

Phase Transitions of Canola Oil Sediment

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Canola sediment was obtained from an industrial filter cake by solvent extraction. When heated in the differential scanning calorimeter (DSC) (5–100°C), the sediment exhibited a single narrow melting peak at around 74.8°C. No solid-state polymorphic transformation of the material could be detected over this temperature range. The X-ray powder diffraction pattern of canola sediment resembled waxes from other sources with an orthorhombic unit cell. The phase transition behavior of canola sediment in oil was studied by both DSC and polarizing microscopy. With increasing ratio of oil/sediment, a reduction in both melting temperature and transition enthalpy was observed. The shape of the supercooling curve resembled that of the melting curve. The induction time was determined by spectrophotometry and was used to calculate the interfacial free energy σ between sediment and oil; $\sigma = 4.71 \text{ erg/cm}^2$. The effect of temperature and sediment concentration on the clouding time of canola oil was studied; the clouding time was the shortest at 5°C.

KEY WORDS: Canola oil, clouding, crystal structure, crystallization, melting, sediment.

Canola oil is the major edible vegetable oil in Canada, accounting for about 60% of deodorized vegetable oil production in the country (1). An increase in the popularity of canola oil can be attributed to its superior nutritional and functional properties. Canola oil has a low content of saturated fatty acids and can be used as salad oil without winterization (2,3). However, in recent years oil processors have reported that canola oil sometimes develops cloudiness on storage, even though it may have passed the cold test (4). The exact reason for this problem is unknown but, by analogy with sunflower oil, sedimentation of waxes in canola oil has been suggested as the major cause. A recent report on the canola sediment indicated that the clouding material consisted mainly of wax esters plus some high-melting saturated triglycerides (4).

Sedimentation of waxes in oil has been extensively investigated in other edible oils, such as sunflower oil, where waxes traditionally cause clouding (5–7). Similar studies, however, have not been made on canola oil. Moreover, little is known about the phase transition behavior of minor oil constituents such as waxes, although great progress has been made on triglycerides where several polymorphic crystal forms have been identified by differential scanning calorimetry (DSC) and X-ray diffraction techniques (8). This information is important because polymorphic crystals have different stabilities and solubilities in oil (8). Studies on other waxes, such as carnauba wax, beeswax and paraffin wax, have suggested that all these waxes have a similar supermolecular structure as revealed by DSC and X-ray diffraction (9–12). However, little is known about the crystalline structure of oilseed waxes.

The phase transition of a crystalline solute is strongly influenced by the presence of solvent. Many studies have been made on the effects of a solvent as a diluent on depressing the melting point of a crystalline solute (13). However, there are relatively few reports on the phase transitions of solid lipids in a liquid oil medium, despite their great importance to a number of industrial processes. In this context, sedimentation in oil can be viewed as a crystallization process, and as such it proceeds *via* nucleation and crystal growth. If the oil is going to develop a sediment, it must become supersaturated to the crystallizing solute. Supersaturation is required for nucleation due to the surface free energy associated with the new phase formation (14). However, for kinetic reasons, supersaturated oil may remain remarkably stable for a period of time. This period will depend on several factors, including supersaturation, temperature and the surface free energy required for creating the new phase (14). Despite the obvious implications, there have been no studies on the surface free energy of sediment in oil. This may be due to the heterogeneous nature of these minor oil constituents.

The importance of studying sedimentation in canola oil is to provide direct information on the stability of the oil and to be able to predict or control the appearance of cloudiness under different conditions, such as wax concentration and temperature. Stability tests conducted on sunflower oil have yielded contradictory results (6,7). Furthermore, canola oil has a different triglyceride composition (1). Therefore, an independent study of this problem is required.

In this report, the phase transition behavior of canola sediment-oil mixtures is considered with sediment isolated from an industrial filter cake collected after winterization. The melting behavior of sediment in pure state and in the presence of oil was studied by DSC and polarizing microscopy. The interfacial interactions between sediment and oil were studied by spectrophotometry. The effect of various conditions, such as sediment concentration and temperature, on the development of the sediment was investigated by polarizing microscopy, while the crystal structure of the sediment was studied by X-ray powder diffraction and DSC.

MATERIALS AND METHODS

Preparation of samples. Canola sediment was obtained by extracting an industrial filter cake, collected after filtration of the winterized oil, with hot chloroform. The excess solvent was removed by vacuum distillation in a rotary evaporator operated at 40°C. The concentrated solution was stored in a refrigerator (0°C) for 24 h to precipitate the solute. The precipitate was then separated from the solution by centrifugation (16300 × *g*) at 5°C. The residual oil in the material was removed by washing twice with cold petroleum ether (2°C). The purified dry material was white and sticky in appearance, and was referred to as canola sediment. The composition of the sediment was determined by gas chromatography by means of the

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experimental procedure, to be described elsewhere (Przybylski, R., unpublished data).

Refined, deodorized and bleached canola oil was obtained from a western Canadian oil processor. Oil was stored at 0°C for one week, and any suspended solid material was removed by filtration through filter paper Whatman No. 541 (Maidstone, England) with diatomaceous earth as a filtering aid. The filtered oil was subsequently considered as sediment-free and used throughout the studies. Solutions were prepared by dissolving a known amount of sediment in oil on weight to weight basis (w/w). Samples with sediment concentration less than 1000 ppm were prepared by diluting a standard 2000 ppm solution with the sediment-free oil.

