Evaluation of Tripalmitin Crystallization in Sesame Oil Through a Modified Avrami Equation

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ABSTRACT: Tripalmitin (TP) crystallization in sesame oil solutions (0.98, 1.80, and 2.62%, wt/vol) was investigated by utilizing a modification of the Avrami equation. The modified equation retains the original correspondence to the nucleation process (i.e., *n*) and crystal growth and simply corrects the value of the crystallization rate constant (*z*) by eliminating the influence of *n*. The energy of activation (E_a) values for TP crystallization in sesame oil solution, calculated with the modified *z*, were quite similar to those calculated with the reciprocal of time required to achieve 50% of TP crystallization ($t_{F=0.50}{}^{-1}$). However, E_a values calculated with *z* from Avrami's original equation were quite different from those obtained with $t_{F=0.50}{}^{-1}$. Thus, *z* and E_a values calculated through the Avrami equation yield erroneous results, especially when comparing crystallization processes having different magnitudes of *n*, as in this study. Additional analysis that considered the viscosity of the TP oil solutions concluded that, at equal supercooling conditions (e.g., 22.0–22.5), the magnitude of *z* and E_a became more dependent upon the crystal growth process as oil viscosity decreased. In contrast, as viscosity of the oil phase increased, the main crystallization process, evaluated through *z* and E_a, was nucleation. Furthermore, within the supercooling interval achieved at the temperatures utilized, the increase in supercooling at constant viscosity conditions (e.g., 5.25–5.5 dynes/cm^2) would produce a higher degree of nucleation without an appreciable effect on TP crystal size. The results obtained indicate that investigating the effects of supercooling, molecular diffusion (i.e., viscosity) and TP concentration on the magnitude of *z* and E_a during TP crystallization in sesame oil requires a multiple variable statistical approach.
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KEY WORDS: Avrami equation, crystallization rate, sesame oil, tripalmitin crystallization.

Tripalmitin (TP) is the triacylglycerol with the highest melting temperature in palm oil and palm stearin, representing 5–11% and 12–56% of their compositions, respectively (1,2). Thus, TP must have a significant effect on crystallization kinetics and polymorphic behavior of palm oil and palm stearin. Palm oil will be the most economical and abundant edible oil worldwide in the near future (3). Thus, there is a need to investigate TP crystallization in model systems with other triacylglycerols (4) or in mixtures with vegetable oils (5,6) to support further developments in palm oil processing (i.e., fractional crystallization) and expand commercial utilization of palm oil or its derivatives.

TP crystallization in a mixture with sesame oil has been investigated under nonisothermal conditions by utilizing reduced viscosity measurements (5). The results obtained indicated that, at TP concentrations <0.98%, triacylglycerols of sesame oil develop mixed crystals with TP. However, at concentrations within the interval of 0.98 to 3.44%, TP crystallizes independently of sesame oil, due to its molecular segregation from the highly unsaturated triacylglycerol phase of sesame oil (5). These results were further confirmed by differential scanning calorimetry and polarized light microscopy, and the polymorph state of TP crystals developed under such conditions (287–299 K) was established (6). All these studies have suggested that viscosity of the liquid phase might become a limiting factor for TP nucleation and crystal growth in sesame oil, especially at TP concentrations <1.80% (5,6).

The Avrami equation (7) also has been utilized to study TP crystallization in solution with sesame oil (6). However, its use was limited to the determination of *n* (i.e., the exponent in the Avrami equation and associated with the nucleation mechanism) and its dependence on temperature. The crystallization rate constant (*z*) included in the Avrami equation (7) and its associated energy of activation (E_a) were not investigated. The Avrami *z* is a composite constant that incorporates nucleation characteristics and growth rate (7,8). However, it has been shown that evaluation of the *z* and E_a by means of Avrami's original equation leads to erroneous results because the *z* is influenced by the magnitude of the nucleation process (*n*) (8). The objective of this investigation was to study TP crystallization in sesame oil by using a modification of the Avrami equation as described by Khanna and Taylor (8). The modified Avrami equation utilized in this investigation retains the original correspondence to nucleation mechanisms (i.e., *n*) and the crystal growth process and simply corrects the value of the *z* by eliminating the influence of *n* (8).

