Influence of Solvent Content on Phase-Transition Temperatures of Oil Sediment and Solution Viscosity in Acetone/Canola Oil Systems

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ABSTRACT: The effect of acetone on phase transition behavior of sediment in canola oil was studied by differential scanning calorimetry under dynamic heating/cooling regimes. The melting temperature of sediment decreased with an increase in the solvent content of canola oil, suggesting an increase in the solubility of sediment in the oil solution. The crystallization of sediment in oil solution was facilitated by acetone, as indicated by the increase in the sediment crystallization temperature. Acetone dramatically reduced the viscosity of canola oil, particularly in the first 30% addition. The reduction of viscosity was far less with further addition of acetone. These results suggested that the optimum range of acetone content needed for sediment precipitation in canola oil would be in the range of 30–40%. A linear relationship was found between the density of canola oil and temperature. The influence of solvent on the density of canola oil/acetone solution can be accounted for by the mixing theory of ideal solutions, whereas the effect of temperature on the dynamic viscosity of oil solution is best described by a modified Arrhenius equation.

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KEY WORDS: Acetone/oil solution, canola oil sediment, crystallization, density, melting, modelling, temperature effect, viscosity.

Canola oil may contain a minor amount of high-melting lipid constituents which, upon precipitation, impart a hazy appearance to the oil (1,2). This also happens with other oils, such as sunflower oil (3–6). The composition of canola oil sediment has been dealt with in recent publications (7–10). These studies have shown that the major component of canola sediment is wax esters of long-chain fatty acids and alcohols.

The haze components must be removed from the oil through winterization prior to packaging for a quality oil product. However, proper control of processing requires information on the composition of sediment as well as its content in oil. In this context, a rapid estimation of the sediment content in oil is critical. Methods developed so far for measurement of sediment content in oil include gravimetric analysis, gas–liquid chromatography, and solvent crystallization (3–6). Of these techniques, solvent precipitation of oil sediment, combined with turbidimetric or differential scanning calorimetric (DSC) measurement, offers some advantages because it is quick and simple. This technique entails the addition of a solvent and low-temperature treatment of the oil solution to bring about crystallization, and measurement of the haze concentration by a turbidimeter or DSC. Previous studies on solvent effects on sedimentation in vegetable oils showed that the addition of an organic solvent, such as hexane or acetone, influenced the physical properties of the oil solution, including the sediment phase-transition temperatures and solution viscosity (7). With acetone, the melting temperature of sediment decreased, whereas the crystallization temperature of sediment decreased or increased, depending on the sediment content in the oil solution. The increase in crystallization temperature of sediment in the presence of a solvent is presumably due to the decrease in oil viscosity. This investigation further studied the influence of acetone/oil ratios on the phase-transition behavior of canola sediment, as well as the viscosity of canola oil/acetone solutions. This should provide information for selecting the solvent concentrations needed for sediment measurement in oil with this technique.

MATERIALS AND METHODS

Refined, bleached, and deodorized canola oil and filter cakes collected after winterization of canola oil were obtained from Western Canadian canola oil processors. Canola oil was stored at 0°C for a week and thereafter filtered with a filter aid of diatomaceous earth (Sigma, St. Louis, MO) to remove any solids. The filtered canola oil was used throughout the study.

Canola sediment was obtained as described previously (8). Briefly, the filter cake from winterization was extracted with hot chloroform, and the extract was concentrated by vacuum evaporation in a rotary evaporator at 40°C. The concentrated solution was stored at 0°C for a week, and the precipitate was separated by centrifugation (16,300 × *g*). The sediment obtained was washed twice with cold petroleum ether (2°C) to remove any residual oil from the material (9).

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Solvent/oil solutions were prepared by mixing appropriate amounts of analytical-grade acetone (Sigma) with canola oil at levels ranging from 10 to 50% solvent (w/w).

Glass capillary viscometers of the Ubbeohde type (International Research Glassware Ltd., Kenilworth, NJ) were employed to measure the kinematic viscosity of oil solutions (11). Isothermal conditions were achieved by a circulating water bath (Haake G, Karlsruhe, Germany). The densities of oil solutions were determined by the pycnometer procedure (12).

