Effects of Crystallization Conditions on Sedimentation in Canola Oil

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The effects of various factors on sediment formation in canola oil were studied. The crystallization temperature of sediment varied with cooling rate, whereas the melting temperature depended on heating rate as well as the cooling rate during sediment formation. The final crystal size depended on cooling rate. The crystal habit of sediment was generally rod-like but could change to a round and leaf-like shape at low cooling rates (<0.5°C/min). Crystal nucleation occurred in the initial stage of crystallization, while crystal growth was observed during the whole crystallization process, decreasing as cooling proceeded. Crystal growth rate of the sediment was proportional to the crystal surface area. Lecithin did not affect the phase transition temperatures of sediment, but retarded crystal growth.

KEY WORDS: Canola sediment, crystal growth, crystal morphology, crystallization, differential scanning calorimetry, hot-stage microscopy, lecithin, melting, wax.

In recent years, the canola oil industry has seen a recurring problem of turbidity during storage of bottled oil (1). This is detrimental to canola oil quality as it influences consumer preference. In sunflower seed oil and corn oil, where clouding is often a problem, the defect is eliminated by winterization.

Winterization involves chilling the oil and removing the solid precipitated material (2). Winterization efficiency is influenced by the rate of cooling, holding temperature and impurities in the oil. These factors affect the rate of the solid's formation and the size and morphology of the solids. Because of oil quality implications, extensive studies on the effects of crystallization conditions on sediment formation in sunflower seed oil have been made (3–7).

Until recently, canola oil has not required winterization. Consequently, there have been few studies on turbidity in canola oil, and the cause of turbidity has yet to be determined (1,8). Because of limited knowledge about canola sediment, it is desirable to understand the influence of various factors on sedimentation in canola oil.

Our previous study dealt with crystal structure and phase transition behavior of canola sediment (8). In the present work, the effects of crystallization conditions on sediment crystal formation are examined. Nucleation and growth mechanisms of sediment were also studied to understand the sedimentation process. Such information could provide insight into the formation and characteristics of sediment in canola oil.

MATERIALS AND METHODS

Preparation of samples. Canola oil used in this study was refined, bleached and deodorized, and it had been stored at 0°C for a week and filtered to remove any solids formed. Canola sediment was obtained by extracting with chloroform an industrial filter cake that was collected after winterization. The residual oil in the sediment was removed by washing twice with cold petroleum ether (2°C). Detailed experimental procedures were described previously (8). Oil solutions of various sediment concentrations (ppm by weight) were prepared by dissolving the required amount of sediment in oil or by diluting a 2000-ppm sediment solution with oil. Oil solutions containing various amounts of phospholipids were prepared by adding lecithin (L-α-Lecithin from soybean, > 98.5% purity; Calbiochem, San Diego, CA) to the oil.

Composition analysis of canola sediment. The composition of canola sediment was determined by the TLC–FID (IATROSCAN) procedure as described by Przybylski and Eskin (9). The first separation was made with hexane/benzene/acetone/acetic acid (44:30:0.8:0.3, by vol), the second with acetone/water/acetic acid (70:1.2:1.5, vol/vol/vol) and the third with chloroform/methanol/water/acetic acid (50:28:3.1:0.3, by vol). All reagents used were of analytical grade and purchased from Sigma Chemical Co. (St. Louis, MO).

Melting and crystallization temperatures of canola sediment in oil. The melting and crystallization temperatures of canola sediment in oil were determined with a polarized-light microscope (IIIRS; Zeiss, Oberkochen, Germany) equipped with a temperature-controlled hot plate (Physitemp, Clifton, NJ). Measurements were made at constant cooling or heating rates from 1–15°C/min. Linear rates of change of temperature were achieved by using a temperature controller (TS-4 ER; Physitemp) and a programmable stepping motor unit (MD2; Physitemp). Precise measurements of temperature were made with a thermocouple attached to the surface of a glass slip on the hot stage.

To prepare samples for microscopic study, drops of hot oil/sediment solution were transferred to a slide slip (26 × 24 × 1.5) and covered by slips of smaller size (22 × 22 × 1.5). Samples were heated to 70°C, held for 10 min to melt any crystals formed during sample preparation, and cooled linearly on the hot-stage polarizing microscope. The crystallization temperature was taken as the temperature where crystals were first observed. In the measurements of melting temperature, samples were cooled at a constant rate of 2.2°C/min from 70°C to room temperature or until crystals were observed. The samples were held at the final temperature for 30 min to allow crystal growth. The melting temperature was determined by heating the samples until the last trace of crystals disappeared.