DSC measurements. The melting behavior of canola sediment was studied by a thermal analyzer (Dupont 9900, Wilmington, DE) equipped with a DSC cell (Dupont 910). Sediment (~3 mg) was weighed into Dupont DSC pans and hermetically sealed. To investigate the melting behavior of sediment in oil, DSC samples were also prepared by adding a specified amount of canola oil into the pans by a microsyringe before the pans were sealed. DSC thermal scans were obtained by heating the samples from 5 to 100°C at 10°C min⁻¹ with an empty pan as an inert reference. The DSC instrument was calibrated with indium while other experimental conditions were essentially the same as described by Biliaderis *et al.* (15). The DSC traces were reported on a constant sediment weight basis; all DSC experiments were conducted in triplicate.

Microscopy. A Zeiss microscope (Zeiss, IIRS, Oberkochen, Germany) equipped with a temperature-controlled hot stage was used for the determination of the melting and crystallization temperatures of sediment-oil mixtures. A drop of a hot sediment-oil solution was transferred to a precleaned glass slide and covered with a slide slip. The slide was placed on the hot plate, whose temperature was controlled by a refrigerated water bath (Haake G, Karlsruhe, Germany). Precise determination of temperatures was made with a thermocouple. Initially, the samples were maintained at 70°C for about 10 min to melt any crystals formed during sample preparation. The samples were then cooled to room temperature at a constant rate, 0.8°C/min, or until sediment crystals appeared as viewed by the polarizing microscope. The samples were held at the lower end temperatures for about 30 min and then heated up until all crystals melted. The crystallization temperature was taken when crystals were first observed, whereas melting temperature was taken when the final crystals disappeared. These experiments were performed in triplicate.

Spectrophotometry. A kinetic study of the crystallization of sediment in canola oil was carried out in a diode array spectrophotometer (8451a, Hewlett-Packard, Palo Alto, CA). The crystallization of sediment was followed isothermally by measuring the transmittance of oil at 600 nm for various time intervals. Sediment-oil solutions were heated at 80°C for about 30 min to melt all crystals before being transferred into a quartz cuvette (12.5 × 12.5 × 45 mm). The temperature of the solution was maintained constant in the spectrophotometer by circulating water through the water jacket of the cuvette holder. Experimental temperatures were chosen so they were higher than the crystallization temperatures and lower than the melting temperatures as measured by the polarizing microscope. At these temperatures, the oil would initially

appear clear, but it would eventually develop turbidity because its temperature was lower than the solubility temperature. The period for the turbidity development is referred to as the latent period or induction time. The induction time was determined graphically from the transmittance-time curve. These experiments were performed in duplicate.

X-ray powder diffraction. An X-ray diffractometer (Philips, PW1710, Cincinnati, OH) equipped with a scintillation counter was used to obtain the diffraction pattern of canola sediment. Diffraction patterns were taken with Cu K α radiation, and the diffractometer was operated at 40 kV and 40 mA. All X-ray diffraction measurements were performed at room temperature (25°C).

Effect of crystallization temperature on the crystal structure. Portions of 500 mL of the 300-ppm sediment solution were prepared by melting the appropriate amount of sediment in canola oil. The solutions were then cooled and stored at the designated temperatures (5 or 32°C) for 4 d. The morphology of the sediment crystals was examined with the polarizing microscope. The sediments were then isolated from the oil at the respective storage temperature as described above. The X-ray diffraction patterns and DSC thermograms of the sediments were obtained as described previously.

Clouding time in canola oil. Oils (120 mL) containing 25–300 ppm sediment were used to fill glass test tubes (16 × 125 mm), and for each sediment level studied two samples were prepared. The solutions were heated at 80°C for 30 min to destroy any crystal history in the oil before being stored at the designated temperatures (0, 5, 10, 25 and 32°C). The clouding time was determined by examining the oil daily by visual inspection as in the cold test (16).

RESULTS AND DISCUSSION

Composition of canola sediment. The canola sediment obtained consisted mainly of saturated long-chain fatty acids and long-chain fatty alcohols (Table 1). The composition of canola sediment resembled sunflower oil waxes

TABLE 1

Composition of Canola Oil Sediment Isolated from an Industrial Filter Cake

Fatty acid (%)		Fatty alcohol (%)	
16:0	3.0	16:0	0.5
18:0	1.8	17:0	0.3
20:0	35.4	18:0	0.4
21:0	0.8	19:0	3.9
22:0	20.4	20:0	0.4
23:0	0.7	21:0	6.7
24:0	8.0	22:0	1.4
25:0	0.6	23:0	4.9
26:0	7.1	24:0	14.3
27:0	0.5	25:0	5.0
28:0	8.9	26:0	23.6
29:0	0.4	27:0	5.7
30:0	3.2	28:0	12.2
31:0	0.1	29:0	1.7
32:0	0.4	30:0	6.7
		31:0	0.2
		32:0	6.2

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with major fatty acids C20:0 and C22:0 and major fatty alcohols C24:0, C26:0 and C28:0 (5,17). However, some differences exist in the relative composition of the alcohols between canola sediment and sunflower waxes. In sunflower waxes, C24:0 is the most abundant alcohol whereas canola sediment contains higher amounts of C26:0.

