3.d. Then the trough was washed with distilled water to remove the released hydrochloric acid. This hydrophobation procedure was repeated twice in order to guarantee complete hydrophobic properties for both glass strips and the top edges of the barriers. Then the glassware was stored in hexane for one night in order to remove excess silicon. At that time the trough and barriers were ready for use.

At the start of an experiment the interfacial trough was placed inside a temperature controlled box consisting of two compartments made of perspex. The trough was housed in the inner compartment of this climate box and its horizontal and vertical position was adjusted with three depth gauge micrometers. The temperature of the liquid in the trough was adjusted by means of circulating air in between the two compartments. The air temperature was regulated with a heat exchanger, placed in a stainless steel tube, connected to the outer wall of this double-walled box. On this tube two small fans were mounted in order to get sufficient air circulation in the system. The complete apparatus was placed upon a marble table in a room free from external disturbing vibrations.

2.2.8.3 Data sampling and data treatment

The displacement of one of the barriers was measured with a glass ruler (Mitutoyo linear Scale, series 529AT-11), equipped with a photo-electric encoder (resolution = 5.0 μm). This linear encoder was connected to a digital counter, supplied with a BCD-interface (Mitutoyo, series 164, type G).

The dynamic surface tension was measured by means of the Wilhelmy plate method. To this end we made use of a roughened glass plate. This plate was suspended from a thin wire, which was shielded from the circulating air in the thermostatted box. This wire was connected to an inductive displacement cell (Bienfait, type Q-11) which was used as the force measuring device. Its analogous signal was fed into a 5 kHz carrier wave amplifier (type : Bienfait). The signals were collected in a IBM PC/XT-286. This signal was digitized with an AD-convertor.

The noise level was reduced by means of electronic filtering at a frequency level exceeding 100 Hz. The time delay, caused by internal filtering in the amplifier ($t_{delay} \approx 0.16$ s), was corrected in the software. Dependent on the dimensions of the Wilhelmy plate (perimeter = 52 mm), the average noise level usually was lower than 0.030 mN/m. However, sometimes low frequency drift effected the measurements in a negative way. In that case the measurement was repeated.

A program was written with Quick basic to obtain direct graphical results of the ellipse. The data for both the displacement of the barrier and the surface tension were fitted with a sine function by means of least square calculations. The variables in this fit procedure were both amplitude and phase angle of the two sine-shaped signals. The amplitudes of the two fitted sine curves were used for the calculation of the dilational modulus and the difference between the two phase angles at t = 0 seconds gave the actual phase angle.

2.2.8.4 Experimental procedures

In the case of measurements with dispersions the trough was carefully filled with a diluted emulsifier dispersion, its preparation being described in section 2.2.1. Usually we prepared an emulsion containing 3% GLP in a continuous phase of either 0.1% sodium caseinate or 2 mMol phosphate buffer. This emulsion was diluted with this continuous phase to a GLP concentration of 0.1% at a temperature of about 50°C.

The temperature of the sample in the trough was measured by bringing a thermometer in the liquid, outside the studied surface area. The experiment was started by expanding the surface area with a factor 3. From this moment the surface tension was recorded in time. When the surface tension had relaxed to an almost constant value, accurate measurements of the dynamic surface tension could be made. At that time the sinusoidal deformation was started. Very often we waited for about 20 hours before the dynamic measurements were performed.

In the case of spreading experiments the trough was filled with the desired water phase. With a micropipet 5 ml of a 5% GLP solution in SBO was spread on the surface as small droplets. Then the surface tension was recorded and dynamic measurements were started at the time, when the surface tension maintained an almost constant value.

Measurements at high temperatures were done as follows. The trough was filled with an 0.1% GLP dispersion in an 0.1% sodium caseinate solution above the crystallization temperature of the α-tending emulsifier. Then the temperature of the air was gradually reduced by lowering the temperature of the heat exchanger. During cooling down, both the surface tension and the dynamic surface tension were followed.

2.2.9 Neutron diffraction

Neutron diffraction experiments were performed at ISIS,

(Rutherford Appleton Laboratory, Didcot, England) in corporation with IRI (Delft, The Netherlands). Our small angle diffraction measurements were conducted with the LOQ spectrometer at ISIS. The spallation neutron source ISIS produces intense neutron bursts 50 times per second by means of collisions of a highly energetic, pulsed proton beam with a Uranium target. The fast neutrons from the target station are slowed down within 25 μs in a hydrogen moderator at a working temperature of 25 K in order to obtain a cold neutron enhanced thermal neutron spectrum. A number of spectrometers are attached to the target station, all with different aims of research, LOQ being one of them. The working of the LOQ spectrometer may be described as follows : A pulse of neutrons travels a distance of $L = 11.4$ m from target to sample and of $l = 4.3$ m from sample to detector. The total travel time t of a neutron from its source to the detector determines its energy or equivalently its wavelength λ (m). The following relations govern the scattering process which is assumed elastic :

$$\lambda = \frac{h}{m \cdot v} = \frac{h \cdot t}{m \cdot (L+l)} \qquad (2.6)$$

$$k_o = \frac{2\pi}{\lambda} \qquad (2.7)$$

where :

h	=	constant of Planck	(J s)
m	=	mass of the neutron	(kg)
v	=	velocity of the neutron	(m/s)
k_o	=	wave number	(m^{-1})

The advantage of such a setup is that no wavelength defining monochromator is needed. A rotating disk chopper at 25 Hz removes alternate pulses from ISIS to avoid frame overlap from adjacent pulses. Neutrons of wavelengths varying from 2 to 10 Å are recorded by a two-dimensional position sensitive neutron detector. The area detector is a multiwire (128x128), $^{10}BF_3$ filled, proportional detector. The position vector r in the plane of the detector determines the momentum transfer Q (m^{-1}) between the neutron and the system under study :

$$Q = k - k_o \qquad (2.8)$$

where k and k_o represent the wave vectors of a scattered and a unscattered neutron respectively. Consequently the momentum transfer Q is equal to :

$$Q = k_o \frac{r}{l} \qquad (2.9)$$

The detector has 64x64 channels, its resolution being 1 cm in both directions, each one of them containing about 80 time of flight channels. They are all handled by an in-house data acquisition system and a Microvax computer. Reduction of the raw LOQ's time of flight data to a composite cross section I(Q) is done by accurate transmission corrections over a wide range of wavelengths.

Dry and hydrated GLP powder samples, containing variable amounts of H_2O/D_2O were brought into circular shaped quartz cuvets. The weight of the samples inside the cells was determined in order to be able to calculate the average cross section of each sample. The cell thickness could be either one or two millimeters, depending on the amount of D_2O and the amount of air present in each gel sample. Each measurement lasted between 1 and 3 hours for each sample depending upon whether $1*10^{+6}$ or $3*10^{+6}$ counts were required for acceptable data statistics.

2.2.10 **Whipping behaviour.**

Usually 250 grams of a dispersion were put into the bowl of an Hobart mixer. The sample was whipped at maximum whipping speed (at motor level 3). After whipping, the overrun and the foam firmness were determined as follows. A foam sample was brought into a small cup of known volume (in our case 221 ml). The weight of the sample was determined and the overrun was calculated with the following formula :

$$\% \text{ Overrun} = \left(\frac{V}{M} * 100 \right) - 100 \qquad (2.10)$$

where V = the volume of the cup (ml) and M = the foam weight of the sample (g).

The foam stiffness was measured with a penetrometer, type : Humboldt MF-6 Co. USA. The measure device either was a cone-shaped body (angle = 45°) its weight amounting to 24 grams or a stainless steel plate (ϕ = 4 cm) having a weight of 55.6 grams. The penetration depth was measured 10 seconds after the test was started.

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3 PRELIMINARY STUDY ON THE MICROSTRUCTURE OF A TOPPING EMULSION IN RELATION TO ITS PHYSICAL PROPERTIES.

3.1 INTRODUCTION

As has been indicated in the introduction, in the food industry technologists have tried to produce whippable imitation products for several good reasons. However, scientific literature on the whipping characteristics of these products is scarce. The main reason for this probably is that research work in this area has been done in industrial laboratories and therefore these studies have not been published. Another reason may be that scientists were not very interested in the physical properties of these rather complicated systems. Indeed, it will appear from this chapter that a number of intriguing physical phenomena in these systems occur which can only be explained partly. Yet, understanding of these phenomena may be of great importance in order to be able to manipulate product properties at will.

The physical properties of dairy cream have been thoroughly investigated. Mulder and Walstra (1974) reviewed the whipping properties of cream. Especially the importance of clumping of fat globules in order to obtain the desired solid properties of the product during whipping is emphasized by these authors. Furthermore, a satisfying mechanism for foam formation and bubble stabilization during whipping of cream is proposed.

Since 1970 different formulations for imitation whipping creams, subject to consumer requirements, have been produced, using knowledge of the physical properties of dairy cream. In this respect one may think of topping powders, frozen imitation creams, frozen whipped toppings and UHT-treated products. Imitation cream, artificial cream and whipped topping are in fact different names to describe similar types of products. These systems usually contain the basic ingredients vegetable fats, proteins, and emulsifiers. They are produced either as powders or as dispersions in liquid state.

Of recent years, changes in food presentation and distribution coupled with the improvements in technology have also widened the application areas of whipping cream. This has induced the production of dairy cream, containing stabilizing additives like emulsifiers and gums (see e.g. Flack, 1985). Furthermore the formulation and manufacture of a spray-dried dairy cream has been published by Kieseker et al (1979). Obviously these products have been developed on the basis of the knowledge obtained from the production of whipped toppings.

It is not possible to investigate all the physical properties of these toppings and newly developed creams. It is clear, however, that these products have one property in common. Foam firmness and stability requires the presence of a network structure in the product. In whipped toppings often structure promoting emulsifiers are used for this aim. The mechanism of this structure formation is not understood.

Andreasen (1973) has briefly studied structure formation in whipped topping. The emulsions that he used for his experiments mainly contained vegetable fat, milk proteins and emulsifiers. He investigated the relation between structure formation and the type of emulsifier, used in the formulation. These emulsifiers, studied, may be divided into two major groups. The first group consists of three so-called α-tending emulsifiers, being acetic esters of monoglycerides (ACTM), lactic acid esters of monoglycerides (GLP) and propylene glycol monopalmitate (PGMP). The second group consists of polyglycerol esters of fatty acid (PGE) and glycerol monostearate (GMS), both showing mesomorphic behaviour with water. Mesomorphism of amphiphiles will be discussed in chapter 4. In the work of Andreasen the relation between structure formation and the presence of α-tending emulsifiers in a topping emulsion, containing a relatively low amount of dispersed phase, is clearly demonstrated. The mechanism of this type of structure formation is not understood.

α-tending emulsifiers are not only applied in whipped toppings. For instance, Wootton et al. (1967) have demonstrated the marked effect of α-tending emulsifiers on the incorporation of air in cake batter systems. According to Wootton these emulsifiers are only active below their melting point. In batters their function is not related to structure formation, but these additives seem to improve bubble stability, though it is not explained what is meant by this improved stability. This is the second important physical property of α-tending emulsifiers. Again this stabilizing mechanism is not well understood. According to Wootton, it seems obvious that the α-crystal modification of the emulsifier is linked with foam stability.

Nielsen (1976) discussed the function of emulsifiers in ice-cream. He clearly demonstrated the positive influence of the presence of small amounts of monoglycerides in ice-cream on the occurrence of particle aggregation and churning effects. There is no literature available on the use of α-tending emulsifiers in ice-cream. It seems contradictory that monoglycerides do promote fat globule aggregation and clumping in ice-cream, while this aggregation effect does not occur in toppings, according to Andreasen (1981). The reason for this contradiction may be explained as follows. It is generally accepted that mechanical clumping is of great importance in ice-cream. This process is probably facilitated, when only relatively small amounts of monoglycerides are present in the o/w-interface of the particles.

From this short overview it clearly appears that the role of α-tending emulsifiers in whippable emulsions and foams is not understood well, despite their wide application. We decided to start a preliminary study on the structural properties of an emulsion, containing an α-tending emulsifier and to relate these properties to the whipping behaviour of this emulsion. We used glycerol lacto palmitate (GLP) as example of such an α-tending emulsifier in our experiments. The reason for this choice was that in literature GLP proved to be a very good example of α-tending behaviour in relation to excellent whipping properties.

Furthermore, it is probably one of the most applied emulsifiers in this food area. As a starting point for this preliminary study we decided to investigate the physical properties of a topping, similar to the type Andreasen (1973) studied.

If the whipping properties of a topping are investigated, one should first start pointing out all the requirements an ideal whippable product should meet. Knowing all these requirements a proper study of the properties of the topping emulsion can be made. An ideal whipped topping should have the following properties :

a) The product must behave like a liquid during whipping and like a solid after whipping. This means that a certain kind of reversible structure should be present in the product, since during whipping physical bonds must be broken and after whipping these bonds should recover within several minutes.
b) Under normal whipping conditions the product should have a sufficient overrun and a small bubble size distribution.
c) Drainage of liquid from the foam after whipping is not allowed.
d) Coalescence and disproportionation of bubbles may not occur in the whipped product. Disproportionation is a destabilization process of a foam, caused by gas diffusion of smaller bubbles towards the larger ones. The driving force behind this process is the aim of a system to reach the lowest state of surface free energy. The process eventually leads to the loss of the smaller bubbles (see e.g. Ronteltap, 1989 and Prins, 1987).

In this chapter the results of these preliminary experiments will be represented and the whipping properties of the emulsion, under study, will be compared with the requirements mentioned above. At the end of this chapter a speculative hypothesis for the microstructure of the fat particle network will be formulated from these results.

3.2 RESULTS AND DISCUSSION.

3.2.1 The structure properties of a whippable emulsion containing glycerol lacto palmitate.

To enable us to evaluate our results obtained for GLP containing toppings, the emulsions that have been investigated by Andreasen (1974) are discussed first. The composition of these topping emulsions is shown in table 3.1. The emulsions were prepared as follows. The ingredients were mixed at 80°C. Subsequently this mixture was homogenized at 80°C at a valve pressure of 20 MPa. After preparation the emulsions were cooled down to 5°C and they were stored at this temperature for 16 hours. Then evaluation of their structure properties was done by using microscopy, rheology and whipping tests.

Table 3.1 : The composition of the topping samples used by Andreasen (1973) in his experiments.

COMPOSITION OF IMITATION CREAM OF ANDREASEN	
25% fat phase (15-35%)	0-16% emulsifier 100-84% fat (hardened palm kernel oil)
75% water phase (85-65%)	2.0% sodium caseinate 10.0% sucrose 0.1% sodium alginate 87.9% water

From ordinary microscopy it appeared that in the case of the stored emulsions containing α-tending emulsifiers, aggregation of the fat globules had occurred. The intensity of this process was largely determined by the amount of emulsifier, added. This aggregation process increased the viscosity of the stored product markedly. However, it was doubtful whether the exact results of these rheological experiments at high shear rates are very reliable because of the possible occurrence of slip.

The results of these rheological experiments are represented in figure 3.1. Considering the whipping properties of these structured emulsions, it appeared that a dosage of about 4-16% of an α-tending emulsifier on fat basis was necessary to obtain a foam with a certain extent of firmness. This amount was subject to the type of α-tending emulsifier, used in the recipe. An explanation for the reason, why a relatively large amount of an α-tending emulsifier is necessary in these products, was not proposed by Andreasen.

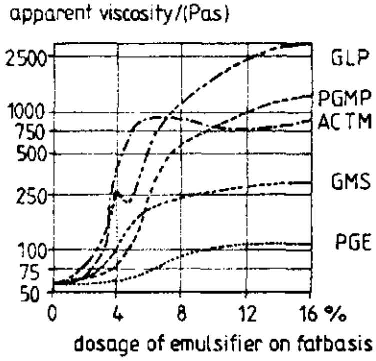

Figure 3.1 : The influence of the emulsifier dosage on the apparent viscosity of the topping emulsions studied by Andreasen. The viscosity was measured with a Haake, Rotovisco at a shear rate of 147 (s^{-1}) at 5°C.

All samples showed a decrease in overrun with an increasing dosage of emulsifier, though at larger emulsifier concentrations toppings containing non-structure inducing emulsifiers showed an increase in overrun. This decrease may be caused by two different reasons. The first reason may be the film destabilizing effect of spreading particles as described by Prins (1987). The presence of emulsifiers, like monoglycerides, strongly increases the potency of particles for film rupture. The second reason probably is the increase in viscosity of the emulsion due to structure formation.

Another important property of topping emulsions which has never been discussed before in literature, is the fact that the particles in topping emulsions are very small compared to the particles present in whipping cream. In the case of whipping cream it has been known for a long time that homogenization considerably impairs whipping properties, particularly in the case of low-fat cream. Probably the tendency for clumping of the dispersed particles is too low according to Mulder and Walstra (1974). In homogenized cream this problem may be solved by the production of a cream, containing suitable sized homogenization clusters (15-20 μm) according to Graf and Müller (1965).

Suppose that partial coalescence is the mechanism that explains structure formation in toppings containing an α-tending emulsifier. Then the contradiction between whipping cream and toppings, containing small particles, can only be understood if partial coalescence occurs much easier in the latter systems. Another explanation would of course be that the aggregation process is caused by a different binding mechanism of the fat particles.

The influence of the physical state of the fat phase on the whipping properties of emulsions, containing different concentrations of ACTM, has also been investigated by Andreasen (1973). It clearly appeared from these experiments that crystallization of the fat phase was necessary to obtain products with a desired degree of firmness. However, it was also demonstrated that fat particle aggregation appeared in all systems, including those which contained 94% liquid oil and 6% ACTM in the crystalline state. Thus, crystallization of the fat phase does not seem to be a prerequisite for the occurrence of particle aggregation. If partial coalescence would be the mechanism that would explain the aggregation of the liquid particles, the crystallized emulsifier itself should cause this process. At least it can be stated that crystallization of the emulsifier is of importance for the occurrence of structure formation. The products containing liquid oil showed a poor overrun, probably caused by spreading of both ACTM and liquid oil (see e.g. Prins, 1987).

The differences in whipping behaviour between the toppings with the three α-tending emulsifiers studied by Andreasen, have not been explained by him. In chapter 5 of this thesis some speculations will be made in order to explain these differences.

Our preliminary experiments were done with emulsions that had a lower dispersed phase concentration than the topping emulsions of Andreasen. We lowered this concentration in order to be able to observe greater differences in structure properties between the emulsions. These results are rather qualitative, but at this stage we were only interested in tracing large effects. Nevertheless, these experiments were quite important, because from the results we obtained the basic knowledge, necessary for further study of these systems. In this preliminary study the following properties of GLP containing emulsions have been investigated :

1) aggregation of fat particles both by visual observations on a macroscopic scale and by means of microscopy.
2) The Adam's consistometer for a rather qualitative judgement on the occurrence of structure formation (see section 2.2.7.1).
3) The whipping properties of these systems, including the determination of a value for the overrun and foam stiffness respectively, according to the methods described in section 2.2.10.

In these preliminary experiments on topping emulsions we briefly studied three important variables, that might have a large influence on the physical properties of the whippable emulsion. These variables were GLP concentration, protein concentration and particle size.

3.2.1.1 The influence of GLP concentration.

The samples were prepared as described in section 2.2.1. The composition of the samples is represented in table 3.2. The GLP concentration was varied between 0% and 40% GLP on fat basis. It appeared that gelation of these systems at 4°C only occurred at relatively high GLP concentration on fat basis ([GLP] ≥ 30%). This seems contradictory to the results of Andreasen, since he already observed large effects at a GLP concentration of about 4% on fat basis. Obviously, this must have been caused by the relatively low dispersed phase concentration that we used in our experiments (see chapter 6). When our emulsions were stored at 20°C for a period of 16 hours after having been kept at 4°C during 2 hours, extensive structure formation also occurred in emulsions containing about 15% GLP on fat basis.

Table 3.2 : The composition of the studied GLP containing topping emulsion.

COMPOSITION OF IMITATION CREAM STUDIED IN THIS THESIS	
8% dispersed phase	70-100 % HCNO 0- 30 % GLP
92% water phase	86.7 % demineralized water 4.0 % corn syrup 1.2 % sodium caseinate 0.1 % sodium alginate

From microscopic investigations on these emulsions we learnt that in all emulsions aggregation of the particles occurs, even if the emulsions are just stored at room temperature. Since the GLP free emulsion also showed particle aggregation, this obviously means that GLP is not involved in this process. When the emulsions are diluted with water, these aggregates redisperse immediately.

Since the viscosity of the emulsion does not seem to have increased after preparation, the interaction between the particles probably is of a rather weak nature. No rheological measurements have been performed in order to characterize this type of aggregation. An explanation for this type of particle aggregation in GLP free emulsions may be that a molecular exclusion effect occurs by the presence of both caseinate and alginate molecules. This causes flocculation of the dispersed particles. A comparable effect has been observed by several investigators in skim milk

(e.g. compare Hansen, 1982 and Grindrod and Nickerson, 1968).

Real structure formation only occurred in emulsions that contained a relatively high GLP level on total fat basis. The particle aggregates, formed in these gelatinized emulsions could no longer be redispersed by dilution with water. Furthermore, the aggregates were much larger and always visible with the naked eye. If such a structured emulsion was heated, coalescence of the aggregated particles occurred at the temperature, where the gel properties were lost. This was checked by means of light microscopy.

The coalescence sensitivity of aggregated particles containing fat crystals as a result of an increase in temperature towards the melting point of the fat is characteristic of partial coalescence (see e.g. van Boekel, 1980 and Melsen, 1987). The two different aggregation types are represented in figure 3.2.

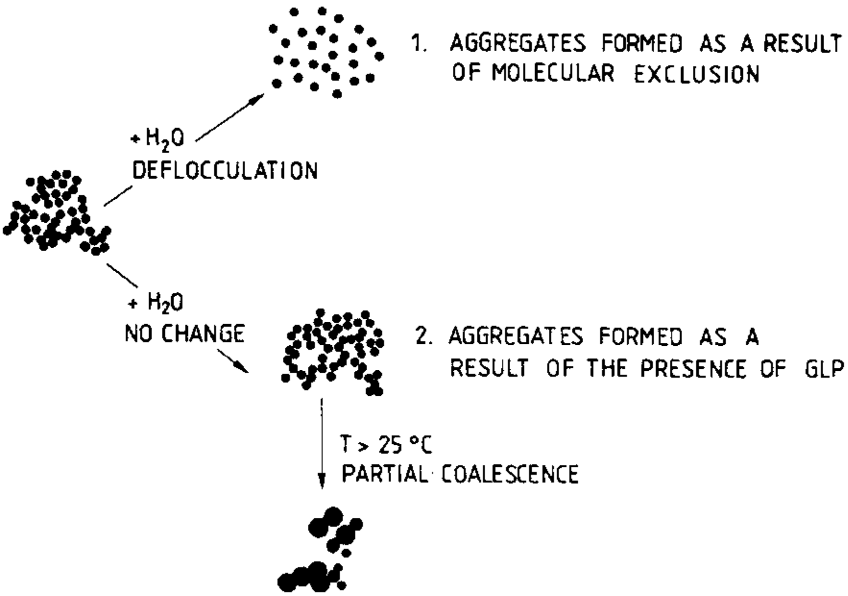

Figure 3.2 : Different types of particle aggregation, occurring in the emulsions investigated.

In table 3.3 the results are shown of the Adam's consistometer test on the systems containing different amounts of GLP. From the results of this experiment it may be concluded that about 13% GLP is necessary in order to obtain a large amount of structure formation in these systems. The firmness of the structure gradually increased at larger GLP concentrations. From the results of a study on the whipping properties of these emulsions, several important conclusions may be drawn.

Table 3.3 : The structure properties of topping emulsions as a function of the GLP concentration, determined with the Adam's consistometer (section 2.2.7.1). The concentration is represented as a percentage on fat basis.

GLP concentration % w/w on total fat basis	Adam's consistometer value
0.0 %	>> 14 (creamed system)
5.0 %	>> 14 (creamed system)
10.0 %	>> 14 (creamed system)
13.0 %	>> 14 (partly creamed system)
15.0 %	>> 14 (not creamed)
17.0 %	10
20.0 %	10
25.0 %	9
33.0 %	6.5

- The overrun constantly reached a higher level at an increasing GLP concentration. GLP free emulsions could not be whipped at all (see figure 3.3). Furthermore, the average bubble size of the whipped product decreased at higher GLP levels. At larger GLP concentrations the bubbles had diameters, ranging between 20 μm and 300 μm. Thus the bubbles were hardly visible with the naked eye.
- Microscopic study revealed that coalescence occurred during whipping of the GLP free emulsion. At increasing GLP levels the effect of particle coalescence constantly decreased. At a level exceeding about 15% on fat basis, the aggregated particles seemed to remain stable during the whipping process. However, if the temperature would rise above 25°C, coales-

cence also occurred in these systems.

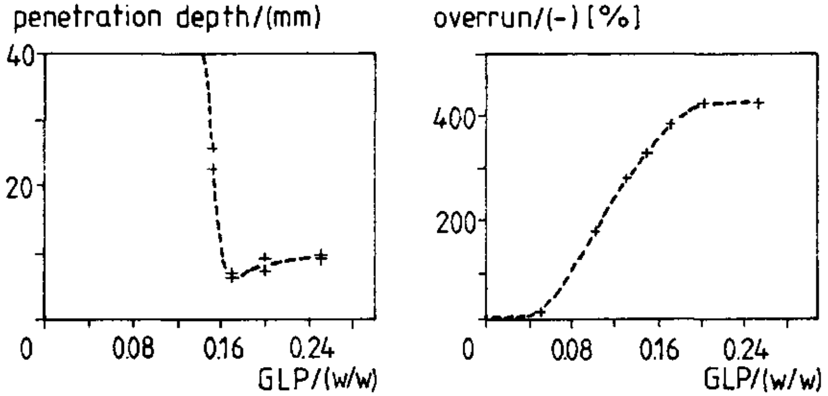

Figure 3.3 : Whipping properties of the topping emulsion at different GLP concentrations on fat basis at 20°C.

- * All the whipped emulsions showed serum separation within a few hours. However, if the gels were stiffer, the bubbles usually became smaller during whipping and the amount of drained liquid decreased too. Serum separation occurs, when the liquid can not be incorporated mechanically in the gel network. The amount of serum, separated after a certain period, is closely related to the irregular nature of the structure, present in the whipped emulsion. This structure consists of large particle aggregates, which are only partly bound to each other.
- * About 15% GLP on fat basis is necessary to obtain increased foam stiffness as can be observed in figure 3.3. This is in good agreement with the experimental results obtained from the Adam's consistometer test on these topping emulsions (see table 3.3).

From these rather rough experiments it may be concluded that GLP indeed plays a very important role in the formation of a network structure in these whippable emulsions. The structure elements of the network are the fat particles.

The effect of the temperature rise from 4°C to 20°C which caused the occurrence of structure formation in the emulsions containing more than about 13% GLP on fat basis has not been discussed in this paragraph. However it seems obvious that crystallization phenomena play an important role in the mechanism of structure formation. The influence of the crystallization of both the fat phase and the emulsifier on structure formation and structure firmness will be treated in chapter 5 and 6.

3.2.1.2 The function of sodium caseinate in whipped topping.

Because it is unknown what the influence of sodium caseinate is on structure formation and whipping properties of topping emulsions, we decided to study this parameter briefly. We used the same emulsion as described in paragraph 3.2.1.1. The GLP concentration in this experiment was 20% on fat basis, whereas the other components had the same concentration as described in the previous paragraph.

Table 3.4 : The influence of sodium caseinate on the structure and whipping properties of the topping emulsion described in paragraph 3.2.1.1. The GLP concentration was 20% on fat basis.

METHOD	SODIUM CASEINATE CONCENTRATION		
	0.4 %	0.8 %	1.2 %
Adam's consistometer test	>> 14 cm	> 14 cm	10 cm
Overrun	428 %	356 %	365 %
Penetration depth	> 40 mm	18 mm	7 mm

In table 3.4 the results of this experiment are shown. It was not possible to prepare a caseinate free topping emulsion, because of the large instability of this specific system. This indicates that sodium caseinate indeed has an important function as emulsion stabilizer at high temperatures. The pH of the emulsion, containing 1.2% sodium caseinate is about 6.9. Thus the caseinate molecules are negatively charged. Therefore, coalescence stability of the emulsion is probably obtained both by electrostatic and steric repulsion.

The reason for the fact that no strong increase in viscosity occurred in the samples containing 0.4% and 0.8% sodium caseinate probably was the coalescence instability of these emulsions. However, from the whipping experiments it may be concluded that the foam stiffness increases at higher sodium caseinate levels. This indicates that structure formation had also occurred in the topping emulsion containing 0.8% sodium caseinate. Furthermore, the overrun decreased at higher protein levels, which may also be related to an increase in viscosity of the whippable emulsion.

It may be concluded from this experiment that the sodium caseinate must have an important function as emulsion stabilizer. However, it is not clear what the function of sodium caseinate is in the mechanism of structure formation. Krog (1977) suggested that proteins have to desorb from the o/w-interface of the fat particles prior to aggregation and that the presence of small molecular surfactants at the o/w-interface may promote this desorption process. When desorption takes place the particles will loose their stability against flocculation or coalescence. If partial coalescence is the mechanism that explains the aggregation instability of the particles, desorption of the protein will certainly facilitate this process, but it is not necessary. For, if crystals are large enough to pierce the thin liquid film between two particles, approaching each other, clumping may also occur. In the paragraph 3.2.2 the desorption of caseinate from the interface of particles will be discussed in detail.

A second important function of the caseinate may be that the protein is involved in foam stabilization during and after the whipping process of α-tending emulsifier containing emulsions.

However, no experimental evidence for this hypothesis can be found in literature. It may be clear that caseinate molecules alone are not able to stabilize the air bubbles of a whipped emulsion. A foam obtained from a whipped sodium caseinate solution is very unstable, since such a foam is destroyed by the process of bubble disproportionation within a few minutes (see chapter 7).

It is known that solid particles are able to stabilize air bubbles by means of Pickering stabilization (see e.g. Darling and Birkett, 1987 or Menon and Wasan, 1988). Bubble stabilization will be obtained, when these solid particles have the proper orientation at the a/w-surface and when they form a network at the interface. Perhaps the same mechanism is applicable to α-tending emulsifier containing toppings. Furthermore, if the particle network itself is in mechanical contact with the a/w-interface, a positive influence on bubble stabilization is expected. Finally, the α-tending emulsifiers themselves may have important bubble stabilizing properties (e.g. Wootton, 1967) by the formation of a crystalline emulsifier film, the nature of which is unknown.

The stability of air bubbles in whipped toppings will be treated further in chapter 7 of this thesis. However, from this short consideration it may be concluded that the exact function of the protein in the investigated topping emulsion is largely unknown.

3.2.1.3 The influence of the homogenization pressure.

Since there are good reasons to believe that the network in topping emulsions consists of aggregated fat particles, it is interesting to study the influence of the particle size on the firmness of the structure in both emulsions and whipped products. An ideal particle network of monodisperse spheres has a network modulus which is independent of the particle size (e.g. van Vliet, 1976 and Papenhuyzen, 1970). If the network structure in our topping emulsions would also be of this ideal nature, we would find the same independence of particle size and network strength.

Unfortunately we have not been able to determine the average particle size in topping emulsions. Spectroturbidimetry as developed by Walstra (1965 or 1968) could not be applied, since the experimental curves obtained for emulsions that contained only 3% GLP on fat basis could not be matched with the theoretical curves (Birtantie, 1985). We can not explain this discrepancy. Furthermore, the Coulter Counter can only be applied to emulsions with relatively large particle diameter. We have only made use of light microscopy in order to get an indication of the particle size. However, very small particles (d < 0.5 μm) can not be observed with this technique.

Table 3.5 : The influence of the homogenization pressure on the structure and whipping properties of the investigated topping emulsion.

Valve pressure (MPa)	10.0	5.0	2.5	1.0
Adam's consistometer test	10 cm	7 cm	13 cm	> 14 cm
Overrun	363%	403%	395%	418%
Penetration depth	7 mm	4 mm	27 mm	> 40 mm

In table 3.5 the results of this experiment are represented. The emulsions which had a formulation as described in paragraph 3.2.1.1. with a GLP concentration of 20% on fat basis were prepared at four different homogenization pressures. It is obvious that the homogenization pressure strongly influences both structure and whipping properties of the topping emulsion. A topping emulsion containing smaller particles showed better structure properties than the system with larger particles. This also influences the firmness of the whipped product in a positive way. Only the emulsion prepared at the highest homogenization pressure showed a decrease in these good properties. Presumably this effect is caused to a large extent by the very irregular nature of the particle network. Microscopy seemed to reveal that emulsions containing larger particles formed larger and more compact aggregates. If this is true, less structure elements would be present for structure formation in the emulsion.

Furthermore, it should not be excluded that smaller particles are more deformed, caused by crystallization of the fat phase (see section 6.4). This may strongly effect the size of the contact area of the aggregated particles and thereby the strength of the bonds between aggregated particles. It will be clear that the influence of the particle size on the rheological properties of structured emulsions is rather complicated. This aspect is briefly discussed in chapter 6.

3.2.2 Structure formation in fat free GLP dispersions.

In paragraph 3.2.1 it has been shown that GLP plays an important role as a structure promoting agent in whippable emulsions. Furthermore it appeared that a rather large quantity of this component on fat basis is necessary in order to obtain the desired structure formation in the emulsion.

With equation 3.1 it can be roughly estimated at what GLP weight fraction the saturation adsorption of a monomolecular layer of GLP molecules at the o/w-interface of the droplets will be exceeded.

$$E_{glp} = \frac{[GLP]}{[GLP]_{sat}} = \frac{X_w \cdot d_{vs} \cdot \rho_{fat}}{6 \cdot \Gamma_\infty \cdot M_w \cdot 1000} \qquad 3.1$$

In this equation E_{glp} is the ratio of the GLP concentration and the GLP concentration at saturation adsorption, X_w is the weight fraction of GLP on total fat basis, d_{vs} is the volume/surface average diameter of the fat particle, ρ_{fat} is the density of the fat phase, Γ_∞ is the saturation adsorption in mol/m^2 and M_W is the molecular weight of the emulsifier.

The first assumption we will make is that all the GLP molecules are equally surface active. The second assumption is that GLP is insoluble both in the oil and water phase at room temperature. These two suppositions are only partly correct, since GLP consists of a mixture of mono- di- and triglycerides. Furthermore, Γ_∞ is not known, but at a first approximation its value will be estimated to be $10*10^{-6}$ mol/m^2 which is a normal value for a low-molecular weight emulsifier. The molecular weight of GLP can of course not be given. As an estimation for this value the molecular weight of mono-lactylated glycerol monopalmitate with M_w = 402 has been used.

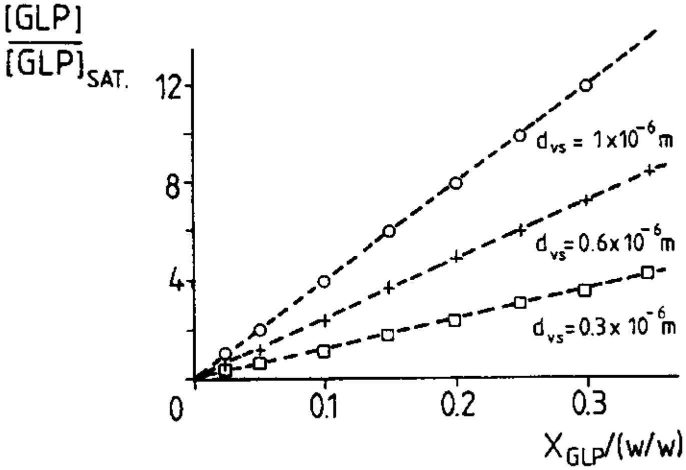

Figure 3.4 : The ratio of the GLP concentration and its saturation adsorption concentration as a function of the weight fraction of GLP on total fat basis at variable diameters.

In figure 3.4 the calculated excess ratio E_{GLP} is shown as a function of the GLP weight fraction on fat basis. From this figure it may be concluded that at a weight fraction of about 20% the adsorption saturation concentration indeed is exceeded with a factor varying between 2 and 8, dependent on the droplet size. A comparable conclusion has been drawn by Darling and Birkett (1987) for the maximum number of monolayers of acetylated monoglycerides present at the o/w-interface of toppings under practical conditions.

In the previous paragraph it has been shown that at a homogenization pressure of 5 MPa instead of 10 MPa structure formation was more pronounced. Thus at an increase in particle size the excess ratio E_{glp} may have increased which sustains the idea that a relatively high GLP/fat ratio may have a positive influence on structure formation in a whippable emulsion.

Obviously, there must be an important reason, why this relatively high emulsifier concentration exerts such an important influence on the structure properties of the whippable emulsion. A possible explanation may be that the formation of multilayered structures at the o/w-interface of the particles is of importance. Several investigators have pointed to the importance of the presence of mesomorphic phases at the o/w-interface of emulsion droplets as a stabilizing factor for these systems (e.g. Friberg, 1971 and Krog, 1977). On the other hand, it has already been stated in the general introduction that, according to Krog (1977) and Andreasen (1973), GLP can not form such mesomorphic phases with water.

However, from the results of our preliminary experiments we got the strong feeling that some kind of gel structure, of which the nature was unknown, is formed at the o/w-interface of the particles. GLP or a fraction of the GLP molecules would be involved in the formation of this structure. With this gel structure the particles are stuck to each other.

If this hypothesis is right, it should be possible to prepare gels containing only GLP and water. However, since GLP is insoluble in water, we decided to test this hypothesis with mixtures consisting of GLP, sodium caseinate and water. The sodium caseinate was added as emulsifying agent for the GLP droplets. It appeared that, when melted GLP was thoroughly mixed with a 2% sodium caseinate solution at 70°C, gelation occurred at a GLP concentration of about 10% after cooling the dispersion to room temperature. Microscopy showed that a network of aggregated particles was formed during this gelation process. Since GLP is insoluble in water, this structure presumably has to be a network of GLP particles. Heating this GLP gel to a temperature above 45°C leads to irreversible loss of this gel. By means of microscopy it was found that coalescence of the particles had occurred. Therefore, this gel seemed to behave in the same way as the GLP containing emulsions described in the previous paragraph.

Having gathered this important knowledge we decided to investigate these structure forming properties of GLP further on gels containing smaller particles. We prepared emulsions with a GLP concentration of 3% and both the sodium caseinate and the sodium chloride concentration were varied. The influence of the NaCl concentration was studied, because we also wanted to get an indication of the fact, whether electrostatic repulsion plays an important role in this particle aggregation and gelation process.

Table 3.6 : The influence of the sodium caseinate and sodium chloride concentration on structure formation in 3% GLP emulsions.