Morphology, distribution of size and growth of canola sediment crystals. The morphology and size distribution of canola sediment crystals were determined by photomicrography. Oils enclosed in slide slips were cooled from 70 to 10°C at a constant rate and maintained at the final temperature for 30 min. With pure canola sediment, samples were cooled from 80 to 20°C. The morphology of the crystals was recorded with a camera (MC100; Zeiss) fitted on top of the microscope. In the growth experiments, oil solutions were cooled at 0.5°C/min from 70 to

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10°C. Micrographs of the crystals were taken periodically during crystallization. Crystal size was taken as the longest dimension of the particles. Coefficients of variation of crystal size were calculated as the standard deviations divided by the mean crystal sizes. Crystallization data were reported on the basis of 100 particles per field.

Differential scanning calorimetry (DSC). The melting behavior of canola sediment crystals, obtained under various cooling conditions, was studied by DSC. A thermal analyzer (Dupont 9900, Wilmington, DE) fitted with a DSC cell (Dupont 910) was used. Samples were weighed into DSC pans and hermetically sealed. An empty DSC pan was used as an inert reference to balance the heat capacity of the sample pan. Sediments were formed *in vivo* in the DSC pans as described below. DSC samples were first held in the DSC for 5 min at 70°C to eliminate any crystal history. They were then cooled at 10°C/min to 10°C, held at this temperature for 5 min, and heated to 70°C at 10°C/min to obtain the first melting thermograms. The samples were subsequently kept at the upper-end temperature for 5 min, and were cooled for a second time but at a lower rate (~0.5°C/min) to 10°C. The samples were re-scanned to 70°C at 10°C/min to obtain the second melting curves. In the crystallization experiments with pure sediment, the DSC samples were scanned (20–80°C) at a constant rate of 1°C/min in both heating and cooling cycles. All DSC data were reported on the basis of constant sediment weight. Calibration and other experimental procedures for the DSC experiments were as described previously (8).

RESULTS AND DISCUSSION

Composition of canola sediment. Table 1 shows that the major components of canola sediment were wax esters, which amounted to 78%. Our previous study reported that canola sediment has physical properties similar to other oilseed waxes (8). These findings further suggest that, as in other oils, waxes are the major clouding substances in canola oil. To avoid turbidity, wax levels in canola oil should be controlled (8).

Morphology and crystallization characteristics of canola sediment. On cooling, molten canola sediment crystallized into crystals with different morphologies depending on the cooling rates (Fig. 1). At high cooling rates, stacked needle-like crystals were formed (Fig. 1a), whereas at low cooling rates tree-like dendrite crystals were produced (Fig. 1b). Formation of dendrite structures suggested that secondary nucleation may occur at low cooling rates.

TABLE 1

Composition of Canola Oil Sediment Isolated from an Industrial Filter Cake Collected After Winterization

Component	Content (%) ± s.d.[a]
Wax esters	78.1 ± 1.0
Triglycerides	Trace
Free fatty acids	0.2 ± 0.1
Free fatty alcohols	2.0 ± 0.1
Diglycerides	2.7 ± 0.2
Others	17.2 ± 0.6

[a] s.d. = Standard deviation.

Figure 2 shows the DSC thermogram of crystallization of canola sediment. Instead of a symmetric single peak observed for melting (8), the DSC crystallization exotherm was characterized by a sharp peak followed by a shoulder. The reason for the appearance of the trailing shoulder is uncertain but is believed to be due mainly to the growth of crystals of slow-crystallizing components. The overall crystallized fraction, expressed as the ratio percentage of the area under the DSC peak at any moment to the total peak area, is also shown in Figure 2. The rate of overall crystallization was not constant, as indicated by the changing slope of the curve. It increased initially and decreased later, levelling off in about 10 min after crystallization started.

Effect of heating and cooling rates on phase transition temperatures. Figure 3 shows the effect of cooling rate on the sediment crystallization temperature as well as the effect of heating rate on the melting temperature of the sediment obtained by cooling at a constant rate of 2.2°C/min. As cooling rate increased, crystallization temperature decreased; whereas, as heating rate increased, melting temperature increased. The effect of cooling rate on crystallization temperature, or heating rate on melting temperature, however, was smaller in oils containing high contents of sediment.