Phase transitions of canola sediment. Canola sediment exhibited a single narrow melting endotherm at around 74.8°C when heated in the DSC (Fig. 1a). Cooling the sample to 0°C and reheating yielded essentially the same DSC trace. The melting temperature of canola sediment was similar to that of sunflower waxes (5) but higher than the melting temperatures of synthetic wax esters with less than 20 carbons in both the acid and alcohol components (18). A single narrow DSC peak indicates that there are relatively few wax esters in the sediment, and all components in the mixture have similar melting properties and crystal forms. Further DSC experiments designated to explore the metastability and solid-state structure of the sediment were carried out. In one experiment, a molten sample (100°C) was quench-cooled to 0°C with liquid nitrogen. The sample was then heated to 100°C at the rate of 10°C min⁻¹. In another experiment, canola sediment was heated to the onset temperature (68°C), or a few degrees below, of the melting endotherm. The samples were held at this temperature for 20 min, cooled

to 0°C and re-heated to 100°C at 10°C min⁻¹. In both cases, identical DSC thermal curves to that shown in Figure 1a were obtained. If the material were metastable, this would not be expected because metastable crystals are very sensitive to the cooling rate and amenable by annealing at around the melting point (8). This finding demonstrates that, in contrast to other lipid species that are often found in several polymorphic forms (8), canola oil sediment is stable and does not undergo solid-state polymorphic transformation.

In the presence of canola oil, the DSC thermal curves of sediment were modified as shown in Figure 1b, c and d. With increasing oil content, the melting peaks of the sediment became broader and less symmetrical and moved to lower temperatures (Fig. 1) while the peak areas were reduced (Fig. 2). A similar melting behavior was reported for solid fats in liquid triglycerides (19,20). A broadened peak would be expected if there is a solubility effect. With increased amount of solvent, the fraction of the solid that dissolves in the liquid phase at any given temperature also increases. More material will therefore melt at a lower temperature, resulting in a broader peak. With heterogeneous materials, such as oil sediment, this effect may be enhanced because different sediment components are likely to have differing solubilities in the oil. The sediment components that have higher solubilities will dissolve at lower temperatures, while those that are less soluble melt at higher temperatures. The reduction of the DSC melting endotherm with increasing oil content may be due to two effects. Firstly, the heat of melting may vary with the melting temperature, which is changed due to the presence of solvent. Secondly, the effect of solvation of the solute will reduce the DSC output of heat for dissolution because solute solvation is exothermic, and it increases with increasing amounts of solvent present (13).

According to the solubility equation for an ideal solution, the reciprocal of melting temperature of a solid is proportional to the logarithm of the molar fraction of the solid (13):

$$\left(\frac{1}{T} - \frac{1}{T_0} \right) = - \frac{R}{\Delta H} \ln x_2 \quad [1]$$

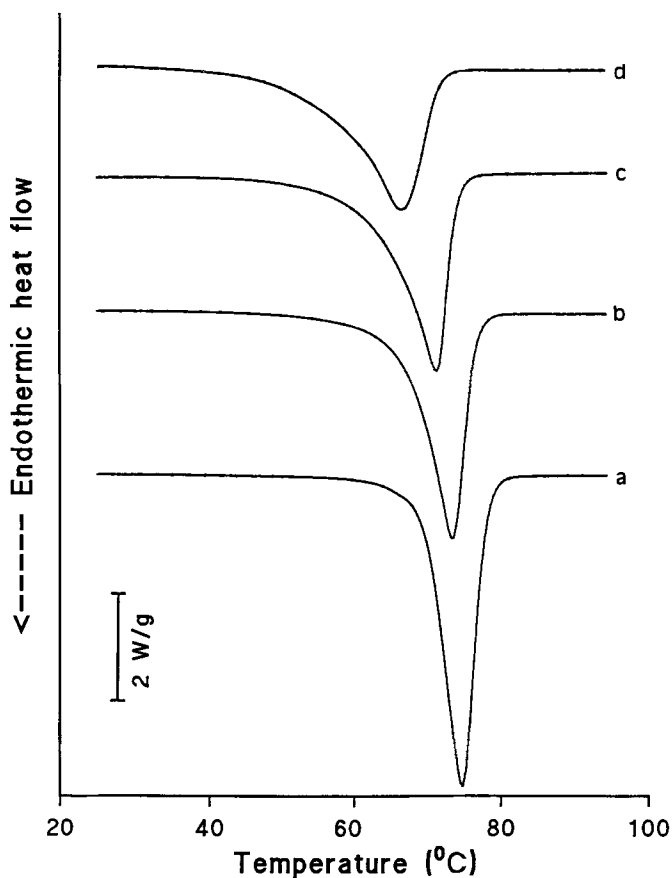


FIG. 1. Differential scanning calorimetry (DSC) thermograms of canola sediment in pure state (a) and in the presence of oil at sediment weight fraction of 80.3% (b), 50.2% (c) and 19.6% (d). Sediment weight fraction (w/w) is based on total weight. DSC heating rate 10°C min⁻¹.

