Water-in-Triglyceride Oil Emulsions. Effect of Fat Crystals on Stability

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ABSTRACT: The influence of low concentrations (0.1–5%) of fat crystals on the stability of water-in-soybean oil emulsions was examined by light scattering and sedimentation experiments. Both the initial flocculation/coalescence rate and long-term stability against water separation were determined. The initial flocculation/coalescence rate increased upon addition of small amounts of fat crystals. When the crystal concentration was increased above a critical concentration (specific to a system), a decrease in the flocculation/coalescence rate occurred. The increased flocculation/coalescence rate is likely the effect of bridging of water droplets by fat crystals. Fat crystal wetting by water is an important criterion for this phenomenon to occur. Emulsion stabilization for crystal concentrations above critical is caused by a mechanical screening of water droplets. The presence of considerable amounts of crystals in oil also lowered the density difference between droplet and medium, and enhanced viscosity. The degree of increase in viscosity depended upon the emulsifier. Both a decrease in density difference and an increase in viscosity play a role in hindering flocculation/coalescence of droplets. In long-term studies of water separation, all concentrations of fat crystals stabilized the water-in-oil emulsions. The droplet size of these emulsions increased until the critical droplet size was approached where the screening effect of crystals on the droplets no longer stabilized the emulsions. The stabilizing effect for emulsions with monoolein was continuously improved by increasing the amount of crystals up to 5%. For lecithin-stabilized emulsions, an optimal effect was achieved for fat crystal concentrations of 1–2%.
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KEY WORDS: Advancing and receding contact angles, emulsifiers, emulsions, fat crystals, food, interfacial tension, oil/water interface, triglycerides, vegetable oils, wetting.

To lower fat consumption, a range of low-fat spreads and margarines has been developed (fat content ≤60%). These spreads consist mainly of water-in-oil emulsions. Their consistency, stability, and texture are often inferior to the original products with 80% fat. One of the critical components in these products is fat crystals, crystallizing from partially saturated oil in the form of colloidal particles. The crystals interact with each other and form a three-dimensional network, with provides a hard, solid character to spreads (1–5). The interactions between the crystals are influenced by adsorption of food emulsifiers (6,7), usually added to the spreads as emulsion stabilizers and controllers of fat crystallization (8–12). The interactions become stronger in the presence of traces of water in the oil (13). Solid fat bridges between crystals may also be formed.

Fat crystals also influence the stability of margarine emulsions. Generally speaking, colloidal particles influence emulsion stability when they are attached to the oil-in-water interface and are preferentially wetted by the continuous phase. This phenomenon was first described by Pickering for oil-in-water emulsions (14), hence the term "Pickering emulsions." Several examples of Pickering stabilization may be found in the literature (15–17). For Pickering emulsions containing fat crystals, stable water-in-paraffin oil emulsions were found, for example, with tristearin crystals attached to the water droplets from the oil side, provided that oil-soluble emulsifiers, such as monoolein or Aerosol OT (sodium dioctyl sulfosuccinate), were present in the oil (18). In dairy applications, a relationship was found between the instability of oil-in-water butterfat emulsions with fat crystals in the oil droplets and the crystal position at the interface (19–21). As the crystals became polar (pierced the oil droplets), the emulsions broke down more easily.

Similar results were found in water-in-paraffin oil emulsions with various surfactants (22). Without crystals, the emulsions were stable. Emulsions with crystals in the oil droplets were unstable if the crystals appeared at the interface, and the instability was promoted by creaming, flow, and turbulence. In margarine-like systems, stable water-in-oil emulsions were formed by adding relatively polar monoglyceride crystals, which could attach to the water droplets from the oil-continuous side (23). Nonpolar triglyceride and fatty acid crystals, which were less polar, gave less stable emulsions.

For emulsions containing fat crystals in the oil droplets, a partial coalescence of droplets may occur (24). The droplets flow together, but retain their identity because crystal structure in the droplets prevents true coalescence. Partial coalescence differs from true coalescence and may have important consequences. Firstly, partial coalescence does not lead to phase separation to the same degree as true coalescence because the globules do not flow together completely. Secondly, due to an irregular form of the aggregates, the viscosity of emulsions may increase. The aggregation may proceed until a continuous network is formed with a solid-like character.

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Stability to partial coalescence is usually lower than to true coalescence in the absence of crystals protruding from the oil droplets because these crystals may contribute to the process by piercing the thin film between the droplets. Partial coalescence is therefore greatly increased by agitation and velocity gradients in the sample (shear).

Particle attachment to the oil-in-water interface is requisite to Pickering stabilization. The attachment may be characterized macroscopically by contact angle measurements in a three-phase-system (19,23). When the contact angle measured through the oil phase is between 0 and 90°, the crystals are preferentially wetted by oil, stabilize oil-continuous emulsions, and destabilize water-continuous emulsions. In the opposite case, when the contact angle is between 90 and 180°, the crystals are preferentially wetted by water, oil-continuous emulsions are destabilized, and water-continuous emulsions are stabilized. Different theories have been forwarded regarding the reasons for stabilization of emulsions by solid particles. For example, the energy required to displace a spherical particle from the interface can be calculated from oil-in-water interfacial tension and contact angle (25,26). Results show that maximum energy is demanded when the contact angle is close to 90°, e.g., when the particles are well wetted by both the oil and water phases in the emulsions. Therefore, it has been suggested that the most stable emulsions will be formed when the contact angle is close to 90°. It has also been assumed that an isolated particle at the interface is trapped in a deep energy well, balanced by the repulsive interaction between particles (27–31).

Wetting of fat crystals, as described by contact angles, is influenced by addition of food emulsifiers to the oil and/or addition of proteins to the water phase. Some studies of this type can be found in the literature (19,23,32). We have studied fat crystal wetting extensively. We found that the polycrystalline fat surface of tristearin β was completely wetted by oil (contact angle $\approx 0°$), while the β' surface of palm stearin was slightly more polar (morphology and orientation effects). Fat crystal wetting was shifted by the addition of emulsifiers. For example, technical lecithins produced rather polar crystals. The most polar crystals (contact angle ~180°) were achieved in the presence of pure soybean phosphatidylcholine (PC). Unsaturated monoglycerides gave less polar crystals, similar to those with technical lecithin. In general, emulsifiers with high hydrophilic–lipophile balance (HLB) values produced the more polar fat crystals.

This study aims to determine how increasing concentrations of fat crystals in oil (0.1–5%) affect the stability of margarine-type emulsions. By variation of emulsifier type and concentration, the effect of fat crystal wetting properties is illuminated. The experiments were performed directly under homogenization, during the rapid coalescence process, and after prolonged storage.

EXPERIMENTAL PROCEDURES

Emulsifiers. The following emulsifiers were studied: pure (>99%) monoolein, unsaturated distilled monoglycerides (Dimodan S), saturated distilled monoglycerides (Dimodan PV), pure lecithin PC from soybean oil (soybean PC, Epikuron 200), and technical lecithins Topcithin and Metarin P. Monoglycerides were supplied by Grindsted Products A/S (Brabrand, Denmark), and lecithins by Lucas Meyer (Hamburg, Germany). Emulsifiers have been further described (purity, source, mole mass, HLB-value, phospholipid composition, hydrocarbon chainlength, polar head group) in a previous publication (6).