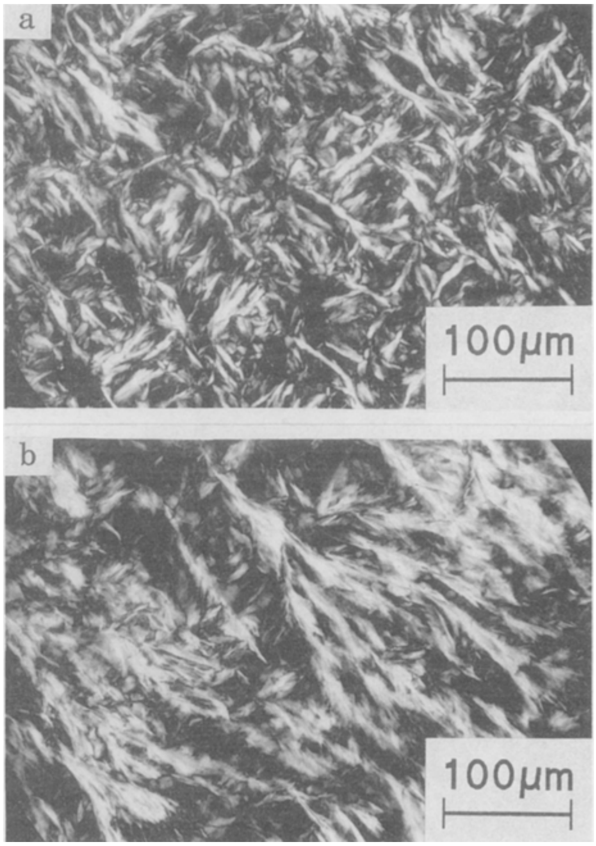

FIG. 1. Micrographs of canola sediment obtained by cooling molten samples at (a) 14.8°C/min and (b) 0.5°C/min.

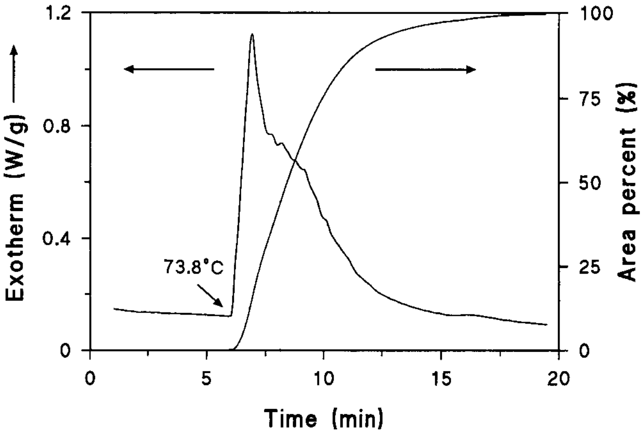

FIG. 2. Differential scanning calorimetry (DSC) exotherm and area percentage of crystallization of canola sediment. DSC cooling rate was 1°C/min.

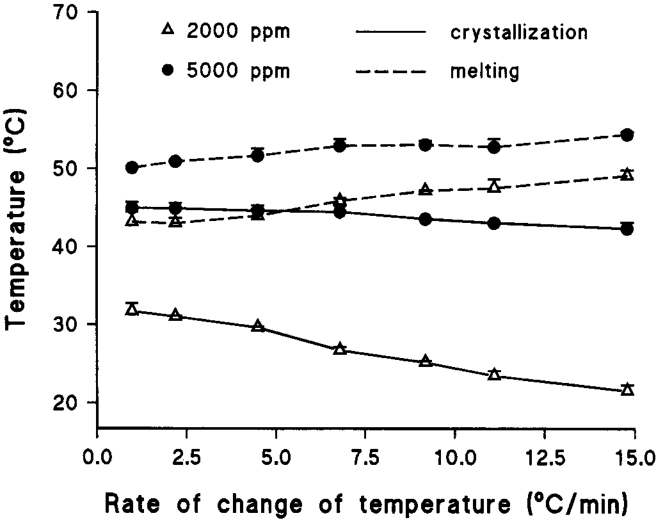

FIG. 3. Crystallization and melting temperatures of canola sediment in oils that contained 2000 and 5000 ppm sediment, as a function of rate of change of temperature.

Figure 4 shows the melting and crystallization temperature difference (ΔT) as a function of the rate of change of temperature and sediment content. The ΔT increased as cooling (heating) rate increased and decreased as sediment content increased. The ΔT between melting and crystallization is an indication of supercooling. The increase in the degree of supercooling with cooling rate may be due to kinetic reasons. At high cooling rates, many nuclei were formed, and crystals were too small to be detected by the microscope for a longer period of time.

The melting behavior of sediment crystals also depended on the cooling rate during sediment formation. This is clearly shown by the DSC melting curves of sediments in Figure 5. On heating, the crystals formed by rapid cooling (~10°C/min) exhibited a melting peak at around 44°C (Fig. 5a), whereas the crystals formed by slow cooling (~0.5°C/min) had a peak at a higher temperature of about 48°C (Fig. 5b). Oils with lower sediment content showed even larger differences between the melting temperatures. However, the cooling rate effect on the crystal melting temperature was not observed in oils containing high sediment contents (>1%). Moreover, the melting temperature of pure sediment did not vary with the cooling rate used in its formation. Thus, the variation in the crystal melting temperature in these oils may not be due to polymorphic crystals, although different crystal habits were observed when sediment was formed at different cooling conditions (see the following section). A factor that could affect the melting temperature of crystals in oil is crystal size. Small crystals were formed in oil by rapid cooling, whereas large crystals were produced by slow cooling. During melting, material dissolving from the