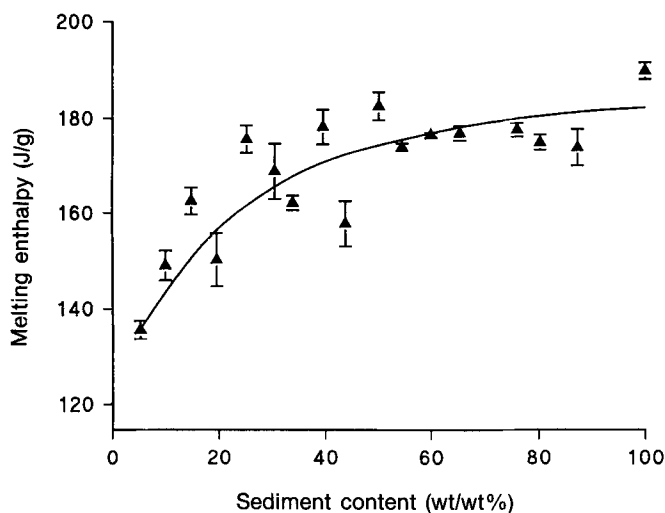


FIG. 2. Differential scanning calorimetry melting enthalpy of canola sediment vs. sediment content in oil.

where T and T_0 are the melting temperatures of the solid in solvent and in pure state, respectively; x_2 is the molar fraction of the solid; ΔH is the heat of fusion of the solid; and R is the universal gas constant. Figure 3 shows such a diagram for canola sediment in oil [an average molecular weight of 700 for sediment was assumed based on a wax ester molecule with average carbon numbers in both fatty acid ($C_{\text{avg}} = 21$) and fatty alcohol ($C_{\text{avg}} = 26$); an average molecular weight of 880 for oil was assumed based on a molecule of triglyceride (fatty acid $C_{\text{avg}} = 18$)]. The melting temperatures of the sediment were taken as the conclusion temperature of their DSC melting peaks. This temperature is considered to represent the melting temperatures of the most stable components in the mixture of sediment. Figure 3 shows that a linear relationship exists between these two parameters, although a deviation of the experimental data from the linear line becomes evident at x_2 larger than 0.7. This is not unexpected because the more concentrated the solution is, the less ideal the system. However, the heat of fusion ($307 \pm 9 \text{ J/g}$) determined from the slope according to Equation 1 is much higher than the DSC experimental value ($185 \pm 1 \text{ J/g}$) determined for pure sediment. Timms (21) also found the melting enthalpies for milk fats, calculated from the linear part of the solubility curves of the fats in oils by means of the ideal solution equation, were almost twice the values as measured by DSC. Nevertheless, Hannewijk *et al.* (22) found the melting enthalpies, calculated by Equation 1, to be similar to the experimental values for pure tri- and disaturated triglycerides in pure unsaturated triglycerides. If the solid phase is heterogeneous, a higher enthalpy derived from Equation 1 may be expected because the melting temperature was taken as the melting temperature of the high-melting components in the mixture, which may need more energy to melt. Norton *et al.* (19) attempted to compare the experimental DSC melting curve of tripalmitin in triolein with that predicted by assuming the ideal solution equation. They found that the heat flow determined by the DSC was lower than the

calculated value and attributed the discrepancy to demixing. If the enthalpy of melting decreases with increasing solvent, as observed in the present study, an overestimation of the heat flow by the ideal equation would be expected because the calculated heat flow is proportional to the enthalpy (19). This may become more pronounced when the melting endotherm is moved to lower temperatures, where a significant reduction in enthalpy values occurs. Timms (21) has also attributed deviation from Equation 1 to differences in the molecular volumes between solute and solvent.

Melting and crystallization temperatures of sediment in dilute systems. When the sediment content in oil is less than 1000 ppm, as is the case in commercial oil, the DSC is not effective in detecting phase transitions of trace sediment in the oil. A polarizing microscope with a hot stage was therefore employed. Sediment crystals larger than $\sim 2 \mu\text{m}$ could be detected as they appear bright under polarized light. Figure 4 shows the microscopic measurements of melting and crystallization temperatures as a function of sediment concentration. The crystallization temperature is always lower than the melting temperature because of supercooling (14). Nevertheless, the crystallization curve resembles the melting curve in shape. The magnitude of supercooling is about $6\text{--}8^\circ\text{C}$ when the sediment concentration is larger than 0.1%; it increases up to 18°C when sediment concentration is less than 0.1%. An increase in supercooling at low sediment concentrations occurs because there is less amount of solute in the oil. The presence of large amounts of dissolved matter facilitates the formation of nuclei, other conditions being equal (14). The canola sediment/oil phase transition curves are similar to those for sunflower wax-oil mixtures as reported by Rivarola *et al.* (5).

The melting curve (or solubility curve) and supercooling curve (or supersolubility curve) can be used to define the boundaries of the binary system corresponding to three different states. When the temperature of a sediment/oil solution is above the melting curve, the oil is not

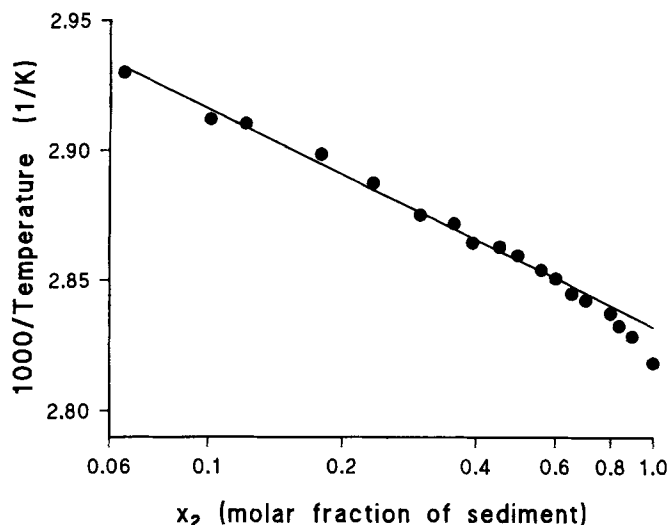


FIG. 3. Differential scanning calorimetry melting temperature of canola sediment as a function of molar fraction of sediment in oil according to Equation 1.