A Dupont thermal analyzer (9900; Dupont, Wilmington, DE), equipped with a Dupont 910 DSC cell, was used for studying the melting and crystallization behavior of canola sediment. DSC samples were prepared by weighing canola sediment into DSC pans, adding a desired amount of acetone/oil solution, and hermetically sealing the pans. The samples were heated in the DSC to 85°C to obtain the melting curves. The same samples were then kept at 85°C isothermally for about 1 min, and cooled to 5°C to obtain the crystallization curves. The DSC heating/cooling rate was 10°C/min. The phase-transition temperatures were taken as the DSC peak temperatures. An empty DSC pan was used as an inert reference. Detailed experimental and DSC calibration procedures were as described previously (8).

RESULTS AND DISCUSSION

Earlier studies reported the effects of solvents (acetone and hexane) on phase transition behavior of sediment in canola oil when the solvent content in the oil was 50% (7). Higher sediment crystallization temperatures were observed in acetone/oil systems at low sediment content (<30%), which suggested that the presence of the solvent greatly facilitated the crystallization process and overrode the solubility effect. The melting temperature of oil sediment in the solvent/canola oil mixture was lower than in oil alone, with hexane exerting the greater effect. This was attributed to the increased solubility of sediment in the presence of a solvent. For an efficient solvent for crystallization, the increase in solubility of sediment due to the introduction of a solvent should be minimal, whereas crystallization of sediment should be facilitated. In this regard, acetone appeared to be a good solvent for precipitation of oil sediment.

Figure 1 shows the typical DSC thermal curves of phase transitions of sediment in a canola oil/acetone solution. An endotherm was observed in heating that corresponded to the melting transition of sediment. Upon cooling, an exotherm concurred with the crystallization of sediment. The effects of acetone/canola oil ratio on the phase-transition temperatures of sediment are shown in Figures 2 and 3. As the acetone content increased from 10 to 50%, the melting temperature of canola sediment decreased (Figs. 2 and 3). The crystallization temperature, however, was less affected by the presence of acetone at high sediment content (Fig. 2), whereas at low sediment content there was an increase in the crystallization temperature of sediment, particularly when acetone content in the oil solution was increased from 10 to 40% (Fig. 3). Moreover, a significant decrease in the melting temperature of sediment occurred at around 30% of solvent. These results suggested that the optimum solvent content in terms of phase transitions of oil sediment was around 30–40% acetone. Interestingly, in sunflower oil, a solvent content of about 50% was reported to be adequate for measuring waxes by the turbidity method (6).

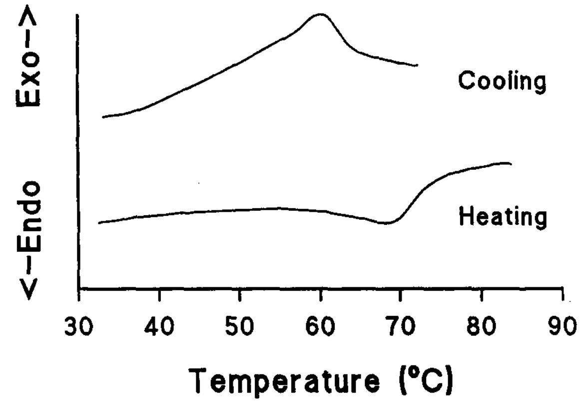

FIG. 1. Differential scanning calorimetric thermal curves of canola oil sediment in an acetone/canola oil (3:7) mixture at 10% sediment content. Endo, endothermic; exo, exothermic.

Figure 4 shows the effect of various amounts of acetone added on the viscosity of canola oil as a function of temperature. The corresponding viscosities of canola oil and acetone are shown in Figure 5. The viscosity of acetone was only a fraction of that of canola oil (a factor of 459 at 0°C), and addition of acetone to canola oil caused a considerable decrease in the viscosity, particularly at low temperatures. Kapseu *et al.* (13) investigated the effect of a number of solvents, including acetone, on the viscosity of cottonseed oil. They found that the ratio of the viscosity of cottonseed oil to that of pure solvents was in the order of 300.