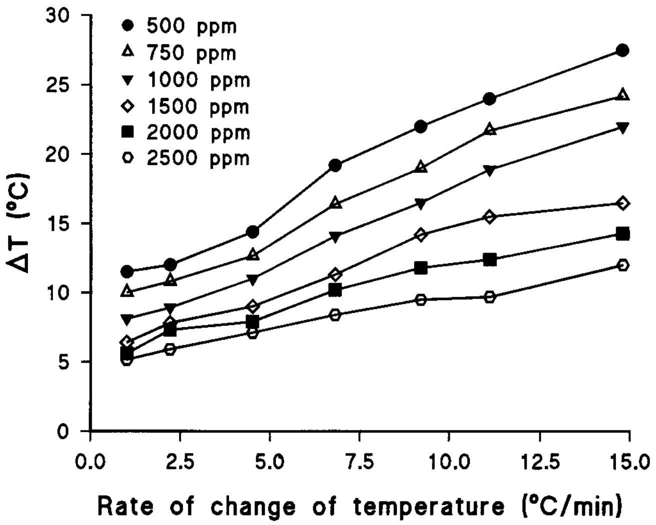

FIG. 4. The melting and crystallization temperature difference (ΔT) of canola sediment in oil at various sediment contents, as a function of rate of change of temperature.

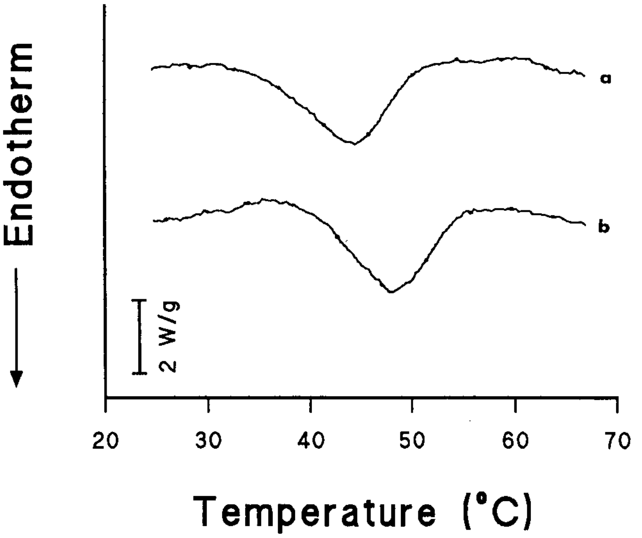

FIG. 5. Differential scanning calorimetry (DSC) melting thermograms of the canola sediments formed at cooling rates of (a) 10°C/min and (b) 0.5°C/min. Sediment concentration was 2500 ppm.

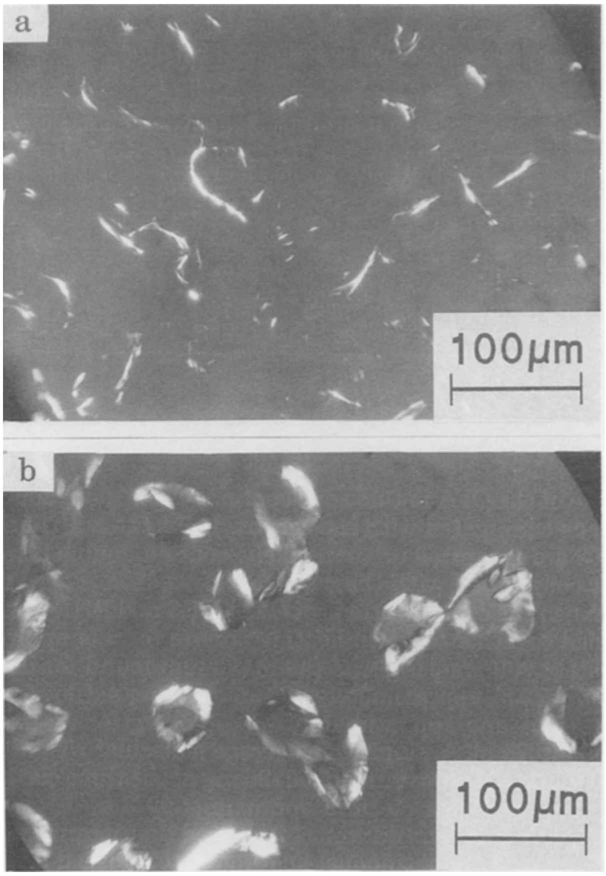

FIG. 6. Micrographs of canola sediment obtained by cooling oil with 2500 ppm sediment at 1°C/min (a) and with 5000 ppm sediment at 0.5°C/min (b).