[NaCl] mMol	SODIUM CASEINATE CONCENTRATION 0.02% pH=5.6	0.2% pH=6.1	2.0% pH=6.7
0.0	flocculation	flocculation	flocculation
0.5	gelation	flocculation	flocculation
1.0	gelation	gelation	flocculation
5.0	gelation	gelation	flocculation
10.0	gelation	gelation	gelation
25.0	precipitation	gelation	gelation
50.0	precipitation	gelation	gelation

The systems were prepared as described in 2.2.1. Different amounts of dry sodium chloride were added to the hot emulsions after homogenization. In table 3.6 the results of these experiments have been represented. The following conclusions can be drawn from these results :

1) Structure formation may occur at all caseinate concentra-

tions, but the extent of this process largely depends on the sodium chloride concentration.

2) The emulsion with a concentration of 0.02% caseinate formed a precipitate instead of a gel at NaCl concentrations higher than about 10 mMol. This is caused by the fact that the GLP particles are susceptible to droplet coalescence at high temperatures at this rather low caseinate concentration. The reason for this will be explained below.

If the saturation adsorption concentration of sodium caseinate at the o/w-interface is 2 mg/m^2, it can be calculated that at a $d_{vs} = 0.5*10^{-6}$ m and at a volume fraction of 0.03 the concentration for saturation adsorption would have to be about 0.07%. Thus, for saturation adsorption the concentration of sodium caseinate can be too low in the 0.02% caseinate containing emulsions.

In order to be able to understand the function of sodium caseinate as a stabilizing agent of the GLP particles in these systems in a better way, we briefly studied depletion of the protein in the gelatinized systems. We determined that in the case of the system containing 0.2% sodium caseinate the amount of protein adsorbed at the o/w-interface was about 0.15 mg/m^2, if the d_{vs} would be $0.5*10^{-6}$ m. Since a sodium caseinate concentration of 0.2% is high enough to cover the total particle interface with a surface concentration of 5.7 mg/m^2 it can be concluded that the amount of protein adsorbed at the particle interface is very low. Although the total interface of the particles in aggregated state is smaller than the total interface of the non-aggregated globular particles, we think that this effect does not explain this large discrepancy. Furthermore the particles are certainly not spherical as will be shown in chapter 6.

The difference in gelation behaviour between emulsions with a varying sodium caseinate concentration is probably by large caused by pH differences. The pH of the emulsion containing about 0.02% sodium caseinate amounted to 5.6, whereas the pH of the dispersion with a sodium caseinate concentration of 2.0% had a pH of 6.7.

Both caseinate molecules and free fatty acids, originating from GLP, may give electrostatic repulsion of particles. This effect strongly depends on pH and salt concentration.

If free fatty acids play an important role in the stabilization of GLP particles at high temperatures, it should be possible to produce stable GLP dispersions, free of caseinate, at a relatively high pH. This hypothesis may be true, since GLP contains about 0.3% free fatty acids. Furthermore GLP is quite susceptible to hydrolysis at high temperatures, according to Schuster (1985), so during homogenization free fatty acids are likely to be formed.

Table 3.7 : The influence of the concentration of a sodium phosphate buffer on structure formation in 3% GLP emulsions at different sodium chloride concentrations.

[NaCl] mMol	PHOSPHATE BUFFER CONCENTRATION (mMol) 0.25	2.5	25.0
0.0	flocculation	gelation	precipitation
2.5	gelation	gelation	precipitation
5.0	gelation	gelation	precipitation
10.0	gelation	gelation	precipitation
15.0	gelation	gelation	precipitation
25.0	precipitation	gelation	precipitation

Therefore, it was tried to prepare stable GLP emulsions in phosphate buffers of different concentration at pH=7.0 containing different amounts of sodium chloride. In table 3.7 the results of these experiments are represented. It appeared that it was indeed possible to prepare fairly stable dispersions of 3% GLP. Most systems quickly formed a gel after cooling down to room temperature on the condition that coalescence did not occur significantly. The high coalescence rate at a phosphate concentration of 25 mMol was probably caused by the relatively high salt concentration. For the same reason this effect may also be observed at low phosphate buffer and high sodium chloride concentrations. However, it is sure that the buffer capacity is also smaller at a phosphate concentration of 0.25 mMol, since the pH of the 3% GLP emulsions had a value of 6.2 instead of 6.9 at the higher phosphate concentration.

Finally, it may be concluded from these experiments on fat free topping emulsions that GLP itself has the capability to form particle gels. It seems that the presence of a fat phase is not a requirement for the formation of a particle network, since GLP itself may be regarded as a supplier of particles. If this hypothesis is correct, we have defined a model system which may be suitable for an easier further study of the micro structure of the whippable emulsion.

The foaming behaviour of these gels has not been discussed yet. However, the foam properties should also be comparable with those of the vegetable fat containing whippable emulsions. These properties will be discussed in the next paragraph.

3.2.3 The reversible whipping properties of fat free GLP gels.

One of the disadvantageous properties of dairy cream is the fact that during prolonged whipping the fat phase eventually churns. Whipped topping, containing a relatively large amount of glycerol lacto palmitate does not have this undesired property. If such a topping emulsion is whipped, the overrun becomes constant after a few minutes and the foam firmness will only slightly change, when whipping is continued. The model system defined in the last paragraph should behave in a similar way.

Therefore 5% GLP gels in the absence or presence of 2% sodium caseinate were prepared and the whipping properties were studied. The GLP concentration was raised beyond the level of the systems described in the previous paragraph in order to increase foam firmness. It was not necessary to add NaCl to these systems, because gelation occurred spontaneously at this GLP concentration. Both overrun and penetration depth were determined as a function of time. The results of these penetration tests can not be compared with those of the systems described in paragraph 3.2, since the penetration was determined with a cone shaped load instead of a disc shaped one (see also 2.2.10).

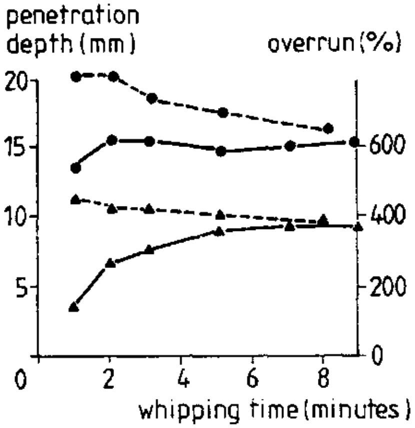

Figure 3.5 : The whipping properties of 5% GLP gels in 2.5 mMol phosphate buffer or in 2% sodium caseinate.
● ● ● : Penetration depth , ▲ ▲ ▲ : Overrun
– – – : Nacas , ——— : Phosphate buffer.

The results of the whipping experiments are represented in figure 3.5. It appeared that these 5% GLP gels had excellent whipping properties. The presence of sodium caseinate certainly influenced the overrun and firmness of the foam. However, it also became clear that GLP alone may be a good foaming agent, which was certainly surprising. In fact, from this experiment it was understood that all basic physical properties of the investigated whippable emulsion may be obtained with a dispersion which only contains the α-tending emulsifier GLP and water. During whipping of the GLP gels no churning effects were observed and it also appeared that the particles did not coalesce. Furthermore both overrun and foam firmness showed a constant value after prolonged whipping. This can only be explained by assuming that the structure of aggregated GLP particles has reversible properties. During whipping the bonds between the particle aggregates are broken. These broken bonds should be restored, at least to some extent, directly after whipping, since the product should have a sufficient yield stress.

This reversible character was investigated further. It was tried to deflocculate a diluted dispersion of aggregated GLP particles by the addition of a 1% solution of the anionic emulsifier sodium dodecyl sulfate. It turned out that this was indeed possible. Mechanical agitation appeared to be useful for this purpose, but it was not necessary to obtain deflocculation. After addition of a sufficient amount of sodium chloride the system flocculated again. The same effects of permanent deflocculation and salt induced flocculation were found in the case of whippable emulsions that contained more than 15% GLP on fat basis.

If partial coalescence would be the cause of particle aggregation occurring in the GLP containing dispersions, this deflocculation effect would be difficult to explain. It seems obvious from this experiment that another particle binding mechanism must be relevant to the system under consideration. Flocculation of particles is caused by attractive van der Waals forces. The DLVO theory learns that flocculation may occur in a secondary or a primary minimum, subject to the level of the repulsive forces that particles exert on each other. In our case the particles are probably covered by a low level of adsorbed caseinate molecules and molecules originating from the emulsifier mixture like e.g. fatty acids, monoglycerides and diglycerides. Thus the particles do not possess a large energy barrier against aggregation in the primary minimum. If this is true, it can also partly be understood that the structure of aggregated particles has a reversible whipping character. If the physical bonds between the aggregated particles can be broken easily during whipping, these bonds will be reformed by the occurrence of a fast flocculation reaction.

Furthermore, the deflocculation effect may be explained as follows. Sodium dodecyl sulfate may adsorb and spread over the interface of aggregated particles, causing electrostatic repulsion between those aggregated particles. If the level of repulsion will be high enough, the particles will separate. By the addition of salt the repulsion will be diminished and the particles will flocculate again.

The DLVO theory may also be applied to the structure of aggregated particles that contain a multilayered gel structure in the o/w-interface of the fat particles, as described in the previous paragraph. However, this flocculation model is not complete, since it does not explain why the aggregated GLP particles or fat particles do not coalesce or sinter. If the particles are totally crystallized, coalescence can not occur. Sintering of the crystals, however, seems to be possible. Andreasen did show that particles which only contained a small fraction of crystallized fat together with a sufficient amount of an α-tending emulsifier would also form rather stable aggregates. Under conditions, where no other repulsive force exists, one would expect these aggregated particles to coalesce. Thus, for the stabilization of the aggregated particles another repulsive force, of which the nature is still unexplained, is necessary. In chapter 5 the nature of this repulsion force will be discussed further.

3.3 WORKING HYPOTHESIS FOR THE REVERSIBLE STRUCTURE FORMATION IN GLP CONTAINING EMULSIONS.

Despite the incompleteness of the model presented in the previous paragraph we wanted to formulate a working hypothesis on the reversible structure formation of aggregated fat particles in GLP containing emulsions. The work described in this thesis will be based on this hypothesis.

1) Above a GLP concentration of about 10% on fat basis aggregated particles are flocculated at ambient temperature. Partial coalescence is of no real importance in the process of structure formation in these whippable emulsions.
2) The flocculation of the fat particles is caused by the

formation of some kind of gel phase of GLP molecules at the o/w-interface of the particles.

3) Crystallization of GLP or of components of GLP plays an important role in the formation of the gel structure present at the o/w-interface of the particles.

4) Sodium caseinate may have an important influence as a stabilizer of the particles in a whippable emulsion at high temperatures. If so, it should desorb from the o/w-interface prior to flocculation. Probably the whipping properties of these emulsions are primarily determined by the presence of GLP.

3.4 SUMMARY.

In this chapter preliminary experiments with the aim to elucidate the microstructure of GLP containing whippable emulsions were discussed. It clearly appeared that the presence of a rather large amount of this emulsifier is closely related to structure formation and gelation phenomena in these kind of systems. Strong evidence has been obtained for the hypothesis that this structure consists of flocculated particles. Partial coalescence or clumping is probably of minor importance.

Furthermore in this chapter it has been shown that a model system only containing GLP and water showed the same physical behaviour as the investigated topping emulsion. This model system will be used throughout this thesis. However, mostly sodium caseinate will be added to this system as a stabilizing agent of the samples at high temperatures.

It is speculated that GLP may be involved in particle aggregation by the way of the formation of a gel structure at the o/w-interface of the particles. With this structure the particles probably stick together. The nature of this specific gel structure is still unknown and will be subject to further study.

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4 A STUDY ON THE GEL STRUCTURE OF GLP CONTAINING EMULSIONS BY MEANS OF X-RAY AND NEUTRON DIFFRACTION.

4.1 INTRODUCTION

In the previous chapter it has been postulated that GLP forms some kind of gel phase at the o/w-interface of fat particles in a whippable topping. However, the nature of this gel phase is not known. In this chapter the possible existence of such a gel phase will be studied.

It is obvious that crystallization phenomena of the GLP emulsifier mixture should play an important role in the formation of such a gel structure. Andreasen (1981) and Krog (1977) indicated that GLP or different α-tending emulsifiers are able to form a rigid α-crystalline film at a soybean o/w-interface. However, the molecular structure of such an interfacial crystalline phase has never been investigated properly.

Boyd et al. (1974) claimed that GLP does not show strong interfacial visco-elastic behaviour at room temperature in contrast to emulsifiers that are able to form mesomorphic phases. From the results of both interfacial rheological experiments and x-ray diffraction they concluded that GLP is not able to form multilayered structures at the o/w-interface. This seems rather contradictory to the observations of Andreasen and Krog, mentioned above. No explanation for this discrepancy is given.

In graph 4.1 the crystallization curve for GLP as determined by DSC is shown at a cooling rate of 2°C/min. In this experiment it is demonstrated that at room temperature a large fraction of GLP crystallizes. This may indicate that the GLP particle gels, described in chapter 3, probably also consist of crystallized GLP molecules. As the gel phase, the existence of which we want to prove, presumably is of crystalline nature, we will discuss lipid polymorphism first.

Mono-, di- and triglycerides show a different polymorphic behaviour. Lutton (1972) has briefly reviewed the possibly occurring polymorphic forms for the major lipid structures. The triglycerides show at least three different crystal modifications being α, β' and β. These three polymorphic forms are mentioned in sequence of increasing thermodynamic stability. From x-ray diffraction studies short spacings can be obtained which are indicative of the lateral packing of the hydrocarbon chains. The different polymorphic forms can be characterized by a subcell structure. The subcell dimensions for the lateral packing of hydrocarbon chains in lipids have been extensively reviewed by Abrahamsson et al. (1978). These dimensions will not be discussed here. We will confine ourselves to note that α is characterized by a hexagonal chain packing structure, β' by an orthorombic subcell with perpendicular positioned hydrocarbon chains and β by a triclinic subcell with parallel positioned chains.

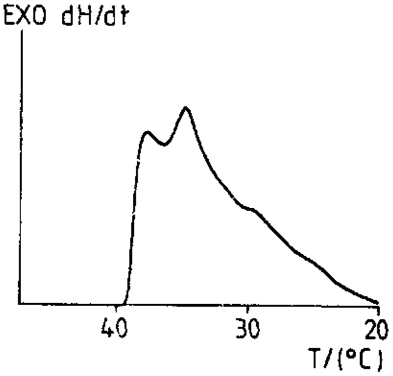


Figure 4.1 : The crystallization curve for GLP determined with DSC at a cooling rate of 2°C/minute.

In the crystal lattice the hydrocarbon chains may be tilted, which indicates a relative displacement of the molecules in the direction of the chain axes. However, in the case of the α-polymorphic form it is known that the hydrocarbon chains are perpendicularly positioned towards the end plane of the methyl groups of the hydrocarbon chains (see also table 4.8).

In table 4.1 the most relevant short spacings of these three polymorphic forms are given for glycerol tristearate as an example of a triglyceride. These values will be used for comparison with our results of x-ray diffraction on both GLP and triglycerides. If the polarity of the lipids increases, like in the case of monoglycerides, new polymorphic forms may be encountered. In this respect the reversible solid-solid α to sub α may be mentioned. Tilting of the crystallized chains occurs more pronounced, since the bulky end groups with two hydroxylic groups require tilting of the chains for reasons of space filling, even in the case of the α form.

Table 4.1 : Literature values for the short spacings of the most important polymorphic forms of lipids containing saturated hydrocarbon chains. For explanation of the symbols see section 2.2.4.

lipid type	α hexagonal	β' orthorombic	β triclinic	Reference
triglycerides				
glycerol tristearate	4.15^{a} vs	4.20^{b} s 3.80 vs	4.60^{a} vs 3.89 s 3.69 s	Lutton (1945^{a}) Simpson (1982^{b})
monoglycerides	sub α α	β'	β	
1-monopalmitin or 1-monostearin	4.14 vs 4.64 w 3.92 m 4.18 vs 3.75 m 3.81 w 3.56 m	4.14 vs 3.87 vw 3.65 w 3.30 w	4.55 4.37 s 3.86 s 3.74 w	Chapman (1962)

In our case the α-polymorphic form must be of great importance, since GLP is an α-tending emulsifier. However, knowledge of the other polymorphic forms will prove to be useful, because GLP is always used in the presence of large amounts of crystallized fat which is likely to produce other polymorphic forms. Furthermore, GLP itself is a mixture of mono-, di- and triglycerides, which are able to form different polymorphic forms as a result of fractionated crystallization.

Since GLP contains a relatively large amount of mono- and diglycerides it may not be excluded that lyotropic phase behaviour of emulsifier molecules plays an important role in the formation of some kind of gel phase at the o/w-interface of the fat particles. Therefore, we will first give a short introduction to this theme.

4.2 THE PHASE BEHAVIOUR OF SURFACTANTS IN THE PRESENCE OF WATER.

In the last twenty years a lot of research has been done on the phase behaviour of emulsifiers in the presence of water. It is well established that many surface active agents show lyotropic mesomorphism, when they are brought into contact with water. Emulsifiers that are dissolved in water above the Krafft temperature may form both micellar solutions or liquid crystalline phases. The Krafft temperature or Krafft point is a specific temperature below which micelles are insoluble. Thus, below this temperature, the monomer solubility is too small for micelle formation.

Tiddy (1980) has written a comprehensive review on lyotropic phase behaviour of water/emulsifier mixtures. There are three well-established classes of liquid crystalline phases, namely the lamellar, hexagonal and cubic phase. All LC-phases have in common that they consist of multilayered emulsifier/water structures and that the hydrocarbon chains of these emulsifiers are in the liquid state. In the lamellar phase the surfactants are arranged in bilayers, separated by waterlayers. The hexagonal phase consists of rod-shaped micelles of indefinite length. The micelles are packed in an hexagonal array. Dependent on the type of hexagonal phase (normal hexagonal or reversed hexagonal), the water molecules or the hydrocarbon chains of the surfactant may form the continuous phase in this mesomorphic structure. The structure of the cubic phase has not been well-established yet. According to Tiddy (1980), at least two types of cubic structures have been found. One proposed structure includes normal micelles packed in some type of cubic array, the other one consists of bicontinuous structures as described by e.g. Scriven (1976).

In many systems a lamellar structure with crystallized hydrocarbon chains is formed below the temperature of the LC-phase. This structure is usually termed as "the gel-phase". The state has been thoroughly analyzed by Vincent and Skoulios (1966) in the case of potassium stearate. The gel phase may exist both in the mono- or bilayer form as has been visualized in figure 4.2. Gel phases always possess a lamellar structure. Gel phases are often metastable. Polymorphic transitions may occur, leading to expulsion of water and subsequent loss of surface active properties.

Since we are primarily interested in the formation of phases with crystallized hydrocarbon chains, these gel phases may be of relevance to our situation. Knowledge of lyotropic mesomorphism of amphiphiles is of great importance for practical purposes. For instance, in the case of biological systems the phase behaviour of phospholipids has been thoroughly studied. Luzatti (1968) and Williams and Chapman (1970) have reviewed the phase behaviour of these phospholipids in the presence of water. With regard to foodstuffs many surfactants that show lyotropic mesomorphism are applied. Krog and Lauridsen (1976) and Krog (1974) have reviewed the phase behaviour of the most important food emulsifiers. In this introduction on phase behaviour of surfactants we will briefly discuss mesomorphism of monoglycerides in the presence of water, since this class of amphiphilic components is most related to α-tending emulsifiers. Lutton (1965) proved that monoglycerides may form all the liquid crystalline phases that have been described above, subject to the temperature, hydrocarbon chain length (C_{12}-C_{22}) and the emulsifier/water ratio.

The most commonly used industrial monoglycerides in foodstuffs are glycerol monopalmitate and glycerol monostearate. Therefore, as an example of mesomorphism in monoglycerides, we will discuss the phase diagram of 1-monopalmitin/water systems as determined by Krog and Larsson (1968). If a sample of this emulsifier is heated in the presence of about 30% water, nothing will happen until the temperature is raised to about 60°C. Then the lamellar phase or the neat phase is formed. At this temperature the hydrocarbon chains are in the liquid state. If this LC-phase is cooled, a gel phase may be formed with a hydrated bilipid layer structure, as shown in figure 4.2.c. Larsson (1964) found that the chains of the lipid molecules are tilted about 54° towards the water layer plane. The lateral packing of the chains can be described by a hexagonal subcell and is usually termed α according to Larsson (1967[a]), which is the same subcell as found for the α-form of triglycerides.

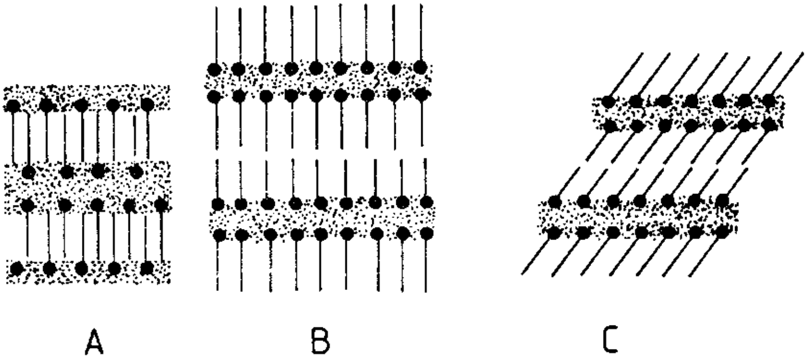


Figure 4.2 : The schematic structure of three possible lamellar gel phases formed by surfactants in contact with water below the crystallization temperature of their hydrocarbon chains.

This gel phase of the monoglycerides is metastable and eventually transforms into anhydrous β-crystals and water. This process is preceded by the formation of α-crystals and water. Often the dispersion of microcrystals in water is referred to as coagel. Monoglycerides with a chain length shorter than C_{14} do not form a gel structure, but on cooling they directly crystallize in the water free β-form.

The water layer thickness of the lamellar gel phase of monoglycerides under normal conditions does not exceed 20 Å (Larsson,

1967^b). In the presence of excess water a dispersion is formed. The particles in this dispersion consist of concentric bilipid layers of monoglyceride molecules alternating with thin shells of water.

As has been indicated in the previous chapter α-tending emulsifiers do not show lyotropic mesomorphism according to for example Schuster (1985), Boyd (1974) and Andreasen (1973). Therefore it may seem rather contradictory to expect the formation of a gel phase as in the case of monoglycerides in α-tending emulsifier containing emulsions. However, there are some striking similarities in the physical behaviour of our GLP gels and that of the gel phases of monoglycerides. It is known that the α-gel phase of a 10% glycerol monostearate dispersion has excellent whipping properties, such as a high overrun and an acceptable firmness of the foam (Krog, 1977). If polymorphic changes to the β-polymorphic form occur, these good foam properties are completely lost. Thus, the whipping behaviour of the α-gel phase of the dispersion state of monoglycerides is in good agreement with the fact that the α-crystalline form of α-tending emulsifiers is related to good foam properties. Furthermore, the dispersion state of monoglycerides in the presence of excess water as described by Larsson (1967^b) is, to a certain extent, comparable with our GLP gels.

On the other hand, the GLP molecules or a fraction of the molecules may well form a rigid α-crystalline film at the o/w-interface. Such a rigid crystalline film could stabilize aggregated particles against coalescence. When this hypothetical mechanism would account for the stability of the GLP gels, we do not have to explain the question, why a gel phase would be formed in a system that does not show lyotropic mesomorphism.

The proper technique to study lipid polymorphism and mesomorphic behaviour is a combination of small and wide angle X-ray diffraction (SAXD and WAXD). Furthermore, neutron diffraction has proved to be a useful technique for structural analysis of gel phases and LC-phases of phospholipids (see e.g. : Büldt et al. , 1979 ; Zaccai et al. , 1979 ; or Worchester and Franks, 1976).

Polarization microscopy is also used extensively for the detection of mesomorphic phases. For a detailed review on lyotropic mesomorphism and microscopy may be referred to Hartshorne (1974). In the phase study presented in this chapter we have applied x-ray diffraction, neutron diffraction and microscopical methods.

4.3 RESULTS AND DISCUSSION

4.3.1 The swelling properties of GLP.

As indicated in the introduction, Larsson (1967^b) showed that the swelling properties of the phases of monoglycerides in contact with excess water are limited. However, industrially prepared monoglycerides always contain free fatty acids. Krog and Borup (1973) indicated that, when these free fatty acids are neutralized, the swelling capacity can be greatly increased.

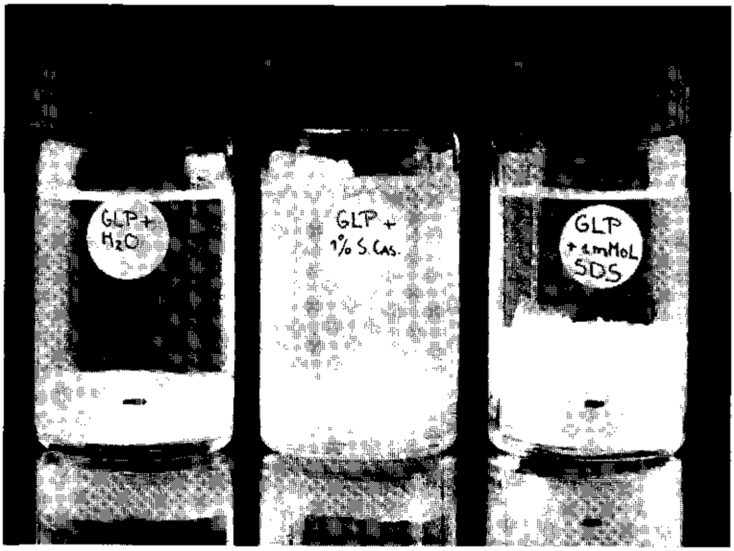


Figure 4.3 : Photograph showing swelling of crystallized GLP at room temperature due to the addition of SDS to the water phase.

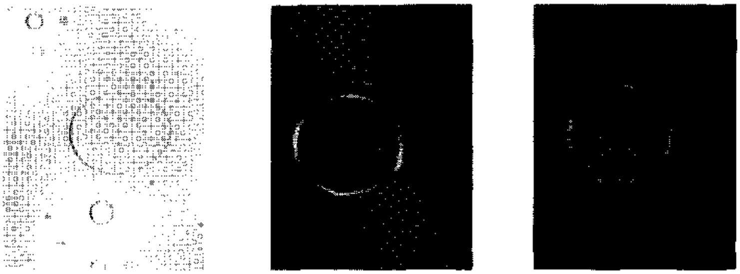
The same effect is observed, when ionic surfactants are added to these systems. This swelling process seems to be in agreement with our observation in chapter 3 that particle aggregates of GLP gels become deflocculated by the addition of a sufficient amount of sodium dodecyl sulfate.

If crystallized GLP is brought into contact with water, no macroscopical swelling is observed. However, when SDS is added to the water phase, swelling occurs gradually (see figure 4.3). If this effect is only typical for gel phases, we would have an argument that GLP may indeed form a gel phase at the o/w-interface of the particles. However, it may not be excluded that solubilization of emulsifier molecules, adsorbed at the o/w-interface, takes place, followed by deflocculation due to electrostatic repulsion of SDS molecules. Such an effect could also occur in the case of a particle gel consisting of flocculated, water-free α-crystals.

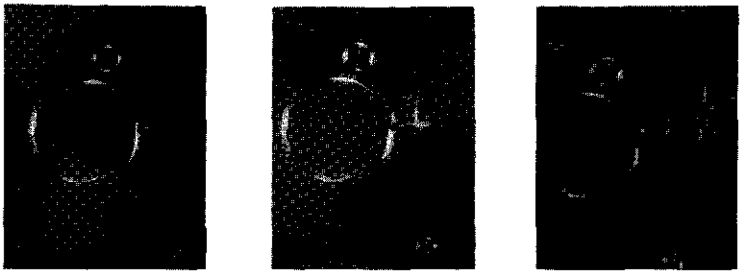
It may be that with microscopy we have observed swelling of GLP as a result of hydration. In figure 4.4 some photographs are shown of a microscopical sample of liquid GLP droplets in contact with water. This sample was cooled down from 50°C to room temperature. At a temperature of about 42°C many of the larger droplets showed rupture phenomena at the o/w-interface. This was followed by the expulsion of liquid drops of emulsifier.

The expulsion effect may be explained as follows. Crystallization phenomena start at the o/w-interface, where a rigid crystalline film is formed. If water penetrates into the droplets, the pressure inside the droplets will increase. If the pressure exceeds the maximum value which can be counterbalanced by the crystallized interface, fracture of this film is likely to occur, followed by the expulsion of the interior liquid fraction of the particle.

When smaller crystallized particles ($d \approx 2\mu m$) are observed with the polarization microscope between crossed polars, it is obvious that the particles show strong birefringence effects in the form of a Malthezer cross (see figure 4.4).



T = 49.0°C T = 43.5°C T = 41.0°C



T = 39.5°C T = 37.5°C T = 20.0°C

Figure 4.4 : Microscopical observations on the rupture behaviour of crystallizing GLP droplets in contact with water during cooling to room temperature.

Therefore the crystallized particles may contain spherically multilayered structures with regular radial repetition as has been seen in the case of liquid crystals (e.g. Hartshorne, 1974). This birefringence effect sustains the idea of the formation of a multilayered crystalline film around the GLP droplets. However, it does not give conclusive information on the formation of swollen GLP layers at the oil water interface. Walstra (1967) studied the crystal habit of fat globules in milk and butter. He distinguished four types of crystallization behaviour from the appearance of the particles between crossed nicols. These four types are shown in figure 4.5. In the case of the O type, either crystals are absent or they are too small to be observed. The N type particles (needle-type) contain small or large crystal needles. The L type

(layer-type) particle shows the same birefringence effect as particles containing layers of liquid crystals. The M type (mixed-type) is a mixture of the N and L type. Walstra assumed that the L-type particles are made up of tangentially oriented needles and the crystal needles are probably oriented in the o/w-interface.

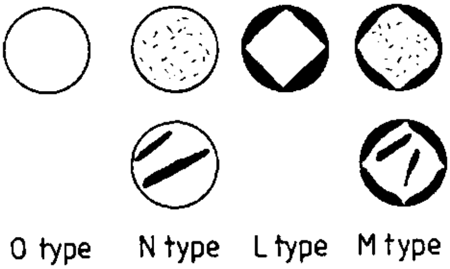


Figure 4.5 : Four possible crystallization types observed by Walstra in milk fat globules with polarization microscopy.

According to Van Boekel (1980) the L and M type are frequently associated with the occurrence of partial coalescence. Thus, this may suggest that the particles in the GLP gels are bound as a result of partial coalescence. Therefore our microscopical observations indicating the formation of a gel phase at the o/w-interface of fat particles is certainly not conclusive. However, it can be concluded from the results presented in this paragraph, that some additional qualitative results have been obtained which may sustain the idea that swelling of GLP as a result of the uptake of water may occur below the melting point of the emulsifier.

4.3.2 X-ray diffraction on water-free and water containing GLP samples.

The first series of x-ray diffraction experiments we will discuss were performed on water-free GLP samples and on GLP particle gels, containing 15% of this α-tending emulsifier in a 2% sodium caseinate solution. These gels were prepared as described in section 2.2.1. The water-free GLP sample was brought in melted state in the sample holder and was kept at room temperature for one day prior to the diffraction measurements.

In table 4.2 the results of both WAXD and SAXD measurements are represented. Both samples show an interference maximum at about 4.13Å. The meaning of this value is that the hydrocarbon chains are indeed crystallized in the α-polymorphic form characterized by a hexagonal subcell as described by Larsson (1967^a). In the case of the gel samples we also found a weak reflection corresponding to a spacing of 4.62Å. This probably means that part of the GLP gel sample is also crystallized in the β-modification.

Table 4.2 : X-ray diffraction maxima for water-free GLP samples and 15% GLP gels in 2% sodium caseinate at room temperature. (Detection with the photographic technique).

	WATER-FREE GLP sample		15% GLP GEL sample	
	d (Å)#	Intensity	d (Å) (N=5)	Intensity
WAXD	4.14	very strong	4.13 ± 0.01	very strong
			4.62 ± 0.01	weak
	12.3	weak		
	13.4	weak	15.7 ± 0.3	very weak
	17.0	weak	21.1 ± 0.3	very weak
	27.0	very weak	31.5 ± 0.5	medium
	32.1	very weak		
SAXD	45.2	extremely strong		
	52.5	very strong		
	67.8	strong	63.2 ± 0.2	incomparable
	135	strong		

\# The spectrum of almost any sample was measured twice and the results represented in the tables of this chapter represent the mean value of these two measurements, unless mentioned otherwise.

It should be emphasized that these two samples differ from each other in two respects. First of all the gel sample contains water which might influence the crystal modification of the emulsifier, because hydration of specific emulsifier components may induce fractionated crystallization. The second important distinction is that the gel sample contains very small GLP particles, as a result of homogenization. In the next chapter the results of DSC experiments will show that the crystallization of GLP is indeed influenced by the interfacial area of the samples.

The reflection values 45.2Å and 52.5Å found for the water-free GLP sample presumably represent long spacings of tilted bilipid layers. Krog and Borup (1973) mentioned a value of 54.9Å for the bilipid layer thickness of the non-aqueous α-crystal modification of distilled glycerol monostearate. The reflection of about 135Å in the case of the dry sample we can not explain. Perhaps, as a result of fractionated crystallization part of the emulsifier molecules form a lattice cell containing more than two molecules as in the case of a bilipid layer. The reflection of 67.8Å could then represent a second order value of this spacing.

From the results of table 4.2 we can certainly conclude that the gel sample with 15% GLP contains a lamellar structure: The SAXD reflection maximum of about 63Å ($N_{measurements} = 5$) represents the long spacing of dry or hydrated crystallized bilipid layers. The other intensity maxima have spacing ratios 1/2 to 1/3 to 1/4 compared to the spacing of 63.2Å, which is indicative of the presence of such a lamellar structure in the gel sample.

The question, whether these bilipid layers are hydrated or not can only be solved, if the value of the long spacing of the bilipid layers of crystallized GLP particles in a dehydrated gel sample is known. Therefore we decided to perform x-ray diffraction on spray-dried GLP emulsions, since with these samples we could exclude a possible effect of particle size differences.

The powders were prepared as described in section 2.2.1.2. In this way a dry GLP powder was obtained containing particles smaller than about 0.5 μm in diameter. This powder was stored at room temperature for several weeks in order to realize complete crystallization of the emulsifier particles and to obtain an "equilibrium state".

In table 4.3 the results of x-ray diffraction experiments on this powder sample are represented. Furthermore, results are included for a sample which was first dried against SiO_2, because the spray-dried powder sample contained about 3% water. In this table the values of the detected reflections are compared with those obtained for the bulk GLP sample (see also table 4.2).

Table 4.3 : Comparison of X-ray diffraction measurements on spray-dried and bulk GLP samples in the absence of water (Photographic detection).

	bulk GLP	spray-dried GLP powder	SiO_2 dried GLP-powder
	d (Å)	d (Å)	d (Å)
WAXD	4.13 (vs)	4.13 (vs)	4.10 (vs)
		4.61 (w)	4.57 (w)
	17.0 (w)	14.2 (w)	13.9 (w)
	27.3 (ew)		
	32.1 (m)		
SAXD	45.2 (es)		
	52.7 (vs)	56.1 (s)	54.8 (s)
	67.8 (vs)		
	135 (m)		

It is clear that homogenization of GLP has a large influence on the crystallization behaviour of the emulsifier, as detectable with this technique. The x-ray diffraction pattern for the homogenized powder sample shows large similarity with the gel sample containing 15% GLP. The inexplicable high values found in the spectrum of the dry, bulk GLP sample are not recovered in the case of the powder sample. Furthermore, the short spacings are in good agreement with those obtained for the 15% GLP gel sample. The value of 4.61Å may be indicative of the occurrence of polymorphic changes or of fractionated crystallization in the case of samples with large surface area. For comparison, a wide angle spectrum of the spray-dried GLP powder is shown in figure 4.6 as detected with a powder diffractometer (see section 2.2.4).

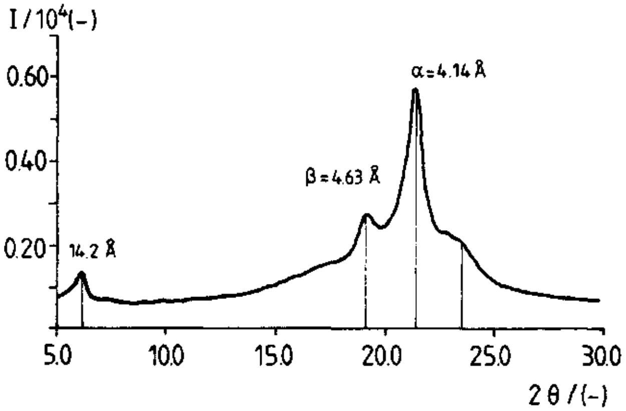


Figure 4.6 : A wide angle x-ray diffraction spectrum for the spray-dried GLP powder determined with a powder diffractometer at room temperature.

It is not clear, whether the powder sample has a lamellar structure, since we have not found reflections of second or third order, though the value of 14.2Å may be indicative of the fourth order. However, a long spacing of about 55Å may fit in well with the thickness of a dry bilipid layer of GLP molecules. Complete hydration would then lead to a long spacing of about 63Å, as has been found in the case of the gel samples of table 4.2.

We investigated this assumption further by means of a hydration experiment with this spray-dried GLP powder sample. To this end the powder was brought into contact with demineralized water at room temperature. After about 24 hours we performed small angle x-ray diffraction on both dry and wet samples using the position sensitive detection (PSD) method. For comparison a GLP-gel was also studied with this technique.

In figure 4.7 the SAXD curves of these three samples are represented. Figure 4.7.A shows a single, sharp Bragg peak of the 20% GLP gel. After desmearing (section 2.2.5) a value of 61.9Å is found for this long spacing which is lower than the value found with the photographic technique. Furthermore, the spectrum does not show a second or third order maximum, though the fourth order maximum may be present (d = 15.6Å). From the two diffraction spectra in figure 4.7.B and 4.7.C it is obvious that hydration has indeed occurred at room temperature. However, the spectrum of the wet sample also indicates that part of the GLP is not hydrated at this temperature, which is contradictory to the spectrum shown in figure 4.7.A.

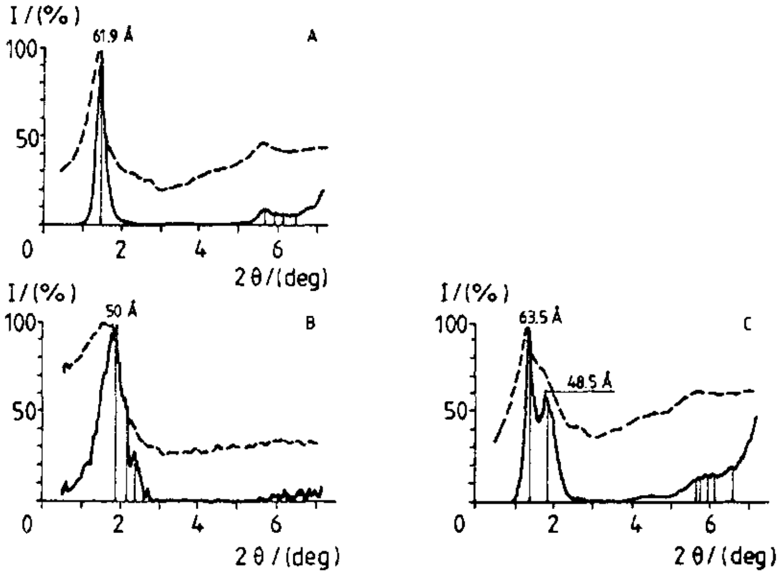


Figure 4.7 : SAXD curves obtained at 20°C for a 20% GLP gel and for a dry and hydrated spray-dried GLP powders. The results were obtained with the position sensitive detector (section 2.2.5.) Both smeared and desmeared curves are represented.