Figure 6 shows that the viscosity of oil solution decreased dramatically (by 55–70%) after addition of only 10% acetone.

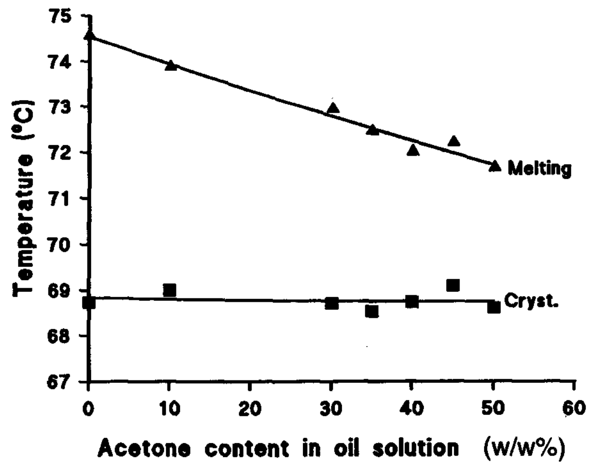

FIG. 2. Phase-transition temperature of canola oil sediment in acetone/canola oil mixtures (40% sediment content) as a function of solvent content. Cryst., crystallization.

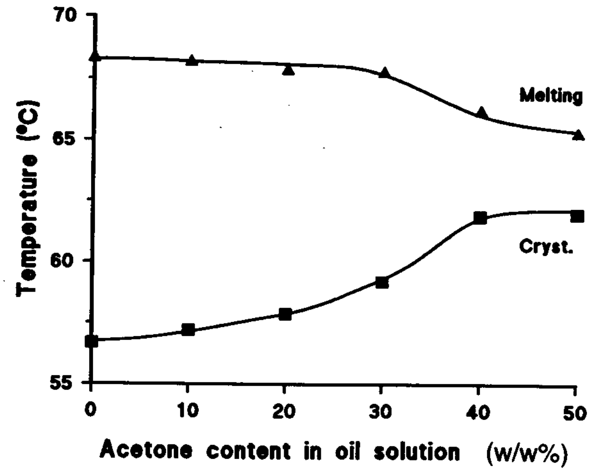

FIG. 3. Phase-transition temperature of canola oil sediment in acetone/canola oil mixtures (10% sediment content) as a function of solvent content. Cryst., crystallization.

With an increase in the solvent content, the viscosity was further reduced, but at lower rates, when the solvent content was greater than 40%. Sedimentation in canola oil is a crystallization process, and the reduction of the oil viscosity will greatly facilitate the crystallization (14). However, addition of solvent may also increase the solubility of sediment (7), negatively influencing the crystallization process. It will also dilute the concentration of cloudiness formed if an excess amount of solvent is used, influencing the sensitivity of turbidity measurement, particularly at low sediment content. In this regard, addition of 30–40% acetone appeared to be optimum to induce maximum reduction in viscosity and less change in solubility.

The dynamic viscosity (μ) of a solution can be obtained by means of the following equation:

$$\mu = \rho v \qquad [1]$$

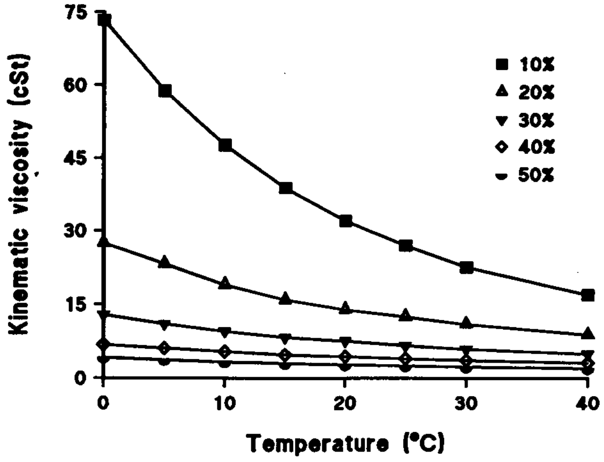

FIG. 4. Viscosity of canola oil/acetone solutions as a function of temperature. The numbers in the figure are the solvent content (%, w/w).

