

Weak Gels of Fat Crystals in Oils at Low Temperatures and Their Fractal Nature

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ABSTRACT: The formation of fat crystal gels in soybean oil has been studied by sedimentation in a low concentration region at 10–25°C. At 10°C, weak gels were formed with 1% crystals, and no gels formed at concentrations of 2–5%. At temperatures of 15–25°C, no gels were formed at concentrations of 1–5%, and samples sedimented. Stronger gels of fat crystals were formed with ~10% fat crystals at all temperatures examined. Formation of weak gels is a consequence of the fractal nature of fat crystal aggregates and sediments. At low temperature, the interaction is weak. The fractal dimension is then high, and the floc size is large for low crystal concentrations. These large flocs form a three-dimensional network that act as a weak gel and withstand gravitational force. When the temperature is increased, the fat crystal interaction becomes stronger, fractal dimension decreases, and floc size decreases. Smaller flocs have a higher density, pack more easily, and sediment. Similar effects are observed when the concentration of fat crystals is increased at low temperature due to a decrease in floc size.

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KEY WORDS: Dispersions, fat crystals, foods, fractals, sedimentation stability, temperature, triglycerides, vegetable oils, weak gels.

Fat crystal dispersions in oils are essential components of foods, such as margarine, butter, spreads, and chocolate (1–3). Fat crystals may also be used as thickeners of triglyceride oils in food, feed, or technical applications. Rheology and sedimentation of fat crystal dispersions are essential quality properties and depend both on adhesion between fat crystals (4–7) and structures formed. Attempts have been made to describe the structure of fat crystal networks, and some dated theories simplified the network as an arrangement of chains of flocculated fat crystals in three perpendicular directions throughout the sample (8–10). During the last few years, however, attempts have been made to apply fractal models to fat crystal structures in oils (11). This approach is promising, because the appearance of crystal networks resembles fractals described elsewhere (12,13). The aim of this study is to determine the sedimentation of small concentrations of fat crystals in oil to detect formation of weak gels. The fractal

approach is used to understand and explain the trends observed.

EXPERIMENTAL PROCEDURES

Materials. A fully hydrogenated palm oil (palm stearin) from Karlshamns AB (Karlshamn, Sweden) was used as solid fat crystals. Palmstearin has a mole mass of 756 g/mol on average and an iodine value of 2.6. Its density is assumed to be the same as the density of tristearin β crystals, $\rho \approx 1$ g/mL. It is stable in the polymorphic β' form, which has a melting point of 57–59°C. The β' form occurs in palmstearin when crystallized from organic solvents, such as acetone. Palmstearin was recrystallized in acetone prior to use to produce well-defined crystals. Dry crystals were characterized with respect to the melting point, polymorphic form, morphology, and specific surface area. The latter, determined by BET at Chalmers Institute of Technology (Gothenburg, Sweden), was 9.6 m²/g, which corresponds to average spherical particle diameter of ~0.6 μ m. Acetone for recrystallization of fat crystals was of analytical grade and supplied by Merck (Darmstadt, Germany). Refined soybean oil from Karlshamns AB was used as the oil phase. The interfacial tension between the oil and distilled water is slightly above 30 mN/m. This high value indicates that the oil is pure with respect to surface-active components. The oil has an iodine value of approximately 130 (~2.5 double bonds per hydrocarbon chain on average) and a melting point of approximately –20°C. The oil was not further purified prior to use. Density of the oil was 0.92 g/mL at room temperature and 0.91 g/mL at 35°C.

Methods. Simple sedimentation experiments provide a useful method for a qualitative comparison of adhesion between particles in dispersions. As adhesion between particles increases, the particles can stick to each other, form larger flocs and more bulky sediments. Increased repulsion has the opposite effect—the particles do not stick to each other, they pass each other when settling and form denser, more compact sediments (4,7). For sample preparation, a desired amount of fat crystals (palmstearin β') was weighed in a test tube together with oil. Calibrated test tubes (with steps of 0.1 mL) with tight locks were used. After dispersing with a vibromixer, the samples were put into a vacuum dryer to evaporate traces of water and to evacuate air. The samples were allowed to settle in a water bath at a specified temperature for about

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three weeks or until the sediment volumes were constant with time. The accuracy of sediment volume determination was ± 0.05 mL, less than 1% of the total sample volume (~ 5.5 mL).