A : 20% GLP gel in 3.33% sodium caseinate solution.

B : Dry, spray-dried GLP powder sample.

C : Hydrated, spray-dried GLP powder sample containing 67% water.

The shift of the long spacing towards a desmeared value of about 63.5Å in the presence of water is larger than the value of the long spacing found in the case of the 20% GLP gel sample being 61.9 Å. The desmeared value for the long spacing of the dry bilipid layer is much smaller than the value obtained by the photographic technique. For the dry powder sample we found a value of about 50Å after desmearing, whereas the value of the smeared curve was about 55Å. This lower value may be related to the applied desmearing technique. The signal for the dry sample was quite broad, compared to the signal obtained for the hydrated gel phases thus markedly effecting the calculation of the exact value of the long spacing for the dry bilipid layer.

The fact that hydration may occur below the crystallization temperature of the emulsifier sample is of great importance. This observation means that an α-crystalline gel phase can actually be formed in systems which do not show lyotropic mesomorphic behaviour. It is known that heating of β-crystals of cetostearylalcohol in the presence of water may lead to the formation of a stable α-hydrate according to e.g. Junginger et al. (1979) and de Vringer (1987). This hydration process occurs about 20°C below the melting point of this gel phase. Furthermore, it is well known that β-crystals of monoglycerides like GMS have the ability to form an α-gel phase just below the Krafft point, when these crystals are heated in the presence of water. Obviously, water can penetrate into the crystal lattice of these amphiphiles.

From the results of this paragraph it may be concluded that an α-gel phase may be formed in GLP particle gels and that hydration in fact may occur well below the crystallization temperature of the hydrocarbon chains of the emulsifier. At this moment the exact values for the dry and hydrated bilipid layers can not be given, because the applied detection methods show different values.

4.3.3 The influence of NaCl on the swelling properties of the α-gel phase of GLP.

The long-term stability of the α-gel phase of monoglycerides or other emulsifiers in aqueous systems is of great importance for a successful application of these additives in foods, when they are used in the gel state (Krog, 1977). From literature it is known that the presence of small amounts of fatty acids may strongly increase the swelling capacity of both mesomorphic and gel phases of monoglycerides or phospholipids (see e.g. Krog and Borup, 1973). This swelling leads to a strong increase in the stability of the gel phase. The swelling capacity depends both on the pH and the salt concentration.

We studied the possible influence of the free fatty acids, which are usually present in GLP in a relatively low amount, on the state of swelling of the GLP bilipid layers in 15% GLP particle gels containing 2% sodium caseinate. To this end we added dry sodium chloride to the GLP dispersions directly after homogenization. The pH of these gels amounted to a value of about 6.10. In table 4.4 the results of these x-ray diffraction measurements are represented.

Table 4.4 : The influence of added NaCl on the long spacing of hydrated GLP gels containing 15% emulsifier and 2% sodium caseinate. Long spacings were obtained from the photographic detection method.

[NaCl]	0 mM	5 mM	10 mM	50 mM
	d (Å)	d (Å)	d (Å)	d (Å)
WAXD	4.13 vs	4.14 vs	4.14 vs	4.14 vs
	4.62 w	4.61 w	4.62 w	4.62 w
	15.9 w	15.6 w	15.9 w	15.7 w
	21.3 vw	21.0 vw	21.0 vw	21.3 vw
	31.5 m	32.2 m	31.5 m	31.5 m
SAXD	63.3 vs	63.1 vs	63.3 vs	62.0 vs

The spacings of the gel phase were not influenced markedly at sodium chloride levels lower than 50 mMol. If we compare the long spacings with those obtained by Krog and Borup (1973) for neutralized GMS gel samples, we can see that these results are in good agreement. They showed that both the lamellar phase and the gel phase of neutralized GMS are very sensitive to low levels of sodium chloride which is expressed in table 4.5.

Table 4.5 : The influence of the NaCl concentration on the swelling capacity of neutralized distilled GMS/water systems containing 70% water as determined by Krog and Borup (1973).

Concentration of added NaCl	Lamellar phase, 60°C		α-Gel phase, 25°C	
	d (Å)	dw (Å) *	d (Å)	dw (Å)
0.0 mMol	128.1	90.0	191.2	136.3
1.7 mMol	126.0	87.9	190.0	135.1
6.8 mMol	125.0	86.9	64.2	9.3
17.1 mMol	126.0	87.9	64.5	9.6
49.6 mMol	123.0	84.9	62.9	8.0
68.4 mMol	61.8	23.7	63.7	8.8
244.0 mMol	56.1	18.0	61.5	6.6

* d = Thickness of hydrated bilipid layer.
d_w = Water layer thickness.

Especially the α-gel phase shows this effect. Krog and Borup have prepared these neutralized systems by the addition of NaOH. We estimated that for neutralization they must have used about 10 mMol NaOH. Thus, these systems already contained 10 mMol of sodium ions, which is about the same concentration as we had in our gels, originating from the added sodium caseinate. We do not know the pH of Krog's neutralized gels, but presumably the pH of his systems exceeded the value of 7.0.

Compared with Krog's results it seems that the lamellar gel phase of GLP behaves likewise to the gel phase of GMS in the presence of similar amounts of sodium chloride. The fact that he found a large swelling effect of the gel phase at very low sodium chloride concentration is probably caused by the high pH of his samples. Extreme swelling of the gel phase of GLP under practical conditions will therefore never occur, which is of great importance for its application in whippable emulsions.

4.3.4 Neutron diffraction on GLP containing samples.

Neutron diffraction has proved to be a very useful technique for structure analysis of mesomorphic and gel phases of surfactants during the last two decades (see e.g. Worchester and Franks, 1976 or Büldt et al. , 1979). The reason for this is the great difference between the neutron coherent scattering amplitudes of hydrogen and deuterium. This difference is also greater than the coherent scattering amplitudes for other atoms found in surfactants. In principal, this relatively great difference makes it possible to locate water molecules within the structure of a multilayer, which of course offers very vital information on the structure of the multilayer.

Since we wanted to obtain more knowledge on the hydration properties of GLP, we decided to perform neutron diffraction on three different types of GLP samples which were hydrated with variable amounts of D_2O. The first series of samples was prepared from the GLP-powder as described in section 2.2.1.2 and they were hydrated at room temperature. The second series of diffraction experiments was performed with a freeze-dried GLP powder, free of any other additional component. The preparation of this sample is described in section 2.2.1.3. This freeze-dried powder sample was also hydrated with D_2O at room temperature. The third series of samples consisted of GLP gels, which were obtained by heating variable amounts of D_2O and GLP to a temperature of about 60°C in sealed bottles and subsequently cooling them down to ambient temperature under vigorous mixing. The differences between the three samples were thus related to composition, average particle size and temperature at which the samples were wetted with D_2O.

In figure 4.8 the combined neutron diffraction spectra of a D_2O-free and a 30% D_2O containing freeze-dried GLP sample are represented. The Q-value ($Å^{-1}$) represents the momentum transfer which is related to the long spacing d in the following way :

$$Q = \frac{2\pi}{d} \qquad (4.1)$$

The cross section on the Y-axis is defined as the probability of scattering of an incident neutron into unit solid angle. The cross section is corrected for sample background by substraction of an empty can run and it is normalized for the sample density. As one can see, the accuracy of the two diffraction peaks, indicated by the vertical lines in the spectra is quite satisfying. It is obvious from these two spectra, that the GLP bilayers swell in the presence of water, because Q decreases from approximately 0.112 ($Å^{-1}$) to a value of 0.096 ($Å^{-1}$).

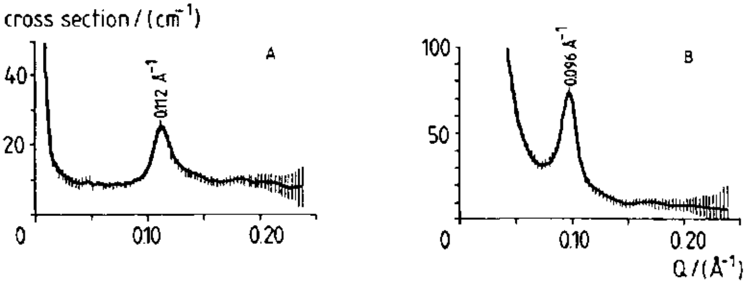


Figure 4.8 : Neutron diffraction spectra for dry and hydrated GLP-particles at ambient temperature.
A : Freeze-dried GLP-powder containing 100% GLP (section 2.2.1.3).
B : The same GLP sample, containing 30% (w/w) deuterium oxide.

It is very remarkable that at low Q-values the scattering cross section increases so dramatically. From a physical point of view this cross section should be related to the distribution of inhomogeneity in scattering power of the sample, arising from differences in constitution of different particles, from differences in size and shape of particles and/or from voids in between particles (for further information, see chapter 6).

In figure 4.9 the results of neutron diffraction experiments with the three types of gels are represented. This figure shows the measured long spacing of the α-gel phase of GLP as a function of the D_2O concentration in weight percentages. From this figure it is obvious that the values for the long spacings of the fully hydrated gel phases depend on the type of sample examined. The differences are not due to experimental error, because this figure clearly shows that the values of the long spacing for sample B and C are quite constant at high D_2O concentrations.

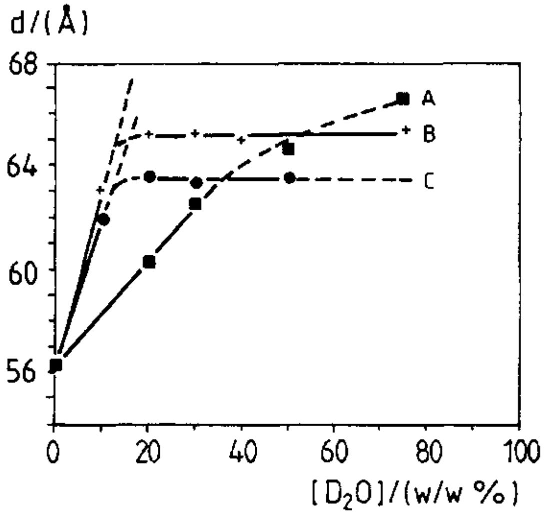


Figure 4.9 : The long spacing of the three different types of GLP samples as function of the weight percentage deuterium oxide as determined with neutron diffraction at ambient temperature.
A : Spray dried GLP-powder containing 60% GLP (section 2.2.1.2).
B : Freeze dried GLP-powder containing 100% GLP (section 2.2.1.3).
C : Melted GLP.

Our explanation for this effect is that fractionation of components at the interface of the particles probably causes differences in the composition of the gel phase which, in turn, may cause differences in the value of the long spacing at the point of maximum hydration. Gels that were prepared by hydrating powder samples at room temperature significantly showed higher values for the long spacings of the completely hydrated samples. The value of 63.5Å for the long spacing of sample C at maximum swelling conditions agrees well with the value found for the gels with x-ray diffraction with the photographic technique. In the next chapter the results will be shown of crystallization and melting properties of GLP samples in the absence and presence of water as detected with DSC.

Besides figure 4.9 nicely demonstrates the competition effect between GLP and the relatively strong hydrophilic protein and sugar fraction for hydration by the added D_2O. If we compare the value of the long spacing of this sample at high D_2O level with the one obtained from x-ray diffraction with the PSD-method (figure 4.7), we must conclude that the latter method gives a significant lower value for the long spacing. Again this may be related to the accuracy of the desmearing method applied in x-ray diffraction.

From the results of this specific paragraph in combination with the results of x-ray diffraction it may indeed be concluded that GLP forms an α-gel phase at a temperature well below the melting temperature of the emulsifier mixture in the presence of water. Besides neutron diffraction has indicated that the value of the hydrated long spacing of the α-gel phase seems to depend on the way a sample is prepared. A model for the structure of this gel phase will be presented in the general discussion at the end of this chapter.

4.3.5 X-ray diffraction on emulsions with a variable fat to GLP ratio at room temperature.

It is of course important to know that GLP may form an α-crystalline gel phase in the presence of water. However, it is of still greater importance to know whether the same effect occurs when GLP is present in an oil or fat phase. Therefore, we have performed x-ray diffraction experiments on gelatinized emulsions with variable GLP to fat ratios. With this technique we also briefly studied the crystallization of water free GLP/fat mixtures.

In table 4.6 the results of x-ray diffraction measurements performed on these lipid mixtures are represented. Prior to these measurements the samples were stored at 4°C in a refrigerator. It can be observed that hardened coconut oil (HCNO), just like GLP, shows a complicated x-ray diffraction pattern. Fat crystallization probably occurred both in the α and β'-polymorphic form as it appeared from the measured short spacings of 3.81Å and 4.17Å (for comparison see table 4.2). The spacing at 4.17Å could be a mixed reflection of the α- and β'-polymorphic form. Probably the values of 34.3Å and 37.6Å are representative for long spacings of crystallized triglycerides, though tilting must have occurred then. Furthermore, it could not be excluded that the spacing of 121.8Å is indicative of the existence of a subcell that contains more lipid molecules. However, since the diffraction patterns in the small angle region, representative of the long spacings, found for these fat/GLP mixtures, are too complicated to be explained, we will only consider the short spacings.

Table 4.6 : WAXD and SAXD measurements on dry GLP/HCNO mixtures at room temperature. Detection was performed with the photographic method.

	HCNO fat	100% GLP 0% fat	80% GLP 20% fat	60% GLP 40% fat
	d (Å)	d (Å)	d (Å)	d (Å)
WAXD	3.81 (s)		3.81 (m)	3.81 (m)
		4.13 (vs)	4.13 (vs)	4.12 (s)
	4.17 (m)			
	4.29 (w)			
			4.61 (m)	4.62 (w)
	11.9 (ew)	13.4 (w)	14.0 (m)	14.0 (m)
		17.0 (w)	16.6 (ew)	
		27.0 (vw)		
		32.1 (vw)		
SAXD	34.3 (vs)		35.5 (m)	34.9 (m)
	37.6 (m)	45.2 (es)		
		52.5 (vs)	53.5 (m)	52.6 (s)
		67.8 (m)		
			106 (vw)	105 (vw)
	121.8 (m)	135 (m)		
age	34 days		36 days	62 days

Mixtures of GLP and HCNO seem to crystallize at least partly in the α-polymorphic form, which may be expected from the α-tending character of GLP. Probably a part of the molecules is crystallized in the β'-form, since the spacing 3.81 is also found. This may be indicative of the occurrence of fractionated crystallization, which would be expected to come about in these complicated mixtures.

Table 4.7 : WAXD and SAXD measurements on emulsions with a variable fat to GLP ratio at room temperature in order to prove the formation of an α-gel phase in these systems. Detection was performed with the photographic method.

	100% GLP[a] 0% fat	80% GLP[a] 20% fat	60% GLP[a] 40% fat	50% GLP[b] 50% fat	30% GLP[b] 70% fat
	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)
WAXD		3.81 (ew)		3.82 (m)	3.82 (s)
	4.13 (vs)	4.13 (vs)	4.13 (vs)	4.15 (vs)	4.15 (vs)
					4.30 (w)
	4.62 (w)	4.61 (w)	4.63 (w)	4.64 (w)	4.62 (w)
	15.7 (vw)	16.0 (w)	15.5 (ew)	15.4 (w)	15.6 (vw)
	21.1 (vw)	21.3 (vw)	22.2 (ew)	20.8 (vw)	22.6 (w)
	31.5 (m)	32.1 (s)		35.5 (s)	35.6 (s)
SAXD				48.8 (w)	49.3 (w)
	63.2 (s)	63.7 (vw)			64.6 (ew)
					130.0 (m)
exposure time	24 (hrs)	72 (hrs)	72 (hrs)	90 (hrs)	90 (hrs)
sample age		10 days	52 days	13 days	12 days

a : Emulsions containing 15% dispersed phase.
b : Emulsions containing 40% dispersed phase.

In our case it is more important to know what happens in the presence of water. In table 4.7 the results are shown of diffraction measurements performed on gels with a variable GLP to fat ratio. This table shows that only in the case of a rather high GLP/fat ratio the long spacing indicative of the α-gel phase could be detected. At lower GLP/fat ratios it can be observed from the short spacings that fractionated crystallization may have occurred in the samples. Both short spacings indicative of the α-polymorph and β'-form are represented in the diffraction pattern. The short spacing of 4.15Å may be a mixed reflection of the 4.13Å spacing of the gel phase and the 4.20Å spacing of the β'-polymorph. The reflection of 35.5Å could probably mean fractionated crystallization of the fat sample itself (see also table 4.6).

Summarizing, it can be concluded that the existence of the α-gel phase could not be shown in emulsions with a relatively high fat/GLP ratio. However, it is not known how many bilipid layers are in fact necessary to obtain a reflection that will be strong enough to be detectable. In this respect it is good to realize that, because of the size of the particles, the number of stacked bilipid layers is strongly restricted. For instance, in the case of a whippable emulsion, which has a 30% GLP to fat ratio and a mean particle diameter of about 0.5 μm, the maximum number of repetitive stacked bilipid layers in the interface would be about 3 (see figure 3.4). Besides, if it is assumed that only about 50% of the total GLP fraction forms part of this gel phase, we would only have 1 or two bilipid layers. If this is true then it can be imagined, that even at a relative GLP concentration of 60% the detection of the long spacing may become impossible. Therefore, it may not be excluded that the α-gel phase may be present at the interface of fat particles in the case of relatively low GLP/fat ratios.

4.4 GENERAL DISCUSSION.

Normally one should investigate the total phase diagram of an amphiphile, before it may be concluded at what temperature or at what concentration a certain phase exists. However, in the case of GLP/water mixtures such an attempt would not be successful for several reasons. First of all, GLP has a very complicated composition which prevents an equilibrium state for crystallized GLP in the presence of water to be obtained within acceptable time. A second important reason is the almost complete insolubility of GLP in water. The structural parameters of the gel phase may therefore strongly depend on the total interfacial area of the system. Furthermore, great differences in pH or salt content will be encountered between systems with low and high water concentrations, which makes preparation of samples with comparable particle size impossible.

One possible way to tackle this specific problem would be to produce spray-dried powder samples and subsequently to hydrate these powders at different temperatures and at different water activities below the melting point of the hydrocarbon chains of the lipid mixture. However, this phase diagram would then become dependent on the size of the emulsifier particles, as shown in the paragraph where the results of the neutron diffraction measurements at room temperature were represented. Therefore we have not performed such a time-consuming study. In chapter 5 we will show some x-ray diffraction results dealing with the temperature influence on the formation and stability of the α-gel phase of GLP. From those results it will be attempted to compose a hypothetical phase diagram for the gel phase of GLP, despite all the problems that have just been described.

From the results shown in this chapter it may be concluded without doubt that GLP is able to form a stable α-gel phase below the melting temperature of its hydrocarbon chains. The structural parameters of this gel phase have not been discussed yet. It is not known which part of the molecules of the GLP mixture are structure elements of this gel phase. It may be clear from the introductory part of this chapter that the monoglyceride fraction alone is not able to produce a stable α-gel phase. Therefore it seems obvious that diglycerides, like glycerol dipalmitate and glycerol lacto palmitate or perhaps even a triglyceride, like glycerol dilacto palmitate, should play an important role in the formation and stabilization of the α-gel phase.

Mixtures of saturated lipids usually crystallize in the α-polymorphic form before transition to the β' or β-polymorphic form occurs. These transitions to the more stable form can be strongly delayed or even stopped, when the lipid mixture is very complex. Furthermore, it can also be expected that bulky head groups may prevent the occurrence of polymorphic transitions. On the other hand, tilting of the hydrocarbon chains may accomplish the space filling requirements of the lattice structure. This actually occurs in the case of monoglycerides. The stability of the α-gel phase of GLP may thus be related both to a complex composition of the emulsifier mixture in the gel phase and to the presence of the bulky lactate esters in the water layer.

We will now try to propose a possible structure model for the α-gel phase of GLP, a model which will still be quite speculative. In table 4.8 long spacings for different crystal modifications of some relevant triglycerides and 1-monoglycerides are given. It obviously appears from this table that the 1-monoglycerides should have tilted chains in all three different polymorphic forms. In the case of the α-gel phase of the monoglycerides the tilt angle equals a value of 54° according to Larsson (1967).

Table 4.8 : Literature values for the long spacings of the different polymorphic forms of some triglycerides and 1-monoglycerides according to Chapman (1962).

long spacings (Å)	α	β'	β
tripalmitin	45.6	42.6	40.6
tristearin	50.6	47.2	45.0
1-monopalmitin	(45.6)	45.8	45.8
1-monostearin	(?)	50.0	50.0

We have found that the long spacing for the dry bilipid layer of GLP probably has a value between 50Å and 56Å, subject to the applied detection method, but probably the second value is more reliable. Suppose, the gel phase contains both mono- and diglycerides. Then, as a rough approximation, the estimated average length of a molecule, present in the bilipid layer, could equal the length of one glycerol monostearate molecule. With a tilt angle for the α-gel phase of GMS of 54° the value for the long spacing of this dry bilipid layer with the hydrocarbon chains in perpendicular position towards the end plane of the lattice would be about 62Å. This means that the hydrocarbon chains in the gel phase of GLP should be tilted without doubt. Furthermore, a physical reason for tilting may be that the lactic acid esters, which are probably present as polar head groups in the gel phase, require tilting of the hydrocarbon chains for geometrical reasons. The value for the tilt angle of the gel structure can not be given, because we do not know the composition of the gel phase. However, from the results of the neutron diffraction experiments we can estimate, whether hydration leads to an increase in this angle.

If it is assumed that the tilt angle of the gel phase does not change as a result of hydration, the volume fraction of water at maximum swelling condition can be calculated, with equation 4.2 :

$$\frac{V_{GLP}}{V_{(GLP + D_2O)max}} = \frac{d_a}{d_{a+w}} \qquad (4.2)$$

where V_{GLP} represents the volume of one dry bilipid layer and $V_{(GLP + D_2O)max}$ the volume of the same bilipid layer at maximum swelling condition. The factors d_a and d_{a+w} represent the long spacings of the dry and hydrated gel phase, respectively. To be able to calculate the D_2O concentration in weight percentages, equation 4.2 has to be converted into formula 4.3 :

$$\frac{M_{GLP}}{M_{GLP} + \dfrac{M_{D_2O} * \rho_{GLP}}{\rho_{D_2O}}} = \frac{d_a}{d_{a+w}} \qquad (4.3)$$

In this equation M_{GLP} represents the mass of the GLP bilipid layer and M_{D_2O} the mass of the water molecules at maximum swelling condition. ρ_{GLP} is the density of the emulsifier mixture which is about 1020 kg/m^3 at 20°C and ρ_{D_2O} is the density of deuterium oxide at the same temperature which is approximately 1110 kg/m^3.

From neutron diffraction as well as x-ray diffraction measurements it appeared that d_a = 55-56Å. In the case of the freeze-dried GLP sample, applying neutron diffraction, we found a value for d_{a+w} equal to approximately 65.2Å and for the gel sample, hydrated above the transition point of the emulsifier, a value for d_{a+w} equal to 63.4Å. From equation 4.3 it then follows that the two different gel phases would be completely hydrated at a D_2O concentration of about 15% and 12% respectively. On the basis of these calculations one might be inclined to conclude from figure 4.9 that the tilt angle is independent from the water concentration. However, it should again be emphasized that it is not known which part of the total emulsifier mixture actually becomes hydrated in the presence of water. If it is supposed that only 50% of the mixture is hydrated, the tilt angle has to change significantly. Yet we think that if the tilt angle increases this effect will be of minor importance.

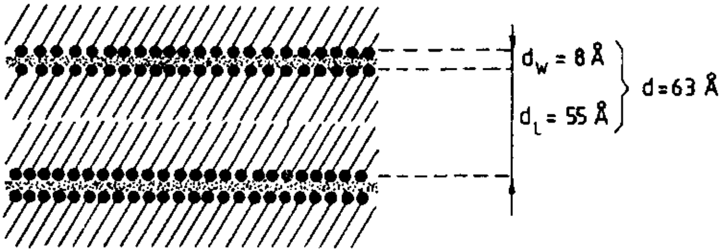


Figure 4.10 : A schematic molecular model for the α-gel phase of glycerol lacto palmitate hydrated above the crystallization temperature of the emulsifier.

Figure 4.10 represents a schematic molecular structure for the α-gel phase of GLP, which was hydrated above the transition point of the emulsifier. In this model it is assumed that the dry bilipid layer thickness amounts to a value of 55Å. If the dry bilipid layer thickness is correct, the water layer thickness of the gel phase would only be 8 Å or 9 Å. This probably is the maximum swelling thickness of the bilipid layer in the case of gels which are obtained for GLP samples that are brought in contact with water at a temperature above the transition point. In the case of spray-dried GLP samples, which are wetted at room temperature, the value for this water layer thickness probably is a few Ångstroms larger. However, when speaking of the water layer thickness of the gel phase of GLP one should realize that the layer, in which water molecules can be found, is much thicker, say 15-20 Å.

4.5 SUMMARY

In this chapter the existence of an α-gel phase in particle gels containing GLP and water has been shown with both x-ray diffraction and neutron diffraction studies. This gel phase consists of hydrated bilipid layers of amphiphilic molecules, originating from the total GLP fraction. The hydrocarbon chains of these amphiphiles are crystallized in the α-polymorphic form. At maximum swelling condition the gel phase has a hydrated bilipid layer thickness of about 63-65 Å which is dependent on the history of the sample prior to wetting.

This α-gel phase of GLP is presumably present at the o/w-interface of the fat particles at a GLP/fat ratio higher than 20%, subject to the size of the particles, in whippable toppings. The α-gel phase is probably also responsible for the reversible whipping behaviour of GLP containing emulsions. However, we were not able to detect the presence of this gel phase in emulsions containing less than 80% GLP on dispersed phase basis. This could have been caused by the fact that the number of stacked bilipid layers is too small to be detectable.

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5 TEMPERATURE DEPENDENT PHASE BEHAVIOUR OF THE GEL PHASE OF α-TENDING EMULSIFIERS.

5.1 GENERAL INTRODUCTION.

In the previous chapter it has been shown that GLP forms an α-gel phase below the crystallization temperature of its hydrocarbon chains. All experiments were performed at room temperature. In this chapter a study will be presented on the temperature at which the gel phase of GLP arises and in addition, its melting properties will be investigated. Furthermore, the phase behaviour of an acetylated monoglyceride (ACTM) sample, being an example of another α-tending emulsifier, will be shown. We have briefly studied the properties of this commercial emulsifier in order to learn whether the formation of an α-gel phase is a common phenomenon in these complicated amphiphilic systems.

The proper technique to detect phase transitions in a system like mixtures of an α-tending emulsifier and water is differential scanning calorimetry. Additional information on the occurrence of fractionated crystallization may be obtained from these measurements. Fractionated crystallization of GLP from an oil phase would sustain the hypothesis that GLP is able to form an α-gel phase at the o/w-interface of fat particles in whippable emulsions.

5.2 RESULTS AND DISCUSSION

5.2.1 DSC-measurements on dry and hydrated α-tending emulsifiers.

In figure 5.1 crystallization curves for dry GLP samples are represented as measured with DSC at two different cooling rates. When the crystallization of GLP is measured at a cooling rate of 2°C/minute, it is observed that crystallization starts at 39°C and that two peaks are found at 38°C and 34°C respectively. At a cooling rate of 0.2°C/minute crystallization starts at a higher temperature. It seems likely that at this cooling rate fractionated crystallization occurs, resulting in the formation of two relatively large fractions near the initial temperature of crystallization. The results of SAXD experiments, represented in table 4.2, also indicated the possible occurrence of fractionation during crystallization. It is important to realize that a different temperature history of the sample may result in a different crystallization behaviour, since this might cause differences in composition of the α-gel phase or even the occurrence of polymorphic transitions in this phase.

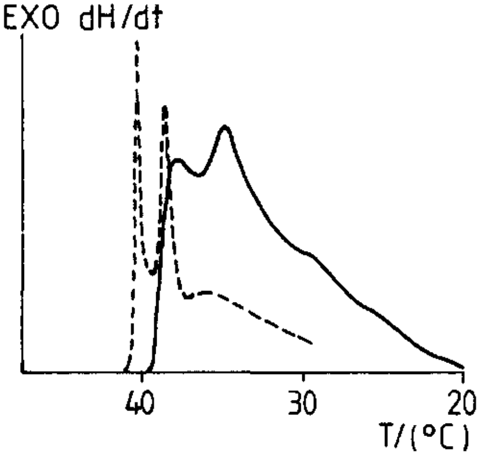


Figure 5.1 : Crystallization curves of dry GLP at two different cooling rates.
(———) : Cooling rate = 2.0°C/minute.
(- - -) : Cooling rate = 0.2°C/minute.

In table 5.1 the crystallization heat is represented for the curves of figure 5.1. It can be stated that this heat effect amounts to about 110 J/g, though this value is not quite accurate. DSC is not a very reliable method for calculation of the total heat flow, because the position of the base line in the cooling curves is quite uncertain. Yet the heat value of about 110 J/g will be used as a reference value for the crystallization of GLP from oil-emulsifier mixtures. Furthermore, this table indicates that the two fractionated peaks represent about 45% of the total heat content of the α-polymorphic form of GLP. In this chapter it will be shown that this amount is frequently encountered when crystallization occurs in GLP/oil mixtures.

Table 5.1 : Heat of crystallization for GLP at two different cooling rates.

Cooling-rate	important fractions	Total heat of crystallization (J/g)
2°C/min	-	102 J/g (40-10°C)
2°C/min	-	113 J/g (40-11°C)
0.2°C/min	19 J/g (41.0-39.2°C) 30 J/g (39.2-37.0°C) + 49 J/g (45%)	89 J/g (41-30°C)

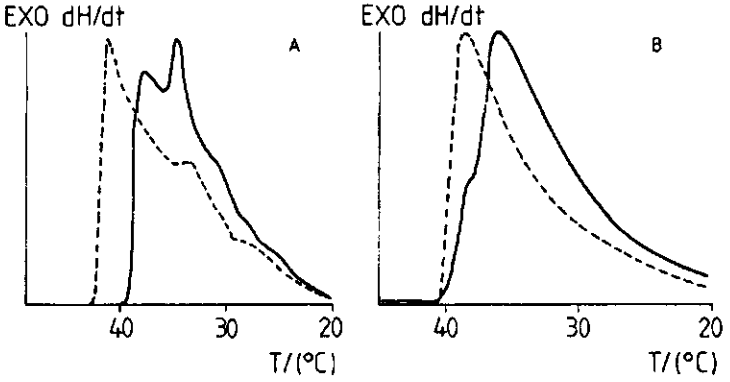


Figure 5.2 : The influence of water on the crystallization behaviour of α-tending emulsifiers as measured with DSC at a cooling rate of 2°C/min.
Fig 5.2A = GLP ; Fig 5.2B = ACTM.
(———) = water-free emulsifier.
(– – –) = emulsifier droplet in contact with a droplet of water.

In figure 5.2 the results are shown of the cooling curves of GLP and ACTM in the presence and absence of water at a cooling rate of 2°C/minute. From these cooling curves it appears that water causes a significant raise in the initial crystallization temperature of the emulsifier samples. Sodium caseinate does not influence this effect, because a comparable temperature shift was found in the absence or presence of this protein.

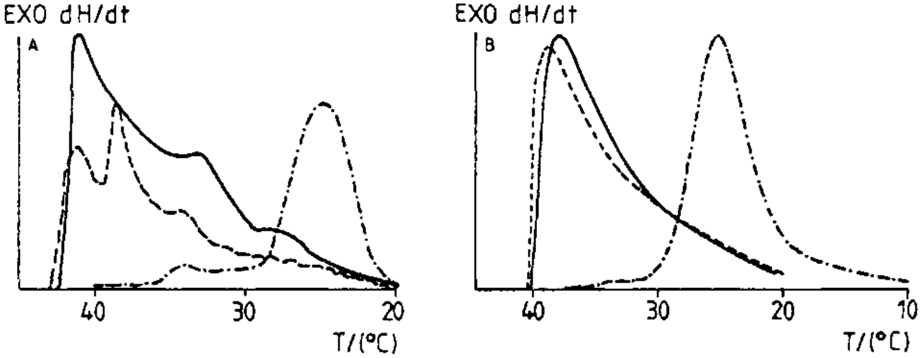


Figure 5.3 : The influence of homogenization on the cooling thermograms of two α-tending emulsifiers determined by DSC at a cooling rate of 2°C/min.
Fig 5.3A = GLP ; Fig 5.3B = ACTM.
(———) = droplet of water against a droplet of emulsifier.
(– – –) = 8% emulsion in 2% Nacas, homogenized at 10 MPa.
(–•—•–) = The same emulsion, but spray-dried.

As expressed in figure 5.3, homogenization does not markedly influence the temperature at which crystallization starts. Only at a very high homogenization pressure of 20 Mpa we found that the temperature at which crystallization starts is suppressed to a value of 38°C which was determined at a cooling rate of 0.2°C/min. Moreover, the thermograms of the water-free, spray-dried emulsions showed that the initial crystallization temperature strongly decreases. In this specific case it was observed that a small fraction of GLP crystallizes over a broad temperature range at a relatively high temperature. This may be due to initial crystallization in the relatively large particles present in the emulsifier powder, an effect which is also suggested by van den Tempel (1968).

The temperature shifts occurring in the cooling curves are important observations, because they mean that homogeneous nucleation is not the mechanism that causes initiation of crystallization in the emulsifier mixtures. Skoda & van den Tempel (1963) and Phipps (1964) showed that in finely dispersed triglyceride emulsions homogeneous nucleation is likely to occur because of the shortage or absence of catalytic impurities, which could act as heterogeneous nuclei. Skoda & van den Tempel (1963) and Walstra & Beresteyn (1975) pointed to the fact that monoglycerides strongly increase the initial temperature of crystallization of the triglycerides. These authors explained this effect by suggesting that micelles of monoglycerides, present in the oil droplets, may act as catalytic impurities. Another possible explanation may be that nucleation is promoted by mono- and diglycerides adsorbed at the o/w-interface according to Skoda & van den Tempel (1963) and van den Tempel (1967), because these amphiphiles are already oriented in a favourable position for crystallization at the interface.

In the case of the α-tending emulsifiers the mono- and diglycerides may also play an important role in the initiation of the crystallization of the complete mixture of glycerides. It is also possible, however, that the α-gel phase fraction itself initiates crystallization of the samples at the o/w-interface of the particles.

In table 5.2 it is shown that neither homogenization nor the presence of water significantly change the measured heat effect in the temperature range of 20-50°C at a cooling rate of 2°C/min. This also is a strong indication for the occurrence of heterogeneous nucleation in the majority of the emulsifier particles, because otherwise the measured heat effects in this temperature range should have been significantly lower.

The influence of water on the phase behaviour of α-tending emulsifiers was further studied by means of heating experiments. In order to exclude possible effects of difference in particle size between dry and wet samples we decided to study this behaviour on spray-dried emulsifier powders (see section 2.2.1). The emulsifier was completely crystallized before the powder was brought into contact with water.

Table 5.2 : The influence of homogenization on the heat of crystallization of some GLP-samples at a cooling rate of 2°C/minute.

Sample	Total heat of crystallization
<u>Droplets</u>	
GLP/water	107 J/g (43-21°C)
GLP/Nacas	83 J/g (43-17°C)
<u>Emulsions</u>	
50% GLP in 10% Nacas	92 J/g (43-16°C) (Sorvall)
10% GLP in 1% Nacas	110 J/g (43-16°C) (Sorvall)

In figure 5.4 these heating thermograms are shown in the case of a GLP and an ACTM powder produced at a homogenization pressure of 10 Mpa. It is obvious that the melting curves of both emulsifiers are shifted a few degrees towards a higher temperature, when the emulsifier particles are brought into contact with water. This experiment strongly indicates hydration of α-tending emulsifiers below the crystallization temperature of the hydrocarbon chains of the amphiphiles. Such an effect was expected to occur since in chapter 4 it had already been shown that a GLP-powder forms an α-gel phase at room temperature when it is dispersed in water.

The heating curves suggest that a large part of the emulsifier molecules participates in the hydration process, because the shift observed almost accounts for the complete melting curve. This effect was not expected to occur so explicitly. If the gel phase would be a part of the total emulsifier sample, it would have been likely that the melting peak of the hydrated emulsifier, in comparison with the dry sample, would have been broader or would even have been split up in two peaks. Instead the endothermic heat peaks of the hydrated samples are significantly sharper than those of the dry samples which may be indicative of better fitting of molecules with the bulky head groups into the crystal lattice of the α-gel phase.

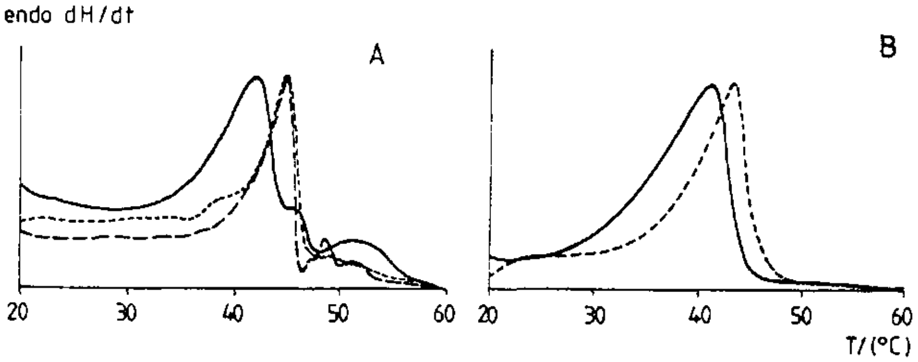


Figure 5.4 : Heating curves of completely crystallized dry and wet spray-dried emulsifier powders. Fig 5.4A = GLP ; Fig 5.4B = ACTM.
(———) Dry emulsifier powder.
(— — —) 50% Powder + 50% water.
(-------) 25% powder + 75% water.

Table 5.3 : The influence of water on the heat of melting of GLP particles in spray-dried powders. The rate of heating was 1°C/minute.