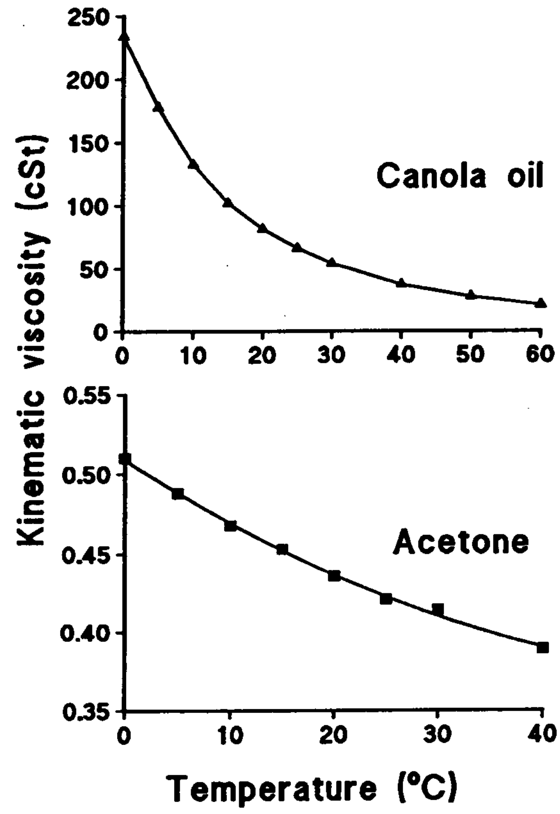

FIG. 5. Influence of temperature on the viscosities of canola oil and acetone.

where v is the kinematic viscosity, and ρ the temperature-dependent density of the solution. Figure 7 shows the density of canola oil as a function of temperature. A linear relationship was found between the density of canola oil (ρ_o) and temperature, T (°C):

$$\rho_o = kT + c \qquad [2]$$

where k and c are -7.096×10^{-4} and 0.9354, respectively. This finding was consistent with that reported by Noureddini

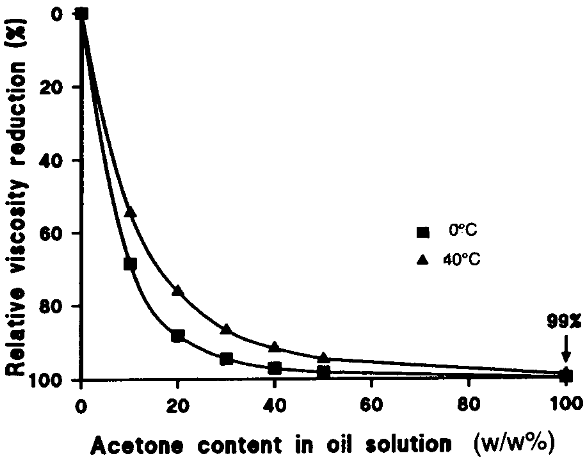

FIG. 6. Viscosity change of canola oil solution with acetone content at 0 and 40°C. The relative viscosity reduction (%) is defined as the viscosity difference between canola oil and the oil solution divided by that of canola oil.