Fat crystals. Fully hydrogenated palm oil (palm stearin) from Karlshamns AB (Karlshamn, Sweden) was used as the source of solid-fat crystal. It had an average mole mass of 756 g/mol and an iodine value of 2.6. Purity and density were not specified. It is stable in the β' polymorphic form, having a melting point of 57–59°C. The α-form appears in rapidly cooled palm stearin and has a melting point of about 46°C. The fatty acid composition of palm stearin was 53% C16:0 (palmitic acid, P), 42% C18:0 (stearic acid, St), 2% C18:1 (oleic acid, O), and 3% other. The composition of triglycerides was 3% POO/MPP, 23% PPP, 37% PPSt, 26% PStSt, and 11% StStSt, where M stands for C14:0 (myristic acid). These data were obtained from the supplier.

The desired amount of dry crystals was added to the emulsion and was homogenized by ultra-turrax. Crystals were recrystallized from acetone. The specific surface area of the crystals (9 m^2/g) was determined by BET adsorption measurements at Chalmers Technical University (Gothenburg, Sweden) with nitrogen gas.

Oil. A refined soybean oil from Karlshamns AB was used as the oil phase. The interfacial tension between this oil and distilled water is slightly above 30 mN/m. This high value indicates a high purity with regard to surface-active components (monoglycerides <0.05%, diglycerides <0.7%, free fatty acids <0.03%, lecithins <1 ppm). The iodine value of this oil was about 130 (~2.5 double bonds per hydrocarbon chain on average), and the melting point was about −20°C. The fatty acid composition was 10.6% C16:0, 3.6% C18:0, 18.2% C18:1, 56.7% C18:2 (linoleic acid, Le), 9.5% C18:3 (linolenic acid, Ln), 0.3% C20:0 (arachidic acid), 0.4% C22:0 (behenic acid), and 0.7% others. The triglyceride composition was: 23.7% LeLeLe, 1.5% LeLeLn, 31.2% OLeLe, 11.6% OOLe, 2.6% OOO, 13% PLeLe, 1.3% PLeLn, 2.6% PLeP, 7.7% POLe, 3.0% POO, 0.7% POP, and 0.5% POSt, and 0.5% StOO. These data were obtained from the supplier, and the oil was not further purified prior to use.

Other chemicals. Double-distilled water was used as the water phase in all experiments. Acetone, for recrystallization of solid fat (palm stearin), was of analytical grade and supplied by Merck (Darmstadt, Germany).

Water droplet size by light diffraction. To determine particle size distribution by light scattering in the Mastersizer from Malvern Instruments (Spring Lane, Malvern, Worcestershire, England), a laser beam (He/Ne, $\lambda = 633$ nm) passes through a sample, and the scattered light is collected by a detector in the forward direction. Small particles scatter light at large angles and large particles at small angles (Fig. 1). The optical para-

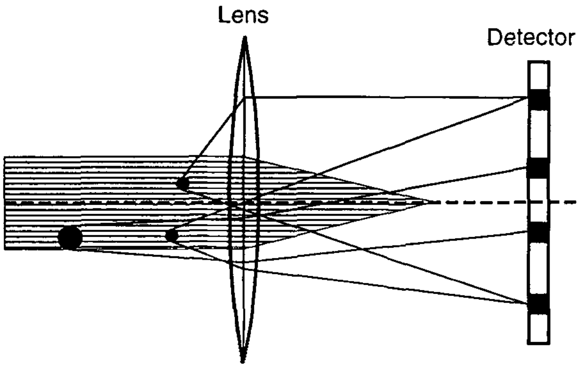

FIG. 1. A schematic picture for particle-size analysis by light diffraction. Small particles scatter light at large angles, and large particles at small angles.

meters for particles (refractive index n_{water} and light absorption coefficient k) and medium (n_{oil}) are important in the conversion of diffraction patterns to particle-size distributions by an algorithm based on the Mie theory. The relative refractive index for water droplets in soybean oil is <1 ($n_r = n_{water}/n_{oil} \approx 1.33/1.46 \approx 0.9$), and the water droplets are assumed to have a rather low absorption coefficient ($k_r \leq 0.01$). For $n_r < 1$, the only available presentation that transforms the scattering pattern to size distribution in the Mastersizer is for $n_r = 0.5$ and $k_r \approx 3$ (highly absorbing particles with low refractive index). Using this presentation, the distribution results may only be used for qualitative comparisons between samples. Trends are more suitable for comparison than numeric values. Generally speaking, using an inappropriate presentation usually leads to tails in the particle-size distributions. These tails are shifted from smaller to larger particle sizes as the n_r ratio decreases (33).

The particle distribution determined from light diffraction is a volume or weight distribution. The distribution is characterized by mean value D[4,3], median value D[v,0.5] and mode (peak) value. The mean value is strongly influenced by larger particles in the sample since their contribution to total particle volume in the sample is large compared to that from smaller particles. For a normal size distribution, mean, median, and mode values are the same. For a volume distribution that is skewed to larger particles (with a tail), the median value is larger than the mode value, and the mean value is often the largest. Mode values are generally influenced least by the presence of tails and have been preferentially used in this study for discussion purposes.

Conventional Fourier optics with lenses of 45, 100, and 300 mm focal lengths were used in our measurements for the appropriate particle-size intervals (0.1–80, 0.5–170, and 1.2–600 μm).

Preparation of emulsions. Soybean oil and emulsifier were weighed at room temperature to produce the desired oil composition. Emulsifier was then dissolved or dispersed by increasing the temperature prior to water addition by weighing. The mixture was homogenized by Ultra-Turrax T 25 (Janke & Kunkel GmbH, IKA-Labortechnik, Staufer, Germany). The influence of rotation speed on the droplet size of the emulsion was determined for emulsions containing 5% water and 2% lecithin (Topcithin) in oil. Increased rotation speed gave smaller water droplets (Fig. 2). This trend level led off at higher speeds.

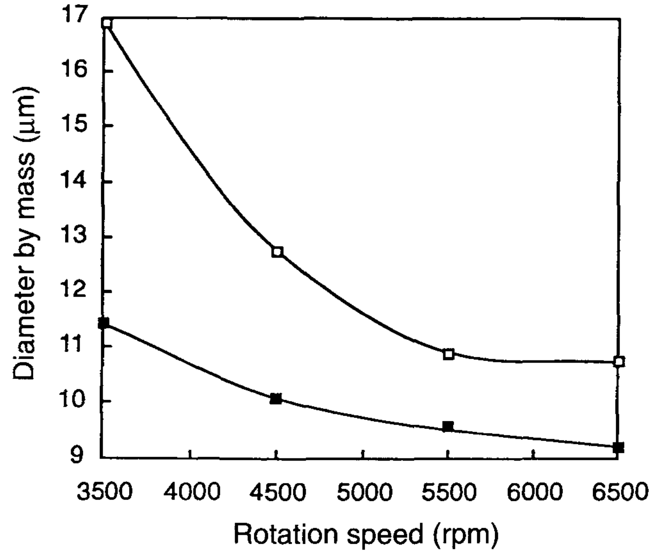

FIG. 2. The influence of rotational speed of ultra-turrax in rpm on the droplet size of water-in-oil emulsions that contain 5% water and 2% Topcithin (Grindsted Products A/S, Brabrand, Denmark) in refined soybean oil. Homogenization time was ~2 min. ■, Median D[v,0.5] and □, mean D[4,3] values.

Dry fat crystals (0.1–5%) with a well-known surface area were successively added to each emulsion sample. A homogenization step and a droplet size measurement were performed after each addition of fat crystals. Homogenization time was restricted to 2 min, and rotation speed to 5500–6000 rpm to avoid heating and undesirable melting of fat crystals.