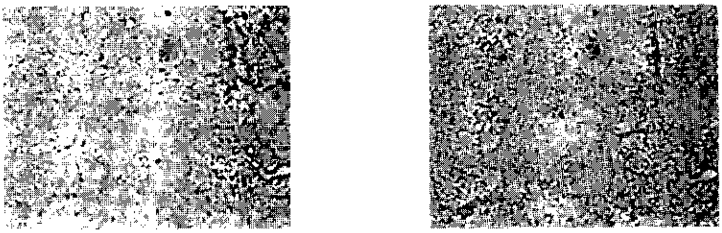
Sample	Total heat of melting
100 % powder 0 % water	116 J/g (26-57°C)
50 % powder 50 % water	125 J/g (31-55°C)
25 % powder 75 % water	105 J/g (31-55°C)

Table 5.3 represents the measured endothermic heat effects as a result of melting of GLP. From these results it can be concluded that the melting enthalpy of GLP is about 115 J/g which is just a little higher than the heat effect we measured in the cooling experiments. This means that the total GLP mixture crystallizes

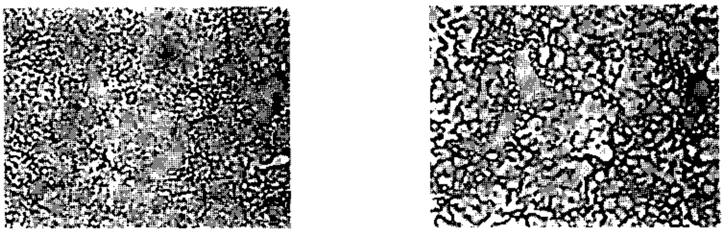
almost completely during cooling down at a rate of 2°C/min to a temperature of 20°C. For comparison the melting enthalpy of the α-polymorphic form of equimolar mixtures of cetyl- and stearyl-alcohol has a value of 128 J/g according to de Vringer (1987), which is in acceptable agreement with our results. Therefore, hydration occurs in the completely crystallized state of the chains of an α-tending emulsifier.

5.2.2 X-ray diffraction on dry and hydrated α-tending emulsifiers as a function of temperature.

In this paragraph the results will be presented of temperature dependent x-ray diffraction experiments carried out on the two α-tending emulsifiers studied. In fig 5.4 we showed that the main GLP fraction of the hydrated sample has melted at a temperature of about 46°C. In fig 5.5 a few micrographs (800x) are re-



T = 44°C   T = 45°C



T = 46°C   T = 48°C

Figure 5.5 : Micrographs (800x) of the gel structure of aggregated GLP particles in sequence of increasing temperature.

presented of the microscopical appearance of the structure of a 20% GLP-gel in a 3.3% sodium caseinate solution in sequence of increasing temperature. These micrographs clearly indicate that the aggregated particles coalesce at a temperature of about 46°C.

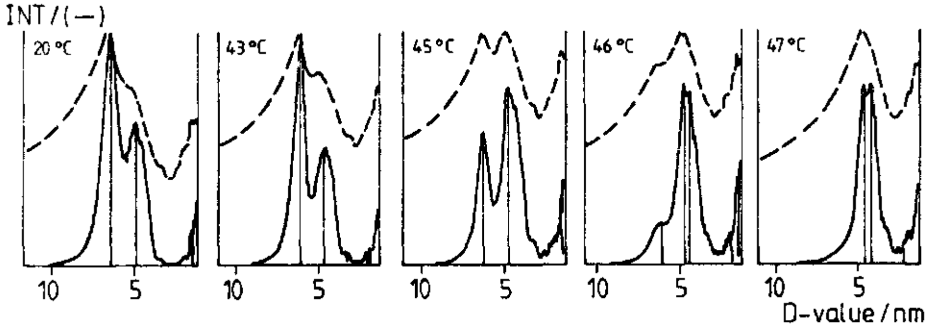


Figure 5.6 : X-ray diffraction curves of hydrated spray-dried GLP powders at increasing temperature. The results were obtained with the PSD.
(− − −) : Smeared curve.
(———) : Desmeared curve.

In figure 5.6 the SAXD curves of the hydrated GLP powder at different temperatures are shown. These curves are not corrected in such a way that the peak heights can be compared with each other. The intensity of the SAXD reflections decreases at increasing temperature. These curves indicate that partial hydration of the particles has occurred at room temperature (see also section 4.6). The long spacing of 62Å gradually disappears at increasing temperature, indicating that the α-gel phase melts over a wide temperature range. Furthermore, this experiment gives evidence for the assertion that GLP does not show mesomorphism above the melting temperature of its hydrocarbon chains. When dehydration occurs and the particles are flocculated in a primary minimum, the liquid particles are no longer stabilized against coalescence. Partial coalescence as a model for the aggregation of the GLP particles would give a comparable effect though (e.g. van Boekel, 1980). At 46°C the long spacing of the lamellar gel phase could indeed hardly be detected anymore which correlates nicely with the microscopical observation of droplet coalescence at this temperature.

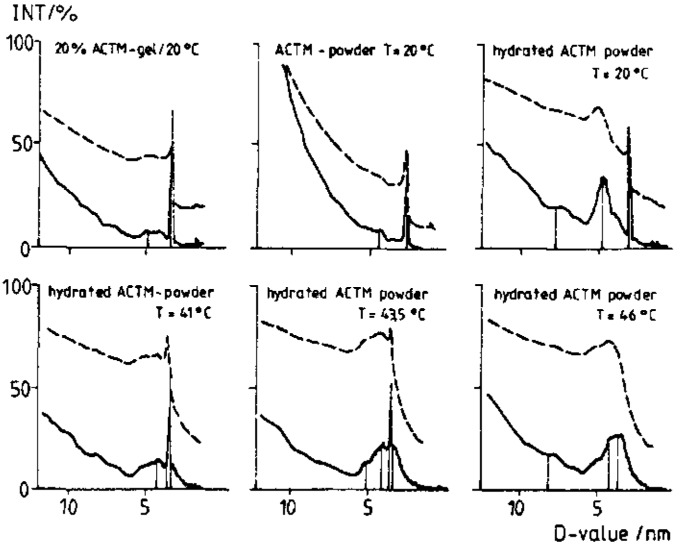


Figure 5.7 : X-ray diffraction measurements on dry and hydrated ACTM spray-dried powder samples and on a 20% ACTM-gel at increasing temperature.
(— — —) *Smeared curve.*
(———) Desmeared curve.

In figure 5.7 and table 5.4 the results of x-ray diffraction measurements performed at different temperatures with the dry and hydrated ACTM samples are shown. Also the result of a SAXD curve of a 20% ACTM gel, prepared at a homogenization pressure of 10 MPa followed by subsequent cooling to room temperature, is included. These results strongly differ from those obtained for GLP. It appeared that the long spacing of the dry emulsifier sample had a value of about 31.5Å, whereas the value of the hydrated sample amounted to about 33.7Å. Martin & Lutton (1972) reported that pure 1-acetyl-3-mono-glycerides, when crystallized in the α-modification, form monolayer crystal structures. For instance, the long spacing of crystallized, pure, 1-acetyl-3-glyceryl palmitate has a value of 30.2Å according to these authors. This value fits in fairly well with the long spacing of 31.5Å that we found for the dry ACTM powder sample. Besides, Vincent and Skoulios (1966) and Luzatti (1968) reported the existence of a monolayer type gel phase in the case of long chain potassium fatty acids.

Table 5.4 : The values for detected spacings of dry and hydrated ACTM samples at different temperatures with the PSD.

Sample	Temperature	Important long spacings (Å)		
20% ACTM gel	20.0°C	49.0	33.6	16.9
dry ACTM powder	20.0°C	48.9	31.8 s	16.0
	39.0°C	50.1	31.5 m	15.8
	41.5°C	49.2	31.5 w	----
	43.5°C	51.9	----	----
hydrated ACTM powder (70% water)	20.0°C	51.0	33.6 s	16.8
	41.0°C	40.8	33.8 m	----
	43.5°C	48.8	34.1 m	----
	46.0°C	----	----	----

Analogous to the results of GLP we found that hydration increases the temperature at which the long spacing of 33.7Å could still be detected, which is also a strong indication of this spacing, representing a hydrated crystal structure. In contrast to GLP gels, the ACTM gels were not stable. The samples showed strong shear-thinning behaviour. Microscopy revealed that the aggregated particles themselves are unstable. Apparently, a network of sintered crystals seemed to be formed. Partial coalescence may be excluded, since the particles are completely crystallized before they come into contact with water. Perhaps ACTM forms the so-called coagel state, which is often encountered in the case of amphiphiles that show polymorphism (e.g. Vincent and Skoulios, 1966 and Larsson, 1967). Furthermore, particle aggregates could not be disaggregated with SDS, in contrast to what had been found with the GLP gels. After a few days a weak macroscopical gel was formed in these samples, though, presumably caused by swelling of the hydrated crystals as a result of the uptake of SDS molecules in the crystal lattice of ACTM.

The main conclusion of this paragraph is that hydration of α-tending emulsifiers occurs below the melting temperature of the hydrocarbon chains of the emulsifiers. To a certain extent this is in contrast with literature concerning lyotropic mesomorphism, because it is often stated that hydration occurs near the cloud point of the amphiphiles. See for instance Hauser (1984) in the case of phospholipids and Krog and Lauridsen (1976) in the case of monoglycerides.

5.2.3 DSC-measurements on samples containing both GLP and an oil or fat phase.

In this paragraph the results of DSC-measurements on mixtures of GLP and an oil or fat phase will be shown. X-ray diffraction experiments, represented in chapter 4, could not prove that an α-gel phase is formed in emulsified GLP/oil mixtures with a mean particle size of about 0.5μm and a GLP/fat ratio lower than 0.8. Therefore, we tried to obtain evidence for this hypothesis with DSC measurements.

The crystallization behaviour of GLP/oil mixtures was studied with five different oils or fats. These samples were in sequence of increasing melting point : Medium chain length triglycerides (MCT-oil), Soy bean oil (SBO), Hardened coconut oil (HCNO), Hardened palm oil (HPO), and tripalmitin (GTP).

In figure 5.8 the crystallization curves of the three fat samples are represented at a cooling rate of 2°C/min together with the cooling curve for GLP. In the case of SBO and MCT no crystallization effects could be detected in the studied temperature range. GTP shows two peaks, probably caused by an occurring polymorphic transition during cooling. GLP has a crystallization curve situated between those of GTP and HPO in the cooling diagram.

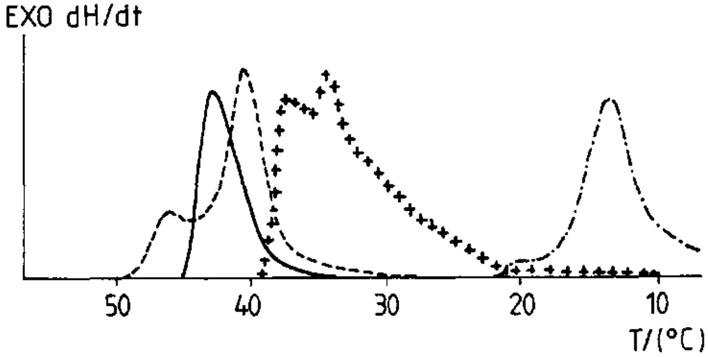


Figure 5.8 : DSC cooling thermograms of the three different fats and GLP used in the study on the formation of an α-gel phase in GLP/oil mixtures. The cooling rate = 2°C/minute.
(———) = HPO ; (— — —) = GTP ; (—•—•—) = HCNO (+ + +) = GLP.

In figure 5.9 the cooling curves of 15% GLP solutions in the mentioned oil phases are represented. From now on distinction will be made between oils that have a higher or lower crystallization temperature than GLP. If we first consider the results of the mixtures composed of GLP and a fat phase with a lower melting point, it is obvious that crystallization starts between the initial crystallization temperature of GLP and of the oil phase itself. Here we may have an indication for the occurrence of fractionated crystallization of GLP components from the oil phase. In the case of the GLP/SBO mixture the initial crystallization temperature is highest. This may be a result of the relatively low solubility of the saturated GLP glycerides in the largely unsaturated oil fraction of the SBO sample. All three samples show two small initial peaks, which may indicate the occurrence of fractionated crystallization of the GLP fraction itself.

In the case of fats that have a higher melting point than GLP the overall picture is different. The samples studied show a small decrease in the initial crystallization temperature of the total fat phase. This may be caused by a reduced amount of catalytic impurities, present in the oil/emulsifier mixture, which then results in delayed crystal formation. However, GLP molecules may also retard the incorporation of triglycerides into the crystal lattice. This latter hypothesis assumes the occurrence of fractionated crystallization of triglycerides from the total oil/emulsifier mixture. The confirmation of this hypothesis can not be obtained from these thermograms. However, it seems obvious that the high melting fats start crystallization, certainly in the case of GTP and that the polar molecules present in the GLP mixture are probably not involved in nucleation.

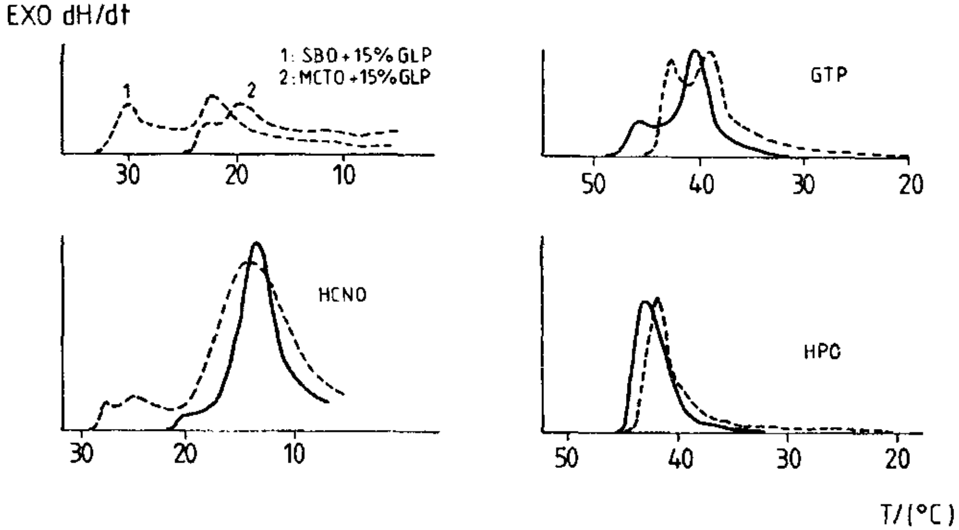


Figure 5.9 : Cooling thermograms of 15% GLP solutions in the 5 different oil samples. The cooling rate = 2°C/min.
(———) Cooling curve of the fat phase.
(— — —) Cooling curve of a solution of 15% GLP in an oil phase.

As we have shown that the crystallization temperature of GLP is markedly influenced by the presence of water, we also tried to prove such an effect in the case of oil-emulsifier mixtures. Again we will distinguish between fats with a lower and a higher melting point than GLP. Furthermore, the possible influence of the particle size will be included, since exhaustion of the more polar components of the total GLP fraction by interfacial adsorption is likely to occur.

In figure 5.10 the results are represented of DSC experiments with 15% GLP in oil solutions in contact with water including both bulk droplet experiments and emulsions. From the course of these curves the following conclusions can be drawn:

1) As has been found in the case of GLP, the presence of water increases the initial crystallization temperature of the oil/emulsifier mixture. The experiment with the HCNO sample probably shows that part of the total GLP fraction crystallizes separately from the total oil/emulsifier mixture. The large bulk fat peak is not influenced by the presence of water, whereas the small initial peak is shifted towards a higher temperature as would be expected, when hydration occurs.

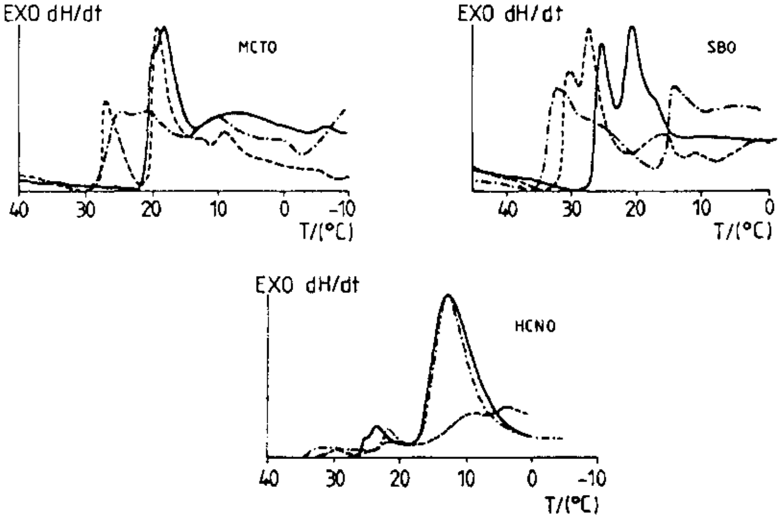


Figure 5.10 : The influence of water on the crystallization of GLP from 15% GLP in oil solutions. The cooling rate = 2°C/min.

(———) : Water-free emulsifier/oil mixture (15% GLP).

(—•—•—) : Droplet of emulsifier/oil mixture against water droplet.

(— — —) : The same sample emulsified in a 10% Nacas solution with a sorvall mixer at a 1:1 ratio.

Table 5.5 : The crystallization heat of GLP/oil samples in the presence and absence of water. Results were obtained from the curves of fig 5.10.

Sample	Important fraction Values calculated on GLP basis	Total heat of crystallization on GLP basis
MCT oil/15% GLP		
Water-free sample	49 J/g (37%) (22.0-13.0°C)	133 J/g (22 to -9°C)
Against droplet of water	48 J/g (44%) (30.0-16.2°C)	108 J/g (30 to -3°C)
Emulsion (50%) (+ 10% Nacas) Sorvall	17 J/g (17%) (29.0-21.5°C) 34 J/g (34%) (21.5-11.0°C) + -------------------------- 51 J/g (51%) (29.0-11.0°C)	100 J/g (40 to -10°C)
Soybean oil/15% GLP		
Water-free sample	25 J/g (20%) (28.0-23.0°C) 55 J/g (42%) (23.0-15.0°C) + -------------------------- 80 J/g (62%) (28.0-15.0°C)	131 J/g (28 to -4°C)
Against droplet of water	40 J/g (43%) (36.0-17.5°C)	93 J/g (36 to 0°C)
Emulsion (50%) (+ 10% Nacas) Sorvall	17 J/g (19%) (34.0-28.5°C) 26 J/g (30%) (28.5-22.5°C) + -------------------------- 43 J/g (49%) (34.0-22.5°C)	88 J/g (34 to 0°C)
Coconut fat/15% GLP		
GLP-free HCNO	3 J/g (3%) (23.0-20.0°C) 81 J/g (72%) (20.0-10.0°C) + -------------------------- 84 J/g (75%) (23.0-10.0°C)	113 J/g (24 to 0°C)
Water-free sample	13 J/g (11%) (27.0-18.5°C) (87 J/g on GLP basis).	120 J/g (27 to 0°C)
Emulsion (50%) (+ 10% Nacas) Sorvall	1.0 J/g (3%) (33.5-27.0°C) 3.2 J/g (11%) (27.0-19.0°C) + -------------------------- 4.2 J/g (14%) (33.5-19.0°C) (28 J/g on GLP basis).	29 J/g (34 to 0°C)

2) Compared to the results of the droplet experiments, emulsification lowers the temperature at which initial heat effects as a result of crystallization are detected. However, this temperature is still higher than the temperature in the case of the water-free emulsifier/oil samples.
3) The cooling curves seem to indicate the formation of two relatively large fractions during crystallization which may be due to fractionated crystallization of components of the total GLP.

This also appears from the measured heat effects, as represented in table 5.5, though these values are less accurate than those obtained for pure GLP, since the amount of emulsifier in the oil fraction is only 15%. In the case of the water-free emulsifier/oil and the droplet experiments the measured heat values may indicate that the complete GLP fraction crystallizes prior to the oil fraction in which it was dissolved, because these values are comparable with the enthalpic value of 110 J/g obtained for GLP itself. Furthermore, the heat effects in the case of the emulsions containing SBO or MCT as solvent for GLP are in good agreement with the results obtained for the droplet experiments.

In all the cases studied it was found that at relatively high temperatures the cooling curves contained two exothermic peaks, corresponding to a fraction of 40-60% of the total GLP sample. Perhaps these two peaks represent crystallization of the α-gel phase active components, though evidence for this hypothesis can not be given. Fractionation is likely to occur because it does not seem very likely that the complete fraction of lactylated components will be incorporated in the lattice of the gel phase both for steric and hydrophilicity reasons.

The result of the emulsified HCNO sample is rather contrary to the results of the non-homogenized samples, because only a relatively small part of the total emulsifier/oil fraction crystallizes during cooling to 0°C. We are not able to give a satisfying explanation for this specific effect. Without doubt, HCNO is the best solvent for GLP molecules of the three studied samples, but still we would not have expected that a good solvent would retard or prevent the formation of a gel phase during cooling, since hydration seems to be the most favourable energetic state.

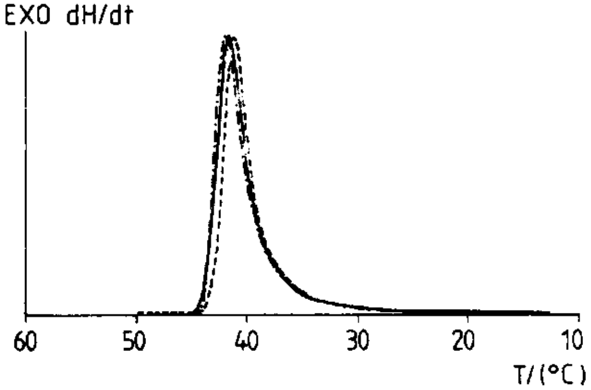


Figure 5.11 : DSC measurements showing the influence of water on the crystallization of 15% GLP solutions in HPO. The cooling rate = 2°C/min.
(———) water-free 15% GLP solution in HPO.
(—·—·—) droplet experiment.
(— — —) emulsion prepared with the sorvall mixer.

In figure 5.11 the results are represented of comparable DSC-experiments with fats that have a higher melting point than GLP. As would have been expected, water has hardly any influence on the initiation of crystallization of the emulsifier/oil mixtures. Systems emulsified with the sorvall apparatus show a small decrease in temperature at which the beginning of crystallization can be detected. This may be the result of a shortage of nuclei in the droplets necessary for the crystallization of the fat phase. When this kind of systems is homogenized at a pressure of 10 MPa, it becomes clear that GLP or at least a fraction of GLP crystallizes prior to the fat phase in which it was dissolved. As an example of this effect, the cooling curves of 10% HPO emulsions containing 2% sodium caseinate are represented in the presence and absence of GLP in figure 5.12. It is obvious that fat crystallization starts at a far lower temperature for a finely dispersed GLP-free HPO emulsion than in the case of the GLP containing sample.

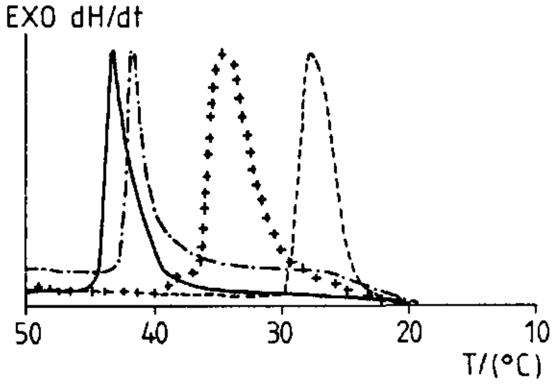


Figure 5.12 : The effect of homogenization on the crystallization curves of 10% fat phase containing GLP-free HPO emulsions and the same HPO emulsions containing 17% GLP on dispersed phase basis. The emulsions also contained 2% sodium caseinate. The cooling rate was 2°C/minute.
(———) HPO emulsion (Sorvall prepared).
(— — —) HPO emulsion (prepared at a pressure of 10 MPa).
(—•—•—) 17% GLP/HPO emulsion (Sorvall prepared).
(+ + +) 17% GLP/HPO emulsion (prepared at a pressure of 10 MPa).

As shown in figure 5.4, the melting curves of spray-dried emulsifiers shift to a higher temperature, when the samples are heated in the presence of water. In the case of samples that contain a large amount of fat in combination with GLP this is not found, because the endothermal peak of the melting fat phase overshadows the melting peak of the α-tending emulsifier. Therefore, we prepared a spray-dried topping powder that contained 80% SBO and 20% GLP on dispersed phase basis according to the procedure described in section 2.2.1.2. This powder sample was stored at room temperature during a period of one week after which DSC measurements were performed.

In figure 5.13 the melting curves of both a dry powder sample and a sample which was dispersed in water at room temperature are represented. These curves clearly show that in the case of the wetted sample the complete melting curve is shifted towards a higher temperature. This can only be explained by assuming that hydration of GLP has occurred, resulting in the formation of an α-gel phase. This gel phase melts at a lower temperature than the pure GLP gel phase. Thus the melting properties of the gel phase are influenced by the presence of an oil or fat phase which of course may be expected to occur.

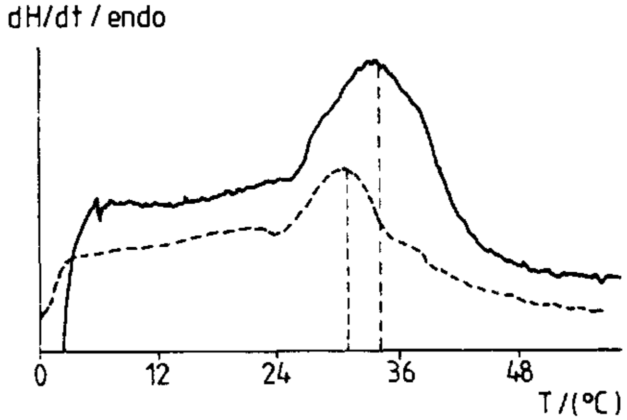


Figure 5.13 : The melting curves of spray-dried topping powders containing 20% GLP and 80% SBO on dispersed phase basis in the absence and presence of water.
(----) : Dry powder sample.
(———) : 50% powder + 50% H_2O (The dispersion was prepared at 20°C).

Finally, it may be concluded from all the obtained results described in this paragraph that GLP or a fraction of GLP most probably forms an α-gel phase, when crystallization occurs in mixtures of an oil phase and GLP in the presence of water. In the next paragraph the mechanism of this gel phase formation will be discussed.

5.2.4 General discussion.

The results of this chapter, obtained from combined DSC and SAXD measurements, provide strong evidence for the formation of a hydrated crystalline phase below the crystallization temperature of α-tending emulsifiers, like GLP and ACTM. The presence of water markedly influences both the crystallization and melting properties of these emulsifiers.

The melting temperature of the emulsifiers is shifted towards a higher temperature, when they are brought into contact with water. Such an effect has been observed with several other amphiphile/water mixtures. For instance Lawrence et al. (1967) showed that water increases the melting point of long chain alcohols, crystallized in the α-modification, for about three degrees. De Vringer (1987) found a comparable temperature effect for equimolar mixtures of cetyl- and stearylalcohol and for polyoxyethyleen glyceryl monostearate (PGM_{20}). On the other hand, the melting temperature of monoglycerides (e.g. Krog and Lauridsen, 1976) or phospholipids like lecithin (e.g. Hauser, 1984) decreases in the presence of water.

Up to now proper phase studies performed at temperatures, where chain crystallization occurs are rather scarce. Kodami and Seki (1983) have shown that several long chain amphiphiles, like phospholipids or potassium stearate, show stepwise chain melting as a result of hydration at increasing water content and they discovered a reversible coagel to gel transition in these systems, however, a molecular interpretation is not given for these effects. It is not known whether this reversible gel to coagel transition is a generally occurring phenomenon with amphiphiles. In this respect it may be noted that Krog and Lauridsen (1976) indicated that monoglycerides also show a reversible coagel to gel transition, since β-crystals hydrate a few degrees below the melting temperature of the hydrocarbon chains, leading to the formation of an α-gel phase.

It is obvious that the melting temperature of crystallized chains of an amphiphile depends, not only on the water concentration and hydrocarbon chain length, but especially on the nature of the polar head group. Hydration of the head group may cause both an increase or a decrease in the melting temperature of the chains, dependent on the fact whether hydration leads to an increase or a decrease in the lattice energy of the crystalline amphiphile. In the case of the studied α-tending emulsifiers both a decrease in steric headgroup repulsion between molecules in opposite layers and formation of hydrogen bonds may play an important role in the raise in the melting point.

In the previous chapter it was maintained that a proper phase diagram of GLP/water mixtures can not be given. Yet, on the basis of the results obtained from combined SAXD and DSC measurements, we will try to define phase diagrams for the two studied α-tending emulsifiers GLP and ACTM. From the experimental results represented in chapter 4 and 5 it may be concluded that GLP is very stable in the α-crystalline modification. The two spray-dried α-tending emulsifiers, which were stored either at 4°C or at room temperature for a period longer than 6 months, proved to be stable in the α-modification. When these samples were brought into contact with water at room temperature, hydration, though not completely, occurred within 12 hours as observed with SAXD. The intensity of the reflection of the long spacing of the gel phase of the α-tending emulsifiers gradually decreased at increasing temperature. Presumably, this indicates that during chain melting the gel phase progressively dissolves in the melted fraction of the emulsifier. Therefore, an exact melting point of the α-gel phase cannot be given. However, both from x-ray diffraction and DSC it can be concluded that the terminal melting points of the completely hydrated gel phase of GLP and ACTM are roughly 46°C and 44°C, respectively. It is doubtful whether in the case of the hydrated ACTM phase the term α-gel phase is allowed to be used. Perhaps it is better to refer to this system as hydrated crystals or as a coagel phase, like the type described by Kodama and Seki (1983).

The α-gel phase of GLP is also very stable at 4°C. Over a period of one month no coarsening of the aggregated particles was ever observed and the spacing of 63Å did not disappear nor could we detect the formation of different polymorphic form with SAXD. This is a very important observation, since it makes GLP to be a versatile agent for industrial application as an inducer of long-term stable aggregation of fat particles in emulsions. From the results of this chapter concerning hydration of ACTM we must conclude that this α-tending emulsifier is not a good stabilizer of aggregated particles. This assumption is in good agreement with the observation made by Andreasen (1973), that ACTM-containing topping emulsions do not show a gradual increase in viscosity of topping emulsions at relatively high emulsifier concentrations (see also figure 3.1). Furthermore, Wilton and Friberg (1971) showed that polymorphic transitions in an α-gel phase stabilized o/w-emulsion of GMS in soybean oil caused a complete breakdown of this emulsion. The same effect was indicated by Fukushima and coworkers (1976) for emulsions stabilized by cetylalcohol or by stearylalcohol. They also showed that mixtures of these two alcohols could stabilize these emulsions and polymorphic transitions were not observed.

Thus these results seem to indicate that the formation of mixed crystals is favourable for the stability of the α-gel phase of an amphiphile. Other scientists also reported such an effect like the stabilization of the gel phase of monoglycerides by small amounts of fatty acids (Krog and Borup, 1973) or by the addition of lecithin (Kurt and Broxholm, 1968). Crystallization in the α-modification is a prerequisite for the formation of gel phases, though the reason for this is not known. Besides, Krog and Lauridsen (1976) assert that emulsifiers, which are non-polymorphic and stable in the α-modification, may form gels with water which show a long-term stability (e.g. : sodium stearoyl lactylate, tetraglycerol monostearate and polysorbates). Therefore, it is clear that α-tending emulsifiers, which are believed to be non-polymorphic as a result of mixed crystal formation, are potential gel phase forming amphiphiles. The stability of the α-polymorphic form of GLP or ACTM is probably determined for an important part by steric repulsion of the bulky head groups of the lactylated and acetylated components respectively. Hydration of the head groups may provide an additional stabilizing effect.

In figure 5.14 two still rather speculative phase diagrams of mixtures of water and the studied α-tending emulsifiers are represented. The low water concentration region has not been studied intensively. We have to add that these diagrams may depend on the particle size, since fractionation of specific components at the o/w-interface may cause differences in crystallization behaviour and in the temperature at which the samples were brought into contact with water. Furthermore, the melting line, indicated as T_m, may not be regarded as the cloud point, since complete phase separation will occur above the melting temperature of the emulsifiers.

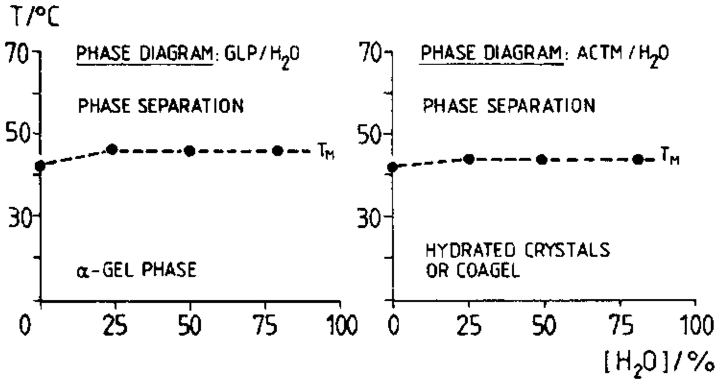


Figure 5.14 : The phase diagrams of the α-tending emulsifiers GLP and ACTM and water in the temperature range of 4-60°C. The T_m-line indicates the melting temperature of the α-modification of the emulsifier.

The crystallization temperature of all the samples containing the α-tending emulsifier GLP or ACTM is increased in the presence of water, as indicated in section 5.2.1. One way to achieve such an effect is by the presence of micelles of mono- and diglycerides in the liquid emulsifier sample, which could act as heterogeneous nuclei, according to e.g. Skoda and van den Tempel (1963). However, another possible mechanism may well be interfacial nucleation, since water may orient polar amphiphiles at the o/w-interface. Besides, the low curvature of the oil-water interface is more favourable for initiation of crystallization than the high curvature of spherical micelles, though the extent of this specific effect probably is of minor importance. Especially, the DSC experiments between contacting droplets of an α-tending emulsifier and water suggest the occurrence of such a nucleation process. Interfacial nucleation could be regarded as an important prerequisite for the formation of the α-gel phase of the emulsifier mixture at the interface of the fat particles. For, if the aggregated fat particles are supposed to be stabilized by an α-gel phase, this phase should be present at the interface.

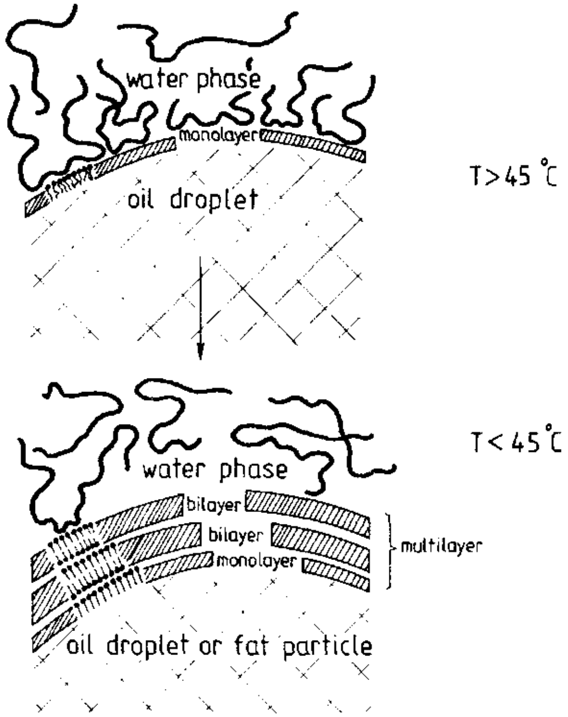


Figure 5.15 : Model of the temperature dependent α-gel phase formation at the o/w-interface of fat particles in an emulsion which contains both sodium caseinate and GLP.

In this interfacial nucleation process in principal many polar amphiphilic components should play a role. For, if an interfacial gel phase, consisting of only monoglycerides in the first bilayer, would be formed, we would have a situation as in a topping emulsion containing monoglycerides. It has already been stated that these emulsifiers do not cause extensive fat particle aggregation. The relative stability of GMS containing topping emulsions may be explained either by specific interactions between this specific α-gel phase and the present proteins according to Barfod and Krog (1987) or by possibly occurring polymorphic transitions in this gel phase leading to increased interaction of the proteins with lipid molecules present at the interface.

In the case of GLP containing topping emulsions we suggest a temperature dependent model as shown in figure 5.15. At a temperature exceeding the melting point of the amphiphile mixture the emulsion is stabilized by the proteins that are usually present and perhaps by the relatively more hydrophilic components of the added emulsifier. Below the melting point of the emulsifier an α-gel phase is formed at the o/w-interface, the stabilizing proteins desorb from the interface and subsequently spontaneous flocculation occurs.

The particles do not coalesce because of the stabilizing repulsive hydration force exerted by the hydrated emulsifier molecules. Aggregated particles coalesce when the gel phase melts, because the stabilizing repulsive hydration force will be lost at this temperature. Therefore, these emulsions show irreversible behaviour during a temperature cycle around the crystallization temperature.

The last ten years a better insight into hydration forces has been obtained. Israelachvili (1985) has written a comprehensive review on the nature and on how to measure these forces. Hydration forces are only active over a very short range of at most about 40Å. If electrostatic repulsion is of no importance, thus in the case of neutral amphiphiles or ionics at high salt levels, amphiphiles may form mesomorphic structures as a result of the van der Waals attraction force. If no other repulsive force would exist, the van der Waals interaction would eventually cause complete phase separation, but the repulsive solvation forces will stabilize these structures. In this respect it is significant to mention that Parsegian and co-workers (1979) and Lis and Parsegian (1982) have shown that hydration forces form a strong barrier to both bilayer aggregation and fusion of phospholipid membranes. Their measurements indicated that the repulsive hydration force roughly decays exponentially with a constant decay factor of about 2.5Å. The gel phase of GLP is probably also stabilized by such a repulsive hydration force. The van der Waals attraction causes the emulsifier or fat particles to be flocculated in a relatively deep energy minimum, because of the short range repulsive nature of the hydrated bilipid layer. However, this energy minimum is not so deep that the particles can not be disaggregated by the shear forces exerted during a whipping process. Thus, the gel phase is closely involved in the reversible whipping properties of GLP containing topping emulsions. In the next chapter order of magnitude calculations will be presented on the strength of both interparticle bonds and on the modulus of particle gels.

5.3 SUMMARY

In this chapter it has been shown by means of DSC and SAXD that α-tending emulsifiers like GLP or ACTM are hydrated below the crystallization temperature of their hydrocarbon chains. GLP forms a hydrated bilipid layer structure, whereas ACTM forms a monolayer type hydrated structure.

The α-gel phase of GLP is very stable. The α-polymorphic form probably is the only crystal polymorph that is formed in the temperature range of 0-45°C and the addition of a sufficient amount of water leads to gradual hydration of these α-crystals. Above the melting temperature of the gel phase dehydration occurs. Water obviously has lattice structure inducing properties, since both the crystallization and melting temperature of the α-tending emulsifiers is significantly raised in the presence of water.

When GLP is dissolved into an oil or fat phase above its melting point, it crystallizes separately from the oil phase. The presence of water strongly promotes this process. Probably nucleation starts at the oil-water interface itself, though it may not be excluded that micelles of a more polar nature can also act as heterogeneous nuclei.

This knowledge is highly relevant for a better physical understanding of this system, since it was postulated in chapter 3 that the α-gel phase of GLP probably sticks fat particles together in a whipped topping to form large particle aggregates with reversible properties.