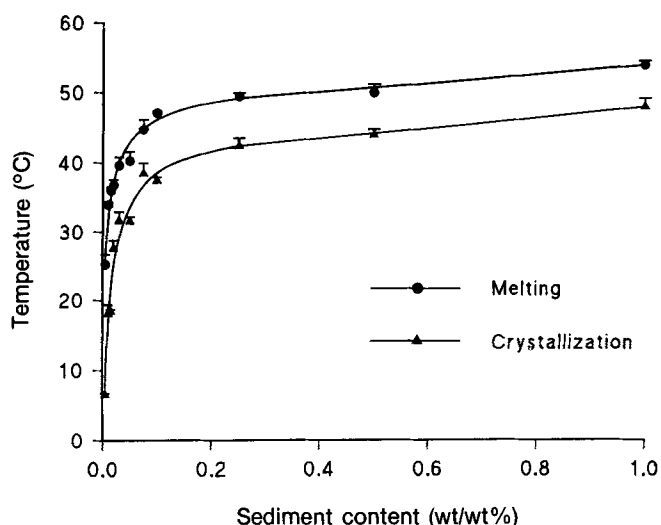


FIG. 4. Melting and crystallization temperatures of canola sediment in oil, measured by polarizing microscopy, vs. sediment content.

saturated and will not undergo phase transition (stable solution). Below the crystallization temperature, crystallization of sediment occurs instantaneously, and the oil is unstable. The oil at temperatures between the melting and crystallization temperatures is metastable. Such a solution can be stored without inducing crystallization of sediment for a period of time. The induction time for crystallization varies from a few minutes to many days, depending on factors such as supersaturation and temperature (14). It is clear that an understanding of the kinetics of a metastable solution is of practical importance because oils that develop turbidity during storage are in a metastable state. The existence of the metastable solution is generally attributed to the excess surface free energy at the boundary separating solid and liquid phases (14).

Sediment-oil interfacial free energy and crystallization kinetics. The surface free energy can be calculated from the induction time, which in the present study was determined by spectrophotometry. A typical data set is shown in Figure 5, which gives the transmittance of an oil solution as a function of time at a constant temperature. The transmittance of the oil remains constant up to a certain period, after which it decreases rapidly and finally levels off. The first period of constant transmittance is known as the induction period during which nucleation mainly occurs (14). Following nucleation, rapid growth of the crystals occurs, resulting in a rapid decrease in transmittance. The final change in transmittance is mainly due to the recrystallization process (14). If the induction period is essentially devoted to nucleus formation, then the induction time (τ) is inversely related to the rate of nucleation (J) by the following equation (14):

$$\ln \tau = \text{constant} - \frac{\ln J}{4} \quad [2]$$

The rate of nucleation can be expressed by the classical nucleation equation (23):

$$J = A \exp\left(-\frac{\Delta G^*}{kT}\right) \quad [3]$$

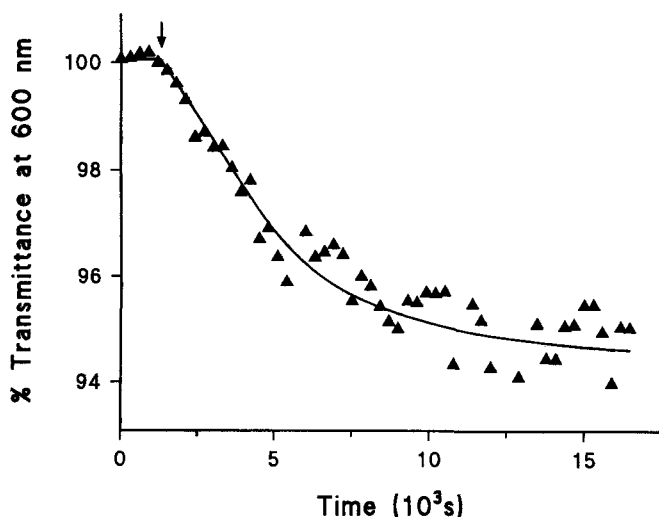


FIG. 5. Transmittance-time curve of oil (200 ppm sediment, 26°C) measured by spectrophotometry showing the development of turbidity after an induction time (indicated by the arrow).

where the pre-exponential coefficient A is a constant and ΔG^* , the activation energy for nucleation. The activation energy ΔG^* can be calculated by the following equation (23):

$$\Delta G^* = \frac{16\pi\sigma^3 v^2}{3k^2 T^2 (\ln S)^2} \quad [4]$$

where σ is the surface free energy between solid and liquid phases (erg/cm²); v , the molecular volume of the solid (cm³/molecule); k , the Boltzmann constant (1.38×10^{-16} erg/K); T , the temperature (K); and S , the supersaturation of the solution. Substituting Equations 3 and 4 into Equation 2, we obtain:

$$\ln \tau = \text{constant}^* + \frac{4\pi v^2}{3k^3} \cdot \frac{\sigma^3}{T^3 (\ln S)^2} \quad [5]$$