The influence of fat crystals in the continuous oil phase. Fat crystals in the continuous phase of emulsions contribute to light scattering and interfere with water droplet size determination. To determine this background light scattering, measurements on fat crystal dispersions, including emulsifiers, in oil were performed. The dispersions were treated in the same manner as emulsions (homogenization at 5500–6000 rpm for 2 min) prior to measurement. The presentation during background measurements was the same as for the emulsions ($n_r = 0.5$, $k_r = 3$). A comparison of median D[v,0.5] and mean D[4,3] droplet sizes with and without background correction is done in Figure 3A, and a comparison of schematic scattering patterns in Figure 3B. The following samples are compared: (1) a dispersion of 1% palm stearin β in soybean oil, (2) water-in-oil emulsion (5% water and 2% Topcithin in soybean oil) without fat crystals in the oil, (3) as (2) with 1% palm stearin β′ in the oil, no background correction, and (4) as (3) with background correction for the crystals.

Despite a large difference in the mean and median size of

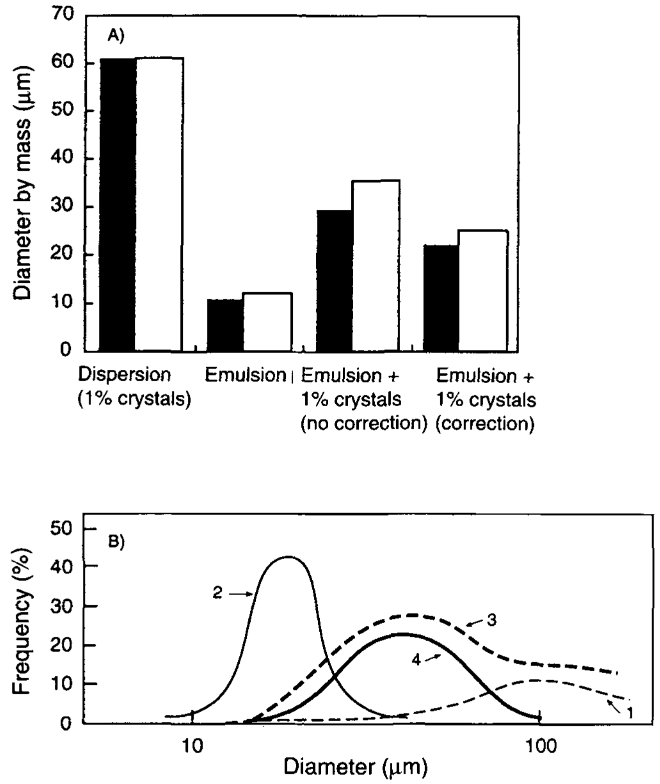

FIG. 3. A comparison of particle-size distributions for the following samples: (1) a dispersion of 1% fat crystals in oil, (2) water-in-oil emulsion (5% water and 2% Topcithin in oil) without fat crystals, (3) as (2) with 1% fat crystals in the oil, no background correction, and (4) as (3) with background correction for the crystals. The crystals were palm stearin β′ with a specific surface 9 m^2/g, and the oil was refined soybean oil: A) ■, median D[v,0.5] and ☐, mean D[4,3] values; B) schematic distribution patterns. Company location as in Figure 2.

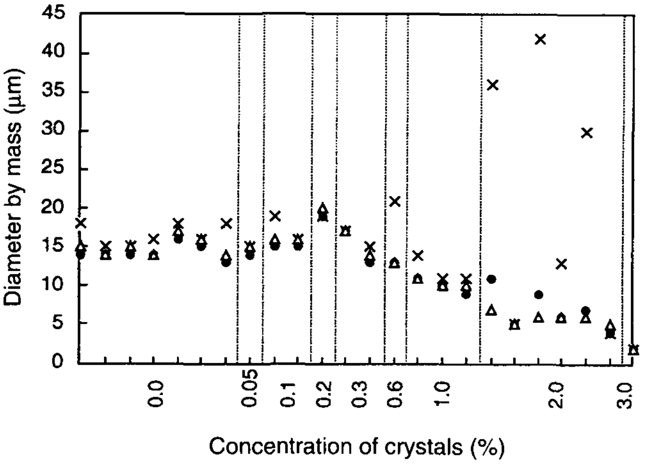

FIG. 4. Droplet size of emulsion containing 20% water and 2% monoolein (batch 1) in oil, as a function of fat crystal concentration in the continuous oil phase. The crystals were palm stearin β′ with a specific surface ~9 m^2/g, and the oil was refined soybean oil: ☐, mean D[4,3], shaded box, median D[v,0.5], and ■, mode values.

fat crystals and water droplets, a background correction shifts the distribution toward smaller particles by about 25%. This shift is expected to be even greater for larger emulsion droplets. The background correction is estimated to be satisfactory up to a crystal concentration of 1–2% for emulsions with monoolein (relatively large droplets), and 3–4% for emulsions with lecithins (relatively small droplets). At higher concentrations of crystals, the concentration of droplets relative to crystals may be too low, giving poor accuracy of determination.

Reproducibility. The reproducibility of droplet size determination by light diffraction was studied for a system with 20% water and 2% monoolein (batch 1) in soybean oil. The results are presented in Figure 4. For low concentrations of fat crystals (<1%), all diameters were similar and reproducible. However, at higher concentrations of crystals, poor reproducibility of mean and median values was observed. The distributions then displayed tails for large particle sizes, which influenced mean and median values. Mode values were influenced least. These results indicate that the mode values are most suitable for qualitative analysis of trends in the systems examined.

Sedimentation experiments. Sedimentation (or creaming) studies are often used to evaluate emulsion stability (14,23,34). If sedimentation (or creaming) occurs, an increase in sediment volume is observed in flocculating emulsions (35). Coalescence leads to faster sedimentation and lower sediment volumes.

In our study, the following emulsions in soybean oil were prepared: 4% monoolein in soybean oil + 20% water, and 0.5% technical lecithin (Topcithin) in soybean oil + 25% water. The emulsions were transferred to test tubes, and increasing amounts of fat crystals (0.1–4%) were added to the oil phase of each emulsion. After homogenization, the emulsions were allowed to settle for prolonged periods, and appearance was checked systematically. Because both crystals and water droplets contributed to the sediment volumes of these emulsions, no direct conclusions could be drawn concerning flocculation or coalescence due to the presence of crystals. In the case of monoolein, some air was trapped in the samples, giving a nonsedimenting foam zone in the top of the samples. The air could not be removed by vacuum due to simultaneous evaporation of water droplets. Phase separation of water was monitored as a function of concentration of the amount of fat crystals while the crystal size and type was kept constant.

Microscopy. Light microscopy was applied to detect any extensive differences in the emulsion image due to fat crystal addition or due to storage. The microscope used was a Zeiss Axioplan (Carl Zeiss, Oberkochen, Germany); the objective was Plan Neofluar with DIC (differential interference contrast) prisma. Photographs were taken with an MC 100 video camera and Sony Printer and were observed at room temperature.