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6 VISCO-ELASTIC PROPERTIES AND FRACTURE BEHAVIOUR OF GELATINIZED EMULSIONS CONTAINING GLP.

6.1 INTRODUCTION.

In the two previous chapters it has been shown that the α-tending emulsifier GLP forms an α-gel phase below the melting point of the hydrocarbon chains of the emulsifier molecules in the presence of water. It was postulated that this α-gel phase is formed at the o/w-interface of the fat particles in which the emulsifier was dissolved. Within this hypothesis it is thought that the fat particles in the whipped emulsion are tightly bound to each other with this gel phase.

In chapter 3 it has been shown that during prolonged whipping of a topping emulsion containing a relatively high amount of GLP, the overrun and foam stiffness do not change significantly. This implies that the network of particle aggregates, present in these emulsions should be able to restore itself after disturbance leading to fracture or yielding of this network. Such a continuous restoration of a network after disturbance can only be understood, if breaking and formation of bonds between the structure elements is reversible within a certain time scale.

This reversible behaviour should be related to specific rheological properties of such a particle network. In this chapter a rheological study on this reversibility is presented. The shape of the individual particles and the microstructure of the particle network has been investigated too, because these parameters may largely influence the rheological and fracture behaviour of particle gels. In the last paragraph of this chapter some order of magnitude calculations for the stiffness of these gels will be shown.

6.2 RHEOLOGICAL AND FRACTURE PROPERTIES OF VISCO-ELASTIC GELS.

Relevant literature on the rheological and fracture properties of visco-elastic foodstuffs is very scarce. In this chapter much use was made of the comprehensive thesis of Luyten (1988) on this specific subject. Though this thesis has been written for cheese, being an example of such a visco-elastic product, this work obviously has a more general applicability.

According to Reiner (1971) a descriptive definition for rheology is the science which studies the deformation of a material as a result of an applied stress (force/unit area) at a certain time scale. By the term time scale one should understand the period of time at which a force is exerted on the studied material. In the context of this definition materials may be divided into three, distinct groups i.e. elastic, viscous and visco-elastic materials.

The first two groups consist of materials of which the ratio between stress and strain (or strain rate) is time scale independent. An ideal elastic or Hookean material will deform fast to a certain deformation as a result of the exerted stress. When this applied stress is taken away, the material will readily regain its original shape. Thus all the elastic or stored strain energy is released. In the case of linear viscous or Newtonian liquids the ratio between stress and deformation rate is constant and is called the viscosity (Ns/m^2). In the case of a viscous material all the added energy will be dissipated, meaning that the shape of the material after the moment of stress removal is completely retained after it has been taken away.

Visco-elastic materials show both kinds of properties, but the extent depends on the time scale of the experiment. At relatively short time scales the material will behave in a more elastic way, whereas at long time scales viscous effects become of major importance. On a microscopical level this can be explained as follows. At a relatively short time scale many bonds will contribute to the structure of a material and during deformation elastic energy may be stored in them. However, eventually at relatively large time scales bonds may break spontaneously due to heat movement, resulting in a process of energy dissipation. In a stressed material broken bonds do not reform aselectly but preferentially in a stress free state. This process results in viscous flow and thus in permanent deformation. The amount of energy dissipation at a certain deformation rate is reflected in the value of the viscosity.

Rheological experiments can be accomplished in many ways. They all have in common that both the stress and the deformation or deformation rate of the material is measured during a certain period of time. The rheological experiments done in this study were uniaxial compression tests between two flat plates, performed with a tensile and compression testing instrument (see chapter 2). Therefore the formulas for stress and strain used in this chapter will directly refer to this type of test.

The stress σ (N/m^2) in a sample is defined as the force F exerted on it per unit area A :

$$\sigma = \frac{F}{A} \qquad (\ 6.1\ )$$

In the case of an uniaxial compression test the stress is not constant during deformation, because sample deformation causes an enlargement of the total loaded sample surface. Thus the actual stress should be calculated from the new surface area which of course will depend on the sample strain. If it is assumed that the volume of a cylindrical test piece remains constant, which will probably be not too far from reality, the stress-bearing area A_t (m^2) equals :

$$A_t = \frac{H_0 A_0}{H_t} \qquad (\ 6.2\ )$$

where :

H_0 = Initial height of the sample (m)
A_0 = Initial stress bearing area (m^2)
H_t = Sample height at time is t (m)

To compare rheological experiments a size independent measure has been defined for the deformation of a sample which is called the strain. According to Whorlow (1980) the strain may be regarded as the deformation relative to the original dimensions of a material as the original distance between the considered different points approaches to zero. For the dimensionless strain the sign ϵ is usually taken. Several formulas exist for the calculation of a value for the strain of a deformed sample (Peleg, 1977 and 1984).

At relatively small deformations the relative strain in a sample may be calculated as being the Cauchy strain ϵ_c (-) :

$$\epsilon_c = \frac{\delta H}{H_0} \qquad (6.3)$$

where δh is the change in sample height and H_0 is the initial height of the gel sample. However, at larger deformations the Hencky, true or natural strain ϵ_h (-) is frequently used :

$$\epsilon_h = \int_{H_0}^{H_t} \frac{dH}{H} = \ln \frac{H_t}{H_0} = \ln (1 - \epsilon_c) \qquad (6.4)$$

where H_t is the sample height after a certain deformation. Since ϵ_h takes into account any strain change in a deformed material this value is a better representation for the real strain in a sample. Thus the Hencky strain definition will be used in all our real stress and strain calculations.

The compression rate V_{def} (m/s) is defined as :

$$V_{def} = \frac{dH}{dt} \qquad (6.5)$$

As the height of the sample decreases during compression, the relative rate of deformation according to the Hencky definition will increase, when using a constant compression rate. Therefore the Hencky strain rate $\dot{\epsilon}_h$ (s^{-1}) will be used to express the real deformation rate of a sample in a compression test :

$$\dot{\epsilon}_h = \frac{d\epsilon_h}{dt} = \frac{dH}{H_t dt} = \frac{V_{def}}{H_t} \qquad (6.6)$$

Especially at relatively large compressive deformations the strain rate may increase significantly, which may be of great importance for the behaviour of time-dependent materials as it will appear later.

The formulae for ϵ_h and $\dot{\epsilon}_h$ only count for the overall strain and strain rate. However, the values for the three-dimensional strain and strain-rate may locally differ from the overall values as a result of e.g. friction and barreling (Luyten, 1988 and van Vliet et al. , 1989).

The ratio between stress and strain is defined as the modulus E (N/m^2) of a material. For a linear elastic material this ratio is constant, but most materials show non-linear behaviour at relatively large deformations accompanied by flow or fracture phenomena. The initial slope of the stress-strain curve may then be used as an acceptable estimation of the Young modulus at the considered $\dot{\epsilon}_h$, if the consequences of non-linear behaviour are absent at this level of deformation :

$$E = \left(\frac{d\sigma}{d\epsilon} \right)_{\epsilon \longrightarrow 0} \qquad (6.7)$$

Knowing the shape of the stress-strain curve is of great importance. For instance if the slope of this curve is decreasing this may be indicative of energy dissipation due to yielding or local fracture inside the material according to Calzada and Peleg (1978) and van Vliet et al. (1989). On the other hand if the slope increases, this may be indicative of the occurrence of different structural changes like e.g. the straightening of coiled chains in a rubber-like material (Treloar, 1975) or non-homogeneous deformation (van Vliet et al. , 1989).

Visco-elasticity may strongly influence the rheological behaviour of a material :

1) The stress required to obtain a certain strain level for a sample decreases at longer time scales. Consequently the amount of stored energy per unit volume decreases at a decreasing strain rate.
2) The value of the modulus will decrease at longer time scales.
3) Part of the deformation is permanent.

Therefore it will not be surprising that visco-elasticity will also largely influence the fracture properties of a gel sample. For completely elastic materials the so-called LEFM theory (Linear Elastic Fracture Mechanics) has been developed (see e.g. Ewalds and Wanhill, 1984). This theory has been extended for materials that show limited flow near a crack tip, which is the point from where fracture proceeds. This theory is called the EPFM theory (Elastic Plastic Fracture Mechanics). A start for a qualitative theory on fracture of visco-elastic systems has been given by Luyten (1988) and van Vliet et al. (1989). On account of the importance of yielding and fracture in the case of our GLP gels, which are visco-elastic (see further on), we will now briefly discuss the major features of fracture of visco-elastic gels.

A material will fracture, when a crack, slit or different kind of defect grows, ultimately resulting in a situation, where the material falls apart. Materials will start fracturing if the internal cohesive or adhesive forces are not able to counterbalance the stress exerted locally. The fractured area will grow spontaneously if the amount of strain energy which releases during fracture is at least equal to the energy which is necessary for the formation of new fractured area. Thus in fracture two different stages may be distinguished namely fracture initiation and fracture propagation.

Fracture always starts near defects, inhomogeneities or slits. This is caused by the fact that the stress in the neighbourhood of defects is higher than the overall-stress in the sample. This effect is called stress concentration. The extent of stress concentration depends both on the shape of an irregularity and on the mechanical connections between rows of structure elements carrying the stress in a network of a certain material. If such connections exist, the local stress at the crack tip will be increased more than far from this tip. This effect is called notch sensitivity. A notch insensitive material contains only a negligible number of these connections or none at all.

Whether fracture will propagate depends on the possibility of energy transport to the newly-formed crack tip. This will only occur in a notch sensitive material, where energy may be transported perpendicularly to the stress trajectories. Therefore in the case of a visco-elastic material we should consider the energy balance near the crack tip in the applied stress time scale.

For a LEFM material the following equation counts for the specific fracture energy R_S (J/m^2) for an elliptical crack in a large plate :

$$R_S = \frac{\pi \sigma_f^2 l}{2 E} \qquad (6.8)$$

where σ_f is the overall stress at fracture, l is the crack length and E is the modulus of the material. This formula is deduced from the balance between the energy that is released during fracture of a certain material and the energy which is necessary to form new surfaces. It is actually the lower limit for spontaneous crack growth of a LEFM material (Luyten , 1988).

The total amount of energy that has to be supplied to a material to produce a fracture surface of one unit length is defined as the material toughness R (J/m^2). Its value obviously is much larger than R_S for several reasons. Part of the supplied energy is stored in the material as strain energy and part of it may be used for energy dissipation, expressed as flow. Furthermore, fracture surfaces are often not smooth but rather rough (Andrews, 1980). For limited flow the fracture parameters may be estimated by EPFM, which assumes that flow occurs just in the vicinity of the crack tip, because only in this region the yield stress of the material is reached. EPFM may not be used anymore, when the yield stress of the material is much lower than the fracture stress and not too much different from the overall stress at fracture far from the crack tip according to van Vliet et al. (1989). For then, extensive flow will occur in the material at relatively large stresses. This flow process will obviously consume the greater part of the energy supplied. Different energy dissipation processes, occurring at large deformations, may be flow of liquid through the matrix or relative movement of structure elements caused by internal friction between those elements (Luyten, 1988 and van Vliet et al. , 1989)

Summarizing it can be concluded that a possible attack towards a proper study of fracture parameters for a visco-elastic material may be the determination of the following energy balance according to e.g. Atkins and Mai (1985), Luyten (1988) and van Vliet et al. (1989).

$$W = W' + W'' + W_f \qquad (6.9)$$

where : W = The total energy input (J/m^3)
W' = The stored strain energy (J/m^3)
W'' = The energy dissipation component (J/m^3)
W_f = The energy used for the formation of new fracture surfaces (J/m^3)

In this chapter we will not elaborate equation 6.9, because the compression measurements performed, appeared to be unsuitable for a semi-quantitative calculation of the individual components. However, for a qualitative interpretation of the experimental results the concepts underlying 6.9 are certainly useful.

6.3 DISCUSSION ON METHODS FOR RHEOLOGICAL AND FRACTURE MEASUREMENTS ON PARTICLE GELS.

There are various ways to deform a material in order to gather knowledge about the rheological and fracture properties of a visco-elastic material (e.g. Whorlow, 1980 and Luyten, 1988). In this study only uniaxial compression tests were applied. In these tests a cylindrical test piece is deformed at a constant compression rate between two plan parallel plates, whereby the force is recorded as a function of time. Compression has a few drawbacks compared to e.g. tension if one wants to get fundamental information about fracture properties (Peleg, 1977 and 1984 or Luyten 1988). The major disadvantages are :

1) Friction between the test piece and the plates may result in increased stress values. The extent of this effect strongly depends on the sample height to diameter ratio (Chu and Peleg, 1985 and Luyten, 1988).
2) Values for σ_{max} and ϵ_{max} found in compression are usually higher than in the case of bending or tension methods (e.g. Pollak and Peleg, 1980 and Luyten, 1988). This may imply fracture or yielding processes to occur before σ_{max} or ϵ_{max} is reached, which makes it difficult to determine the values for these parameters. This effect is possibly caused by the limited speed of crack growth, resulting in that it takes a certain time before a crack starting in the center of a sample can be seen at the outside.
3) Compression tests are unsuitable for the determination of a material's notch-sensitivity. To this end bending tests or especially tension tests are more suited. In the case of these tests fracture stress and fracture propagation is studied as a function of the length of a notch introduced prior.

We have chosen to perform compression tests primarily because of the relatively experimental simplicity. GLP gels are difficult to handle, since local fracture or permanent sample deformation occurs very easily, making tension and bending tests extremely difficult to carry out. Cutting tests as described by Atkins and Vincent (1984) might prove to be an elegant alternative for proper study of the toughness and the specific fracture energy of visco-elastic gels. Then the energy balance 6.9 could be estimated.

Friction has influenced the results of our compression tests to a certain extent, because during compression barreling was observed. Consequently, values obtained for fracture stress and strain may be too high. However, this effect was probably not of great importance. Compression causes water to separate from the gel samples, especially at low volume fractions of dispersed phase ($\phi < 15\%$). This water may act as a lubricant, which gives a reduction of friction.

Furthermore, it has already been stated that friction becomes of greater importance at relatively low height to diameter ratios. We applied a value for this ratio equal to about 1.3. It was not possible to increase this ratio towards a much higher value, because the preparation of undamaged specimens would become too difficult.

6.4 RESULTS AND DISCUSSION

6.4.1 The microstructure of GLP particle gels.

In chapter 3 a few experimental results on the whipping properties of 5% GLP gels in aqueous solutions containing 2% sodium caseinate were shown. These whipping properties probably are closely related to the formation of the α-gel phase of the GLP. The microstructure of these gels and the structure of the individual GLP particles will also be of great importance for the rheological properties of these GLP gels and their whipped products. In the present paragraph the microstructure of these gels will be treated into further detail. In the next paragraph we will present a few results of experiments dealing with individual GLP particle shape estimation.

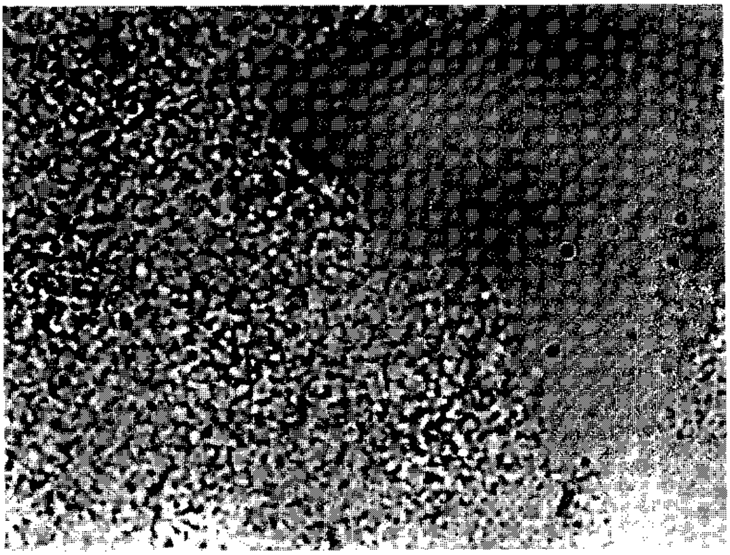

Figure 6.1 : A micrograph of the structure of a diluted 5% GLP gel in a 2% sodium caseïnate solution at a magnification of 1000x determined at ambient temperature.

In figure 6.1 a micrograph is shown of the gel structure of a diluted sample of a 5% GLP gel in a 2% sodium caseinate solution at a magnification of 1000x. Presumably the gel structure consists of flocculated GLP particles in a continuous water phase. It is not known, whether part of the α-gel phase of GLP will go into the water phase during gel phase formation. This effect, sometimes referred to as the so-called Lanza process, can only occur if the contact angle is very small which might be the case for GLP particle gels. However, we think that the individual particles will remain intact during the interfacial crystallization process of the GLP molecules. This process then causes the formation of crystalline shells around the particles (see section 4.3). Of course swelling will cause a reduction in the attractive forces between the bilipid layers of the gel phase, but presumably the van der Waals forces will be strong enough to keep the bilipid layers aggregated, if the distance between the bilipid layers is smaller than 10 Å (see section 6.4).

The micrograph represented in figure 6.1 also shows, despite its low measure of sharpness, that the individual crystallized GLP particles are not spherical, but they seem to have a cylindrical or platelet-like geometry. For geometrical reasons it is to be expected that the shape of the liquid GLP particles will not remain spherical during gel phase formation. The reason for this is that crystallization of the GLP mixture in the form of lamellar structures of bilipid gel layers demands these particles to adopt a flat structure. In this respect one should realize that the formation of a multi-lamellar structure of crystalline bilipid layers from the original sphere geometry would be the most favourable energetic state from a thermodynamic point of view. Of course this is only valid when side effects of this gel phase with respect to the continuous water phase could be disregarded. Therefore crystallization of the particles should cause them to deform into small cylinders or platelets. Buchheim et al. (1985) showed with transmission electron microscopy that fat particles which contain a relatively high level of an α-tending emulsifier, like GMO (glycerol monoöleate) or PGMS (propylene glycol monostearate) also strongly deform in contact with water. They stated that the fat particles in a topping powder change from spheres into platelets when the powder is wetted, especially in the case of GMO.

In figure 6.2 the result is shown of a SEM-micrograph for a comparable GLP gel as described just before. From this picture it also appears that the GLP particles become strongly deformed from their originally spherical geometry into anisometric particles. However, this photograph should be looked at with care, because the applied cryo-technique may have caused the formation of water crystals. Yet we think that this SEM-micrograph supplies circumstantial evidence for the formation of anisometric particles below the melting temperature of GLP.

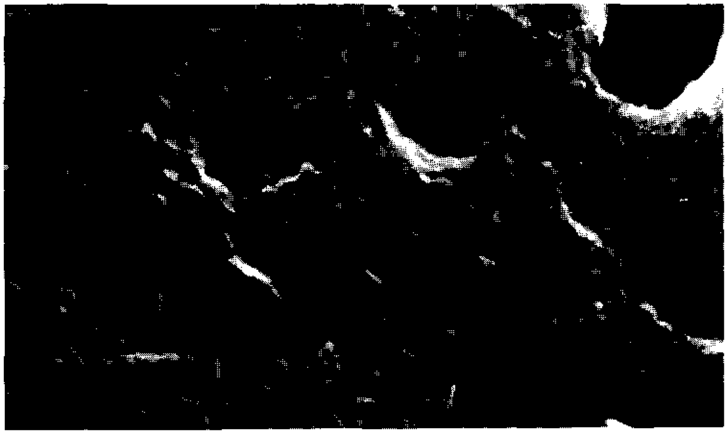

Figure 6.2 : A SEM-micrograph of the gel structure of a 10% GLP particle gel in a 2% sodium caseinate solution at two different magnifications.

Particle geometry changes of course should have a large influence on the rheological properties of whipped toppings, since in the case of an increased contact area between the aggregated particles the physical bonds between the particles will become effectively stronger. This effect should therefore be included in our model calculations for the modulus of the GLP particle gels in the last part of this chapter. In the next paragraph we will make an attempt to estimate the shape of the GLP particles by means of the results obtained with capillary viscosimetry.

6.4.2 Estimation of the shape of GLP particles in diluted GLP dispersions.

In order to be able to know the shape of GLP particles in aqueous dispersions we applied capillary viscosimetry. To this end the viscosity of these dispersions should normally be measured in a Couette-type apparatus, where the samples are placed in the annular gap between two concentric cylinders and where one of the cylinders rotates at constant angular velocity. However, it is doubtful whether in our case this method would be sensitive enough to measure the viscosity at low volume fraction. Therefore we applied capillary viscosimetry which usually gives accurate and reproducible results for the viscosity of the dispersion.

However, the great disadvantage of this method is that over the cross-section of the capillary there is a gradient in shear rate, which may strongly effect the viscosity measurements in the case of dispersions of non-spherical particles. This may be explained as follows. At a low shear rate small, anisometric particles do not become oriented by the velocity gradient in the liquid. Brownian movement causes the particles to be isotropically distributed in the liquid. At an increasing shear rate the viscosity of the dispersion decreases as a result of increased orientation of the particles. Since the viscosity of a dispersion of non-spherical particles therefore depends on the shear rate of the experiment, it may be clear that precise particle shape calculations from the viscosity obtained by this method are impossible. Nevertheless we will represent some results of our measurements and calculations, since we believe that still some relevant conclusions may be drawn from them.

In the beginning of this century Einstein proved that the viscosity of a diluted dispersion of rigid spherical particles ($\phi < 0.01$) may be calculated by :

$$\frac{\eta_s}{\eta_0} = \eta_r = 1 + \nu\phi \qquad (6.10)$$

where η_s is the viscosity of the dispersion, η_0 the viscosity of the continuous phase of the dispersion and ϕ the volume fraction of dispersed particles. The ratio of η_s and η_0 is defined as the relative viscosity η_r. In equation 6.10 ν represents a form factor and in the case of spherical particles ν is equal to 2.5. For the situation of non-spherical particles this factor will be larger.

According to e.g. Blom (1986) by the so-called rotary Péclet number, $Pé_r$, an estimation can be made of the ratio of hydrodynamic forces, which tend to orient the particles in the flow field, and Brownian motion. This Péclet number is defined as :

$$Pé_r = \frac{\dot{\gamma}}{2\ D_r} \qquad (\ 6.11\ )$$

where $\dot{\gamma}$ (s^{-1}) is the shear rate of the flow field and D_r (s^{-1}) is the rotary diffusion constant. At high $Pé_r$ the particles will become oriented in the flow field and at low $Pé_r$ Brownian motion determines the orientation of the particles in the liquid.

According to Blom et al. (1986) the diffusion rotary constant for prolate ellipsoidal particles can be calculated by the following set of equations :

$$D_r = \frac{k\ T \cdot (\ R^2 \alpha_{/\!/} + \alpha_{\perp}\ )}{16\ \pi\ \eta\ a_{/\!/}\ a_{\perp}{}^2 \cdot (\ R^2 + 1\ )} \qquad (\ 6.12\ )$$

where : k = The constant of Boltzmann (J/K)
T = Temperature (K)
η = Viscosity (Pa·s)
$a_{/\!/}$ = length of vertical semi-axis (m)
$a_{\perp}$ = length of horizontal semi-axis (m)

where :

$$R = \frac{a_{/\!/}}{a_{\perp}} \qquad (\ 6.13\ )$$

$$\alpha_{\perp} = \frac{R^2}{R^2 - 1}\ (\ 1 - \beta\ ) \qquad (\ 6.14\ )$$

$$\alpha_{/\!/} = \frac{2}{R^2 - 1}\ (\ R^2 \beta - 1\ ) \qquad (\ 6.15\ )$$

and where :

$$\beta = \frac{\cosh^{-1} R}{R\ (\ R^2 - 1\ )^{0.5}} \quad (\ R > 1\ ) \qquad (\ 6.16\ )$$

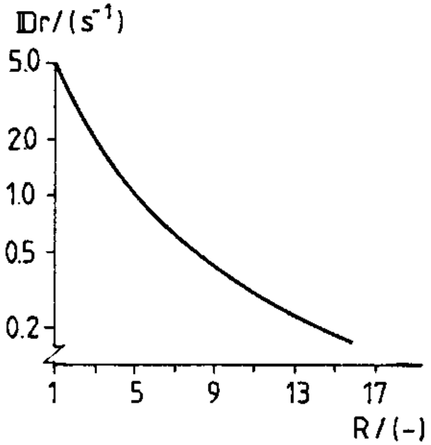

Figure 6.3 : The rotary diffusion constant of prolate ellipsoidal particles as a function of the axial ratio R, calculated with equation (6.12), where the mean particle diameter was estimated to be 0.5μm.

By this set of equations the rotary diffusion constant for prolate ellipsoidal particles can be calculated as a function of the ratio of the two axes of symmetry. If the mean particle radius of the liquid GLP particles is estimated to be 0.25 μm, D_r can be calculated as a function of the axial ratio. In figure 6.3 results of these calculations are represented for particle dispersions at a temperature of 30°C.

According to Blom et al. (1986) the mean shear rate in the capillary of the ubbelohde can be calculated by the following formula :

$$\bar{\dot{\gamma}} = \frac{a\ P}{3\ L\ \eta} \qquad (\ 6.17\ )$$

where a is the radius of the capillary, P is the mean hydrostatic pressure and L is the length of the capillary. From equation 6.17 it follows that in our case the mean shear rate would be about 1220 s^{-1}. Therefore $Pé_r$ for prolate ellipsoidal particles should have a value which would strongly exceed the value of 1.

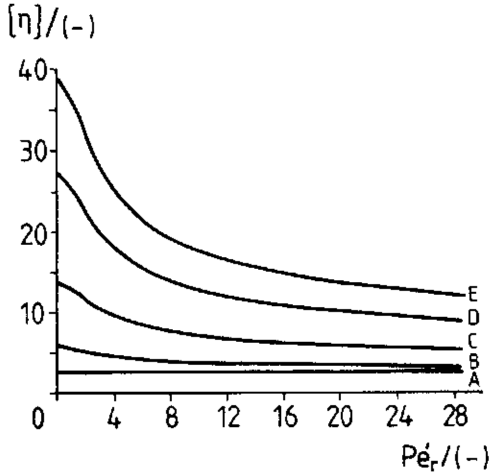

Figure 6.4 : The intrinsic viscosity of prolate ellipsoidal particles as a function of the rotary Péclet number calculated by Scheraga (1955) for several axial ratios.
A : R = 1 , B : R = 5 , C : R = 10 , D : R = 16 , E : R = 20.

Scheraga (1955) developed a theory which predicts the intrinsic viscosity [η] (m^3/kg) of a diluted dispersion of non-spherical particles as a function of the rotary Péclet number. The intrinsic viscosity is defined as :

$$[\eta] = \lim_{C \to 0} \frac{\eta_r - 1}{C} = \frac{\nu \phi}{C} \qquad (6.18)$$

where C (kg/m^3) is the concentration of the dispersed particles. In figure 6.4 the results of this theory for prolate ellipsoidal particles have been represented for several axial ratios.

First we will consider the data of our rheological experiments. In figure 6.5 a typical result is represented of the determined relative viscosity as a function of the weight fraction of GLP in a 0.1% sodium caseinate solution. Usually a linear relation was found in the concentration region up to about 0.4% GLP. At higher emulsifier concentrations flocculation occurred which markedly effected the viscosity.

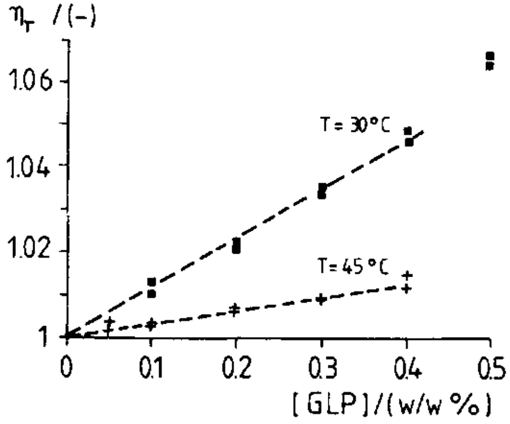

Figure 6.5 : The relative viscosity of GLP dispersions in a 0.1% sodium caseinate solution as a function of the GLP concentration determined by means of capillary viscosimetry at 30°C and at 45°C. The emulsions were prepared at a homogenization pressure of 10 MPa at 70°C.

In figure 6.6 the experimentally determined form factors ν of the GLP particle dispersions are represented as a function of temperature. From this figure it appears that ν is equal to 2.8 at a temperature of 45°C. This can be expected, since the particles should be spherical when the GLP mixture is in almost completely melted state, which is the case at this temperature (see figure 5.4). Below the melting temperature the value ν strongly increases, probably as a result of two phenomena, firstly swelling caused by hydration and secondly particle shape changes caused by crystallization of the emulsifier.

In fact the form factor ν as represented in figure 6.6 should be regarded as an apparent form factor ν^*. This is caused by the fact that the effective volume fraction of GLP increases as a result of hydration. Therefore ν should be corrected for swelling of the dispersed particles.

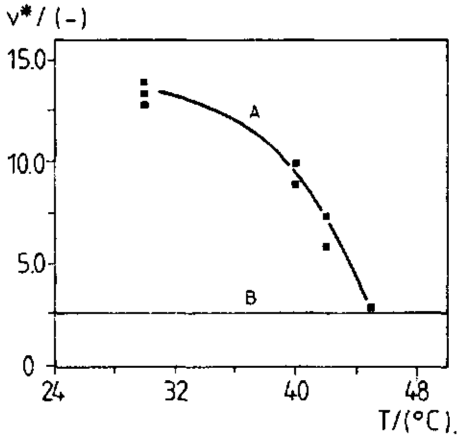

Figure 6.6 : The apparent form factor ν^* of GLP particle dispersions as a function of temperature. A : experimental data , B : theoretical line for spheres.

If the particles are supposed to be prolate ellipsoids, the actual value of ν can be roughly estimated with the following two equations :

$$\eta_r = 1 + \nu f_s \phi_{GLP} \qquad (6.19)$$

where :

$$f_s = \left(\frac{d_a + d_w}{d_a} \right)^2 \qquad (6.20)$$

and :

f_s = the swelling factor (-)
d_a = the thickness of the dry bilipid layer (m)
d_w = the thickness of the same hydrated layer (m)

At 30°C, the temperature at which the crystallization of GLP is complete, we found for the apparent form factor ν^* a value of 13.4 ± 1.2 (N=5). After correction for swelling, as indicated above with $f_s \approx 1.31$, the value for ν becomes 10.2 at 30°C.

Now the question is what would be the real value of the rotary Péclet number for prolate ellipsoids in the case of our experiments. If the axial ratio would be relatively large, say larger than 20, $Pé_r$ would become much higher than 1000 (see figure 6.3). This would fit in nicely with the results of figure 6.4, where one can see that for high rotary Péclet numbers the intrinsic viscosity goes down to a value lower than 14. However, we think that such an axial ratio probably is not realistic. Both the SEM-micrographs and the photographs obtained from light microscopy provided us with the idea that the particles would have an axial ratio between 5 and 10.

There may be several reasons for the over-estimation of the axial ratio with these calculations. First of all it has already been stated that the type of flow, used to estimate the particle shape, is in principle wrong (see e.g. Simha, 1940). Secondly we cannot estimate a reliable value for D_r, because the size distribution of the particles is unknown. Thirdly the particles, differing in size as a result of the homogenization process, may also have different shapes, because one may expect the smaller particles to become deformed strongest. Finally it is not known, whether the particles may be regarded as prolate ellipsoids, although the results of microscopy seem to point to this type of geometry.

From the results of the last two paragraphs it may be concluded that GLP particles which are smaller than 0.5 μm in diameter become deformed from their original, spherical shape as a result of interfacial crystallization phenomena. The exact geometry of the particles still remains unknown, but probably the particles adopt a cylindrical structure.

6.4.3 Rheological and fracture properties of GLP containing gels.

As indicated in the introduction of this chapter we are very interested in the mechanism which explains the reversible whipping behaviour of a topping emulsion, which contains a relatively large amount of GLP on fat basis. To obtain a better insight in this behaviour, rheology can certainly be of help. However, the second reason, just as important as the first one, is the fact that we wanted to obtain circumstantial evidence for the hypothesis that the α-gel phase of GLP determines the rheological and fracture properties of emulsions containing at least 20% GLP on fat basis. We were in need of extra evidence, because the results of the diffraction measurements, presented in chapter 4, conflicted with the hypothesis.

To this end we first studied the behaviour of gels containing 100% GLP on dispersed phase basis. To exclude possible effects, caused by a variable dispersed phase concentration, experiments were performed both in the range of 8 to 15% and at 40% dispersed phase concentration. These gels were prepared as described in section 2.2.1.1. Uniaxial compression tests were performed on cylindrical specimens with a tensile and compressional testing apparatus, as described in section 2.2.7.2.

In figure 6.7 stress-strain curves for 12% and 40% GLP gels at variable deformation rate are represented. From these figures it appears that the gels show very time scale dependent rheological and fracture behaviour. The shape of the stress-strain curves can be characterized as follows. The curves start with a sharp increase, followed by a maximum and a progressive decrease at high V_{def} or a semi-plateau at low V_{def}. We can draw the following major conclusions from the shape of these stress-strain curves.

1 GLP particle gels behave like visco-elastic materials.
2 All samples yield after a small deformation (say about 5%) and show plastic fracture behaviour.

and show plastic fracture behaviour.

3 At a certain extent of deformation the stress is lower with decreasing deformation rate.

4 The fracture strain increases with decreasing strain rate.

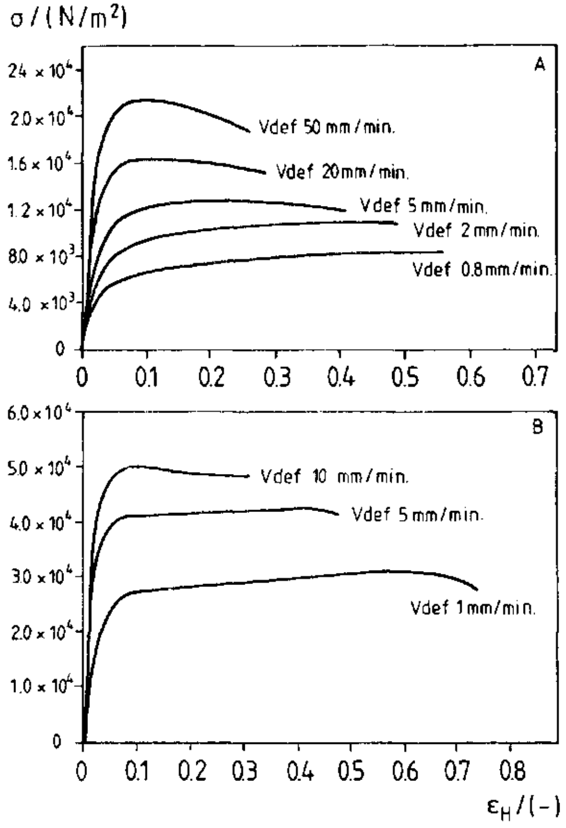

Figure 6.7 : Stress-strain curves for a 12% GLP gel in a 2% sodium caseinate solution (A) and a 40% GLP gel in a 5.33% sodium caseinate solution (B). The samples were stored at 20°C directly after preparation and the samples were allowed to age for a period of 18-24 hours prior to the experiment.

These conclusions are based on the following considerations. The initial slope of the curves decreases at decreasing strain rate, which may be indicative of visco-elasticity. The linear restress-strain curve already starts to decrease at deformations larger than about 2%. This slope decrease may be caused by initial yielding phenomena (see e.g. van Vliet et al. , 1989). One can expect such rheological behaviour for a solid or semi-solid material. When the gels are deformed further, the stress increases up to a maximum value. At still larger deformations visible fracture will eventually occur. The region of maximum stress to fracture stress forms a relatively large part of the stress-strain curves at low deformation rates. Especially in this region plastic fracture occurs. At high compression rates the gels relatively show a more brittle-like fracture behaviour.

At a relatively high deformation rate the maximum stress is higher than the fracture stress observed, but in general it may be stated that in all cases the fracture stress is smaller than the maximum stress level. The reason for this effect can be explained as follows. The stress-strain curves were recalculated from the measured force-time curves and these calculations were frequently performed up to the point of maximum registered force. However, this was not always correct. Very often it was observed that just before or right at the point of this force maximum vertical tension slits appeared on the outside of the gel specimens at low V_{def}. In the case of high compression rates we could not make an accurate estimation of the moment at which macroscopical fracture did occur, because these samples often failed in shear. Thus it may not be excluded that the final parts of the curves obtained for samples which were compressed at high strain rates are unrealistic.

The occurrence of plastic flow can explain the differences in the observed fracture strain levels. Qualitatively this can be made clear as follows. During the plastic flow process microscopic cracks will be formed which may heal again, because inherent to visco-elastic materials new bonds may be formed between the structure elements, in this case bonds between both GLP particles and particle aggregates (see e.g. Luyten, 1988 and van Vliet et al. , 1989). It takes time to form these new bonds. At a high deformation rate the process of restoration of new, stress-free bonds is far more exceeded by the effect of strain induced structure breakdown, consequently ϵ_f will be relatively small. At relatively low deformation rates the effect of new bond formation becomes of importance. Thus as a result of the latter effect ϵ_f will increase at decreasing strain rate.

A second order effect may be that it takes time to fracture a material, especially in the case of visco-elastic materials, because in the latter case both fracture initiation and fracture propagation are hindered or delayed when matrix flow occurs. Now, if the deformation rate is high, the stress will reach a high level too, because the material will react more elastically. Subsequently the level of stored energy will also be large and this amount of stored energy may be used for yielding and eventually fracture processes. The growth of fracture surfaces will continue relatively fast, if matrix flow is of minor importance which is to be expected at high deformation rates. In the case of low deformation rates yielding processes occur at a much lower stress level and consequently plastic flow may delay both fracture initiation and propagation.

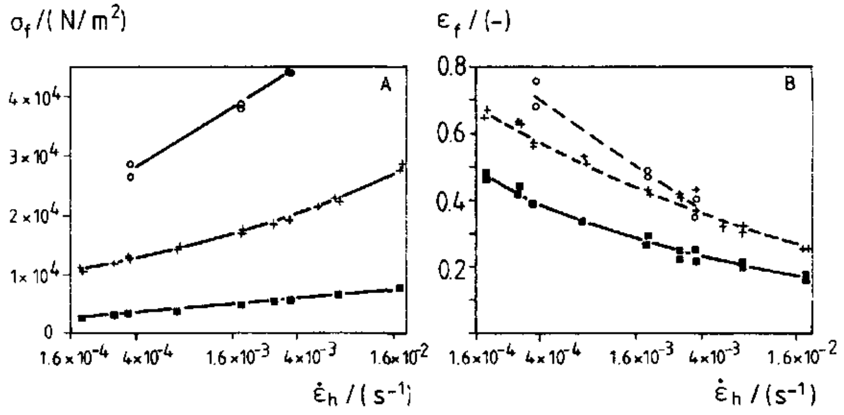

Figure 6.8 : The fracture stress and fracture strain as a function of the Hencky strain rate for gels with variable GLP concentrations.
A = Fracture stress versus $\dot{\epsilon}_h$, B = Fracture strain versus $\dot{\epsilon}_h$.
▪ : [GLP] = 8% , + : [GLP] = 15% , o : [GLP] = 40%.