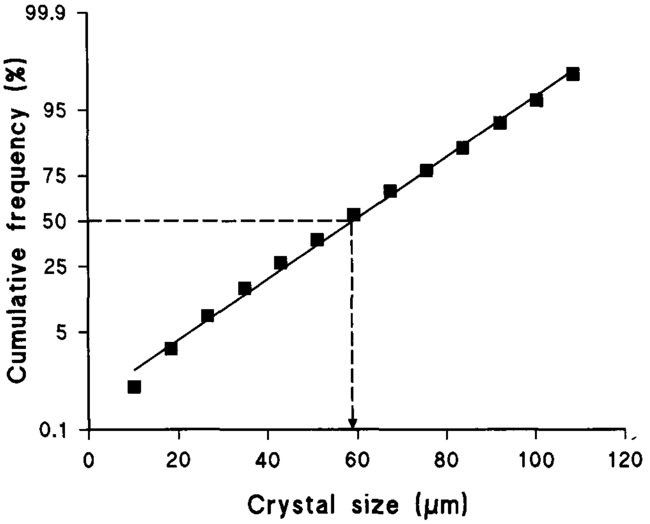

FIG. 7. Cumulative frequency of crystal size as a function of crystal dimension in 5000 ppm sediment oil. Cooling rate was 1°C/min.

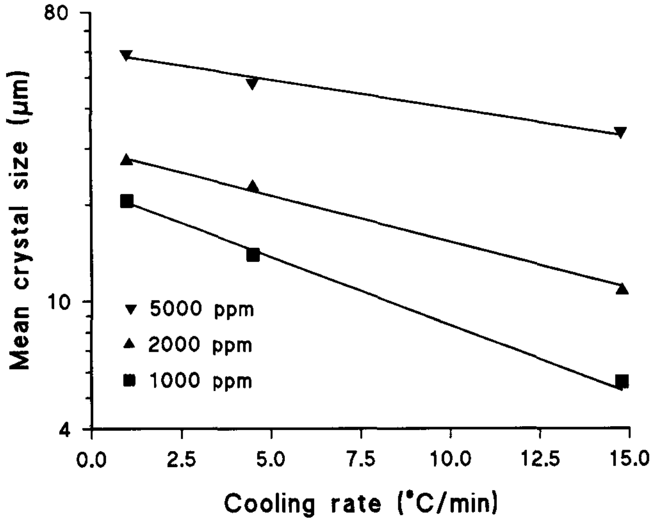

FIG. 8. Mean size of sediment crystals as a function of cooling rate in oil at various sediment concentrations.

crystals must diffuse from the crystal surface to the bulk solution, and crystals of smaller sizes facilitate the process of dissolution because of the large contact area. This effect is less significant at high sediment contents (10).

Effect of cooling rate and sediment concentration on crystal habit. The crystal habit of canola sediment crystallized in oil was influenced by the cooling rate as well as by the sediment concentration. In most cases, they were needle-like or rod-like crystals (Fig. 6a). However, at low cooling rates (<0.5°C/min), crystals exhibited round-shaped and leaf-like appearance (Fig. 6b). Crystals produced in oils that contained higher sediment contents exhibited normal rod-like crystals. This indicates that the crystal morphology of oil sediment depends on both the cooling rate and the crystallizing solute concentration. Sunflower oil wax crystals reportedly changed in shape when wax concentration was higher than 1% (3). Kellens *et al.* (11) reported that tripalmitin crystals could have different morphological appearances, depending on crystallization temperature or on whether it crystallized from a melt or from transformation of less stable crystals (11). These authors found four β'-microstructures for tripalmitin, which included grainy, fibrous, feathery and lamellar structures.

Effect of cooling rate and sediment concentration on crystal size. A typical data set of the frequency distribution of size for sediment crystals in oil is shown in Figure 7, plotted as the cumulative frequency vs. particle size on a probability scale. The mean particle size for the crystals in the sample was estimated from the regression line (12) as the x-value at $y = 50\%$. Figure 8 shows the effect of cooling rate on the crystal size at three sediment concentrations. The mean size of the crystals in oil that contained 1000 ppm sediment decreased from 21 μm to about 6 μm when the cooling rate increased from 1°C/min to 15°C/min. In addition, the concentration of sediment in oil also affected sediment particle sizes. Crystals in oil that contained 5000 ppm sediment were about three times larger than those in oil containing 1000 ppm sediment. However, it must be pointed out that crystal size would not increase monotonically with concentration, and further increases in concentration may result in decreases in crystal size (10).

Rivarola *et al.* (3) found an exponential equation that correlated the crystal size of waxes in sunflower seed oil with the final cooling temperature. The dependence of crystal size on cooling rate for canola sediment can also be described by a similar equation:

$$x = ae^{-b\lambda} \quad [1]$$

where x is the mean crystal size (μm), λ the cooling rate (°C/min). Both a (μm) and b (min/°C) are constant coefficients equal to 22 and 9.3×10^{-2} for 1000 ppm, 30.2 and 6.9×10^{-2} for 2000 ppm, and 59.7 and 3.9×10^{-2} for 5000 ppm, respectively.