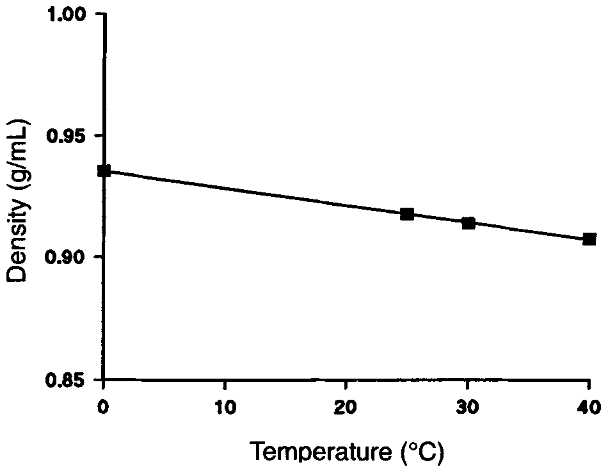

FIG. 7. Influence of temperature on the density of canola oil.

et al. (15), who investigated the temperature effect on density for a number of vegetable oils, including rapeseed oil.

In a mixture of oil/acetone, the reciprocal of density of the mixture (i.e., total volume) is equal to the sum of partial volumes of the component solvents, i.e.:

$$\frac{1}{\rho_{\text{mix}}} = \sum \frac{w}{\rho} = \frac{w_o}{\rho_o} + \frac{w_a}{\rho_a} \qquad [3]$$

where ρ_{mix}, ρ_o, and ρ_a are densities of the mixture, oil, and acetone, and w_o and w_a are weight fraction of oil and acetone, respectively. Substituting w_o by $(1 - w_a)$ and rearranging Equation 3 yielded:

$$\frac{1}{\rho_{\text{mix}}} = \frac{1}{\rho_o} + \frac{\rho_o - \rho_a}{\rho_o \rho_a} w_a \qquad [4]$$

Figure 8 shows the reciprocal of density of the oil solution as a function of acetone content. As predicted by Equation 4, a linear relationship was obtained. In addition, the density of acetone (ρ_a), calculated from the slope of the regression line by using Equation 4, agreed well with the experimental value (0.7905) by calculation, compared to 0.7908 by experiment.

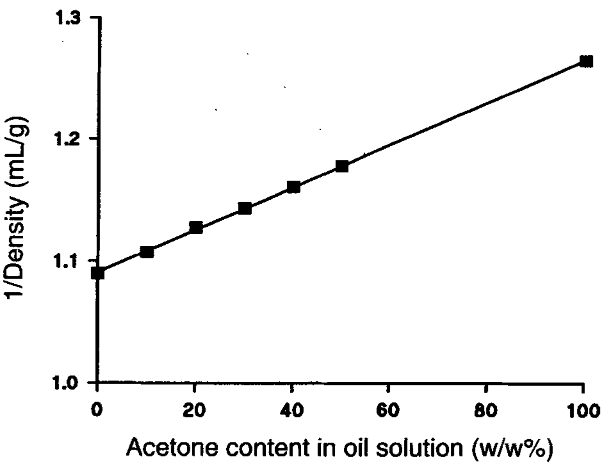

FIG. 8. Relationship between the density of canola oil/acetone solution and its solvent content at 25°C.

Table 1 tabulates the dynamic viscosities of acetone/canola oil solutions by applying Equations 1–4. Modelling of the temperature effect on the dynamic viscosity of oils is important and has been investigated by various workers (11,13,16,17). Equations of various forms have been used in their studies. These consist of two two-parameter (Eqs. 5, 6), and four three-parameter equations (Eqs. 7–10), i.e.:

$$\ln \mu = a + b \ln T \qquad [5]$$

$$\ln \mu = a + \frac{b}{T} \qquad [6]$$

$$\ln \mu = a + \frac{b}{T + c} \qquad [7]$$

$$\ln \mu = a + \frac{b}{T} + \frac{c}{T^2} \qquad [8]$$

$$\ln \mu = a + \frac{b}{T} + cT \qquad [9]$$

$$\ln \mu = a + bT + cT^2 \qquad [10]$$

where a, b, and c are constants, and T is temperature (K). The goodness of the equations to describe the temperature dependence of oil viscosity can be further studied by utilizing the viscosity data for the homologous oil solutions in Table 1. Generally, the four three-parameter equations (i.e., Eqs. 7–10) gave a better fit than the two two-parameter equations (i.e., Eqs. 5, 6), with a mean deviation of about 1% for canola oil by the former, compared to about 5% by the latter. Of the two two-parameter equations, Equation 6 gave a better fit to the data; whereas Equation 7 was the best among the four three-parameter equations. Figure 9 shows both the experimental data (symbols) and the values predicted by Equation 7 (lines) as a function of temperature. The corresponding constants for Equation 7 are tabulated in Table 2.