In figure 6.8 both the fracture stress and fracture strain are represented as function of the Hencky strain rate for three GLP gels at different emulsifier concentrations. These figures again clearly show the time-dependent fracture properties of these gels. At higher GLP concentration we found that the fracture strain was larger at comparable strain rate levels. It may well be that at higher GLP levels the relatively higher regularity of the gel network increases the possibility of matrix flow. This would also be consistent with the results for ϵ_f found for the 40% GLP gel. At longer time scales we found an increase in fracture strain, whereas at shorter time scales the strain line touches the line of the 15% sample, because flow is expected to occur more extensively at longer time scales. However, this explanation is still rather speculative.

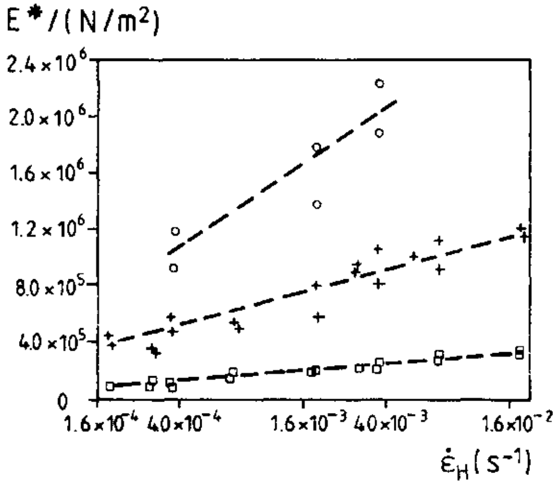

Figure 6.9 : The apparent Young modulus as function of the initial Hencky strain rate for GLP gels at variable GLP concentration.
▪ : [GLP] = 8% , + : [GLP] = 15% , o : [GLP] = 40%.

In figure 6.9 apparent Young moduli for the GLP gels at variable emulsifier concentration are represented as a function of the Hencky strain rate. In the case of solid or semi-solid materials the linear region of the stress-strain curve may be very small (e.g. smaller than $\epsilon_h = 10^{-3}$ according to Papenhuijzen, 1970 or Kamphuis, 1984). In the next chapter we will present some data supporting such a small linear region for GLP containing particle gels. Thus the calculated modulus values should actually be regarded as apparent moduli, E^*, since the width of the linear region is probably smaller than the ϵ range over which E^* has been calculated.

These curves show again that GLP gels exhibit time-dependent rheological behaviour. The slope N of the log E^* versus log $\dot{\epsilon}_h$ plot seems to be rather constant. In the case of the 8% and 15% gels we found a value for N of 0.26 and in the case of the 40% samples of about 0.33. However, the latter N-value is not very reliable, since in this case compression experiments were only performed in a relatively small range of strain rates.

The N-value is often used for rheological characterization of a material. A completely elastic material should give a N-value equal to zero. The higher this value will be the more viscous a material is. Luyten (1988) found an average N-value of 0.17 for several types of Gouda cheese, which is regarded to be a visco-elastic material. Furthermore, she reported a value of N equal to 0.06 for whipped cream, obtained by calculations from experimental data of Dickie and Kokini (1982). Whipped cream is believed to behave like a rather elastic foodstuff, because of the presence of a continuous network of partially coalesced fat globules. Thus the relatively high N-value observed for GLP gels is consistent with our hypothesis of GLP gels to consist of a reversible network of flocculated fat particles and probably not of a network of partially coalesced fat particles.

Comparable results can be obtained from the slope of a plot of the logarithm of the stress versus the logarithm of the Hencky strain rate. These results are represented in figure 6.10 for both a 15% GLP gel and a 40% GLP gel at several levels of deformation. The value of the slope for the 15% gel sample amounts to N = 0.21, whereas the value for the 40% gel sample amounts to N = 0.25 at deformations larger than 2%, values that are somewhat lower than the slope of the Log E^* - log $\dot{\epsilon}_h$ plots. Thus the linear region is at least smaller than the 2% deformation level. These N-values are fairly constant in the increasing part of the stress-strain curves. Only at the maximum stress level the slope decreases slightly.

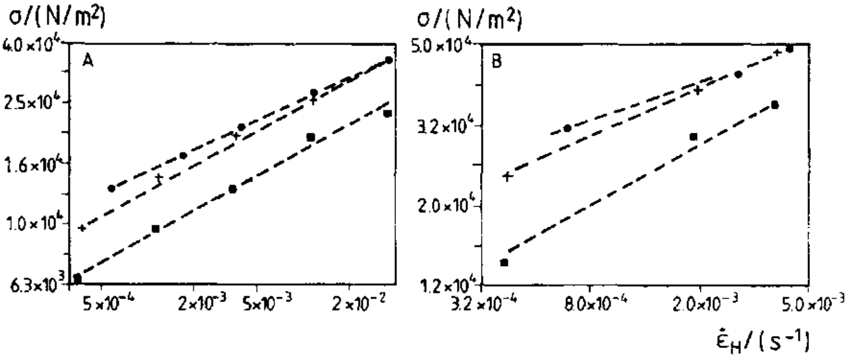

Figure 6.10 : Influence of the strain rate on the stress of a 15% GLP gel (A) and a 40% GLP (B) at variable deformations.
■ : ϵ_h = 0.02 , + : ϵ_h = 0.05 , ● : ϵ_h at maximum stress level.

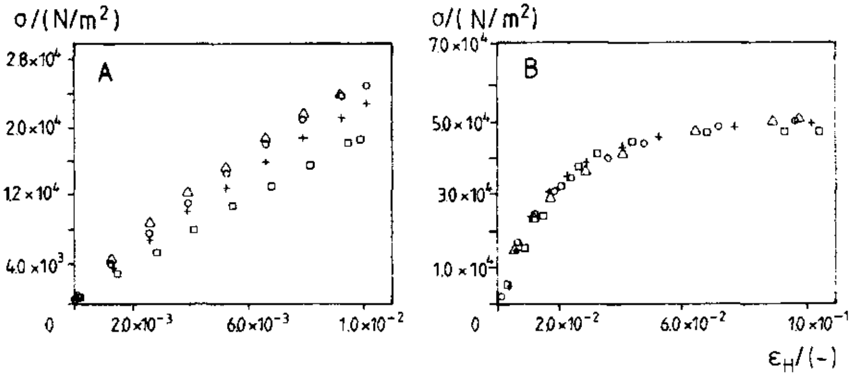

Figure 6.11 : Cycle compression experiments performed with 40% GLP gels at a strain rate of $3.7*10^{-3}$ s^{-1}. A : ϵ_h = 0.01 and B : ϵ_h = 0.1.
□ = First cycle , + = second cycle , O = third cycle , △ = fourth cycle.

By means of cycle compression tests we tried to study the reversible properties of the GLP gels further. For this purpose gels were deformed up to a certain strain level after which the applied stress was released at the same deformation rate. After four minutes the gels were compressed again. In figure 6.11 the results of such an experiment are shown for a 40% GLP gel at two different strains e.g. at ϵ_h = 1% and 10% respectively. In the latter case it was found that permanent deformation had occurred after each compression cycle. Therefore each time a new initial sample height was used in our calculations.

The results of this experiment were rather surprising, especially at $\epsilon_h = 0.01$. We would have expected reversible properties to be found, meaning that the height of the stress-strain curve would remain the same or at most would not decrease too much. However, we found that cycle compression in the apparent linear region led to an increase in height of the stress-strain curve. In our opinion this effect can only be explained by assuming that even a small deformation of the material results into a change of the microscopical structure of a GLP gel. In this respect one might think of stretching and compression of chains, causing additional particles or particle aggregates to form new bonds and thus to become mechanically effective as structure elements of the gel network or resulting in an increase in the contact area between the aggregated particles. Consequently the actual linear region indeed can only exist at very small deformations.

If we consider the same cycle experiment, yet performed at larger ϵ_h, it can be concluded that the gels show reversible behaviour in the applied time scale of about four minutes. This conclusion is based on the fact that the samples do not return to their original geometry when the stress is released, yet, all curves have approximately the same shape.

Especially from figure 6.12 it appears that GLP gels show reversible behaviour in the time scale considered. If the complete stress-strain curve of a gel which had undergone 4 compression cycles at a constant ϵ_h of 0.1 is compared with curves obtained for the two gels that had not been deformed earlier, it appears that these different curves do not differ significantly.

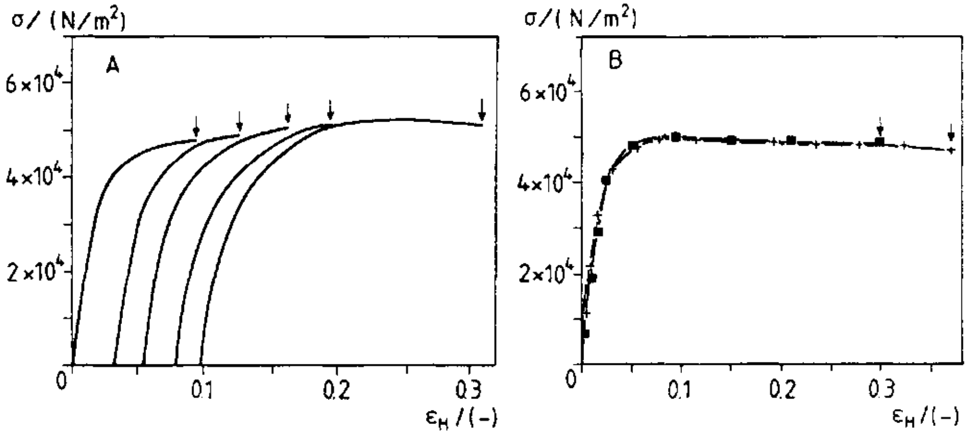

Figure 6.12 : The influence of cycle compression on the shape of stress-strain curves of 40% GLP gels at a Hencky strain rate of $3.7*10^{-3}$ s^{-1}.

A : The complete stress-strain curve for a 40% GLP gel which had undergone 4 compression cycles at $\epsilon_h = 0.1$.

B : The real stress-strain curve shown for two 40% GLP gels.

Qualitatively this reversible behaviour can be explained as follows. In the case of GLP gels, yielding processes start to occur at deformations larger than about 5%. At these deformations a gel starts flowing. If the stress is released, it is observed that the sample has a new shape, which is caused by these flow phenomena. When the sample is compressed again, it will start flowing at approximately the same yield stress. Finally it is observed that the material fractures at the same ϵ_f, as would have been found if the sample was deformed directly up to ϵ_f. Summarizing it seems reasonable to conclude that GLP gels have reversible properties in the time scale that we studied.

6.4.4. The influence of sodium caseinate on the rheological and fracture properties of 10% GLP gels.

In chapter 3 and 5 it has been stated that the caseinate molecules should desorb from the interface of the fat particles below the crystallization temperature of GLP. If this assumption would be true, the presence or absence of caseinate in these gels would not be of any influence on the rheological and fracture properties of the GLP gels. To test this we performed compression experiments with 10% gels prepared in 2.0 mMol phosphate buffers, pH = 6.8 and in 2% sodium caseinate solutions having a comparable pH value.

It appeared to be very difficult to prepare these two types of emulsions with comparable average particle size. It would have been better to homogenize both samples in the phosphate buffer and to add a caseinate solution to one of these emulsions afterwards. However, this method appeared to be unsuccessful, because stable emulsions in phosphate buffer could only be prepared at a maximum GLP content of about 5%. As an indication for the instability of a 10% GLP containing emulsion prepared in phosphate buffer, the pH of the gel reduced to a value of 4.8 coming from 6.8. This caused the occurrence of coalescence in this emulsion at a high temperature (see section 3.2.2). Dilution of the emulsion with the phosphate buffer or a 20% sodium caseinate solution caused these gels to become too weak to handle properly.

Therefore we decided to compare the rheological results obtained for 10% GLP gels prepared in a 2% sodium caseinate solution with those obtained for the same gels but prepared in a 2.0 mMol phosphate buffer. We realize that in this case the size of the GLP particles in the phosphate buffer will be somewhat larger than the size of particles in the caseinate solution.

In figure 6.13 the results for the Young modulus of these two gel types are represented as a function of the Hencky strain rate. From this figure it appears that the modulus of the phosphate buffer gels is somewhat lower than the modulus of the samples prepared in the sodium caseinate solution at the same strain rate. In our opinion the larger average particle size of the former gels can be related to this difference. The network of these samples probably is more inhomogeneous as a result of this difference in particle size.

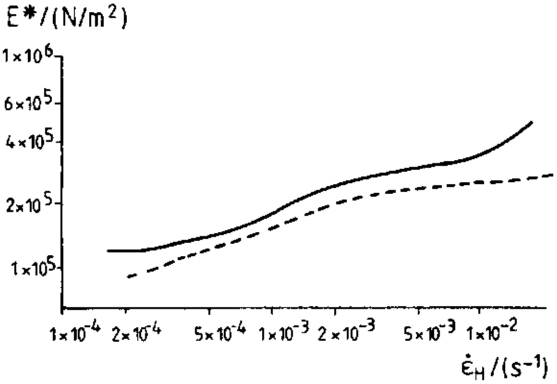

Figure 6.13 : The Young modulus as function of the Hencky strain rate for 10% GLP gels with a different continuous phase composition.
—— = Gel in 2.0% sodium caseinate solution.
– – – = Gel in 2.0 mMol phosphate buffer.

The slope of the log E^* versus log $\dot{\epsilon}_h$ plots is rather similar namely $N \approx 0.29$ for both systems, which is an important observation, because this clearly points towards the fact that the character of the physical bonds could be the same in both cases.

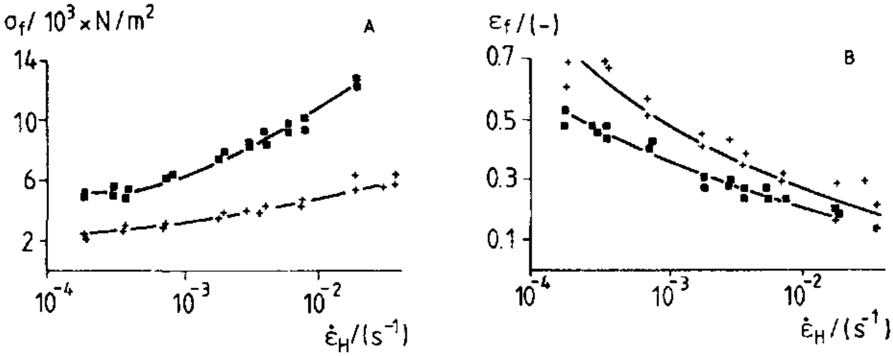

Figure 6.14 : The fracture properties of 10% GLP gels with different continuous phase composition.
A : Fracture stress as function of the Hencky strain rate.
B : Fracture strain as function of the Hencky strain rate.
▪ = Gel in 2.0% sodium caseinate, + = Gel in 2.0 mMol phosphate buffer.

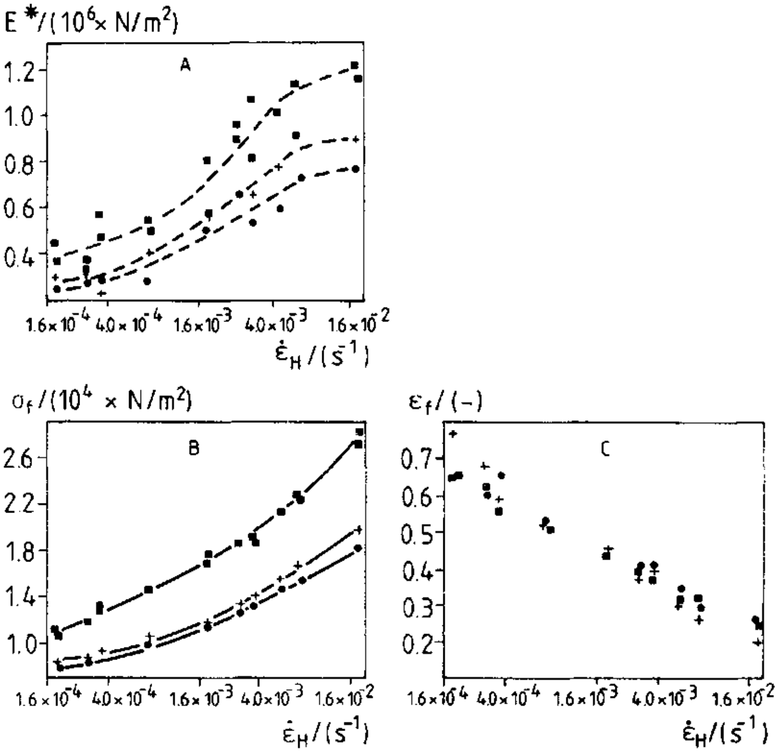

Figure 6.15 : The rheological and fracture properties of 15% GLP gels in 2.0% sodium caseinate solutions prepared at variable homogenization pressures.
A : Young modulus as function of the Hencky strain rate.
B : Fracture stress as function of the Hencky strain rate.
C : Fracture strain as function of the Hencky strain rate.
Homogenization pressure : ■ = 10 MPa. , + = 1 MPa. , ● = 0.1 MPa.

The idea of larger inhomogeneity of the gel structure in the phosphate buffer is not completely consistent with the results of the fracture properties for these gels. In figure 6.14 it is shown that the fracture stress is much lower in the case of the gels prepared in phosphate buffer, which is in good agreement with the above mentioned explanation. However, the fracture strain is larger for these gels, which was rather unexpected. Perhaps in the case of the gels prepared in phosphate buffer formation of new bonds between particles and particle aggregates occurs faster, because these particles are not partly stabilized by adsorbed caseinate molecules (see e.g. chapter 7). However, this explanation still is rather speculative.

In this respect it may be relevant to regard the rheological and fracture properties of 15% GLP gels prepared at variable homogenization pressures in 2% sodium caseinate solutions which are represented in figure 6.15. There we can see that the modulus and the fracture stress decrease at increasing particle size, whereas the fracture strain does not change significantly within the limit of detection.

Though there are differences between the results of the rheological and fracture properties of gels prepared in 2 mMol phosphate buffer or in 2% sodium caseinate buffer, we still think it is reasonable to conclude that the gel network properties are mainly determined by GLP. The presence of sodium caseinate is of minor importance for the rheological behaviour of these gels which appears strongest from the time dependent behaviour of these gels.

6.4.5. The Influence of an oil or fat phase.

In this paragraph the influence of an oil or fat phase on the rheological and fracture properties of GLP containing emulsions will be presented. The purpose of this paragraph is to show that the rheological properties of these dispersions are primarily determined by the α-gel phase of GLP, which is supposed to be present at the o/w-interface of the dispersed particles. In our opinion these particles are bound to each other with this gel phase.

In figure 6.16 the stress-strain curves of gels containing 40% dispersed phase, consisting of 32% hardened coconut oil (HCNO) and 8% GLP in a 5.3% sodium caseinate solution are shown at variable deformation rates. These gels had undergone a cooling cycle prior to the compression test in the following way. The hot emulsion samples were cooled to 4°C directly after preparation in a refrigerator and stored at this temperature for 1 hour. Next the samples were stored overnight at the measuring temperature.

Figure 6.16 indicates that these gels behave strongly time-dependent, just like the GLP gels. The fracture strain increases with decreasing deformation rate as one would expect to occur for systems that show plastic fracture behaviour. However, it was quite surprising for us to find that at a relatively low strain rate the fracture stress increased again with the strain rate. This might be explained by assuming that extensive structure formation takes place at these relatively long time scales for this specific type of gel. Only at low deformation rates the time scale of the experiment is long enough to allow this strong crack healing effect, implying the formation of sufficiently new bonds during deformation. If this explanation is right this is another indication for the reversible properties of this specific type of gels.

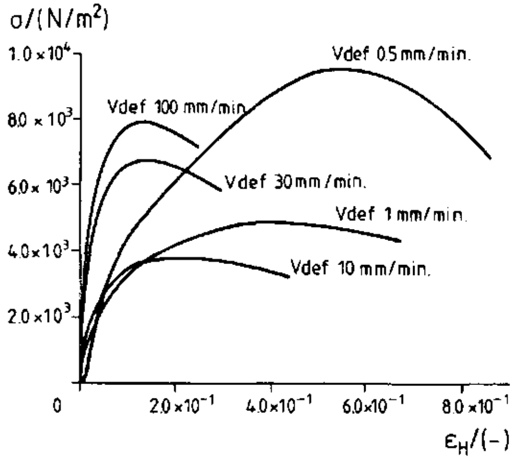

Figure 6.16 : The stress-strain curves for particle gels containing 40% dispersed phase (32% HCNO + 8% GLP) in a solution of 5.3% sodium caseinate. The compression tests were performed at 20°C. The emulsions were temperature cycled prior to the compression tests.

For comparison in figure 6.17 the stress-strain curves for a 40% GLP gel and a 32% HCNO / 8% GLP gel are represented together in one figure at three different deformation rates. These curves show that at the same deformation rate the fracture strain seems to be independent of the type of gel, which is an indication for the fact that in either case the gel properties are determined by GLP. The fracture stress levels are significantly higher for the 40% GLP gels. At 20°C one can expect the HCNO/GLP mixture to be almost completely solid after the temperature cycle mentioned, just like GLP. Thus the difference in strength between the two gel types is not related to the solid fat level in the particles.

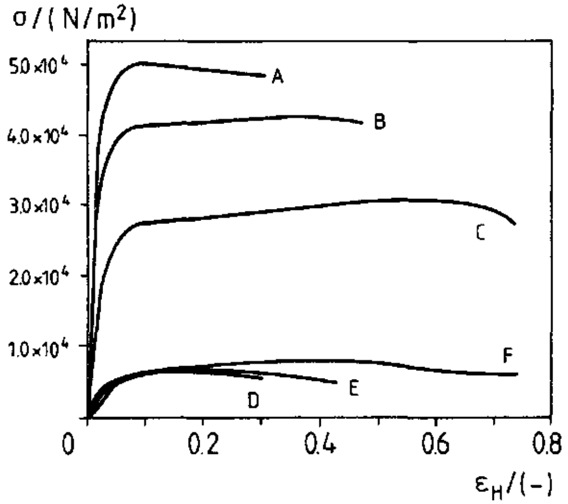

Figure 6.17 : Stress-strain curves for a 40% GLP gel and a 40% gel containing 32% HCNO and 8% GLP on dispersed phase basis in 5.3% sodium caseinate solutions (T=20°C) at variable deformation rate.
A : 40% GLP / V_{def} = 10 mm/min , D : 40% GLP/HCNO / V_{def} = 10 mm/min.
B : 40% GLP / V_{def} = 5 mm/min , E : 40% GLP/HCNO / V_{def} = 5 mm/min.
C : 40% GLP / V_{def} = 1 mm/min , F : 40% GLP/HCNO / V_{def} = 1 mm/min.

In our opinion this specific effect is closely related to differences in particle shape between these two systems. In the case of pure GLP gels one can expect the particles to deviate stronger from a spherical geometry than the particles containing a mixture of HCNO/GLP, because the GLP particles should consist of gel phase multilayers at a level of at least 50%, whereas the particles of the latter system only contain a maximum of about 2 repetitive bilipid layers (see section 3.2.2).

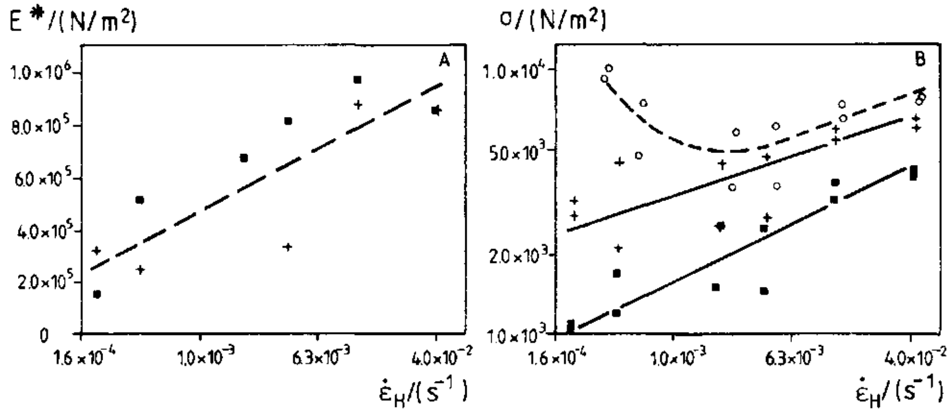

Figure 6.18: The apparent Young modulus (A) and the stress (B) at different strain levels as function of the Hencky strain rate for 40% particle gels containing 32% HCNO and 8% GLP on dispersed phase basis (T=20°C).
Graph B ; ■ : ϵ_h = 0.02 , + : ϵ_h = 0.05 , o : ϵ_h at maximum stress level.

In figure 6.18a apparent moduli for the temperature cycled samples and in figure 6.18b stress data at three different Hencky strain levels are shown as a function of the Hencky strain rate. Considering the apparent modulus graph, it is obvious that the data are not very accurate. Especially in this case it appeared to be difficult to make an accurate estimation of the initial slope of the force-time curves. If linearity between the log E^* - log $\dot{\epsilon}_h$ data is assumed, the slope of this line would be about 0.25. The slope of the line in the log σ - log $\dot{\epsilon}_h$ plot at small deformations is 0.26 which is in good agreement with the value for N mentioned before. This value also corresponds reasonably well with the N-value found for gels, containing 40% GLP on dispersed phase basis. This could be interpreted as an indication of the fact that the relaxation behaviour of the mechanically effective bonds is the same for both types of gel (Luyten, 1988). However, at the level of maximum stress it is apparent that the line tends to bend towards higher stress levels again at strain rates lower than about $3*10^{-3}$ s^{-1}. Plastic flow starts to become dominant at this time scale and seems to be more relevant in the systems containing a mixture of the α-tending emulsifier and HCNO than in pure GLP gels.

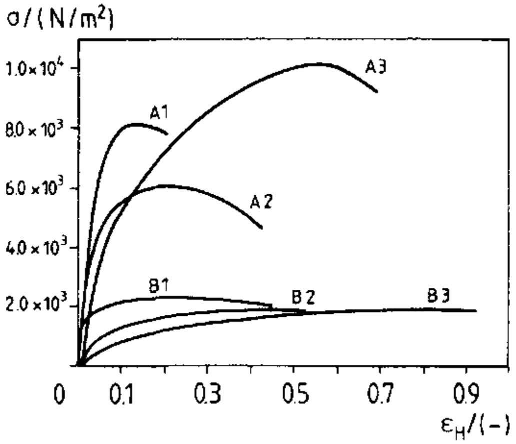

Figure 6.19 : The influence of the temperature history on the stress-strain curves for 40% gels, containing 80% HCNO and 20% GLP on dispersed phase basis measured at three different strain rates (T=20°C).
A) With temperature cycle, B) without temperature cycle.
1 : V_{def} = 100 mm/min, 2 : V_{def} = 5 mm/min, 3 : V_{def} = 0.5 mm/min.

In figure 6.19 another example of stress-strain curves for gel samples, containing 32% HCNO and 8% GLP are shown for three different strain rates. In this figure, a distinction has been made between samples which had undergone a temperature cycle and samples which had been stored at 20°C directly after sample preparation. In the latter samples crystallization of the fat/emulsifier is not complete. In this case the stress levels are significantly lower. This may be related to the fact that the particles probably are far less deformed from a spherical geometry, because part of the fat phase still is in the liquid state. Consequently the bonds between the aggregated particles are weaker. We think that from these results it may be concluded that both the rheological and fracture properties of gels containing 80% HCNO and 20% GLP on total dispersed phase basis are determined by the amount of solid fat and the shape of the particles.

In this respect we were anxious to learn, whether gels could be prepared from emulsions that contain a completely liquid oil fraction in the presence of GLP. Therefore emulsions were prepared with the same ratio between triglycerides and GLP as the HCNO/GLP systems, but the HCNO fraction was replaced by soybean oil (SBO). Indeed stable gels could be formed from these emulsions at a 40% dispersed phase level. Gelation occurred during cooling of the emulsion to room temperature without the necessity of a temperature cycle. In figure 6.20 the stress-strain curves of these gels are shown at variable deformation rate.

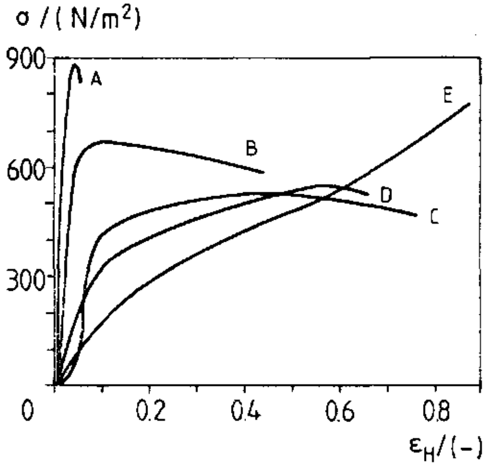

Figure 6.20 : Stress-strain curves of gels containing 40% dispersed phase in a 5.3% sodium caseinate solution. The dispersed phase was composed of 32% SBO and 8% GLP. Measurements were performed at 20°C.
A : V_{def} = 100 mm/min , B : V_{def} = 30 mm/min , C : V_{def} = 10 mm/min
D : V_{def} = 5.0 mm/min , E : V_{def} = 0.5 mm/min.

This graph shows that the maximum stress levels are much lower (about an order of magnitude) than the stress values found for the HCNO containing emulsions. In our opinion this is closely related to the shape of the particles. In fact it may well be that the particles in these specific gels have a spherical geometry. Again we observed that these gels show strongly time dependent rheological and fracture properties. Another striking point is that, just as it had been found in the case of the HCNO containing samples, at small deformation rates the fracture stress levels become higher than those levels found at higher deformation rates.

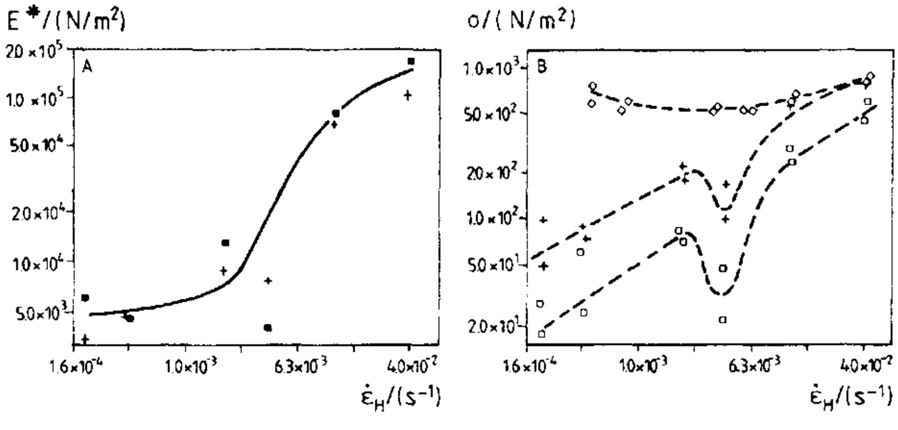

Figure 6.21 : The apparent Young modulus ■ and +, (A) and the stress (B) at different strain levels as function of the Hencky strain rate for 40% particle gels containing 32% SBO and 8% GLP on dispersed phase basis (T=20°C). Graph B: □ : $\epsilon_h = 0.02$, + : $\epsilon_h = 0.05$, ◇ : ϵ_h at maximum stress level.

In figure 6.21a plots of the apparent Young modulus and the stress at several states of deformation as function of the Hencky strain rate are represented for the same SBO/GLP gels. In this case we did not find a linear relationship between Log E^* and log $\dot{\epsilon}_h$. If we would draw a straight line through the experimental data, a slope of value 0.73 would be found, which strongly points towards the visco-elasticity of these gels. Presumably relaxation behaviour of the bonds in the considered time scale is different from the other gels. If it is supposed that GLP also primarily determines the rheological properties of these gels, at least a second order effect should influence the values of these Young moduli.

Up to now we do not have a satisfying explanation for this high N value. We do not think that this value is related to the deformability of the partly liquid particles because of the following reason. The deformability of the particles will mainly be determined by the stiffness of the gel phase layer, which is supposed to surround the particles. The Young modulus of this surfactant layer probably has a value of about $1*10^{+8}$ N/m^2 or perhaps even higher. To deform a particle this gel phase layer has to be bent. According to e.g. Luyten (1988) the displacement Y_{max} (m) in the center of a cylindrical beam can be roughly estimated by equation 6.21 :

$$E = \frac{\sigma\ L^2}{6\ D\ Y_{max}} \qquad (\ 6.21\ )$$

where :

E = Young modulus (N/m^2)
σ = applied stress (N/m^2)
D = diameter of the beam (m)
L = length of the beam (m)

If, as a first order approximation, it is supposed that the gel phase layer may be regarded as a beam, it is very easy to see from equation 6.21, assuming D to be 0.0125 μm, which is the thickness of two hydrated bilipid layers (see chapter 4 and 5) and L to be equal to 0.25 μm that Y_{max} will be extremely small under the stresses applied. Thus these SBO/GLP particles may be regarded as undeformable spheres.

In figure 6.21b it is obvious that at rather small deformations a distinct dip is found in the log σ - log $\dot{\epsilon}_h$ curve at a time scale of about 5 minutes which points to a strong non-linear effect. The HCNO/GLP gels also showed a small indication of such non-linear behaviour. Although this effect may be related to GLP gels we have no explanation for this phenomenon up to now.

Summarizing from the experimental results presented in this chapter we think that it is reasonable to conclude that the relaxation spectra are similar for both pure GLP gels and gels containing 20% GLP and 80% HCNO. This means that the type of bonds probably is of the same nature. The behaviour at rather large deformations sustains this idea. Our interpretation of this comparable behaviour is that the α-gel phase of GLP, present at the o/w-interface of the fat particles, primarily determines the rheological and fracture properties of these gels.

6.5 MODEL CALCULATIONS FOR THE MODULUS OF GLP CONTAINING GELS.

In order to be able to compare our results for the Young moduli of the studied gels with the results of theoretical predicted moduli, we will first discuss the intermolecular forces between two particles. In our systems containing aggregated, non-charged bilipid layers the only relevant interactions are hydration repulsion and van der Waals attraction (see chapter 4 and 5). Both the case of interacting spheres and platelet-like structures will be dealt with in this paragraph. The calculations should be regarded as order of magnitude estimations, since many structural parameters of the α-gel phase are still unknown. Furthermore, it has already been indicated that more knowledge on the geometry of the particles should be obtained in the future. The calculations shown below are performed for particles that are only surrounded by 1 bilipid layer at the interface of the particles.

According to e.g. van Vliet (1976), if $H \ll a$, the van der Waals interaction energy between two spherical particles is roughly given by :

$$V_a = - \frac{a\,A}{12\,H} \qquad (\ 6.22\ )$$

where :

V_a = Attraction energy (J)
a = Particle radius (m)
A = Hamaker constant (J)
H = Interparticle distance (m)

According to Parsegian et al. (1979) or Lis et al. (1982) the hydration interaction energy between two spherical vesicles can be described by the following empirical equation :

$$V_r = \pi\, a\, \lambda^2\, P_o\, e^{-H/\lambda} \qquad (\ 6.23\ )$$

where :

V_r = Hydration energy (J)
a = Particle radius (m)
λ = Decay length of hydration force (m)
P_o = Osmotic pressure at bilayer contact (N/m^2)

In this formula for the hydration energy use has been made of the Derjaguin approximation (Derjaguin, 1934), because the original empirical equation only counts for flat plates of interacting bilipid layers. The sum of the van der Waals attraction and the hydration repulsion gives the total interaction energy V_t (J) between two particles as a function of the interparticle distance.

According to Verwey and Overbeek (1948) in the case of two flat semi-infinite plates at distance H, ignoring retardation, the equation for V_a (J/m^2) is given by :

$$V_a = \frac{-A}{12\,\pi\,H^2} \qquad (\ 6.24\ )$$

and according to e.g. Parsegian et al. (1979) V_r (J/m^2) is equal to :

$$V_r = P_o \lambda e^{-H/\lambda} \qquad (6.25)$$

For the calculation of the total interaction energy between spherical particles the radius of the spheres was assumed to be 0.25 µm. Other values for the different parameters in equation 6.22-6.25 were obtained from Jönsson and Persson (1987) who theoretically determined phase equilibria for the lamellar mesophase ($T>60°C$) of 1-acylglycerols in the presence of small amounts of an anionic surfactant. According to these authors the Hamaker constant A for monoglycerides in the liquid state is equal to $6.0*10^{-21}$ J , $P_o = 1.25*10^8$ N/m^2 and $\lambda = 2.22$ Å. However, it should be emphasized that the values for these parameters are in fact unrealistic for GLP containing dispersions, because of the following reasons. The hydration repulsion curve of the gel phase of GMS probably differs from the curve for the same emulsifier at high temperatures, which again will differ from the curve for GLP multilayers in the solid state. Furthermore, the value for the Hamaker constant may be wrong, although for phospholipids, like DPPC, the same value is used by other authors, e.g. Lis et al. (1982). Therefore these curves should only be regarded as a mere indication of the level of interaction forces between particles which are aggregated as a result of van der Waals attraction.

In figure 6.22 plots are shown of these interaction energy curves for both spheres and flat plates. In the case of the plate model for the lamellar mesophase of monoglycerides an energy minimum at $d \approx 16$ Å is found. This fits in very well with the experimental value of 16 Å obtained for the waterlayer thickness d_w of the lamellar mesophase phase of GMS at 60°C (see Krog, 1973). Spherical particles may approach closer as shown in figure 6.22, because the minimum energy level is found at an interparticle distance of about 12 Å.

According to Krog (1973) the gel phase of GMS has an average waterlayer thickness d_w of about 14 Å at low salt concentration which proves that the hydration repulsion interaction should indeed be lower in the case of the gel phase. In the case of the gel phase of GLP hydration repulsion should even be much smaller, because, if it is supposed that the tilt angle does not change as a result of hydration, the minimum water layer thickness would only be about 9 Å in the case of samples that were wetted above the melting point of the emulsifier mixture (see section 4.3.4).

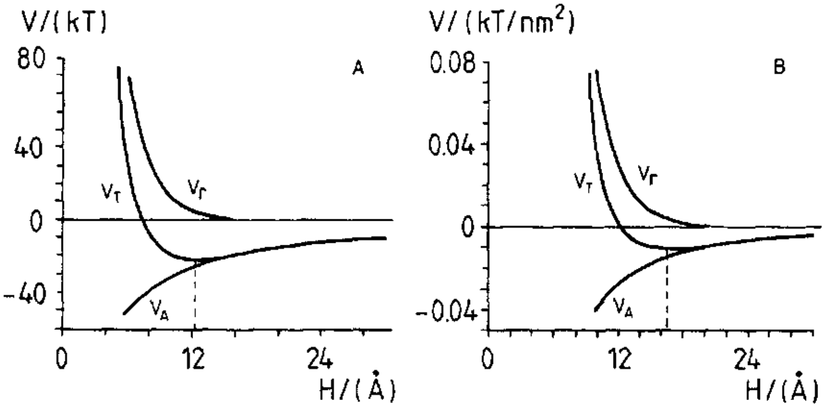

Figure 6.22 : The theoretical interaction energy curves for monoglycerides calculated with equation 6.22-6.25 both for two spheres (A) and two flat plates (B) as a function of the interparticle distance.
1 : Hydration repulsion energy 2 : Van der Waals attraction energy
3 : Total interaction energy

Now, suppose that the GLP particles may be regarded as particles which contain only one bilipid layer at the o/w-interface of these particles. Then, if those particles have deformed into platelet-like structures, the area of closest bilayer contact may increase markedly compared to the case of aggregated spheres. If the contact area approaches an average value of 0.01 μm^2, the interaction energy becomes 5 times larger than the energy in the case of spheres and at an area of closest contact of 0.1 μm^2 this factor would become 50 (also see figure 6.22). Thus one can imagine that the particle geometry may have a tremendous influence on the value of the modulus of a particle gel.