Equation 5 can be used to calculate the surface free energy σ because all the parameters in the equation are either constants or can be measured. Figure 6 shows the experimental induction time according to Equation 5. From the slope of the regression line, the σ value was estimated to be 4.71 ± 0.18 erg/cm² for canola sediment in oil. This value is comparable with literature values of 7–10 erg/cm² for long-chain hydrocarbons in their own melts (24). Phipps (25) obtained a surface free energy of 8.3 erg/cm² for α -tripalmitin (PPP)/melt, while Ng (26) found a value of 9.45 erg/cm² for β -PPP/melt. Surface free energies in solution are usually lower than the corresponding values in melts by about 30% (24). In triolein, the surface free energy of β -PPP decreases to 8.95 erg/cm² (26). The value of the interfacial free energy for canola sediment is lower than that for β -PPP in triolein. This can be understood because sediment is less soluble in oil than PPP, which indicates that there is less interfacial interactions between sediment and oil.

Figure 5 also shows that the transmittance of the oil rapidly decreases after the induction time. This region reflects crystallization, corresponding mainly to crystal growth. The nearly linear decrease in the transmittance

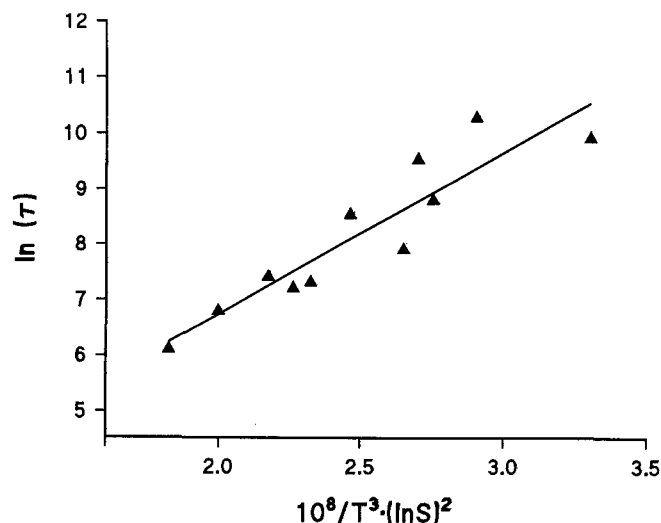


FIG. 6. Induction time for crystallization of canola sediment in oil plotted according to Equation 5.

in this region indicates that the rate of crystal growth or clouding is almost constant. During crystallization, a decrease in supersaturation is accompanied by an increase in crystal growth surface area. These parameters have opposite effects on crystal growth and apparently cancelled each other in oil. Figure 7 shows the slope as a function of the crystallization temperature and sediment content. As can be seen, for a given sediment content, the rate of crystal growth increases rapidly with decreasing temperature, mainly due to increasing supersaturation. However, decreasing temperature also causes increase in viscosity

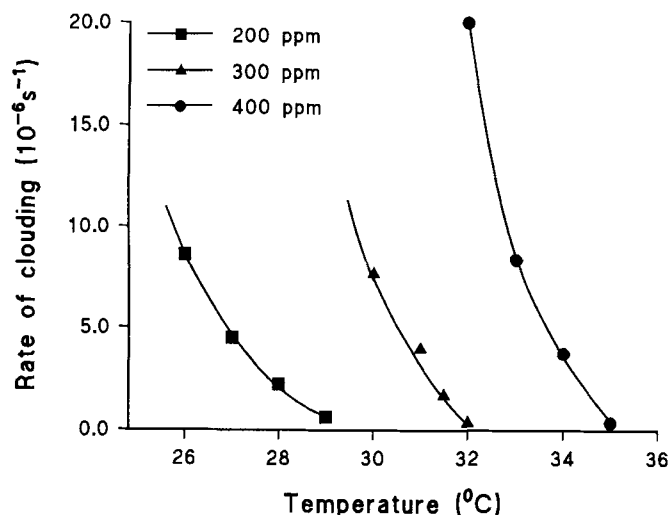


FIG. 7. Clouding rate of canola oil at different temperatures and various sediment contents. The clouding rate was taken approximately as the slope of the linear region of the transmittance-time curve.

of the solution and, therefore, the growth of crystals will eventually decrease when the viscosity effect becomes large (23). A slightly faster increase in clouding rate with decreasing temperature at high sediment contents can be attributed to the larger specific growth surface area (14).

Crystal structure of canola oil sediment. The X-ray diffraction pattern of canola sediment is shown in Figure 8. The X-ray diffraction pattern has the same main features as other waxes of different origin, such as paraffin waxes, beeswax, carnauba wax and montan wax (9-12). Like other waxes, the two strongest peaks occur at short d-spacings of 4.13 and 3.72 Å, while the next two weaker peaks occur at short d-spacings of 2.98 and 2.49 Å. The diffraction peaks in the region of 40-46° 2θ are less resolved and are believed to be due to overlap of peaks from traces of solid fats in the mixture. There are at least two long d-spacings, corresponding to 31.7 and 21.6 Å. Experiments on other waxes have demonstrated that such an X-ray diffraction pattern corresponds to crystals of an orthorhombic unit cell (9-12). It is, therefore, possible that the unit cell of canola sediment crystals is also orthorhombic, with the chains arranged parallel to the c axis. In addition, it seems that all the components of canola sediment are arranged in the same crystal form, although they have different chain lengths. This finding is consistent with the DSC measurement, which shows that the sediment melts like a single substance. According to Lourens and Reynhardt (27), waxes have an amorphous zone, which consists mainly of the chain ends. This may explain why molecules of different chain lengths can form a crystal structure that resembles a single pure substance.