RESULTS

Initial droplet size in different emulsions without fat crystals. Mode values for droplet size distributions of water-in-soybean oil emulsions were determined directly after the homog-

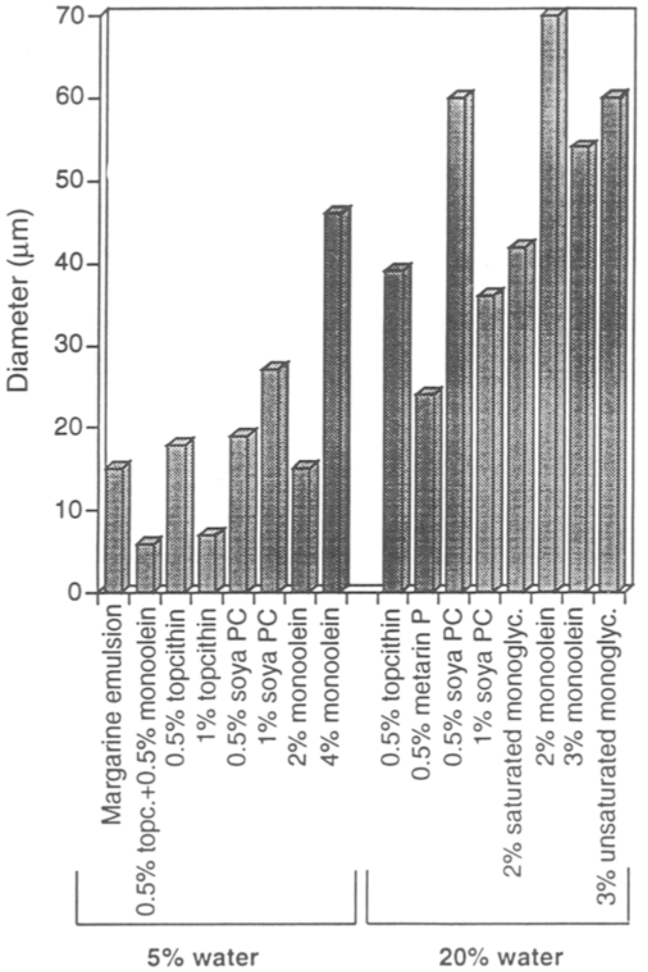

FIG. 5. Droplet size (mode values of volume distribution) of water-in-soybean oil emulsions stabilized by different emulsifiers and containing 5 and 20% water, respectively. Margarine emulsion contains 0.5% Topcithin (topc.) and 0.5% monoolein in oil, and 3% gelatin, 3% spray-dried skim milk, and 2.5% salt in water. PC, phosphatidylcholine; monoglyc., monoglycerides. Topcithin and Metarin P from Grindsted (Brabrand, Denmark).

enization step. Results are presented in Figure 5. Two levels of water in emulsions were tested: 5 and 20%. Emulsifiers were: pure PC from soybean oil (soybean PC; concentrations, 1 and 2%); technical lecithin Topcithin (0.5 and 1%); pure monoolein (two different batches; concentrations, 2, 3, and 4%), unsaturated distilled monoglycerides (Dimodan S, iodine value ≈50; concentration 3%), and saturated distilled monoglycerides (Diomdan PV, iodine value ≤2; concentration 2%). A combination of 0.5% Topcithin and 0.5% monoolein (batch 1) was also investigated. The water phase was double-distilled water in all cases except one. "Margarine emulsion" contained 0.5% Topcithin + 0.5% monoolein (batch 1) in oil, and 3% gelatin, 3% spray-dried skim milk, and 2.5% salt in water.

The results indicate that emulsions are coarser when more water is added, provided the composition of the samples is kept constant. The emulsions were coarser with pure soybean PC compared to technical lecithin. Monoglycerides gave coarser emulsions than lecithins. Unsaturated distilled monoglycerides gave emulsions similar to pure monoolein. There was a difference in droplet size in the presence of the two different batches of monoolein. Saturated distilled monoglycerides gave smaller droplets than unsaturated distilled monoglycerides and monoolein. A combination of 0.5% technical lecithin and 0.5% monoolein gave the finest emulsions. Addition of proteins and salt to the water produced a less stable margarine emulsion.

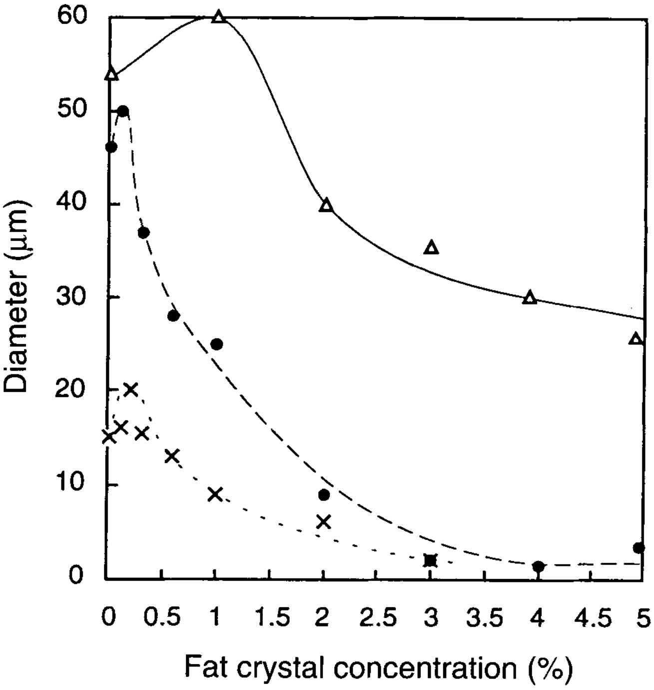

FIG. 6. Droplet size (mode values of volume distribution) of monoolein-stabilized water-in-soybean oil emulsions as a function of fat crystal concentration in oil (% w/w). The crystals were palm stearin β′ with a specific surface ~9 m^2/g. The following compositions were studied: ×, 2% monoolein (batch 1), 5% water; ●, 4% monoolein (batch 2), 5% water; and △, 2% monoolein (batch 1), 20% water.

Emulsions containing lecithins (pure soybean PC and technical topcithin) and monoolein were chosen for further investigations with fat crystals.

Initial droplet size as a function of fat crystal concentration. Results are presented in Figure 6 for emulsions stabilized by monoolein, in Figure 7 for emulsions stabilized by pure soybean PC, and in Figure 8 for emulsions stabilized by the technical lecithin (Topcithin). When crystals were not present, the emulsions stabilized by monoolein gave larger droplets than those stabilized by lecithins. When crystals were added to the oil, no such difference was observed. No systematic differences were observed between the two emulsions stabilized by different lecithins.

The same trend was observed in all cases examined—an increase in the initial droplet size at low concentration of fat crystals with a subsequent decrease at higher concentrations of crystals. Droplet sizes for crystal concentrations of a few percent were generally smaller than for the emulsions without

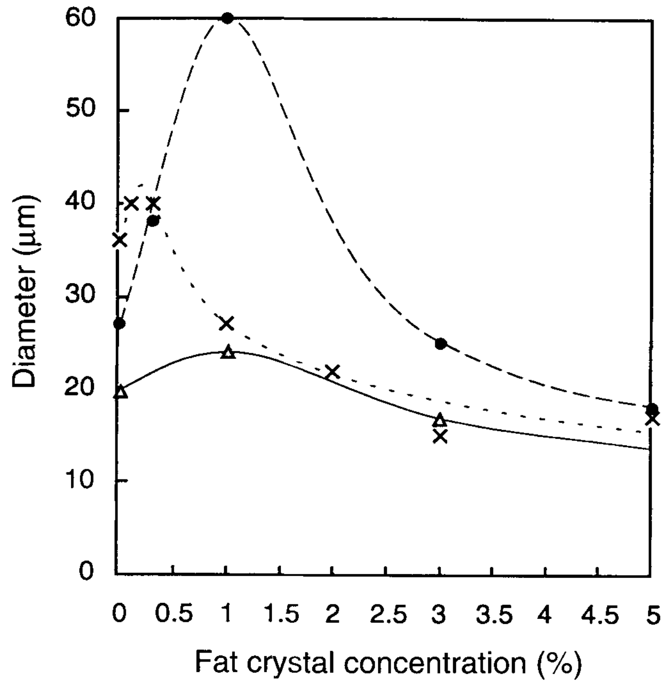

FIG. 7. Droplet size (mode values of volume distribution) of soybean phosphatidylcholine (PC)-stabilized water in soybean oil emulsions as a function of fat crystal concentration in oil (% w/w). The crystals were palm stearin β′ with a specific surface ~9 m²/g. The following compositions were studied: ×, 1% soybean PC, 20% water; ●, 1% soybean PC, 5% water; and △, 0.5% soybean PC, 5% water.