We will now proceed with the estimation of a theoretical value for the modulus of GLP particle gels. According to van Vliet (1976) an ideal particle network consists of particles which are arranged in a statistical network of chains, all of them contributing to the rigidity of this network to the same extent. For the moment we will suppose that this is also valid for our GLP gels. As has already been said the total interaction energy between two spheres covered with one bilipid layer can be roughly given by :

$$V_{tot} = - \frac{a\ A}{12\ H} + \pi\ a\ \lambda^2\ P_0\ e^{-H/\lambda} \qquad (\ 6.26\ )$$

Consequently the total force between these droplets is equal to :

$$F = \frac{\delta\ V_{tot}}{\delta\ H} = \frac{a\ A}{12\ H^2} - \pi\ a \lambda P_0\ e^{-H/\lambda} \qquad (\ 6.27\ )$$

For an estimation of the Young modulus this equation should be linearized in the equilibrium state, thus in the situation, where $F = 0$ and $H = H_o$. From series expansion it follows, to a first approximation, that the interaction force between two spherical particles in the state of equilibrium is equal to :

$$F_{Ho} = \triangle H\ [\ - \frac{a\ A}{6\ H_o{}^3} + \pi\ a\ P_0\ e^{-Ho/\lambda}\ ] \qquad (\ 6.28\ )$$

where :

$\triangle H$ = extension of the distance between two droplets (m)

From 6.28 the shear stress σ_s per m^2 is obtained by multiplying the force F in each chain by the number of chains per m^2 (see e.g. van Vliet, 1976) :

$$\sigma_S = F_{Ho} * \frac{\phi}{2 \pi a^2} \qquad (6.29)$$

where ϕ is the volume fraction of dispersed particles. Thus for σ_S the following equation is valid :

$$\sigma_S = \frac{\phi \Delta H}{2 \pi a} \left[- \frac{A}{6 H_o^3} + \pi P_0 e^{-Ho/\lambda} \right] \qquad (6.30)$$

It can easily be demonstrated that in the case of small strains the following relation is valid for the shear strain τ_S (-) of the particle network (van Vliet, 1976) :

$$\tau_S = \frac{\Delta H}{a} \qquad (6.31)$$

Thus the shear modulus G (N/m^2) of the network becomes :

$$G = \frac{\sigma_S}{\tau_S} = \frac{\phi}{2 \pi} \left[- \frac{A}{6 H_o^3} + \pi P_0 e^{-Ho/\lambda} \right] \qquad (6.32)$$

In our case we should know the value of the Young modulus. If no significant volume change occurs during deformation, the Young modulus E will become (according to e.g. Reiner, 1971) :

$$E = 3 * G \qquad (6.33)$$

Thus the theoretical modulus is equal to :

$$E = \frac{3 \phi}{2 \pi} \left[- \frac{A}{6 H_o^3} + \pi P_0 e^{-Ho/\lambda} \right] \qquad (6.34)$$

The hydration repulsion energy curve for GLP is unknown. Thus an estimation for the parameters λ and P_0 has to be made. We will do this with the aid of the equations 6.24 and 6.25. Summation of V_r and V_a gives the total interaction energy for two infinite plates as a function of the distance between these plates. Differentiation of this function gives the interaction force between these two plates :

$$F = \frac{A}{6\ \pi\ H^3} - P_0\ e^{-H/\lambda} \qquad (\ 6.35\ )$$

If it is supposed that $A = 6*10^{-21}$ J and $H = 9*10^{-10}$ m under the condition that $F = 0$ (see chapter 4 and 5), values for P_0 can be estimated for different λ values. These λ and P_0 values are listed in table 6.1. Next with equation 6.27 the equilibrium distance H_0 between two droplets can be calculated. Then the Young moduli can be obtained with equation 6.34. The values for H_0 and E are also represented in table 6.1.

Table 6.1 : Theoretical Young moduli for an ideal network of aggregated, spherical GLP particles calculated for different values of λ , P_0 , and H_0 with equation 6.34, where $A = 6*10^{-21}$ J and $\phi = 0.4$.

λ (m)	P_0 (N/M^2)	H_0 (m)	E (N/m^2)
$2.0*10^{-10}$	$3.9*10^{+7}$	$5.1*10^{-10}$	$4.0*10^{+5}$
$1.8*10^{-10}$	$6.5*10^{+7}$	$5.7*10^{-10}$	$6.0*10^{+5}$
$1.6*10^{-10}$	$1.2*10^{+8}$	$6.1*10^{-10}$	$7.6*10^{+5}$
$1.4*10^{-10}$	$2.7*10^{+8}$	$6.4*10^{-10}$	$9.3*10^{+5}$

For the 40% SBO/GLP gels, which were regarded as systems that contained spherical particles, an experimentally determined Young modulus was found of about $2.0*10^5$ N/m^2 at the highest deformation rate. If the water-layer thickness would be about 9 Å, which is the layer thickness determined by diffraction techniques, we found for the theoretically calculated Young modulus a value between $4*10^{+5}$ and $9*10^{+5}$ N/m^2, subject to the values selected for the parameters of the hydration repulsion curve. Thus there seems to be a reasonable agreement between the experimental and theoretical value for the Young modulus of a 40% SBO/GLP gel. There are a number of reasons why the value of the theoretical modulus E should be different from the experimental value :

1 As has already been stated the hydration repulsion curve for GLP is unknown. However, the values selected for λ and P_0 seem to be realistic, because hydration repulsion should be of less importance than in the case of e.g. phospholipids.

2 The network is supposed to be ideal, which is not the case. In reality a particle aggregate network model should be applied (see e.g. van Vliet, 1976). In the network structure a number of particles are present in aggregates and in this condition they do not act as stress bearing structure elements. Thus the effective volume fraction of particles is lower, although this effect will be of less importance at high dispersed phase concentrations.

3 The experimentally determined modulus, which was used for comparison with the theoretical modulus, probably is too low for two reasons. SBO/GLP gels behave strongly visco-elastic in the applied time scale (see figure 6.21a). Furthermore, it is not certain that the moduli have been determined in the linear region of the stress-strain curves. This latter effect may give both a higher or a lower value for E.

4 It is unknown, whether the particles remain spherical in the case of SBO particles that contain 20% GLP, when they become part of an aggregate, although we think that they may be regarded as undeformable spheres.

5 The real value of the Hamaker constant in the case of a SBO/GLP particle gel is unknown, but it is probably higher than $6*10^{-21}$ J.

The experimentally determined moduli for the 40% GLP gel and the gel which contained 32% HCNO and 8% GLP, are about $2.0*10^6$ and $9.0*10^5$ N/m^2 respectively. In our opinion this higher value is related to changes in particle geometry as a result of crystallization phenomena. An increase by a factor 10 for the pure GLP gel does not seem unrealistic in this respect as has been shown earlier in this paragraph.

Summarizing it may be concluded that the order of magnitude calculations for the theoretical moduli agree reasonably well with the experimental data for the Young moduli of GLP containing particle gels.

6.6 SUMMARY

In this chapter some results were shown of both the rheological and fracture properties of 100% GLP containing particle gels and gels containing 80% fat or oil on dispersed phase basis. The stress-strain curves of these gels appeared to be very similar in several ways, despite differences in composition. For instance, the gels studied showed comparable visco-elastic behaviour and plastic fracture behaviour at comparable time scales, although the SBO/GLP gels showed different behaviour. Furthermore, macroscopical fracture occurred in almost any case at the same Hencky strain at similar deformation rates. For as far as the firmness of the gels is concerned, it has been shown that both the moduli and the yield stress of the gelated systems are probably determined by the amount of crystallized fat present in the particles. This may well be related to the shape of the particles.

In our opinion this can only be explained by assuming that these rheological and fracture properties are closely related to a common mechanism, probably the formation of the α-gel phase of GLP at the o/w-interface of dispersed phase, a hypothesis for which strong evidence had already been represented in chapter 5. Furthermore, the rheological and fracture properties of gels only containing GLP on dispersed phase basis indicate that caseinate does not seem to influence these properties. This is in acceptable agreement with the model for α-gel phase aggregated particles as postulated in the final paragraph of chapter 5.

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7 SURFACE RHEOLOGICAL PROPERTIES OF THE α-GEL PHASE OF GLP

7.1 INTRODUCTION

For practical application a whipped emulsion, like whipped cream, should have a certain firmness after having been whipped. In the case of a whipped topping this can be achieved by the formation of a continuous network of aggregated fat particles (see chapter 3). Hitherto often a relatively large amount of an α-tending emulsifier, like GLP, is added. In the previous chapters the reason for this has been made clear.

In chapter 4 and 5 strong evidence has been given for the hypothesis that GLP may form an α-gel phase at the o/w-interface of fat particles. In chapter 3 and 6 it has been shown that emulsions which contain a large amount of this emulsifier on dispersed phase basis form gels below the crystallization temperature of the emulsifier mixture. These gels consist of a three-dimensional network of dispersed particles and it is postulated that these particles are connected to each other with this α-gel phase. This network structure has reversible properties, which means that during whipping the bonds between the structure elements become broken by the mechanical agitation, but new bonds are quickly formed at rest.

Another important property a whipped emulsion should have, is foam stability for a relatively long time, e.g. a few days. It seems very unlikely that coalescence of the bubbles can still be of importance in the whipped product, since they are encapsulated in the network structure of particle aggregates. This does not mean, however, that the bubble size distribution can not change as time proceeds, because the bubbles should also be stable against the process of disproportionation. As indicated in chapter 2 this process causes the gradual shrinking of the smaller bubbles in the foam as a result of gas diffusion, while the larger bubbles will grow in size.

In this chapter we will present a study of the surface rheological properties of GLP containing emulsions, because these properties may be closely related to the stabilization against the process of disproportionation (e.g. Ronteltap et al. , 1989).

7.2 BUBBLE DISPROPORTIONATION

Disproportionation is gas diffusion from smaller bubbles to bigger ones. The driving force for this process is the difference ΔP_{tot} between the Laplace pressures ΔP of two bubbles with different radii. Equation 7.1 shows that the Laplace pressure difference over a curved interface of a bubble is proportional to the surface tension and inversely proportional to its radius.

$$\Delta P = \frac{2\,\tau}{r} \qquad (7.1)$$

where :

τ = Surface tension (N/m)
r = Bubble radius (m)

This equation shows that the Laplace pressure is higher for smaller bubbles. Consequently for the pressure difference ΔP_{tot} between two bubbles of different size the following equation is valid :

$$\Delta P_{tot} = \Delta P_1 - \Delta P_2 = \frac{2\,\tau_1}{r_1} - \frac{2\,\tau_2}{r_2} \qquad (7.2)$$

According to Henry's Law, the solubility of a gas is proportional to its pressure. Thus in the neighbourhood of a small bubble the gas solubility is higher than close to a large one. As a result of the concentration gradient gas transport will occur from smaller to bigger bubbles.

By assuming that this transport is only governed by diffusion de Vries (1958) showed that as a result of disproportionation the square of the bubble radius decreases proportional to time. Relation 7.3 gives the equation of the Vries for the gradual shrinkage of one bubble in favour of a bubble with infinite radius which are separated by a liquid layer of thickness Θ_f :

$$r_t^2 = r_0^2 - \frac{4\ R\ T\ D\ S\ \tau}{P_0\ \Theta_f}\ t \qquad (7.3)$$

where :

r_t = Bubble radius at time = t — m
r_0 = Bubble radius at time = 0 — m
R = Gas constant — $J\ Mol^{-1}\ K^{-1}$
T = Temperature — K
D = Diffusion coefficient — m^2/s
S = Gas solubility — $mol\ m^{-3}\ Pa^{-1}$
τ = Surface tension — N/m
P_0 = Atmospheric pressure — Pa
Θ_f = Film thickness between the two bubbles — m
t = Time — s

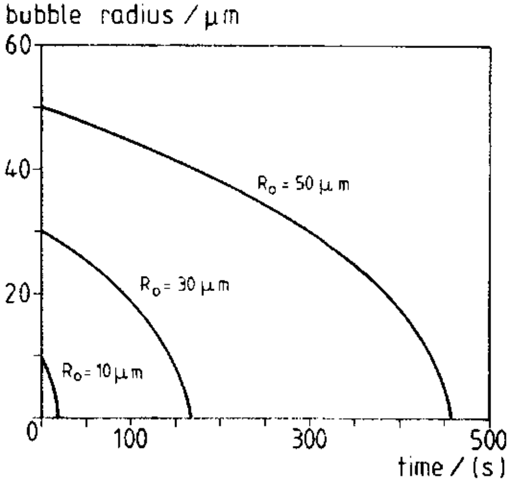

Figure 7.1 : The rate of disproportionation of nitrogen gas containing bubbles with different initial radii, as calculated with equation 7.3 according to the theory of de Vries (1958).

To demonstrate the possible importance of disproportionation in aqueous foams which contain relatively small bubbles, in figure 7.1 three examples are shown of the radii of N_2-filled bubbles as a function of time. The following values for the different parameters have been chosen : $T = 293$ K, $D = 2*10^{-9}$ m^2/s, $\tau = 40$ mN/m, $\Theta_f = 10$ μm and $S (N_2) = 6.9*10^{-6}$ mol Pa^{-1} m^{-3}.

The foams we are dealing with in this study usually contain air, although in practice laughing gas (N_2O), being much better soluble than N_2, is also regularly applied in whipped emulsions nowadays. Despite the fact that the solubility of nitrogen gas in an aqueous phase is rather low, foam destabilization by gas diffusion is expected to occur, as is apparent from figure 7.1, because on average the bubble radius in these whipped products is rather small, i.e. 50-100 μm. Since in whipped products this type of foam deteriorating process does not occur, how can the discrepancy between theory and practice be explained?

First of all the theory of the Vries assumes a constant value of the surface tension during the disproportionation process. For most practical systems, however, this is not a realistic assumption; surface active components are present and consequently, as the surface area of a bubble becomes smaller, the compression of the surface will also lead to a decrease in surface tension. Ronteltap et al. (1989), who extensively studied the stability of beer foam, have extended this theory by the incorporation of the relevant surface rheological properties. Prins (1987) has theoretically shown that a high surface dilational viscosity may greatly enhance bubble stability against disproportionation.

Furthermore, Lucassen (1981) has shown that for a certain value of the surface dilational elasticity E_d the process of disproportionation can be completely prevented. We will discuss this further in the next paragraph. Thus it may be clear that surface rheological properties should be taken into account.

Presumably in the case of whipped cream a network of partly coalesced fat particles, present both in the continuous phase and in the a/w-interface, takes care of the stability of air bubbles against this foam deterioration process (according to e.g. Buchheim, 1978 , Schmidt and van Hooydonk, 1980 and Brooker et al. , 1986). In the case of GLP containing emulsions it may as well be expected that both surface and bulk rheological properties are of great importance. If multilayers of crystallized GLP or a network of GLP particles are present at the a/w-interface, this type of surface layer could give a long-term stability of the air bubbles in the whipped product, according to the mechanism, described by Lucassen.

As has already been indicated in the introduction of this chapter in the case of GLP containing emulsions we are also dealing with the presence of a network structure of aggregated fat particles in the continuous phase of the whipped emulsion. If this network structure is linked with the interfacial layer around the air bubbles, which is rather likely, it is to be expected that both surface and bulk rheological properties are closely involved in the stabilization process against bubble disproportionation.

In this chapter results will be given of a study of the surface rheological properties of GLP containing systems. These properties were determined by means of dynamic surface dilational measurements, performed at small deformations. Our interest in these properties is twofold. Primarily we are interested in a stabilization mechanism against disproportionation. Secondly we think that it is necessary to obtain more knowledge of what substances adsorb to the a/w-interface in systems which contain both proteins, like sodium caseinate, and low-molecular weight surface active components, like monoglycerides or fatty acids. Up to now the latter subject is still rather controversial, although many scientists believe that low-molecular weight surfactants will gradually expel adsorbed proteins from an interface. We will discuss this subject in more detail in section 7.4.1 and 7.4.2 of this chapter.

7.3 SURFACE RHEOLOGY (Dynamic measurements)

A comprehensive review on the subject of surface rheology from a fundamental point of view has been given by van den Tempel (1977). Furthermore, Goodrich (1979) wrote an excellent review on the status of interfacial rheology for the science of fluid mechanics. In this chapter we will only deal with the surface dilational properties, because disproportionation involves purely isotropical surface compression and expansion processes. In our case only measurements close to equilibrium are meaningful, because stabilization should occur in this situation. Under this condition the surface dilational modulus ϵ (N/m) is used frequently. According to e.g. Lucassen and van den Tempel (1972[a]) this surface dilational modulus is defined as the quotient of a local surface tension change $d\tau$ and the corresponding relative area change dA/A of a uniform surface element A :

$$\epsilon = \frac{d\tau}{d\ \ln A} \qquad (7.4)$$

Usually an oscillatory experiment is applied to determine this dilational modulus. Relaxation processes such as diffusion of surface active material between bulk and surface (e.g. Lucassen and van den Tempel, 1972[b]) or relaxation processes within the monolayer itself (e.g. Veer and van den Tempel, 1973) will cause a phase difference θ to occur between a local area variation and the corresponding change in surface tension. This implies that for such a system ϵ is a complex quantity :

$$\epsilon = |\epsilon|\ e^{i\Theta} \qquad (7.5)$$

or :

$$\epsilon = |\epsilon| \cos\Theta + i\ |\epsilon| \sin\Theta \qquad (7.6)$$

where $|\epsilon|$ represents the amplitude ratio between surface stress and strain. The first part of equation 7.6 is the real part of the complex modulus which may be regarded as the two-dimensional "storage modulus" E_d (N/m) :

$$E_d = |\epsilon| \cos\Theta \qquad (7.7)$$

the second part of equation 7.6 is the imaginary part of the complex modulus ϵ. In equation 7.8 it is shown that $|\epsilon|\sin\Theta$ is related to the product of the radial frequency w (rad/s) and a so-called dynamic surface dilational viscosity n_d (Ns/m) :

$$wn_d = |\epsilon| \sin\Theta \qquad (7.8)$$

The product wn_d can be regarded as the surface "loss modulus". In this chapter the quotient of E_d and wn_d, which is equal to the tangent of the phase angle Θ, will often be used :

$$\tan\Theta = \frac{wn_d}{E_d} \qquad (7.9)$$

If $\tan\Theta$ is zero the surface behaves completely elastically during the measurement. For a completely viscous surface $\tan\Theta$ is infinite. Thus the dynamic rheological surface properties can be determined by simply measuring both $|\epsilon|$ and Θ during a sinusoidal surface deformation, performed at small barrier amplitudes according to the method described in chapter 2.

As has already been remarked in the previous paragraph, according to Blank (1968) and Lucassen (1981) disproportionation will not occur if the following condition is satisfied :

$$E_d = d\gamma \,/\, d\ln A > \gamma/2 \qquad (7.10)$$

This relation is based on the fact that, if the surface tension would decrease at least as fast as the relative bubble surface area would decrease as a result of bubble shrinkage, the driving force, the Laplace pressure, would not increase. Thus E_d can be regarded as a useful parameter for the characterization of the sensitiveness of bubbles to disproportionation. However, in this respect it should be emphasized that for long-term stability of bubbles, the bubble surface must behave elastically over a long time scale.

The emulsifier under study, was likely to have solid or semi-solid surface properties (chapter 5), implying surface elastic behaviour (see e.g. Veer and van den Tempel, 1973 and Larsson, 1978) ; it can be expected that a gel phase multilayer (chapter 4 and 5) or a monolayer of crystallized GLP molecules is adsorbed at the a/w-interface. Therefore, we had to build a Langmuir trough which could be used at very small deformations i.e. at relative deformation amplitudes between 10^{-4} and 10^{-3} in order to ensure linear surface rheological behaviour. In practice this meant that we were obliged to measure sinusoidal barrier displacements of 50 μm amplitude in an accurate way. In chapter 2 it has been described, how this has been accomplished.

A disadvantage of the langmuir trough that we designed, is that the sinusoidal deformation is not purely dilational, because the interface is also partly sheared. Thus the rheological numbers are likely to contain a shear component (e.g. Goodrich, 1979). However, we think that for our purpose, which only concerns the tracing of great differences in surface rheological behaviour between completely different systems, this method will give satisfactory results.

Proper dynamic measurements can only be performed after the surface tension of the system has reached a constant value during one deformation cycle, because otherwise both $|\epsilon|$ and Θ can not be determined. Normally this would last about 20 minutes. A problem is the fact that the frequency range, which could be applied in a reliable way with our Langmuir trough was rather small, namely ($0.01 < w < 1.0$ rad/s). Consequently the relevant time scale of the disproportionation process, being a few days for a whipped product, can not be matched with this relatively small frequency range. However, it can be stated that for stabilization of air bubbles against disproportionation only by means of surface properties, at least in the time scale of our dynamic measurements E_d should have a high value and the surface should respond completely elastically in the frequency range applied .

7.4 RESULTS AND DISCUSSION.

7.4.1 **A/w-surface at room temperature.**

In this paragraph some results will be shown of the surface dilational properties of GLP and/or sodium caseinate containing systems. The concentrations which have been used in these experiments are much lower than under practical conditions. Thus the rheological properties of these surfaces can not be translated directly into the properties of surfaces in whipped emulsions. The results of these experiments should therefore merely be regarded as examples of specific behaviour of these components at an interface.

The surface rheological properties of GLP have been studied in two different ways. Part of the measurements were performed by preparing a diluted GLP dispersion, pouring this dispersion in the Langmuir trough and subsequently measuring the surface rheological properties as a function of time at room temperature. A second series of measurements were made up of experiments, where a small amount of a GLP solution in soybean oil (SBO) was spread on a surface of an aqueous phase at room temperature.

First the rheological properties of a surface of a 0.1% sodium caseinate solution will be discussed. The properties of a surface that contains proteins usually is strongly time-dependent. It may take a considerable amount of time before an equilibrium state is obtained. Therefore, experiments were always started by preparing a fresh surface by means of an expansion of the total surface area with a factor 3 within a few seconds. In the case of the 0.1% sodium caseinate solution we found that after about 4 hours a relatively constant value of about 48 mN/m is obtained for the surface tension (also see figure 7.4). This slow surface tension relaxation process may be the result of two different mechanisms :

1) It is known that both unfolding of proteins at an interface and desorption of these molecules usually may take a lot of time (see e.g. Mussellwhite, 1966, Benjamins, 1975, Darling, 1987 and MacRitchie, 1985). In the case of sodium caseinate which is a mixture of proteins, especially the latter process may result in a slow surface tension decrease towards an equilibrium value, because in this state components which are most surface active should be adsorbed at the interface.
2) Sodium caseinate may still contain a small fraction of fat which might cause a slow decrease in surface tension. The same effect has been shown by e.g. Prins (1986) in the case of the a/w-surface of skim milk.

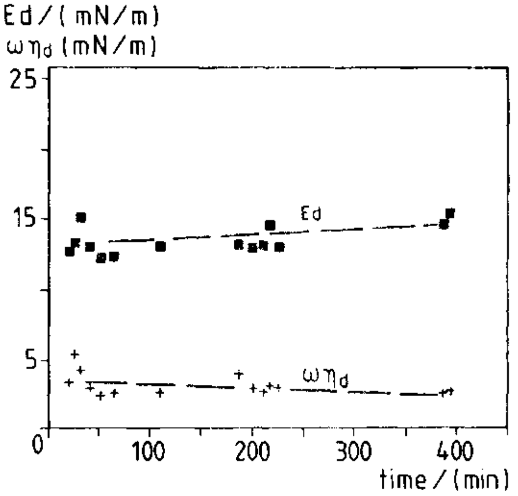

Figure 7.2 : The storage and loss modulus of a surface of a 0.1% sodium caseinate solution determined at a radial frequency of 0.314 rad/s and at a relative amplitude of $2*10^{-2}$ as a function of time.

Presumably the first process is most important, since the τ-value of about 48 mN/m for the equilibrium surface tension of a caseinate solution is usually found by other scientists. This equilibrium value is quite independent from the caseinate concentration, because of the high affinity character of this protein.

In the case of a caseinate containing surface we found the modulus to be constant up to deformation levels of at least 8%. Therefore, we decided to perform our experiments at a relative deformation amplitude of 2% in order to be certain to remain within the linear region of deformation. In figure 7.2 the dynamic surface dilational moduli E_d and wn_d for the surface of a 0.1% sodium caseinate solution are represented as a function of time after initial expansion of the surface. These measurements were performed at a radial frequency of 0.314 rad/s at room temperature.

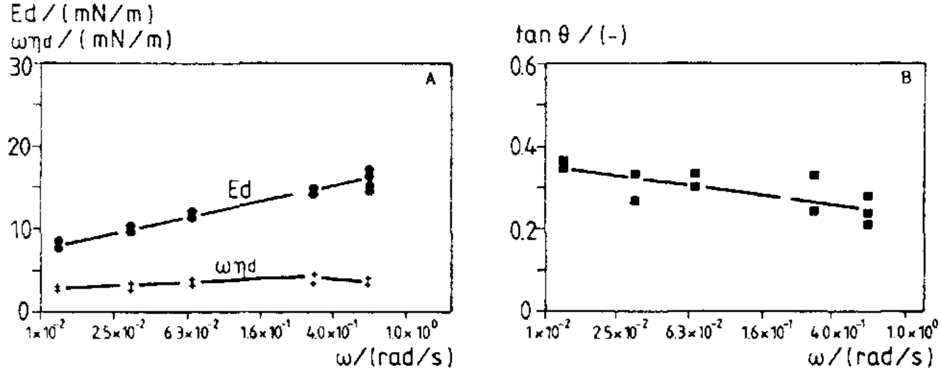

Figure 7.3 : The surface rheological properties of an aged surface of a 0.1% sodium caseinate solution determined at ambient temperature and at a relative amplitude of deformation of $2*10^{-2}$. (The age of the surface is about 20 hours).

It appears that the values for these two moduli are independent of time, although a small decrease in surface tension still occurs. This may also indicate that the surface tension decrease is not related to adsorption of lipids at the a/w-interface, because then we would expect the dilational modulus to increase to much higher values (see e.g. Prins, 1985).

In figure 7.3 the results of the dynamic surface rheological properties of the caseinate solution are represented as a function of the radial frequency. From this figure it appears that the surface behaves visco-elastically, because E_d gradually decreases as a function of the time scale of the experiment. The value of tanθ increases from 0.25 to 0.35 at lower frequencies, which is an alternative way to point to visco-elasticity of a surface layer of adsorbed caseinate molecules.

It may be clear from the results of these surface rheological measurements that disproportionation can not be prevented by a surface layer of adsorbed caseinate molecules (also compare with equation 7.5). Furthermore, it is also not possible that an increase in the bulk protein concentration would lead to an increased surface "stiffness" combined with long-term elastic properties of the surface, since saturation adsorption is already obtained at a very low protein concentration. Thus small bubbles, which are only stabilized by adsorbed caseinate molecules, are supposed to disappear at a rate, as approximately predicted by equation 7.3.

We will now consider similar experiments performed with dispersions, which contained 0.1% GLP as dispersed particles. A distinction will be made between the surface rheological properties of dispersions which were prepared in a 0.1% sodium caseinate solution and in a 2 mMol phosphate buffer of pH equal to a value of 6.9. The preparation of these dispersions has been described in section 2.2.1.1 and the experimental procedure of the surface rheological measurement has been shown in section 2.2.8.4.

In figure 7.4 plots are represented of the surface tension as function of time of the two dispersions under consideration. We have also included a graph for the 0.1% sodium caseinate solution without GLP. From this figure it appears that great differences exist between the "equilibrium" surface tensions of these three systems. It should be emphasized that the dispersion prepared in the phosphate buffer appeared to be very unstable, since the particles formed visible aggregates at the moment when the trough was filled with this dispersion. Of course this may have affected our experimental results, since in this case bulk rheological properties may become of importance too.

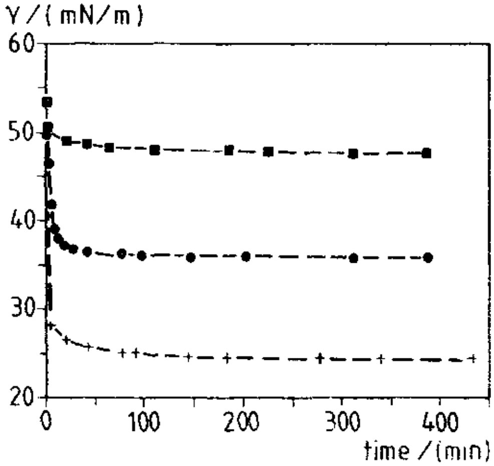

Figure 7.4 : The surface tension as function of time for three different systems as measured at a temperature of 20°C.

■ ■ ■ : 0.1% sodium caseinate solution.

● ● ● : 0.1% sodium caseinate solution containing 0.1% GLP.

+ + + : 0.1% GLP dispersion in a 2 mMol phosphate buffer.

It is not known whether the presence of sodium caseinate does influence the value of the surface tension of a dispersion of GLP particles. It is generally believed that low-molecular weight surfactants may gradually expel proteins from an interface (e.g. Oortwijn and Walstra, 1979 and Darling and Birkett, 1987). If this would be true for GLP particle dispersions, one would expect the equilibrium surface tension to become the same both for dispersions of GLP particles in a phosphate buffer and in a 0.1% sodium caseinate solution. The fact that this was not found, could be explained by assuming that there is an important time dependency. This means that, if we would have waited long enough, the same value for the surface tension in the state of equilibrium would have been obtained for these two systems.

However, it may well be that differences in particle size have caused the equilibrium γ values to be different. For, if the particles in the phosphate buffer are larger compared to the particles in the caseinate containing sample, it seems logical that the composition of the o/w-interface of the GLP particles may be different. The adsorption of these particles at the surface and the spreading process may then give a different composition of the a/w-interface. In section 7.4.2 we will give additional evidence in favour of this explanation.

Let us now first consider the surface rheological properties of these two GLP containing systems and compare these results with those obtained for the GLP-free caseinate solution. In figure 7.5 it is demonstrated for the GLP dispersion in phosphate buffer that the region in which surface stress and strain respond in a linear way, is very small. Linearity is already lost at a relative deformation larger than ca. $2*10^{-4}$, as is apparent from both the $|\epsilon|$ and $\tan\theta$ versus dA/A plots. This strongly points towards solid state properties of this surface.

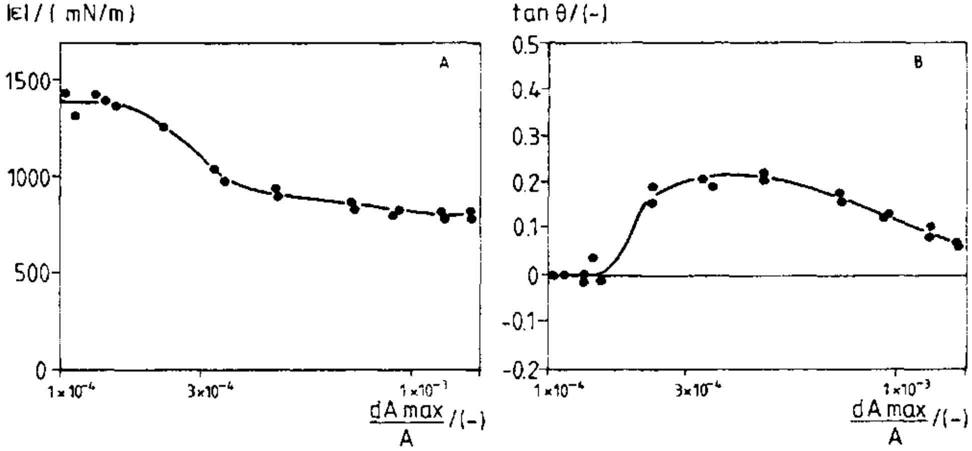

Figure 7.5 : Determination of the linear region of surface stress and surface strain both from $|\epsilon|$ and $\tan\Theta$ for a 0.1% GLP containing dispersion, prepared in a 2 mMol phosphate buffer. The radial frequency = 0.314 rad/s, T = 20°C and the age of the surface = 20 hours.

In chapter 6 it has already been stated that the region of linear behaviour of stress and strain for GLP gels could also be very small. However, it should be emphasized that it is not known, whether it is allowed to make a direct comparison between surface rheological and bulk rheological properties. It may be possible that in a surface dilational experiment different types of physical bonds are broken than in a bulk rheological experiment. In the case of a GLP surface of the monolayer type, physical bonds between crystallized hydrocarbon chains have to be broken, whereas during a bulk rheological experiment it is likely that hydrated bilipid layers of the α-gel phase start shifting over each other under an applied stress.

The dilational modulus of the system in the phosphate buffer has a value of about 1400 mN/m at a radial frequency of 0.314 rad/s, as is apparent from figure 7.5. This is a factor 100 larger than the dilational modulus of the 0.1% sodium caseinate solution. This result shows a strong resemblance with the results of dynamic surface dilational measurements of Veer and van den Tempel (1973) obtained for diluted dispersions of long chain alcohols, like hexadecanol, in the gel state. From the results of our experiments it may be doubted that their rheological experiments have been performed in the linear region, since they used a relative amplitude of about $2*10^{-3}$. If so, it would be likely that their values for the moduli should be even higher. On the other hand they found completely elastic behaviour for these surface layers at time scales shorter than about 10 seconds which might indicate that their measurements have been performed within the linear region.

In figure 7.6 the results are shown of the surface rheological parameters $|\epsilon|$ and $\tan\Theta$ for a 0.1% GLP dispersion in the two different continuous phases as a function of the radial frequency. In the case of the sodium caseinate containing dispersion we were obliged to measure at a relative deformation amplitude of $2*10^{-3}$, because at a smaller deformation amplitude the signal to noise level would become too low. Thus it seems likely that these measurements have been performed beyond the linear region.

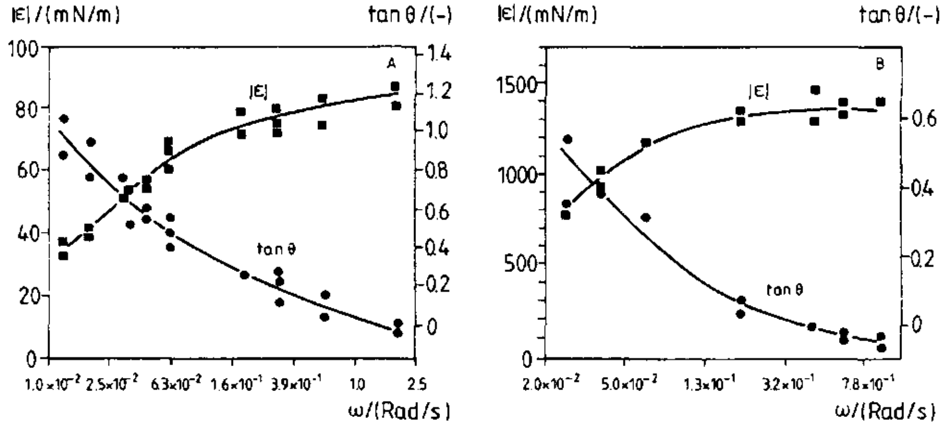

Figure 7.6 : The dilational modulus $|\epsilon|$ and tanΘ for a 0.1% GLP particle dispersion in two different continuous phases as a function of the radial frequency at T = 20°C. The age of the surface = 20 hours.
A : Aqueous phase = 0.1% sodium caseinate solution ; $dA/A = 2*10^{-3}$.
B : Aqueous phase = 2 mMol phosphate buffer ; $dA/A = 2*10^{-4}$.

When the values of the dilational moduli of the two systems are compared with each other, it is quite remarkable to notice such a great difference between these values. The dependence of tanΘ on the radial frequency shows strong resemblance for these two dispersions. At high frequency tanΘ is about zero, meaning that the system responds completely elastically, as one would expect to find for a surface in the solid state. At low frequency the "loss angle" Θ increases to a value higher than 45° which points towards the occurrence of surface relaxation processes at longer time scales. This visco-elastic surface behaviour at low frequencies was to a certain extent surprising, because we would have expected the surface to respond elastically over a wide range of frequencies.

Now the question rises what in fact determines the surface rheological properties of a dispersion which contains slightly soluble surfactant particles. As has already been remarked Veer and van den Tempel (1972) studied the surface behaviour of dispersions of fatty alcohols, like dodecanol and hexadecanol. They concluded from their experiments that in these systems a surface is formed which consists of a monolayer of surfactant molecules in contact with surfactant particles that are present in the surface. This state shows strong resemblance with a monolayer of a slightly soluble surfactant, after collapse has occurred (see Larsson, 1978). According to Veer and van den Tempel the rheological properties of such a surface can be characterized by a high value of the surface dilational modulus accompanied by slow surface relaxation processes. The time scale at which relaxation occurs, is strongly determined by the length of the hydrocarbon chains of the surfactant molecules. They also state that similar behaviour has been found for aqueous dispersions of monoglycerides or fatty acids.

In our case we are dealing with a system of particles which also contain a large amount of slightly soluble surfactant molecules. These particles will adsorb to the a/w-interface, where spreading of surface active components occurs. According to Veer and van den Tempel a monolayer would then be formed in contact with the emulsifier particles "adsorbed". The value of the surface tension is determined both by the monolayer and the particles, since after collapse of a monolayer it is also noticed that the surface tension may drop strongly below the surface tension in the equilibrium state (Veer and van den Tempel, 1972 and Larsson, 1978).

What could be the influence of the sodium caseinate molecules on the surface rheological properties of a dispersion of GLP particles? Normally one would expect the caseinate molecules, if they are adsorbed at the a/w-interface anyway, to become replaced by the low-molecular weight surfactants of the gel phase present at the interface of the particles. However, it has already been noticed that the caseinate containing dispersion appeared to be much more stable than the dispersion which had been prepared in the 2 mMol phosphate buffer. Thus adsorbed caseinate molecules probably form a small energy barrier against particle aggregation its nature being both electrostatic and steric. It may well be that such an energy barrier also prevents surfactant particles to become adsorbed at the a/w-interface. This would explain both the relatively high value for the surface tension of the caseinate containing system and the low value of the dilational modulus compared to the system in phosphate buffer.