Effect of crystallization temperature on physical properties and structure of sediment. Canola oil containing 300 ppm sediment developed turbidity within one day at both 5 and 32°C. The oil at 5°C developed floc-like

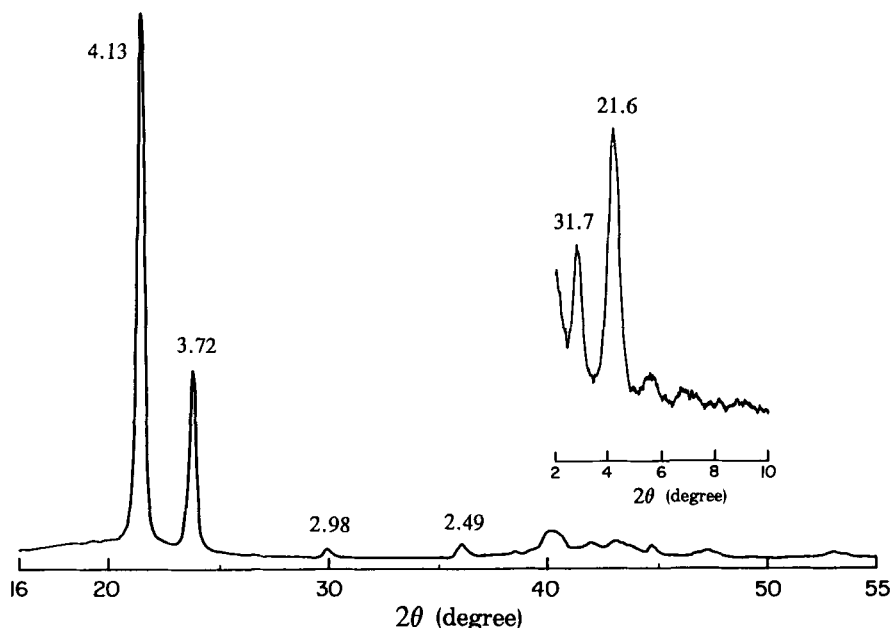


FIG. 8. X-ray diffraction (XRD) pattern of canola oil sediment isolated from an industrial filter cake. The section of the XRD pattern at low angles from 2-10° is shown at top. The major short d-spacings and long d-spacings of the XRD for the sediment are also labelled on the diagram.

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cloudiness whereas the oil at 32°C developed large and separate flakes. It appears that sediment crystals favor the growth direction along their longest axes, resulting in elongated crystals. Crystals grown at the low temperature were small in size, whereas large and often aggregated crystals were observed at the high crystallization temperature. Also, the sediment developed at 5°C was a gum-like material and difficult to filter, compared to that obtained at 32°C, which was powder-like and easy to filter. Figures 9 and 10 show that both materials exhibited the same main structure features under X-rays, with the two strongest peaks at the same short d-spacings. However, at least one peak may be missing in long d-spacings in the sediment isolated at 32°C. When compared with the X-ray diffraction pattern of original material (Fig. 8), an

extra peak was found at a d-spacing of 3.51 Å for both oil sediments. This may be due to a contaminating component from the canola oil. Because the canola oil had been cold-treated, it is likely that this component was stable in oil even at low temperature. However, sediment crystals may act as nucleation sites for the crystallization of this material. The DSC traces of the two sediments are also shown in Figure 11. The endotherm peak for the 32°C sediment occurred at higher temperature than that for the 5°C sediment. The peak temperature of the latter is about the same with that of the original material. However, the melting enthalpy of the 32°C sediment (190 ± 3 J/g) was higher than its 5°C counterpart (155 ± 2 J/g). This may imply that higher-melting components with higher melting enthalpies were segregated in the crystals of the 32°C sediment.

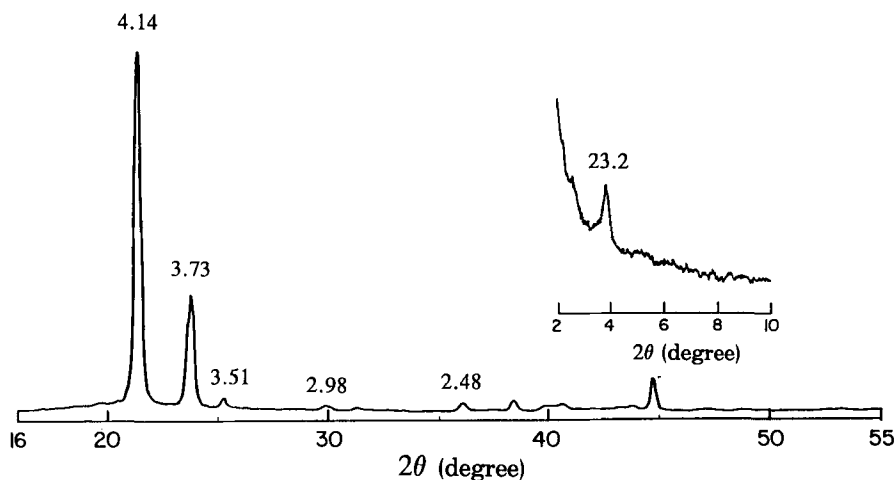


FIG. 9. X-ray diffraction (XRD) pattern of canola oil sediment developed at 32°C. The section of the XRD pattern at low angles from 2–10° is shown at top. The major short d-spacings and long d-spacings of the XRD for the material are labelled on the diagram.