RESULTS AND DISCUSSION

Sediment volume of palmstearin β' crystals is presented in Figure 1 as a function of the crystal concentration in soybean oil. At 15, 20, and 25°C, the sediment volume increased continuously with fat crystal concentration. For concentrations close to 10%, a thick gel was formed where the crystal network filled the entire volume of the sample (~ 5.5 mL). The sedimentation pattern was different at 10°C. A weak gel was formed at a concentration of ~ 1 vol%, and almost no sedimentation occurred. A thick gel was formed at concentrations close to 10 vol%. Apparently, gels at 1 and 10 vol% have different structure, strength, and nature. No gels appeared at the intermediate concentrations at 10°C. Sediment volumes were recalculated to sediment densities (as vol%) in Figure 2. At low fat crystal concentrations, the slope of the relationship "sediment density–volume fraction" is greatest at 10°C and least at 25°C. This indicates that the aggregation state changes more rapidly at low temperature than at room temperature. At high concentrations (≥ 5 vol%), the slopes are generally lower, differences are smaller, and the aggregation state is unchanged.

The application of a fractal approach to sedimentation of fat crystals in oils may shed some light on aggregation phenomena in these systems. In this approach (14), one assumes

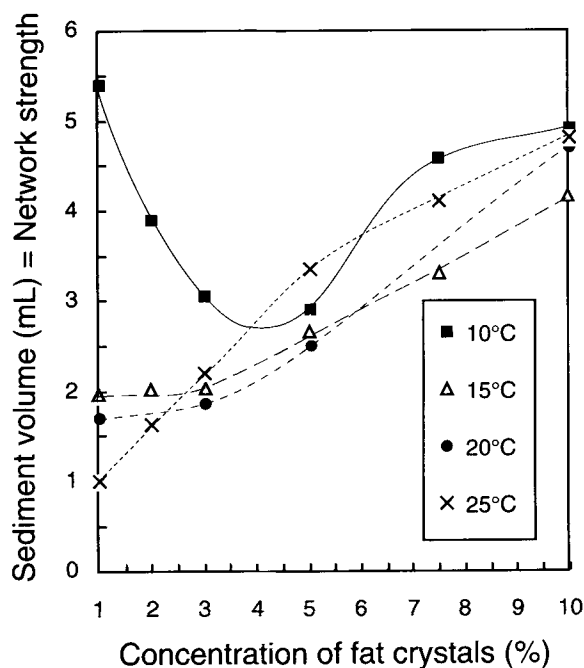


FIG. 1. Sediment volumes (expressed in mL) of palmstearin β' crystals in soybean oil as a function of crystal concentration in the oil (expressed in vol%). The total volume of samples was 5.5 mL. The sedimentation temperature was 10, 15, 20, and 25°C.

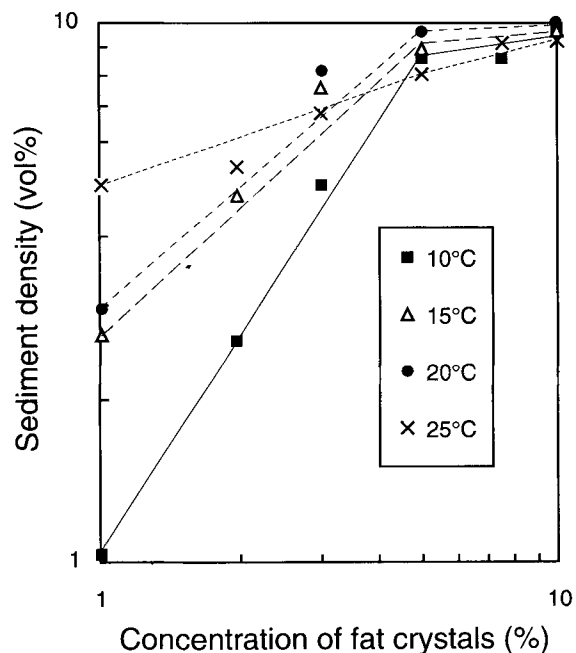


FIG. 2. Sediment density (expressed in vol%) of palmstearin β' crystals in soybean oil as a function of crystal concentration in the oil (expressed also in vol%). The results are recalculated from Figure 1. The sedimentation temperature was 10, 15, 20 and 25°C.