Crystal growth of canola sediment in oil. The growth of sediment crystals in oil was studied during cooling with a slow cooling regime (0.5°C/min). This is comparable with industrial winterization, where crystallization is carried out nonisothermally with decreasing temperature (2). Figure 9 shows the number of crystals in oil that contained 2000 ppm sediment during the course of cooling. As the oil was slowly cooled to the nucleation temperature, which was about 48°C for the oil used, nucleation began to occur and continued as the oil temperature was further decreased. The nucleation process almost ended after about 10 min, which corresponded to about 5°C below the nucleation temperature. Further decreases in temperature did not result in additional nucleation. Figure 9 (inset) clearly shows that nucleation reached a maximum, after which it decreased as the cooling proceeded.

Figure 10 shows the mean crystal size as a function of time during crystallization. Table 2 shows the variations of size in the crystal population from the means. Figure 11 depicts the change of size of individual sediment crystals during crystallization. Crystal growth was fastest in the initial stage. It decreased as the temperature and supersaturation decreased. The final crystal size attained by individual crystals reflected mainly the progressive process of nucleation.

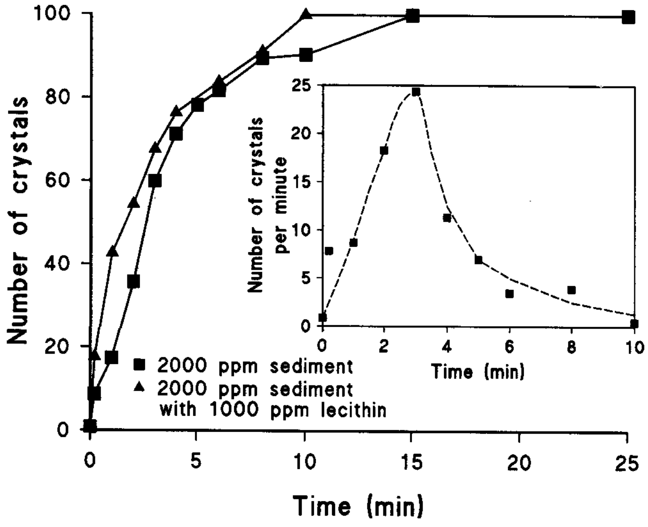

FIG. 9. Number of crystals per field in oil (2000 ppm sediment) with or without lecithin during the course of crystallization. Inset figure shows the rate of increase of crystal number in oil without lecithin.

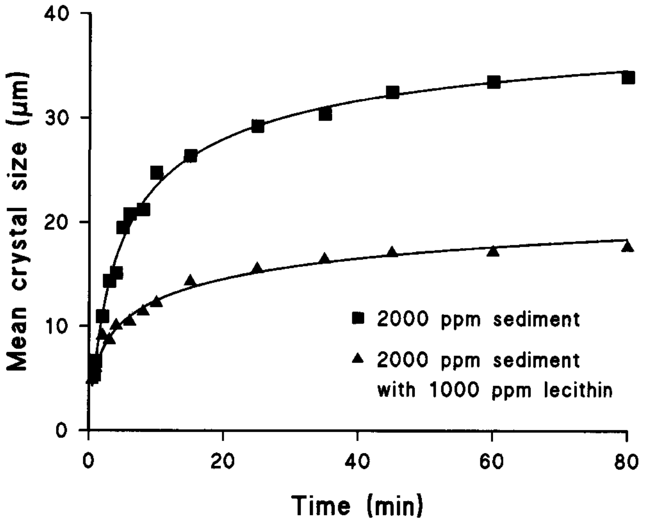

FIG. 10. Mean size of sediment crystals in oil without or with lecithin, as a function of crystallization time.

TABLE 2

Standard Deviations (σ) of Distribution and Coefficients of Variation (σ/mean) of Crystal Size[a]

Time (min)	2000 ppm		2000 ppm (0.1% lecithin)	
	σ (μm)	σ/mean (%)	σ (μm)	σ/mean (%)
1	5.3	80	2.9	58
2	6.6	61	4.1	68
3	9.4	65	6.8	79
4	10.6	70	5.6	56
6	11.6	56	5.6	53
8	12.6	59	5.9	51
10	13.4	54	6.7	54
15	12.8	48	5.9	41
25	12.3	42	6.3	41
35	13.8	45	6.9	42
45	14.9	46	7.1	41
60	13.3	40	7.2	42
80	13.3	39	7.1	40

[a] Values of σ were determined from regression lines as shown in Figure 7 according to Reference 12.

Effect of lecithin on crystallization. Addition of lecithin (up to 1%) to canola oil/sediment solutions did not change the melting and crystallization temperatures of sediment. A previous study on lecithin in sunflower seed oil also reported that lecithin did not change the phase transition temperatures of sunflower wax in oil (5). Figure 9 shows that the increase of the number of crystals with time in the presence of lecithin followed the same trend as that without lecithin. These data suggest that the action of lecithin, which is known as a natural crystal inhibitor in oil, is mainly due to retarding growth of crystals (5). Figures 10 and 12 clearly show that the presence of lecithin greatly reduced the crystal size. With increased lecithin content (Fig. 12), crystal size decreased. However, an increase of lecithin concentration from 0.5 to 1% did not significantly affect the crystal size of the sediment.