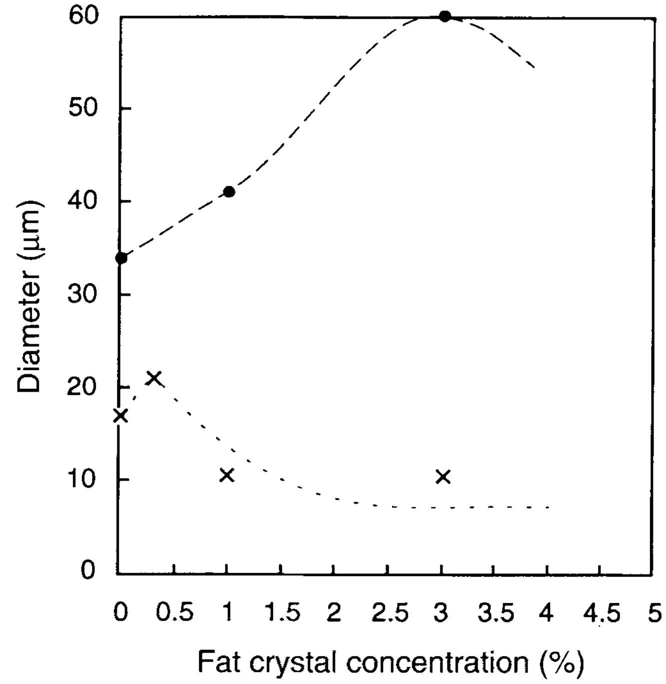

FIG. 8. Droplet size (mode values of volume distribution) of Topcithin-stabilized water-in-soybean oil emulsions as a function of fat crystal concentration in oil (% w/w). The crystals were palm stearin β′ with a specific surface ~9 m²/g. The following compositions were studied: ×, 0.5% Topcithin, 5% water; and ●, 0.5% Topcithin, 20% water. Company source as in Figure 5.

crystals. The critical fat crystal concentration, where a shift from destabiliziation to stabilization was observed, depended on the system.

Sedimentation—long-term stability of emulsions. The influence of fat crystals on long-term stability of emulsions against phase separation of water has been examined in sedimentation experiments. Results for emulsions containing 4% monoolein (batch 2) and 20% water are presented in Figure 9, and for emulsions containing 0.5% technical lecithin (Topcithin) and 25% water in Figure 10, as a function of concentration of fat crystals in the oil phase.

Figure 9 shows that monoolein-stabilized emulsions with 20% water were sensitive to coalescence. About 60–70% of water separates after one day and was almost unchanged after a period of one month. The coalescence rate was high. The coalescence degree became lower upon addition of fat crystals to the oil. The change was gradual with an increasing amount of crystals. More than 0.5% crystals were required to observe any significant difference, and for crystal concentrations ≥3%, no phase separation occurred for one week, and only 10–20% after one month.

The behavior was different for emulsions with 25% water and technical lecithin (Topcithin), as indicated in Figure 10. These emulsions were more stable than monoolein emulsions—the water separation was about 25% after four days and increased to about 40% after one month. The coalescence process was slower in topcithin emulsions than in monoolein emulsions. On a time scale of one week, all fat crystal concentrations stabilized emulsion droplets against coalescence,

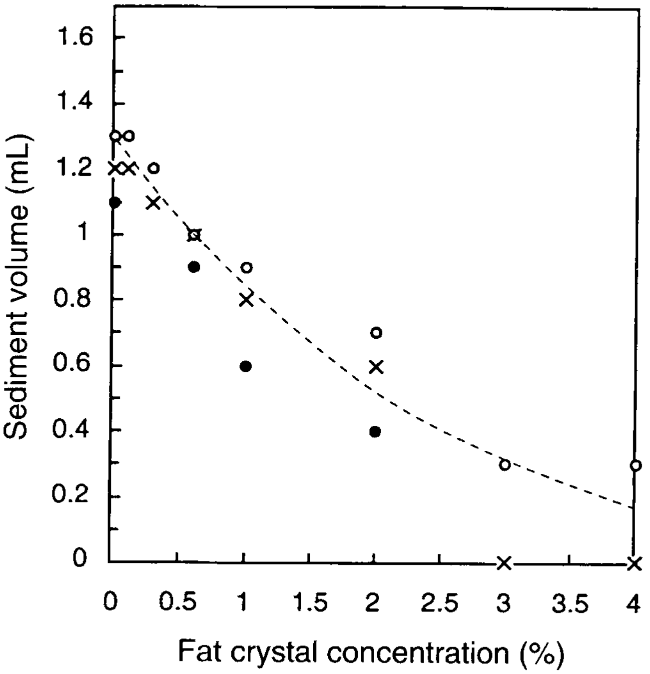

FIG. 9. Water separation (●, after one day; ×, after six days; and ○, after four weeks) of emulsions containing 4% monoolein and 20% water in soybean oil, as a function of fat crystal concentration in the oil. The crystals were palm stearin β′ with a specific surface ~9 m²/g. The total emulsion volume is 7 mL, and the water volume is 1.6 mL.

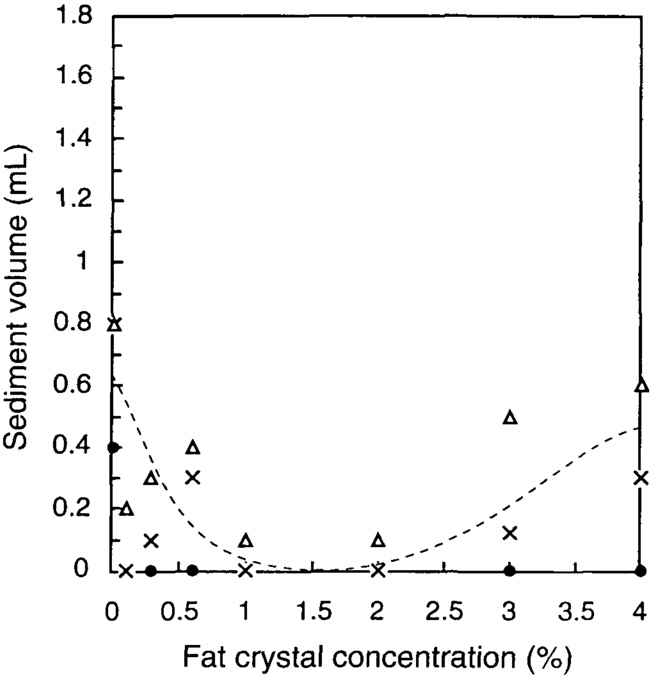

FIG. 10. Water separation (●, after four days; ×, after ten days; and ○, after four weeks) of emulsions containing 0.5% technical lecithin (topcithin) and 25% water in soybean oil, as a function of fat crystal concentration in the oil. The crystals were palm stearin β′ with a specific surface ~9 m^2/g. The total emulsion volume is 6.8 mL, and the water volume is 1.8 mL.

and higher concentrations gave less water separation. For a longer time scale (month), best stabilization occurred for concentrations of about 1–2%.