that the particles aggregate in fractal flocs due to Brownian motion. When these aggregates become large enough, they sediment due to gravity. The anisotropy caused by sedimentation should not change the fractal character of the aggregates due to rotation and random collisions. A relationship between relative floc size (R/r , R is the radius of the fractal floc and r is the radius of the primary particles) and volume fraction of particles in dispersion (ϕ) has been deduced from an expression for sedimentation velocity for fractal aggregates (15). Because the sediment volumes of samples were determined when the sedimentation process was completed (at equilibrium), the sedimentation velocity was 0. Thus we get:

$$\frac{R}{r} \propto \left(\frac{\phi_{\max}}{\phi} \right)^{\frac{1}{3-d_f}} \quad [1]$$

where d_f is the fractal dimension of flocs (sediments), ϕ is the volume fraction of particles in the sample, and ϕ_{\max} is the maximal volume fraction in the sediment (assumed to be equal to the sediment density in vol%). The relationship is plotted in Figure 3. Provided that the ϕ_{\max} and r are constant and the fractal dimension d_f is constant (assumed to be valid for a constant temperature), the floc size decreases exponentially with increasing volume fraction ϕ . And for constant volume fraction ϕ , the floc size is large for a high fractal dimension d_f and small for a low fractal dimension. With this background, the following can be concluded. Fat crystal interaction is weak at low temperature and fractal dimension

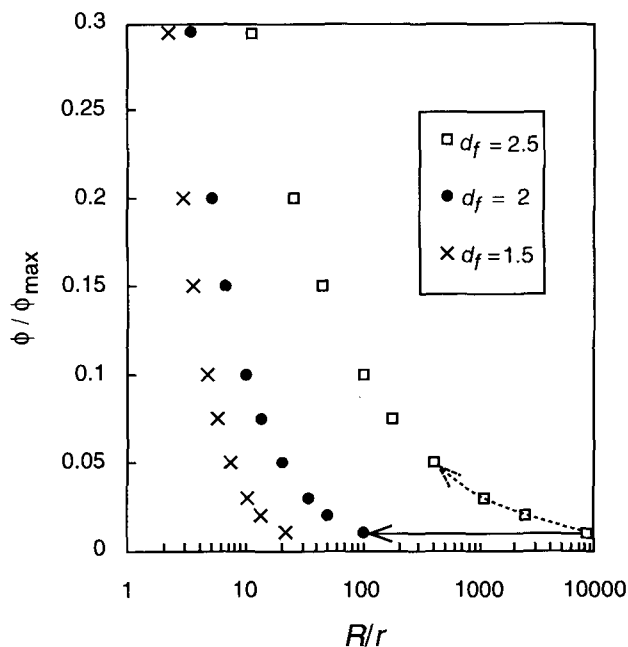


FIG. 3. Theoretical relationship between the volume fraction of particles in the sample (relatively a maximum volume fraction, ϕ/ϕ_{\max}) as a function of the floc size relative to particle size (R/r , R is the radius of the fractal floc and r is the radius of the primary particles). Fractal dimension, d_f is 2.5, 2.0, and 1.5, respectively; \rightarrow , direction of change in floc size R due to increase in temperature at constant crystal volume fraction ϕ ; $\cdots\rightarrow$, direction of change in floc size R due to increase in crystal volume fraction ϕ at constant temperature.

is high. Large flocs are formed, and the effective density is therefore low. At a certain limit, the flocs are so large and voluminous that they cannot sediment, and a weak gel formation occurs. For a hypothetical case of 0.1 vol% fat crystals with a diameter of $d = 0.5 \mu\text{m}$, which can maximally pack to a volume fraction of $\phi_{\max} \approx 0.5$, and having a fractal dimension of $d_f = 2.5$, the floc size is $\sim 10 \text{ mm}$ according to Figure 3. Such large flocs may form a three-dimensional network (weak gel) that can withstand gravity. When temperature increases, particle adhesion is stronger and the fractal dimension decreases, as indicated by a continuous arrow in Figure 3. If the fractal dimension in our hypothetical case is diminished from 2.5 to 2, the floc size decreases from 10 mm to 100 μm , according to Figure 3. These flocs, which are two orders of magnitude smaller, have a much higher effective density, can pack more easily, and may start to sediment. Similarly, when the concentration of fat crystals is increased at low temperature (constant d_f), the floc size decreases (as indicated by a dotted arrow in Fig. 3), and sedimentation occurs. If the concentration in our hypothetical example is increased from 0.1 to 0.2 vol%, the floc size decreases from 10 to 1 mm.

Another way to explain the results would be to assume that the fractal dimension of fat crystal networks is not constant

for a constant temperature but changes with fat crystal concentration, despite a constant interaction strength (the lower the concentration, the lower the fractal dimension and the more loosely-packed flocs). In any case, formation of weak fat crystal gel at low concentration and low temperature is a consequence of the fractal nature of fat crystal aggregates and sediments in combination with a weak fat crystal adhesion at low temperature.

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