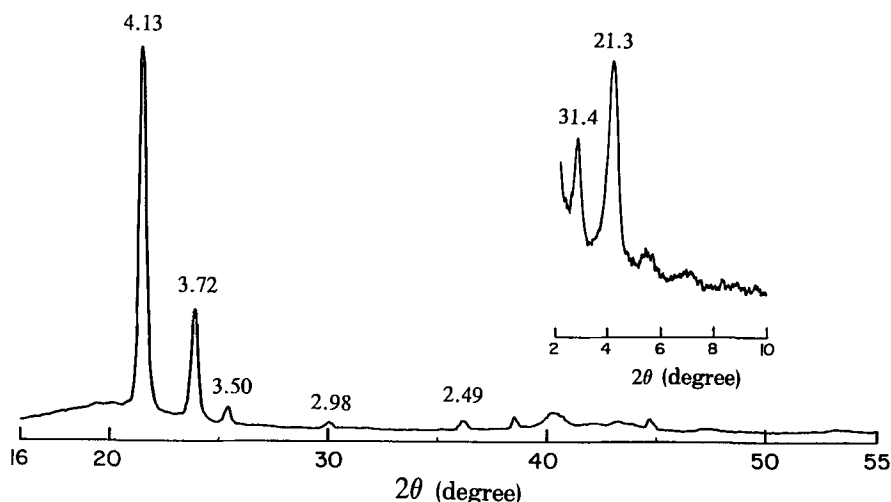


FIG. 10. X-ray diffraction (XRD) pattern of canola oil sediment developed at 5°C. The section of the XRD pattern at low angles from 2–10° is shown at top. The major short d-spacings and long d-spacings of the XRD for the material are labelled on the diagram.

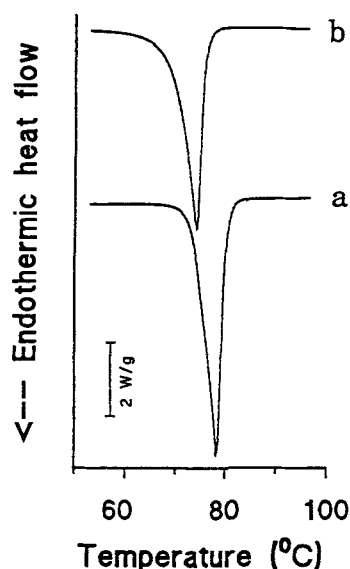


FIG. 11. Differential scanning calorimetry thermograms of canola oil sediments developed at 32°C (a) and 5°C (b).

Clouding time of canola oil. Table 2 summarizes the storage test on canola oil containing various amounts of sediment at different temperatures. When the sediment concentration was higher than 200 ppm, the oil became cloudy in less than one day at any temperature studied with exception of 200 ppm sediment at 32°C. In the concentration range of 75–150 ppm, oil appeared cloudy in about one day at 5, 10 and 25°C, whereas at 0°C it remained clear up to 3 d. In any case, more than 24 h was required for the oil to develop turbidity when the sediment concentration was less than 50 ppm. A previous investigation on cloudiness of sunflower oil has reported that oil stored at 5°C is more stable (6). In contrast to this finding, our data indicate that 5°C may probably be the optimum temperature for turbidity sediment development. The studies on sunflower oil by Turkulov *et al.* (7) revealed that 13°C was the optimum clouding temperature for the oil. In the present study, for sediment concentration <50 ppm, the clouding time at 5°C was 2–3 d while a much longer time was required at 0°, 10° and 25°C. These data can be rationalized on the basis of the temperature dependence of nucleation and crystal growth rates; the former is favored at low temperatures while the latter is facilitated at high temperatures. It appears, therefore, that

the optimum temperature for sediment development in terms of nucleation and crystal growth is 5°C.

Table 2 also shows that the threshold of the 24-h cold test (0°C) for canola oil is about 200 ppm, which is higher than both 80 ppm and 150 ppm of waxes reported for sunflower oil (6,7). However, canola oil is less tolerant to sediment at other temperatures. At sediment content over 50 ppm, the oil became turbid within 2 d even at 25°C. Sunflower oil can remain stable at 25°C for more than 1 wk, even with 100 ppm waxes (6). Canola oil containing less than 25 ppm sediment remained clear at room temperature for more than one month. These results suggest that canola oil should be treated at about 5°C if cloudiness turns out to be a problem, and winterization is required to remove the majority of sediment.

ACKNOWLEDGMENT

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for the financial support.

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[Received October 27, 1992; accepted February 5, 1993]

TABLE 2

Effect of Sediment Concentration on the Clouding Time (days) of Canola Oil Stored at Different Temperatures

T (°C)	Sediment levels (ppm)							
	25	50	75	100	150	200	250	300
0	6	4	3	3	2	1	<1	<1
5	3	2	1	1	1	<1	<1	<1
10	5	2	1	1	1	<1	<1	<1
25	>30	2	1	1	1	<1	<1	<1
32	^a	/	/	>30	23	23	<1	<1

^aClouding time was not determined.