Microscopy. Microphotographs of monoolein emulsions from sedimentation studies are presented in Figure 11, and of technical lecithin (Topcithin) emulsions in Figure 12. The samples were taken after one day of sedimentation. The photographs represent fat crystal contents of 0% (A), 1% (B), and 3% (C). The magnification is 26× for monoolein emulsions (Fig. 11) and 105× for topcithin emulsions (Fig. 12) because the former were much coarser.

Figure 11A indicates that, in the absence of fat crystals in oil, only a few droplets remained in monoolein emulsion after 24 hours' storage. The concentration of emulsion droplets was much higher in the presence of 3% fat crystals in the oil (Fig. 11C). The droplets were very large (up to 1 mm in diameter) but appeared relatively stable on a microscope slide. The situation was intermediate when 1% of fat crystals was present in the oil (Fig. 11B). The water droplets were not as stable then as with 3% fat crystals. The photograph shows how the largest droplets are deformed and flocculated on the microscope slide.

The emulsion stabilized by technical lecithin (Topcithin) (Fig. 12A) was more stable than the monoolein emulsion. The droplets were large (100–500 µm) but were relatively stable and did not separate as a water phase. The droplets became smaller (≤100 µm) in the presence of 1% fat crystals (Fig. 12B) and 3% fat crystals (Fig. 12C).

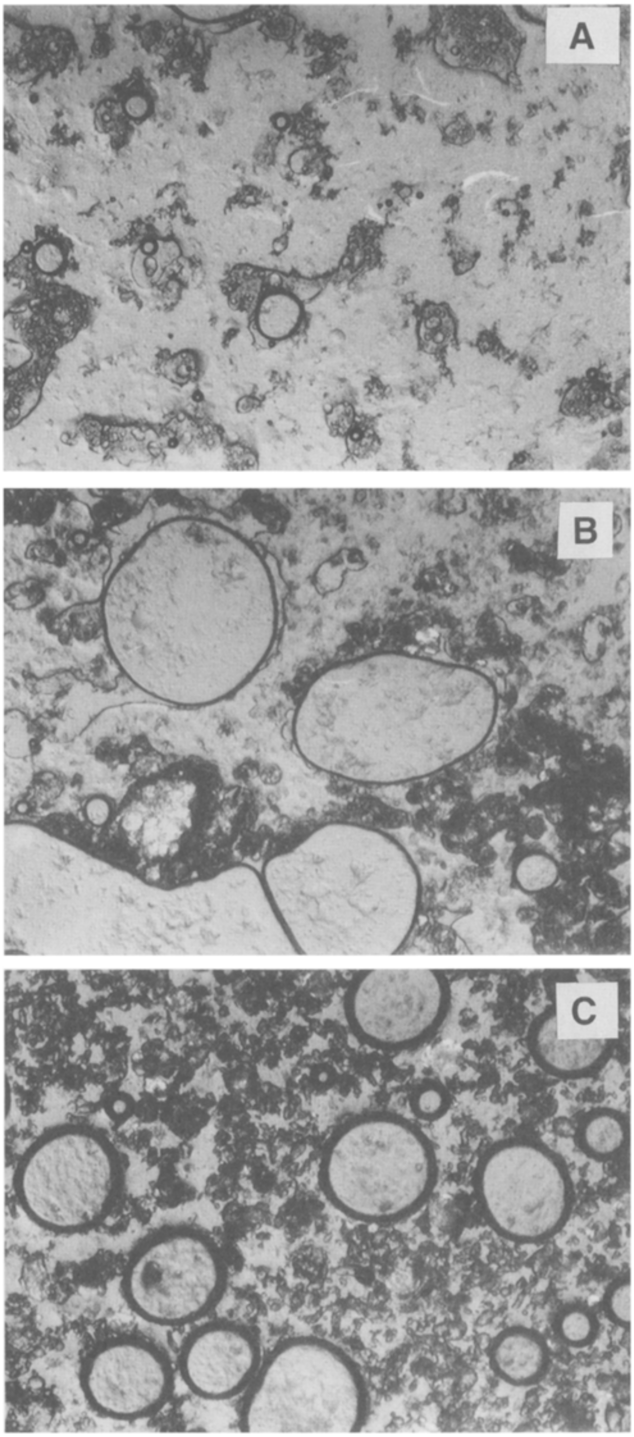

FIG. 11. Light microphotographs of emulsions containing 4% monoolein and 20% water in soybean oil (one day after homogenization). Magnification was 26× (3 mm ≈ 100 µm), the temperature was ~22°C (room temperature). Fat crystal concentrations in oil were: (A) 0%; (B) 1%; and (C) 3%. The crystals were palm stearin β′ with a specific surface ~9 m^2/g.

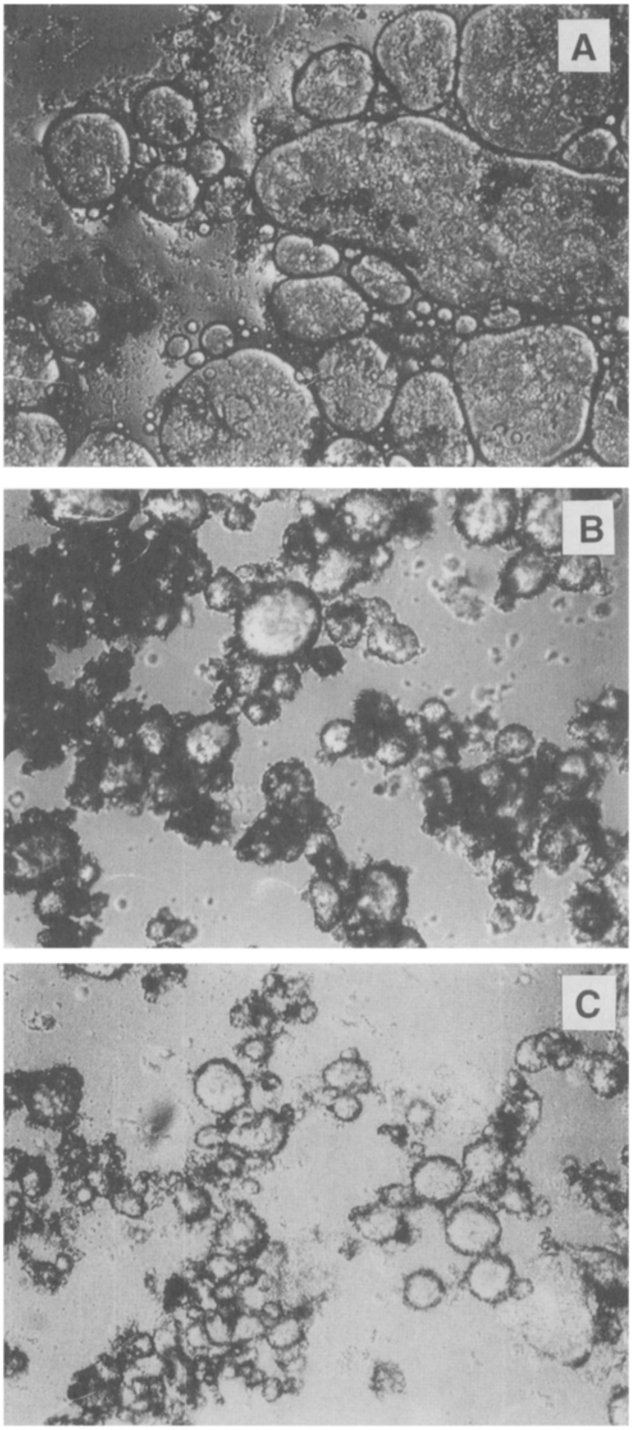

FIG. 12. Light microphotographs of emulsions containing 0.5% technical lecithin (Topcithin) and 25% water in soybean oil (~one day after homogenization). Magnification was 105× (16 m ≈ 100 μm), the temperature was ~22°C (room temperature). The fat crystal concentrations were: (A) 0%; (B) 1%; and (C) 3%. The crystals were palm stearin ß′ with a specific surface ~9 m^2/g. Company source as in Figure 5.