Crystallization kinetics of canola oil sediment. Relatively few studies have dealt with kinetic aspects of crystallization of fats and oils (13). The classical Avrami kinetic

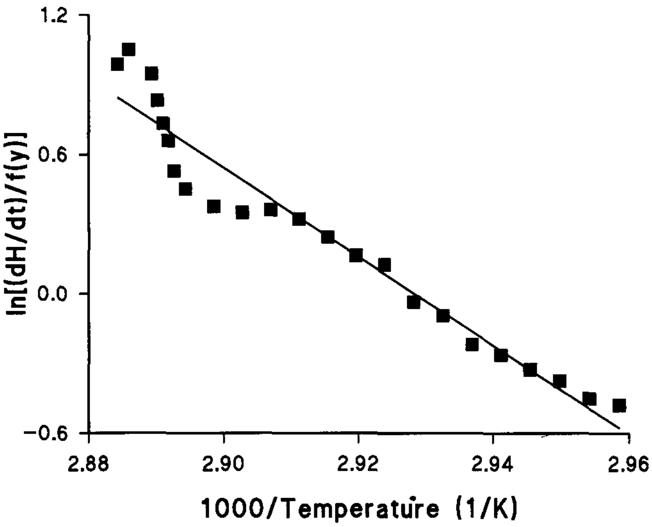

FIG. 11. Size of individual sediment crystals in oil (2000 ppm sediment) as a function of crystallization time. Data for six representative crystals (denoted by A, B, C, D, E and F) are shown in the figure. The solid lines are plotted according to Equation 6.

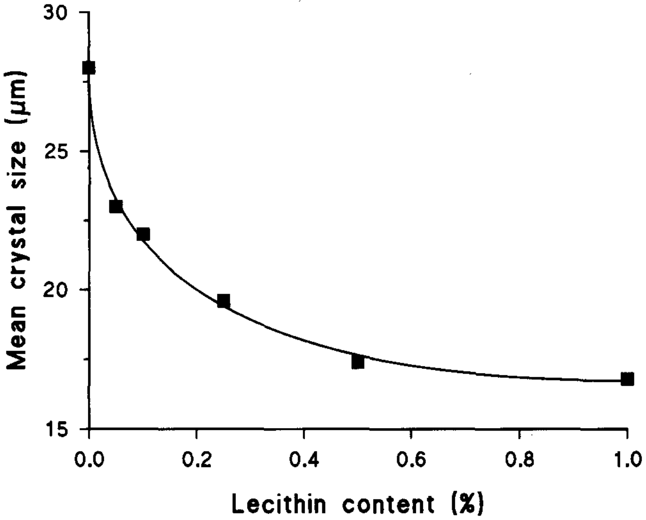

FIG. 12. Effect of lecithin on the mean size of sediment crystals in 2000 ppm sediment oil, formed at a cooling rate of 2.2°C/min.

theory has often been applied in studying crystallization kinetics for materials solidifying from their melts (14–16). Accordingly, the generalized form of transformation rate equation is as follows:

$$\frac{dy}{dt} = K(T)f(y) \qquad [2]$$

where y is the fraction of crystallized phase, t is the time, and $K(T)$ is the crystallization rate constant (a function of temperature T). The exact form of the function $f(y)$ in Equation 2 is $(1 - y)[-\ln(1 - y)]^{(n-1)/n}$, where n is an integer from 1 to 4 (15). According to Sun *et al.* (17), the function $f(y)$ is equal to $(1 - y)$. The latter can be actually considered as a special case of the former (n = 1). Also, when substituting $dy/dt = (1/A)dH/dt$ into Equation 2 based on the Borchardt's assumption (15) and assuming that the crystallization rate constant follows an Arrhenius relationship with temperature, the following modified equation is obtained:

$$\frac{dH/dt}{f(y)} = AK_0\exp\left(-\frac{E}{nRT}\right) \qquad [3]$$

where dH/dt is the rate of heat flow; A, the total area of the DSC crystallization peak; K_0, a constant; R, the universal gas constant; and E, the activation energy of crystallization. Taking the logarithms of both sides of Equation 3 yields a linear relationship. Figure 13 shows the best fit of the DSC crystallization data for pure canola sediment by using this equation and assuming n = 2. Based on the slope of the regression line, the activation energy was about 318 kJ/mol. Due to the heterogeneous nature of canola oil sediment (8), the observed deviation from linearity is not surprising. Further kinetic studies on crystallization of sediment and other fats with the Avrami theoretical approach and its modifications (14,15) would be both of practical importance and of scientific interest.