However, as indicated before, another factor may also be of great influence on the surface rheological properties of the surfactant particles, namely particle size. It may be expected that at high temperatures the coalescence stability of the GLP dispersion, prepared in the phosphate buffer, would be lower than the stability of the same dispersion prepared in a sodium caseinate solution. Furthermore, it should be emphasized again that bulk rheological properties may have influenced our results.

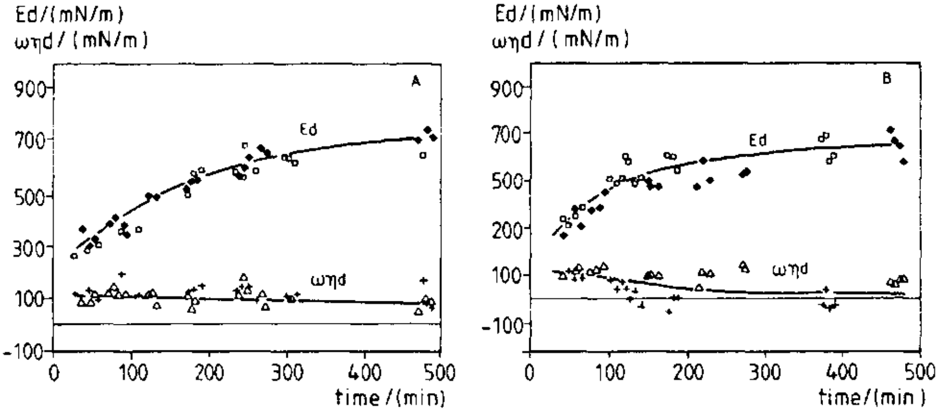

Figure 7.7 : The surface rheological moduli E_d and wn_d for GLP spread from a SBO solution upon two different continuous phases, determined as a function of time after spreading. The age of the surface is about 20 hours, the radial frequency = 0.314 rad/s and T = 20°C.

A : Continuous phase is a 2 mMol phosphate buffer.

B : Continuous phase is a 0.1% sodium caseinate solution.

In order to learn more about the possible influence of sodium caseinate on the surface rheological properties of GLP containing systems, we decided to perform some experiments, where GLP was spread from a soybean oil solution both on the surface of the 2 mMol phosphate buffer and the 0.1% sodium caseinate solution. This procedure is described in section 2.2.8.4. The amount of GLP which was added to the surface exceeded the monolayer concentration with a factor of about 100, so multilayer formation could occur.

In figure 7.7 the results are represented of the dilational moduli E_d and $w\eta_d$ for these two systems as a function of time after spreading. It was observed that the surface dilational modulus $|\epsilon|$ strongly increased and τ decreased as time proceeded. This value of $|\epsilon|$ was not the equilibrium value, since a plot of log $|\epsilon|$ versus log time almost shows linear behaviour. The storage modulus E_d reached a value of about 700 mN/m after 500 minutes, independent from the fact, whether sodium caseinate was present or absent in the water phase. This supports the idea that sodium caseinate is not of great influence on the surface rheological properties of GLP. In the case of GLP particle dispersions, adsorbed caseinate molecules could pose an energy barrier against adsorption of GLP particles at the a/w-interface. Also the surface tension was equal for both systems i.e. τ had a value of about 34 mN/m. This value indicates that τ and $|\epsilon|$ are independent, since e.g. the equilibrium value for τ in the case of the 0.1% GLP dispersion in the solution of 0.1% sodium caseinate amounted to 36 mN/m, whereas the value for the dilational modulus of this system was only about 70 mN/m.

In our opinion the surfaces of these systems are "GLP-surfaces", meaning that GLP components determine the surface rheological properties. In figure 7.8a it is demonstrated that linear behaviour of the surface stress and strain can only be obtained at very small deformation viz. at deformation levels which are at least smaller than $1*10^{-4}$. This figure seems to indicate that the linear region is even smaller than in the case of systems containing GLP particles. This could mean that the composition and/or structure of this type of surface is different from the surface of systems containing GLP particles.

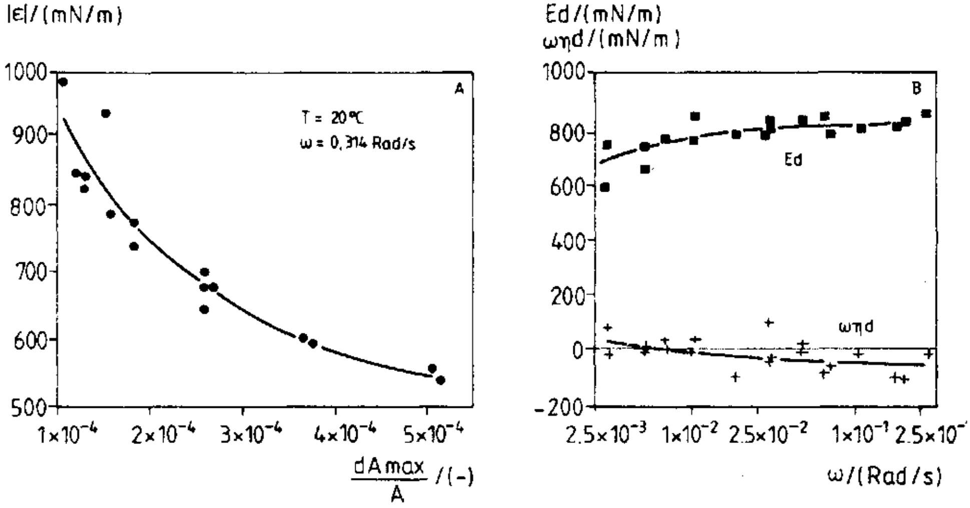

Figure 7.8 : The rheological properties of a surface of a 2 mMol phosphate buffer on which 0.5 ml of a 5% GLP containing SBO-solution was spread at a temperature of 20°C. The age of the surface was 20 hours.
A : The dilational modulus as function of the relative deformation.
B : The dilational modulus and tanΘ as a function of the radial frequency determined at a relative deformation of $1.5*10^{-4}$.

Additional evidence for this assumption can be found in figure 7.8b, where the rheological parameters $|\epsilon|$ and tanΘ for this type of surface is represented as a function of the radial frequency. Here we can see that the surface responds almost completely elastically in the frequency range that has been studied. Consequently this result is contradictory to the result obtained for the surfactant dispersions.

Summarizing it may be concluded that at room temperature the surface rheological properties of dispersions which contain both GLP and sodium caseinate, are mainly determined by the α-tending emulsifier. GLP will provide the surface with solid state properties and that the gel phase of GLP very likely determines these surface rheological properties.

7.4.2 Temperature influence on the surface rheological properties of GLP.

In chapter 5 it has been shown with DSC experiments that the gel phase of GLP will melt at a temperature of about 47°C. In principle, it is possible to measure the occurrence of a phase transition in the surface with the aid of surface rheology. This can be done by means of the determination of the π/A-curve at temperatures below and above the cloud point of the surfactant (see e.g. Larsson, 1978). However, this must also be possible with dynamic surface tension measurements. Furthermore, the latter type of measurements have the advantage that time dependent effects can be noticed.

In the case of GLP one would expect the surface dilational modulus to increase strongly during cooling of a dispersion of GLP particles. Furthermore, it is likely that, as a result of the crystallization of adsorbed surfactant molecules, relaxation processes will shift towards lower frequency. We decided to verify this idea for GLP by measuring the surface rheological properties of a 0.1% GLP dispersion in a 0.1% sodium caseinate solution during a gradual temperature decrease. During this experiment the temperature decreased at a rate of approximately 1°C/minute.

In figure 7.9 the results are shown of both $|\epsilon|$ and tanΘ as function of the temperature for two systems which have the same GLP concentration, however, which differ from each other in particle size. The first system had been obtained by dilution of a 1% GLP dispersion, prepared in a 1% sodium caseinate solution, with a 0.1% sodium caseinate solution at high temperature towards the desired concentration of 0.1% GLP. The second system has been prepared under the same homogenization conditions. However, the emulsion itself was prepared with a low sodium caseinate to GLP ratio (This emulsion contained 0.1% sodium caseinate and 3% GLP). This caused the pH of this specific emulsion to drop to a very low value of about 4.8 during the homogenization process, causing this emulsion to be unstable. Normally we did not have any problems with the preparation of emulsions at this composition. However, in this case we think that the free fatty acid content of the GLP was too high.

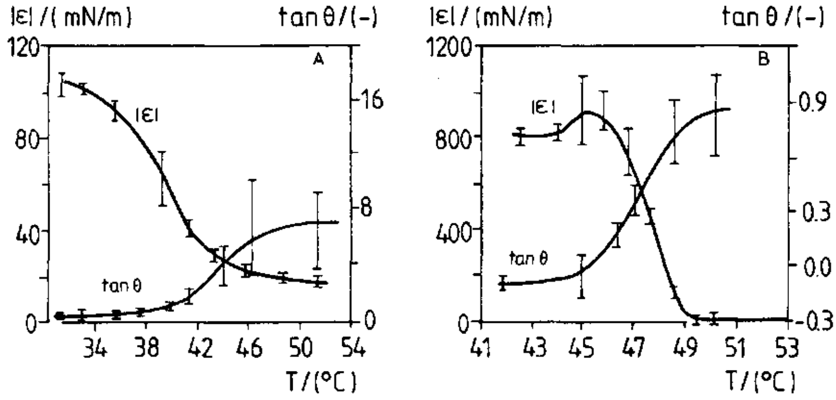

Figure 7.9 : The surface rheological properties of a 0.1% GLP dispersion in a solution of 0.1% sodium caseinate determined as function of temperature, which decreased at a rate of approximately 1°C. The radial frequency = 0.314 rad/s.
A : Measurement for a stable particle dispersion.
B : Measurement for an unstable particle dispersion.

First the results of figure 7.9a will be discussed. At least partly, figure 7.9a may be compared with figure 7.6a, because both samples contain particles of approximately the same size. At high temperature the dynamic measurements were started at a relative deformation amplitude of 0.5%, which was gradually reduced to 0.1% in the temperature range of 30-38°C. Therefore, it seems likely that part of these measurements have been performed outside the linear region.

At temperatures exceeding 46°C the moduli have a value of about 20 mN/m which is similar to the modulus of a sodium caseinate solution at room temperature. However, it is very unlikely that we are dealing with a surface layer which only contains adsorbed caseinate molecules. At high temperature low-molecular weight surfactant molecules probably also determine the value of the surface tension (γ = 27.5 mN/m). At high temperature tanΘ is approximately 7 which means that the surface responds almost completely viscously in the time scale of the experiment applied. Reduction of the temperature leads to an increase in the dilational modulus towards a value of about 110 mN/m at a temperature of 30°C, whereas tanΘ decreases to 0.4.

At a temperature of about 47°C the surface rheological properties start changing. This fits in rather well with the results of DSC experiments which have been given in chapter 5. The results of the dynamic measurements can only be compared with the melting curves of the GLP gels, because the cooling rates applied for the determination of the cooling curves are too high.

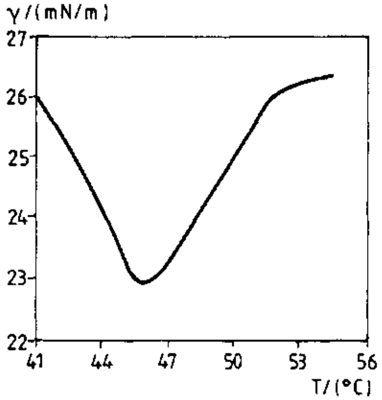

Figure 7.10 : The surface tension versus temperature curve for a surface of a 0.1% GLP dispersion in a 0.1% sodium caseinate solution. The temperature was gradually lowered at a rate of 1°C/minute.

In figure 7.9b the results of the dynamic measurements are shown for the unstable emulsion. Here we can see that the phase transition occurs more pronounced and the transition temperature is about two degrees higher. The dilational modulus reaches a value of about 800 mN/m, whereas tanΘ reaches a value of almost zero at the applied frequency of 0.314 rad/s, just as one would expect to find. Thus, when the α-gel phase of GLP is formed below the cloud point of the emulsifier mixture the surface rheological properties are strongly determined by this gel phase. Furthermore, figure 7.10 strongly points to the occurrence of a phase transition in the surface, because a large dip was found in the τ versus T-curve at the temperature, where the gel phase is supposed to melt.

However, it still remains unknown, whether these rheological properties are determined by a monolayer of surfactant in contact with surfactant particles or that we are dealing with a multilayer of surfactant molecules. According to Veer and van den Tempel (1978) the first explanation is the most likely one.

7.5 GENERAL REMARKS

Three major conclusions can be drawn from the results that have been shown in this chapter.

1) At room temperature the surface rheological properties of systems which contain a relatively large amount of the α-tending emulsifier GLP are strongly determined by the presence of this emulsifier. It is very likely that the α-gel phase of GLP is closely involved in these properties.

2 The surface rheological properties of GLP containing systems are strongly determined by the history of the system (the temperature, the particle size).

3) The surface rheological properties of dispersions which contain GLP, may be influenced by sodium caseinate.

It has been shown that in the case of GLP containing emulsions, a solid surface layer is formed at the a/w-interface. Such a layer could protect air bubbles against disproportionation, if $|\epsilon|$ would be high enough, but this is not the only important prerequisite. The extent of stabilization against this foam deterioration process will also strongly depend on the fact, whether the surface will respond completely elastically or visco-elastically in the relevant time scale. We have shown that relaxation processes in the surface of a dispersion of GLP particles may already occur after a short period of time. Although the dispersed phase concentration was rather low compared to practical conditions, it may be expected that these surface rheological properties, alone, are not sufficient enough for long-term stability of air bubbles against disproportionation.

However, the network structure of aggregated fat particles, present in the continuous phase of the whipped emulsion, is likely to be another important stabilizing factor. It may be expected that this network is connected to the surface layers of the bubbles. This particle network may stop the shrinking process of air bubbles, if the yield stress is at least equal to the Laplace pressure of the bubbles. With equation 7.1 a mean value of the Laplace pressure can be estimated. If it is supposed that the mean bubble radius r is 50 μm and γ is 25 mN/m, ΔP becomes equal to 1000 N/m^2. In chapter 6 it has been shown that at a time scale of about 4 minutes 12% GLP particle gels have a yield stress equal to about 4000 N/m^2. Thus at this time scale and at this dispersed phase content stability of the bubbles against shrinking may be expected. However, it should be realized that also as a result of the visco-elastic properties of GLP particle gels, the stability against disproportionation will be gradually lost.

Summarizing, under normal storage conditions of a few days, it is likely that disproportionation in these whipped emulsions can be strongly delayed, if both the dispersed phase content and the GLP concentration are high enough.

7.6 SUMMARY.

In this chapter results have been given of the surface rheological properties of systems which contain both GLP and sodium caseinate. Knowledge of these properties is of great importance in order to be able to understand better the possible stabilization mechanism against disproportionation in α-tending emulsifier containing whippable emulsions.

It has been found that at room temperature GLP determines the surface rheological properties of dispersions containing 0.1% GLP in a solution of 0.1% sodium caseinate. The surface behaves completely elastically at time scales shorter than about 20 seconds and the modulus reaches a very high value. However, we found that at longer time scales relaxation processes, occurring in the surface layer, become of importance at this dispersed phase concentration. Thus, for the prolonged stability of air bubbles in the foam of a whipped emulsion, also the presence of a continuous network is required.

The surface rheological behaviour is related to the formation of an α-gel phase below the transition temperature of the emulsifier mixture. It has been found that the surface rheological properties, start to come about in the temperature range, where DSC and x-ray diffraction measurements indicate that the gel phase of GLP still exists.

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8 CONCLUDING REMARKS

The aim of this study was primarily to obtain a better insight into the physical properties of whippable emulsions, which contain a relatively high level of an α-tending emulsifier. It is known that these emulsifiers strongly promote spontaneous fat particle aggregation at room temperature, but up to now nobody could explain the reason for this typical behaviour. Although this study was mainly performed on the α-tending emulsifier mixture glycerol lacto palmitate (GLP) and partly on a mixture of acetylated monoglycerides (ACTM), we think that some important general conclusions can be drawn from the results of this study which are important for the physical behaviour of these whippable emulsions.

We have obtained strong evidence for the hypothesis that an α-tending emulsifier may form an α-gel phase at the interface of the fat particles below the crystallization temperature of the emulsifier mixture. This gel phase may be regarded as a lamellar structure of stacked bilipid layers of crystallized surfactant molecules. In the presence of water these bilipid layers become hydrated. We believe that the presence of this α-gel phase mainly determines the physical behaviour of these whippable emulsions. In our opinion, the idea that a gel phase may be formed at the interface of fat particles in an emulsion which contains a large amount of an α-tending emulsifier is completely new. It has always been believed that these emulsifiers are unable to form mesomorphic phases with water. We fully agree with this hypothesis above the cloud-point of the emulsifier mixture. However, in our opinion nobody has ever thought of the idea that an emulsifier which does not form mesomorphic phases above the melting temperature of its hydrocarbon chains, may form a gel phase below the transition point of the surfactant mixture. For, this would imply that water molecules should be able to diffuse through the very hydrophobic region of crystallized hydrocarbon chains, which would be quite surprising. However, from the results that we have obtained from

DSC, x-ray diffraction and neutron diffraction we conclude that this process really occurs at temperatures well below the melting point of the emulsifier.

Another important aspect of the ability of an α-tending emulsifier to form a gel phase is, that this gel phase is stable for a long period of time. It is a well-known fact that monoglycerides are not very functional in this kind of emulsions although they are also capable of α-gel phase formation. Two reasons for this difference in physical behaviour may be relevant in this respect :

1) Monoglycerides are always unstable in the α-polymorphic form. This causes the gradual transformation of α-crystals into the more stable β-modification. This process is attended with expulsion of the water molecules from the lipid bilayers. This may be one explanation for the reason why the whipping properties of emulsions, containing a high level of monoglycerides are poor.
2) An different reason may be that proteins, like sodium caseinate, which are usually present in this type of edible emulsions, are bound relatively strongly to the o/w-interface of monoglyceride stabilized fat particles. This would explain why spontaneous particle aggregation does not occur in emulsions, containing a high level of monoglyceride and sodium caseinate. We have seen that in the case of emulsions which contain a relatively high level of GLP this process occurs at rest.

We think that the gel phase of GLP has long-term stability, because of its complex composition. It is well-known that complicated lipid mixtures will at least initially crystallize in the α-modification. However, if polymorphic transitions into β' or β could occur, this would certainly happen. As this process is very unlikely in the case of an α-tending emulsifier, like GLP, the α-polymorphic form will remain stable. If the α-polymorphic form of

GLP is brought into contact with water, hydration of the bilipid layers will occur. The extent of hydration is expected to depend on the physical properties of the headgroup, e.g. its hydrophilicity, its shape and the presence of ionic components.

In this thesis it has been shown that the α-gel phase of GLP strongly determines the whipping behaviour of o/w-emulsions. The presence of this gel phase presumably causes the fat particles to flocculate spontaneously. These aggregates show reversible behaviour, meaning that a large disturbance of such aggregates, like during whipping, causes the physical bonds between the structure elements to become broken, but that these bonds will become restored fast enough at rest. This is very essential, since the whipped product should have a certain firmness immediately after the whipping process.

Another important requirement a whipped product should meet is long-term stability of the air bubbles in the product. Small air bubbles will gradually disappear as a result of a diffusion process, which is usually referred to as disproportionation. Therefore, the bubbles have to be protected against this process in a certain way. We have shown that it seems likely that the stability of the bubbles in an emulsion containing GLP particles is at least partly controlled by specific rheological properties of the a/w-surface, namely a high surface dilational modulus accompanied by elastic behaviour at short time scales. We believe that the α-gel phase of GLP is closely involved in the formation of a surface layer with such specific properties. However, it seems likely that bulk rheological properties are also involved in the stabilization of the air bubbles.

Summarizing, it can be stated that the whipping behaviour of an emulsion containing a relatively large amount of an α-tending emulsifier, like GLP, is mainly determined by the formation of an α-gel phase at the o/w-interface of the dispersed particles.

SUMMARY

In whippable emulsions, like whipping cream and toppings, the presence of a network structure is required both for reasons of foam firmness and stability. In toppings this is often realized by the addition of a relatively large quantity of a so-called α-tending emulsifier on total fat basis, because such an emulsifier strongly promotes structure formation in these emulsions. The term α-tending means that this emulsifier crystallizes in the α-polymorphic form. It is generally believed that this property is closely related to its function in these systems, although an explanatory mechanism was still unknown. Some investigators have proposed that these emulsifiers may enhance partial coalescence of the fat particles. However they do not give an explanation for the fact that these specific emulsions do not churn, not even after prolonged whipping.

In the introduction we made clear why we decided to study the mechanism of α-tending emulsifier induced structure formation in whippable emulsions. The results of such a study could have a wider applicability, since in many emulsions the presence of a network structure is desired e.g. in pharmaceutical or cosmetic products, such as ointments or creams. For this purpose we made use of a model emulsion showing strong structure forming properties. This emulsion primarily consisted of hardened coconut fat, the α-tending emulsifier glycerol lacto palmitate (GLP), and sodium caseinate.

In chapter 2 the experimental methods are given, which have been used in this study. We have used a number of diffraction techniques to elucidate the crystal structure of the fat particle network, such as small angle and wide angle x-ray diffraction (SAXD and WAXD) and neutron diffraction. Differential Scanning Calorimetry (DSC) has been used extensively to study crystallization processes in these systems. Furthermore, both bulk and

surface rheological methods were applied in order to get a better physical insight into the structure properties of toppings that contain a large amount of GLP.

In chapter 3 preliminary experiments with the aim to elucidate the microstructure of GLP containing whippable emulsions were discussed. It was apparent that the presence of a rather large amount of this emulsifier is closely related to structure formation and gelation phenomena in these systems. Evidence for the hypothesis that this structure consists of flocculated particles was obtained. Partial coalescence or clumping, if occurring anyway, is probably of minor importance in these systems. It was speculated that GLP may be involved in particle aggregation by means of the formation of a gel structure at the o/w-interface of the particles. We supposed that with this gel structure the particles would stuck together, as a result of van der Waals forces.

In chapter 4 strong evidence has been obtained for the hypothesis that this gel structure is of partly mesomorphic nature. The existence of an α-gel phase in particle gels only containing GLP, sodium caseinate and water has been shown with both x-ray diffraction (WAXD and SAXD) and neutron diffraction studies. This gel phase consists of hydrated bilipid layers of amphiphilic molecules, originating from the mixture of emulsifier molecules. The hydrocarbon chains of these amphiphiles are crystallized in the α-modification. At the state of maximum swelling the gel phase has a hydrated bilipid layer thickness between 63-65 Å dependent on the history of the sample prior to wetting. The dry bilipid layer has a thickness of approximately 55-56 Å.

At the end of chapter 3 we postulated that a gel structure is probably present at the o/w-interface of the fat particles at a GLP/fat ratio higher than 20%, dependent on the size of the dispersed particles. However, we failed to detect the presence of the α-gel phase in emulsions containing less than 80% GLP on dispersed phase basis with the applied diffraction methods. This could have been caused by the fact that in these systems the number of stacked bilipid layers present at the o/w-interface is too small to be detectable.

In chapter 5 it has been shown with DSC and SAXD that in the presences of water α-tending emulsifiers, like GLP or ACTM (acetylated monoglycerides) become hydrated below the crystallization temperature of their hydrocarbon chains. GLP forms a lamellar gel phase of hydrated bilipid layer, whereas ACTM only forms a monolayer type of gel phase.

The α-gel phase of GLP is very stable. The α-polymorphic form probably is the only crystal modification that is formed in the temperature range of 0-45°C and the addition of water leads to hydration of these α-crystals. Above the melting temperature of the gel phase dehydration occurs. Water obviously has crystal structure stabilizing properties, since both the crystallization and melting temperature of the α-tending emulsifiers is significantly increased in the presence of water.

When GLP is dissolved in an oil or fat phase above its melting point it crystallizes separately from the oil phase. The presence of water strongly promotes this process. Furthermore, it has been shown that the melting curve of a soy bean oil emulsion containing 20% GLP on dispersed phase basis is shifted towards a higher temperature in the presence of water. The results of these DSC experiments are very important, because they provide additional evidence for our hypothesis that the α-gel phase of GLP is formed at the o/w-interface of the dispersed particles in a whippable emulsion.

In chapter 6 some results were given of a study of the rheological and fracture study on particle gels which consist of 100% GLP and gels containing 80% fat or oil and 20% GLP on dispersed phase basis. The properties of these gels showed strong resemblance in several ways, despite the great differences in composition. As far as the firmness of the gels is concerned, it has been shown that both the moduli and yield stress values of the gelated systems are strongly determined by the amount of crystallized fat present in the particles. This was explained by differences both in particle deformability and particle shape.

The rheological and fracture properties of gels only containing GLP as dispersed phase indicate that caseinate is probably of no influence on this rheological behaviour. In our opinion the rheological and fracture properties of particle gels which contain a relatively large amount of GLP can only be explained by assuming that these properties are closely related to one common mechanism. We believe that this mechanism is the formation of an α-gel phase of GLP at the o/w-interface of the dispersed phase.

In chapter 7 some results have been shown of surface rheological experiments for systems which contain both GLP and sodium caseinate. Knowledge of these properties is of great importance in order to obtain a better insight into the stabilization mechanism against bubble disproportionation in whipped emulsions, containing a large amount of an α-tending emulsifier.

It has been found that at room temperature GLP governs the surface rheological properties of dispersions containing 0.1% GLP in a solution of 0.1% sodium caseinate. Furthermore, we showed that this surface rheological behaviour is closely related to the formation of an α-gel phase below the transition temperature of the emulsifier mixture. These surfaces behave completely elastically at relatively short time scales. At longer time scales relaxation processes, occurring in the surface layer, become of importance. Therefore, we concluded that for prolonged stability of air bubbles in a foam of this kind of whippable emulsions the presence of a continuous network of aggregated fat particles is probably necessary too.

Summarizing, it can be concluded that the whipping behaviour of an emulsion containing a relatively large amount of an α-tending emulsifier like GLP is mainly determined by the formation of an α-gel phase at the o/w-interface of the dispersed particles.

SAMENVATTING

In opklopbare emulsies, zoals slagroom en toppings, is de vorming van een netwerk van geaggregeerde deeltjes nodig om een stevig en stabiel opgeklopt produkt te verkrijgen. In toppings wordt dit vaak verwezenlijkt door de toevoeging van een relatief grote hoeveelheid van een zogenaamde α-tending emulgator, omdat zo'n stof structuurvorming in de opklopbare emulsies sterk bevordert. De term α-tending betekent dat dit soort emulgatoren de neiging vertoont te kristalliseren in de α-modificatie. Het wordt algemeen verondersteld dat dit kristallisatiegedrag nauw verbonden is met de structuureigenschappen van dit type opklopbare emulsies. Echter het hieraan ten grondslag liggende mechanisme was nog onbegrepen voor aanvang van dit onderzoek. Sommige onderzoekers hebben geopperd dat α-tending emulgatoren misschien partiële coalescentie van de vetbolletjes bevorderen. Zij gaan echter voorbij aan het feit dat deze produkten niet karnen tijdens het opklopproces.

In de introduktie is uitgelegd, waarom besloten werd het mechanisme van door α-tending emulgatoren geïnduceerde structuurvorming te onderzoeken. Wij waren van mening dat de uitkomst van een dergelijk onderzoek een veel bredere betekenis zou kunnen hebben dan alleen voor opklopbare emulsies, omdat in vele typen emulsies de aanwezigheid van een netwerk van geaggregeerde deeltjes gewenst is. Hierbij wordt met name gedoeld op produkten van cosmetische en farmaceutische aard, zoals crèmes en zalven.

Bij dit onderzoek zijn wij uitgegaan van een modelemulsie, waarin zich het verschijnsel van structuurvorming in sterke mate manifesteert. De samenstelling van deze modelemulsie bestond primair uit cocosvet, de α-tending emulgator glycerollactopalmitaat (GLP) en natriumcaseïnaat.

In hoofdstuk 2 zijn de experimentele methoden beschreven, die bij dit onderzoek gebruikt zijn. Enerzijds werden technieken toegepast, waarmee bestaande kristalvormen in vet/emulgator deeltjes kon worden bestudeerd, zoals röntgendiffractie (SAXD en WAXD) en neutronendiffractie. DSC (Differential Scanning Calorimetry) is aangewend om kristallisatieprocessen in deze systemen te kunnen onderzoeken. Daarnaast is gebruik gemaakt van zowel bulkreologische als oppervlaktereologische methodieken om een beter inzicht te krijgen in het fysische gedrag van dit soort emulsies.

In hoofdstuk 3 zijn de resultaten van een aantal inleidende experimenten gepresenteerd. Uit deze resultaten is duidelijk gebleken dat de aanwezigheid van een relatief grote hoeveelheid GLP nauw verbonden is met structuurvorming en gelering in deze topping emulsies. Er zijn duidelijke aanwijzingen verkregen voor de hypothese dat de vetbolaggregaten uit gevlokte deeltjes bestaan. Partiële coalescentie, als het al optreedt, is waarschijnlijk van geen belang voor het fysische gedrag van dit soort opklopbare produkten. Tot slot is er gespeculeerd dat de aanwezigheid van GLP leidt tot de vorming van een soort gelstructuur in het olie/watergrensvlak van de gedispergeerde deeltjes. Deze gelstructuur zou de deeltjes met elkaar verbinden.

In hoofdstuk 4 zijn sterke aanwijzingen verkregen voor de theorie dat deze gelstructuur van gedeeltelijk mesomorfe aard is. Met röntgendiffractie en neutronendiffractie is het bestaan van een zogenaamde α-gelfase in deeltjesgelen, die slechts GLP, natriumcaseinaat en water bevatten, aangetoond. Deze gelfase zou bestaan uit gehydrateerde bilipide lagen van moleculen, afkomstig van het GLP. De koolwaterstofketens van deze moleculen bevinden zich in de α-kristallijne toestand. Bij maximale zwelling bedraagt de dikte van één bilipide laag ongeveer 63-65 Å. De exacte waarde hiervan blijkt afhankelijk te zijn van de voorgeschiedenis van de emulgator. De watervrije bilipide laag heeft een dikte van 55-56Å.

Aan het einde van hoofdstuk 3 is gespeculeerd dat er een gelstructuur van GLP aanwezig zou zijn op het o/w-grensvlak van de gedispergeerde deeltjes bij een GLP/vet-verhouding groter dan 20%, dit mede afhankelijk van de grootte van de deeltjes. Wij zijn er echter niet in geslaagd met röntgendiffractie het bestaan van de α-gelfase van GLP aan te tonen in dispersies, die minder dan 80% GLP op vetbasis bevatten. Dit zou mogelijk samen kunnen hangen met de dikte van de multilaag in het grensvlak van de deeltjes, die sterk afhankelijk is van de GLP concentratie.

In hoofdstuk 5 is met behulp van DSC en SAXD aangetoond dat α-tending emulgatoren, zoals GLP of ACTM (geacetyleerde monoglyceriden) duidelijk hydrateren beneden de kristallisatietemperatuur van de koolwaterstofketens. GLP vormt daarbij een lamellaire gelfase van gehydrateerde bilipide lagen, terwijl het ACTM repeterende lagen vormt met de dikte van ca. 1 emulgatormolecuul per laag.

De α-gelfase van GLP is erg stabiel. De α-polymorfe vorm is waarschijnlijk de enige modificatie, die wordt gevormd in het temperatuurgebied tussen 0°C en 45°C. Toevoeging van water leidt tot hydratatie van deze α-kristallijne structuur. Boven de smelttemperatuur van de gelfase treedt dehydratatie en samenvloeiing van de in water onoplosbare emulgatordeeltjes op. Water heeft duidelijk een stabiliserende invloed op het kristalrooster van deze emulgatoren, omdat zowel de kristallisatie- als de smelttemperatuur van de α-tending emulgatoren stijgen ten gevolge van de aanwezigheid van water.

Wanneer GLP opgelost wordt in een olie of vet, boven het smeltpunt van het aldus ontstane mengsel, dan kristalliseert het weer separaat van deze olie. De aanwezigheid van water bevordert dit proces in sterke mate. Verder is aangetoond dat de smeltcurve van een emulsie, welke 20% GLP en 80% soya-olie op disperse fase basis bevat, duidelijk verschuift naar een hogere temperatuur ten gevolge van de aanwezigheid van water. De resultaten van de DSC-experimenten zijn erg belangrijk, omdat ze additioneel bewijs leveren voor de hypothese dat er beneden de kristallisatietemperatuur van GLP een α-gelfase wordt gevormd op het o/w-grensvlak van de gedispergeerde deeltjes.

In hoofdstuk 6 zijn resultaten gepresenteerd van onderzoek naar de reologische en breukeigenschappen van deeltjesgelen, die 100% of 20% GLP op disperse fase basis bevatten. In het laatste geval is naar de invloed van zowel soya-olie als cocosvet op deze eigenschappen gekeken. Het reologische en breukgedrag vertoont voor de verschillende systemen in een aantal opzichten grote overeenkomst. Voor wat betreft de stevigheid van de gelen kan worden opgemerkt dat zowel de elasticiteitsmodulus als de zwichtspanning in sterke mate bepaald wordt door de hoeveelheid kristallijne fase in de deeltjes. Aangenomen wordt dat dit gedrag nauw samenhangt met verschillen in vorm en vervormbaarheid van de deeltjes in het netwerk van vetbolaggregaten.

De reologische en breukeigenschappen van gelen, die 100% GLP op disperse fase bevatten, geven aan dat het natriumcaseïnaat deze eigenschappen niet of nauwelijks beïnvloedt. Naar onze mening wordt het reologische en breukgedrag van deeltjesgelen, die een relatief grote hoeveelheid GLP op vetbasis bevatten, door één algemeen mechanisme bepaald. Wij denken dat dit mechanisme de vorming van een α-gelfase van GLP op het o/w-grensvlak van de disperse deeltjes is.

In hoofdstuk 7 zijn de resultaten gepresenteerd van een studie naar het oppervlaktereologische gedrag van dispersies, die zowel GLP als natriumcaseïnaat bevatten. Kennis van dit soort eigenschappen is van groot belang voor een beter inzicht in mogelijke vormen van stabilisatie tegen disproportionering van luchtbellen in opgeklopte emulsies.

Er is gevonden dat bij kamertemperatuur GLP het oppervlaktereologische gedrag bepaalt van dispersies, die 0.1% GLP in een oplossing van 0.1% natriumcaseïnaat bevatten. Verder is aangetoond dat dit reologische gedrag nauw samenhangt met de vorming van de α-gelfase beneden de kristallisatietemperatuur van de emulgator. Het oppervlak van deze verdunde GLP-dispersies gedraagt zich volkomen elastisch bij relatief korte tijdschalen. Bij langere tijdschalen treden er relaxatieverschijnselen op in het oppervlak.

Daarom is geconcludeerd dat voor stabilisatie van luchtbellen in dit soort opgeklopte produkten contact tussen het netwerk van geaggregeerde deeltjes en de oppervlaktelaag, waarschijnlijk onontbeerlijk is.

Samenvattend kan geconcludeerd worden dat de opklopeigenschappen van emulsies, die een relatief grote hoeveelheid α-tending emulgator op disperse fase bevatten, hoogst waarschijnlijk bepaald worden door de vorming van een α-gelfase in de o/w-grensvlakken van de gedispergeerde vetdeeltjes.

LIST OF SYMBOLS

A	Hamaker constant	J
A	surface area	m^2
A_0	initial stress bearing area	m^2
A_t	stress bearing area at time t	m^2
a	particle diameter	m
C	concentration of dispersed particles	kg.m^{-3}
d_{vs}	volume surface average diameter	m
D_r	diffusion rotary coefficient	s^{-1}
d	long spacing	Å
d_a	thickness of dry bilipid layer	Å
d_{a+w}	thickness of hydrated bilipid layer	Å
d_l	thickness of dry bilipid layer	Å
d_w	water layer thickness	Å
E_d	storage modulus	N.m^{-1}
ew	extremely weak	
E	Young modulus	N.m^{-2}
E^*	apparent Young modulus	N.m^{-2}
f_s	swelling factor	-
F	force	N
G	shear modulus	N.m^{-2}
H	interparticle distance	m
H_0	initial sample height	m
H_o	interparticle distance in energy minimum	m
H_t	sample height after a certain time t	m
l	crack length	m
m	medium	
M_w	molecular weight	g
$Pé_r$	rotary Péclet number	-
P_0	osmotic pressure at bilayer contact	N.m^{-2}
Q	momentum transfer	Å^{-1}
R	axial ratio	-
R_s	specific fracture energy	J.m^{-2}
r	bubble radius	m

s	strong	
V_a	van der Waals attraction energy	J
V_{def}	compression rate	$m.s^{-1}$
V_r	hydration repulsion energy	J
V_{tot}	total interaction energy	J
vs	very strong	
vw	very weak	
w	weak	
X_w	weight fraction of GLP on fat basis	-
γ	surface tension	$N.m^{-1}$
$\dot{\gamma}$	shear rate	s^{-1}
Γ_∞	saturation adsorption	$Mol.m^2$
ΔP	Laplace pressure	$N.m^{-2}$
ΔH	extension of the distance between two droplets	m
ϵ	dilational modulus	$N.m^{-1}$
ϵ_c	Cauchy strain	-
ϵ_f	fracture strain	-
ϵ_h	Hencky strain	-
$\dot{\epsilon}_h$	Hencky strain rate	s^{-1}
ϵ_{max}	maximum strain level	-
η	viscosity	Pa.s
$[\eta]$	intrinsic viscosity	$m^3.kg^{-1}$
η_d	surface dilational viscosity	$N.s.m^{-1}$
η_r	relative viscosity	-
η_s	viscosity of dispersion	Pa.s
η_0	viscosity of the continuous phase	Pa.s
ϕ	volume fraction dispersed particles	-
λ	decay length of the hydration force	m
$\surd$	form factor	-
$\surd^*$	apparent form factor	-
σ	stress	$N.m^{-2}$
σ_f	fracture stress	$N.m^{-2}$
σ_{max}	maximum stress	$N.m^{-2}$
θ	phase angle	rad
w	radial frequency	$rad.s^{-1}$

CURRICULUM VITAE

De auteur van dit proefschrift is geboren op 30 augustus 1960 te 's-Hertogenbosch. In juni 1978 behaalde hij aan het St. Oelbert gymnasium te Oosterhout (NB) het gymnasium β-diploma. Aansluitend hierop is gestart met de studie levensmiddelentechnologie aan de toenmalige Landbouwhogeschool te Wageningen. In november 1984 slaagde hij met lof voor het doctoraal examen met als hoofdvakken levensmiddelenchemie en organische chemie en als bijvak proceskunde.

Vanaf 1 januari 1985 tot 1 september 1988 is de auteur als onderzoeks-assistent werkzaam geweest bij de sectie zuivel en levensmiddelennatuurkunde van de vakgroep Levensmiddelentechnologie. In deze periode werd het in dit proefschrift beschreven onderzoek verricht.

Sedert 1 september is hij als research medewerker werkzaam bij de divisie industriële produkten van DMV Campina bv te Veghel.