DISCUSSION

Different instability mechanisms in emulsions. The main instability mechanisms for emulsions can be identified (35) as: (i) creaming or sedimentation, caused by motion of droplets due to gravity; (ii) flocculation—aggregation of droplets due to collisions of droplets; (iii) coalescence—when the flocculated droplets fuse together; and (iv) Ostwald ripening—diffusional transport of dispersed phase from small to large droplets.

Because the emulsions examined were rather coarse and unstable, Ostwald ripening was of secondary importance. Sedimentation occurred extensively, which was observed in long-term stability experiments. Water separation in these experiments was mainly dependent on the rate of coalescence because the sedimentation rate of large droplets and their aggregates was fast. Consequently, both in long- and short-term experiments, flocculation and coalescence processes were predominant.

Flocculation. Flocculation is the first step in a coalescence process. Three different mechanisms may induce flocculation (35): (i) Brownian (thermal) motion of droplets; (ii) Shear (orthokinetic flocculation); and (iii) gravity. Brownian flocculation only dominates for small particles and may be neglected for the emulsions examined.

Flocculation and disruption of droplets by shear occurs during the emulsification process. The shear flocculation rate increases with droplet size, with volume fraction of droplets, and with shear rate, but decreases with increasing viscosity of the oil phase.

Gravity-induced flocculation probably dominated in the short-term light-diffraction experiments and in the long-term sedimentation experiments. The gravity-induced flocculation rate increases with increasing volume fraction of droplets, increasing density difference oil/water, and increasing droplet or aggregate size. The flocculation rate decreases with increasing viscosity of the oil phase, and increasing fractal dimension of flocs.

Coalescence rate. The coalescence of flocculated or concentrated emulsion consists of four main steps (35): (i) consolidation (the emulsion structure changes from loosely aggregated to more compact); (ii) drainage of film between droplets; (iii) rupture of film; and (iv) merging of droplets. The last step is fast for water droplets with low viscosity, but it can be slow for oil-in-water emulsions that contain semisolid fat droplets [partial coalescence (24)].

The influence of some experimental parameters on the coalescence rate is presented in a qualitative way in Table 1 (from Ref. 35).

Emulsions without fat crystals. The composition of emulsions studied and experimental parameters are summarized in Table 2. The interfacial tension between oil and water (γ_{ow}), the contact angle for fat crystals at the oil/water interface (θ), and relative increase of oil viscosity due to addition of fat crystals (η_{disp}) were taken from our previous work (7). Droplet diameters (mode values) were obtained from light diffraction experiments of volume distributions (Figs. 5–8), where d_i represents the droplet size of the emulsion without crystals in oil and d_e is the droplet size of the emulsion with 3% crystals in oil. The critical concentration (C_{crit}) is the

TABLE 1
The Influence of Some Parameters on the Emulsion Coalescence Processes[a]

Increase in parameter	Consolidation	Film drainage	Film rupture
Droplet viscosity	—	—	Slower
Continuous phase viscosity	Slower	Slower	—
Droplet size	Slower or quicker	Slower	Quicker
Volume fraction of droplets	Quicker	Quicker	—
Density difference	Quicker	Quicker	—
Interfacial tension	Slower	Quicker	Slower
Surface viscosity	—	—	Slower
Surface elasticity	—	Slower	Slower
Adhesion	Slower	Quicker	—
Repulsion	Quicker	Slower	Slower
Thickness of adsorbed layers	Quicker	Slower	Slower
Solubility of emulsifier in droplets	—	Quicker	Quicker

[a] Reference 35.

TABLE 2
Characterization of the Emulsion Systems Studied[a]

Emulsifier and its concentration (%)	C_{water} (% w/w)	γ_{ow} (mN/m)	θ_0 (°)	d_i (μm)	d_e (μm)	η_{disp} (relative)	C_{crit} (% w/w)	d_{crit} (μm)	t (μm)
Monoolein									
2	5	~4	60°	15	5	++++	0.2	20	0.13
2	20	~4	60°	54	38	++++	1.0	60	0.50
4	5	~2	90°	46	10	+++	0.1	50	0.17
Soybean PC									
0.5	5	~1	~180°	20	17	+++	1	24	0.83
1	5	~1	~180°	28	24	++	1	60	2.0
1	20	~1	~180°	36	15	++	0.3	40	0.1
Topcithin[b]									
0.5	5	~1	~70°	17	10	+	0.3	22	0.17
0.5	20	~1	~70°	34	60	+	≥3	≥60	1.5

[a] C_{water}, water content in emulsion; γ_{ow}, interfacial tension between oil and water; θ_0, contact angle (advancing) for fat crystals at the oil/water interface (measure through the oil); d_i, the initial droplet size of emulsions without fat crystals; d_e, the droplet size of emulsions without 3% crystals; η_{disp}, relative change in the viscosity of the continuous oil phase due to addition of fat crystals (Ref. 7); C_{crit}, critical fat crystal concentration when destabilization of water droplets turns to stabilization (maximum in Figs. 9–11); d_{crit}, droplet size of emulsions at critical fat concentration; t, fat crystal layer thickness around water droplets at critical concentration ($t \approx C_{crit} \bullet d_{crit}/6 \bullet C_{water}$); PC, phosphatidylcholine.
[b] From Grindsted (Brabrand, Denmark).

crystal concentration for maximum droplet size (Figs. 6–8), which represents the concentration when destabilization turns to stabilization. And d_{crit} is the droplet size of emulsions at critical fat crystal concentration.

Several factors influence the initial droplet size of the emulsion systems studied. The droplet size increases with increasing amount of dispersed phase due to an increase in flocculation rate. On the other hand, increasing droplet size should have a preventative effect on the drainage of film during coalescence (Table 1).

The droplets were largest for emulsions stabilized by monoolein, intermediate for soybean PC, and smallest for technical lecithin (Topcithin) (Table 2). The small droplets for lecithins may be due to a low interfacial tension and relatively high viscosity (6) of oil solutions, among other factors, which make the emulsification process more effective. High viscosity also produces slower flocculation after homogenization, according to Table 1. The differences between lecithins may be due to greater uniformity of the technical lecithin in the emulsion.

Emulsions with increasing amounts of crystals. Fat crystals in the oil phase influence several emulsion parameters. The density difference between oil and water diminishes because fat crystals have a density close to water. This decreases gravity-induced flocculation and coalescence rate. A similar effect should be observed with an increase in viscosity of the continuous phase due to the presence of crystals. The viscosity increase is exponential with fat crystal concentration (1,2,20,36). Because the crystal adsorbs to the oil-in-water interface, the interfacial viscosity and elasticity also are expected to increase and slow down the coalescence process.

All these effects contribute to slower coalescence and smaller droplet size for fat crystal concentrations above a certain critical concentration, which is system-specific (Table 2). For lower crystal concentrations, the opposite effects dominate. These effects are most likely caused by bridging of water droplets by fat crystals as described below.