In a study of size distributions and growth mechanisms of microcrystalline precipitates, Berry and Skillmay (18) demonstrated that if the rate of increase of molecules in the crystal is proportional to the crystal surface area, a frequency distribution of size, p(x) vs. x (where x is crystal size), will remain fixed both in shape and in width during growth when the volume is proportional to x^3, and surface area is proportional to x^2. For cylinder-like crystals, this is also valid if the ratio (C) of diameter/length of the crystal remains constant, as shown below.

Because $dN/dt \propto S$, where N is the number of molecules incorporated into the crystal; S, the crystal surface area; and t, the time, dN/dt is proportional to dv/dt, where v is the crystal volume. The increment of volume in the crystal is, therefore, proportional to S, i.e.,

$$dv/dt \propto S \qquad [4]$$

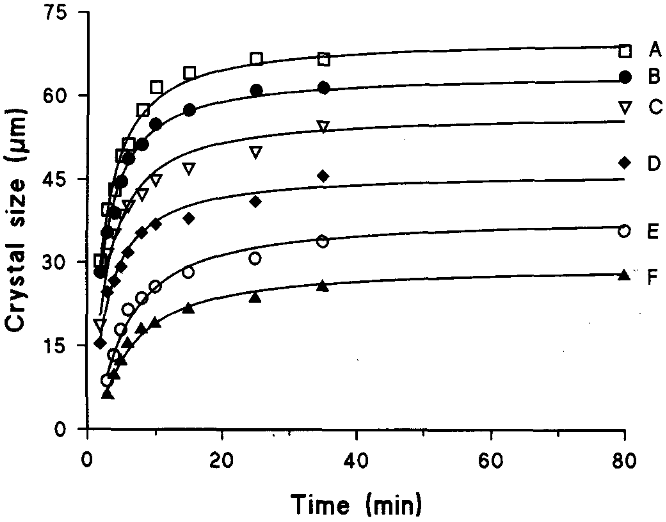

FIG. 13. Crystallization of canola sediment as a function of temperature, plotted according to Equation 3.

The effective surface area for a finite cylinder is $(\pi C^2/2 + \pi C)x^2$, whereas the volume of the crystal is $(\pi C^2/4)x^3$. By substituting them into Equation 4, we obtain:

$$dx = kdt \qquad [5]$$

where k is a growth coefficient characteristic of the system conditions and is assumed to be identical for crystals of all sizes. Equation 5 indicates that the change in size, dx, is the same for all crystals of all sizes and therefore, both the shape and width of crystal size distribution are constant during growth (18).

The shapes of the size distribution for canola sediment crystals were unchanged during growth. Table 2 shows that after a few minutes of crystallization when crystal growth predominated, the standard deviation value, σ, was almost constant, indicating a constant width of size distribution during growth. Figure 11 also shows that the size differences between individual crystals were nearly unchanged during growth, as Equation 5 predicts. These results suggest that crystal growth in canola sediment is proportional to the crystal surface area. Factors that affect crystal surface properties, such as absorption of impurities on the surface, will therefore affect the crystal growth process. In this context, lecithin has been found to be absorbed on the surface of wax crystals (5), and reduced growth rate is expected for canola sediment (consisting of 78% waxes) by this mechanism.

Equation 5 could not be integrated for a nonisothermal crystal growth process, as carried out in this study, because k was temperature dependent. However, the following empirical equation adequately describes the individual crystal growth data obtained in this study:

$$x = C_1 \exp\left(-\frac{C_2}{t}\right) \qquad [6]$$

C_1 and C_2 are constants for a crystal. Figure 11 shows the curves plotted according to Equation 6. Substituting Equation 6 into Equation 5, rearrangement gives:

$$k = \frac{C_2}{t^2} \exp\left(-\frac{C_2}{t} + C_1\right) \qquad [7]$$

Table 3 tabulates the values of k at various crystallization times according to Equation 7. As expected, k was almost constant among crystals of various sizes except for the initial stages of the process; during the initial phase of crystallization, both nucleation and crystal growth occurred simultaneously. These results further support the notion that sediment crystal growth is proportional to the crystal surface area as discussed above.

TABLE 3

Growth Coefficients (k) for Individual Sediment Crystals in Oil Containing 2000 ppm Sediment[a]

	Time (min)			
Crystal	2	10	15	25
A	12.9 ± 0.4	1.03 ± 0.06	0.49 ± 0.03	0.18 ± 0.01
B	11.7 ± 0.4	0.94 ± 0.06	0.44 ± 0.03	0.17 ± 0.01
C	10.5 ± 0.6	0.95 ± 0.10	0.45 ± 0.05	0.17 ± 0.02
D	8.5 ± 0.4	0.81 ± 0.07	0.39 ± 0.04	0.15 ± 0.01
E	5.0 ± 0.6	1.10 ± 0.10	0.54 ± 0.06	0.22 ± 0.02
F	3.5 ± 0.4	0.85 ± 0.06	0.44 ± 0.03	0.18 ± 0.01

[a] The k values are for the six crystals (denoted by A, B,C,D,E and F) shown in Figure 11.

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