In a study on viscosity of oils and fatty acids, Noureddini *et al.* (11) found that Equation 9 was the best for correlating their viscosity data with temperature. Other workers (17) used Equation 8 for vegetable oils, including canola. Comparison of these studies revealed that the constants of Equation 8 ob-

TABLE 1
Dynamic Viscosity (cP) of Canola Oil and Acetone/Canola Oil Solutions at Various Contents of Solvent (%, w/w) and Temperature

Tempterature (°C)	Canola	10%	20%	30%	40%	50%
0	218.4	67.5	24.8	11.5	5.98	3.63
5	165.7	53.9	20.9	9.78	5.29	3.18
10	123.2	43.6	17.0	8.43	4.69	2.82
15	94.4	35.4	14.2	7.30	4.10	2.55
20	75.0	29.0	12.4	6.61	3.77	2.28
25	61.0	24.4	11.1	5.77	3.38	2.10
30	49.5	20.3	9.70	5.12	3.11	1.93
40	33.8	15.1	7.75	4.24	2.64	1.66

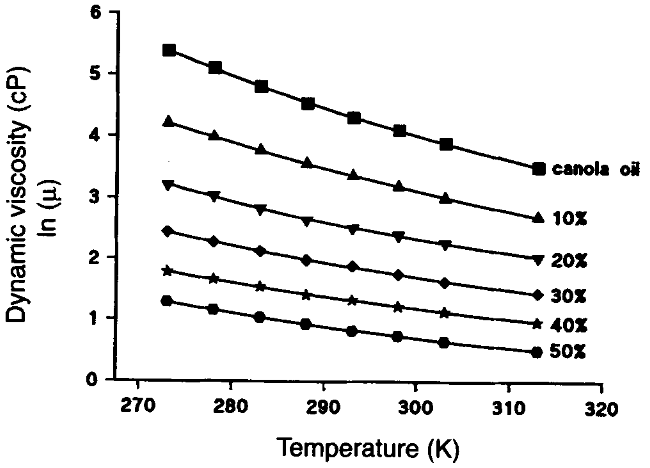

FIG. 9. Dynamic viscosity of canola oil/acetone solutions as a function of temperature at various solvent contents. The lines are plotted by using Equation 7, and the points are experimental data.

TABLE 2
Constants of Equation 7 for Canola Oil and Acetone/Canola Oil Solutions Containing Various Amounts of Solvent (%, w/w)

Acetone	*a*	*b*	*c*
Canola	−1.9847	869.5383	−155.1464
10%	−1.8389	734.8531	−151.8299
20%	−1.6411	606.7171	−147.7674
30%	−1.5741	485.9526	−151.9339
40%	−1.3972	366.9311	−157.9940
50%	−1.3947	260.1528	−176.0885

tained by various workers were significantly different. For example, $a = -4.4068$, $b = 2501.109$, and $c = 5098.307$ were reported for canola oil by Toro-Vazquez and Infante-Guerrero (17), whereas $a = 6.2246$, $b = -5060.580$, and $c = 1.319E + 6$ were obtained in the present study and were in the same order with those reported for vegetable oils by Noureddini *et al.* (11) when Equation 8 was applied. This was unexpected and may suggest that Equation 8 is not stable. Therefore, models other than Equation 8 are preferred.

Analysis of constant, *c*, for Equation 7 in Table 2 showed that this numeric for the homologous oil solutions may be considered constant. Examination of the viscosity data for various oils, as reported by Noureddini *et al.* (11), demonstrated that the average value of constant, *c*, from Equation 7 was about −156. When this fixed value for *c* is used in Equation 7, it gives an average deviation for viscosity of about 3% for oil and its solutions.

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