Coalescence due to piercing of droplets by fat crystals. Fat crystals in the continuous phase of water-in-oil emulsions may participate in flocculation and coalescence processes as

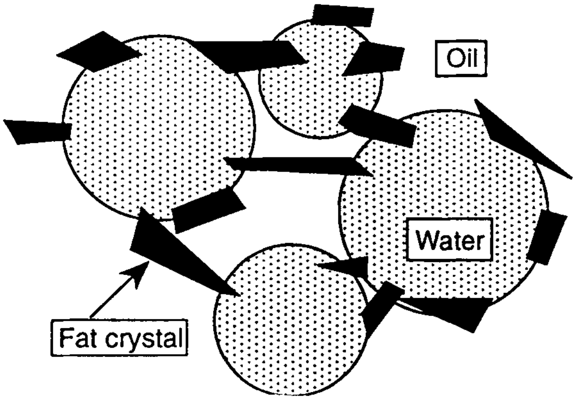

FIG. 13. Schematic picture of destabilizing mechanism for emulsions by fat crystal bridges between water droplets in oil.

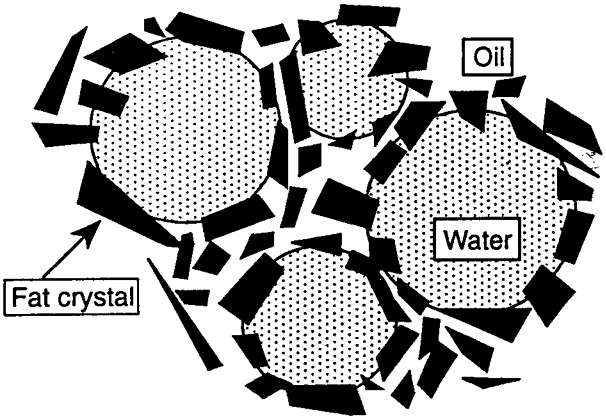

FIG. 14. Schematic picture of destabilizing mechanism for emulsions due to screening of water droplets by fat crystals in oil.

schematically presented in Figure 13. This phenomenon is similar to partial coalescence in oil-in-water emulsions (24), where the droplets coalesce in shear due to fat crystals piercing out from the inside of oil droplets and acting as bridges. The wetting of fat crystals by the water phase, characterized by contact angle in a three-phase contact, is an important parameter in this phenomenon.

The adhesion force, F_b, that keeps two droplets together due to a fat crystal bridge is given approximately by Equation 1 (24):

$$F_b = \frac{A}{s} \bullet \gamma_{ow} \bullet (1 - \cos\theta_0) \qquad [1]$$

where γ_{ow} is the interfacial tension between oil-and-water phases, θ_0 is the advancing contact angle for fat crystal/oil/water (measured through the oil for water-in-oil system); A is the surface area of crystal piercing the droplet; and s is the distance over which the crystal protrudes from the droplet. This force is obtained by the interfacial tension component directed toward the water droplet, by the perimeter of the fat crystal and water droplet cross-section. In an emulsion under dynamic shear condition, maximum floc size is determined by balancing the adhesion force and the shear force F_s pushing the droplets apart (24):

$$F_s = \dot{\gamma}\eta \bullet d^2 \qquad [2]$$

where $\dot{\gamma}$ is the velocity gradient (shear rate), η the viscosity of medium, and d the droplet diameter. As a first approximation, the difference $F_s - F_b$ is the critical force for disruption of flocs (stabilization) in the presence of fat crystal bridges:

$$F_s - F_b = \dot{\gamma}\eta \bullet d^2 - \frac{A}{s} \bullet \gamma_{ow} \bullet (1 - \cos\theta_0) \qquad [3]$$

Comparison between different emulsion systems. From the results in Table 2 and from Equation 3, the following observations may be forwarded. Low interfacial tension should give low adhesion of fat crystal bridges to the droplets (low F_b) and thereby a weak destabilizing effect (high $F_s - F_b$). However, the effect from interfacial tension seems not to dominate in our case. High viscosity of fat crystals in the oil medium for monoolein emulsions (7) seems to be important in disruption of crystal bridges and prevention of coalescence (high F_s) with relatively low critical concentrations for stabilization.

Screening of emulsion droplets by fat crystals. As the concentration of fat crystals in the continuous phase increases, stabilizing mechanisms take over due to increased bulk and surface viscosities and due to decreased density differences. Crystals may mechanically prevent or hinder the droplets from approaching each other (Fig. 14), and thereby from coalescing. The critical concentration should correspond to the droplet surface covered by a layer of fat crystals. The thickness of that layer, t, may be derived from the critical volume fraction of fat crystals in each sample, ϕ_{crit}, divided by $(\phi_{water}/d_{crit/6})$, which represents the droplet area per unit volume of emulsion. Thus:

$$t \approx \frac{\phi_{crit}}{\phi_{water}/\frac{1}{6}\, d_{crit}} \approx \frac{C_{crit}}{C_{water}/\frac{1}{6}\, d_{crit}} = \frac{C_{crit}\, d_{crit}}{6\, C_{water}} \qquad [4]$$

provided that the thickness of the layers is small compared to the water droplets. C_{crit} is the critical fat crystal concentration, and C_{water} is the water content, both in percent. The layer thickness in emulsions, specified in Table 2, is of the order of magnitude 0.1–2 μm. Because the average fat crystal size (calculated from the specific surface and assuming that the crystals are spherical) is 0.7 μm, the crystals adsorbed to monoolein droplets correspond to a monolayer of small particles or a monolayer of long-shaped particles adsorbed flat on droplets. In the case of lecithin, a monolayer of large particles is adsorbed, or more than a monolayer of average particles. Thus, monoolein emulsions demand thinner layers for stabilization than lecithin emulsions. This may be the effect of fat crystal polarity, which is higher in the presence of lecithins compared to monoolein, producing destabilizing effects (crystals may penetrate water droplets). The second effect, observed in all cases except for soybean PC, is that large droplets are less stable and demand thicker layers for stabilization.

Long-term stability. Studies of long-term stability (Figs. 9–12) indicate that water-in-oil emulsions with monoolein and Topcithin are stabilized against water separation for all fat crystal concentrations examined. Initial destabilization by low crystal concentrations, observed in light-diffraction studies, was not observed in sedimentation, most likely due to pronounced hindering effects on consolidation of concentrated systems. The droplet size in sedimentation samples increased directly after sample preparation until the critical droplet size and critical concentration were approached. Then, the crystals present in the sample formed an approximate monolayer on the droplets, protecting the emulsion droplets from further coalescence. The Topcithin emulsions were more stable than the monoolein emulsions. For Topcithin emulsions, the optimal crystal concentration for stabilization appeared at 1–2%, which may be due to formation of an optimal network of fat crystals and water droplets.

Technological consequences. The initial destabilization by small amounts of fat crystals may be an important parameter for the production of margarine and spreads, especially those with low fat content. The destabilization degree may be decisive to the final product properties as well as determining processing properties. The degree of destabilization is probably strongly dependent on the rate of fat crystallization in the oil phase as well as on the amount and form of fat crystals formed. Local variations in the temperature and/or shear may also be important.

The initial destabilization of emulsions by particles may also be an important phenomenon for other applications such as, for example, emulsion polymerization. It also may play a part in emulsion/foam systems such as ice cream.

Long-term stability of oil-continuous liquid products (for example, liquid margarine) may be achieved by well-designed fat crystals. For best stability, the optimal amount of fat crystals as well as the optimal emulsifier and its amount should be determined.

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