EXPERIMENTAL PROCEDURES

Materials. The same batch of whole-seed refined sesame oil, obtained from a local industry (Aceitera San Juan, Salvatierra, Gto. Mexico), was used in all experiments. TP

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(>99% pure) was obtained from Sigma Chemical Co. (St. Louis, MO). A Supelco (Bellefonte, PA) glass column (2.6 m × 2.1 mm), packed with GP 10% SP 2330 on Chromosorb 100/120, was utilized for the gas chromatographic fatty acid analysis; the conditions utilized have been reported elsewhere (6).

Crystallization studies. TP solutions in sesame seed oil were prepared at 0.98, 1.80, and 2.62% (wt/vol). At these concentrations, TP crystallizes independently from sesame oil triacylglycerols (5,6). Complete dissolution of TP in the oil was achieved by heating the dispersion for 30 min at 353 K with constant stirring, and the system was cooled at 1.0 K/min until the desired temperature was reached (±0.2 K). Isothermal crystallization curves of TP solutions were obtained by measuring its transmittance (600 nm) as a function of time at temperatures between 287 and 299 K. A double-beam spectrophotometer with data acquisition system (Shimadzu UV-2101PC; Shimadzu Corp., Kyoto, Japan) and temperature control (Brookfield TC-500; Brookfield Instruments; Stoughton, MA) was utilized. A more detailed description of the methodology utilized has been reported previously (6).

Fractional crystallization, F, as a function of time (t) was calculated as

$$F = (T_i - T)/(T_i - T_f) \quad [1]$$

where T_i is the transmittance of the oil solution at time zero, T is the transmittance at time t, and T_f is the minimum transmittance obtained during the crystallization process. With the modified Avrami equation (Equation 2) as proposed by Khanna and Taylor (8), the index of crystallization reaction, n, was calculated from the slope of the linear regression of $\ln[-\ln(1 - F)]$ vs. $\ln(t)$ by using values of F within 0.25 and 0.75 (7). The overall z was calculated from the intercept, $n[\ln(z)]$ (Equation 3).

$$-\ln(1 - F) = (zt)^n \quad [2]$$

$$\ln[-\ln(1 - F)] = n[\ln(z)] + n[\ln(t)] \quad [3]$$

Crystal morphology was studied with a polarization microscope adapted with a camera (model BX60F/PMC35; Olympus Optical Co., Ltd.; Tokyo, Japan). The objective magnification was 20×, and the ocular magnification was 10×. Temperature control was achieved with a specially built platen, equipped with a heating/cooling system (Brookfield model TC-500). A small volume (≈4 μL) of TP oil solution was dropped on a glass slide, and after placing a cover slip, the system was heated to 353 K for 30 min and then cooled (1.0 K/min) until the desired temperature was reached. After induction of nucleation, pictures of the crystals were taken as a function of time.

Measurements of shear stress. The shear stress (τ) of the TP solutions was determined under isothermal conditions at a shear rate (γ) of 7.92 s^{-1} with a Brookfield DV-II viscosimeter (Brookfield Instruments), equipped with the small-sample adapter (Brookfield 13R) and spindle SC4-18. The volume of sample was always 8 mL, and temperature control was ±0.2 K (Brookfield TC-500).

The solution in the sample container of the viscosimeter was heated at 353 K for 30 min. Afterward, the system was cooled (1.0 K/min) until the desired temperature was achieved within the interval of 287 to 303 K. The equilibrium time for recording the shear stress was 25 s. The value of τ was plotted as a function of relative supercooling, which was defined as $T_s - T$, where T is the isothermal crystallization

TABLE 1
Crystallization Kinetics of Tripalmitin in Sesame Oil at Three Different Concentrations

	Tripalmitin	50% Transformation		Modified Avrami equation		
Temperature (K)	concentration (%, wt/vol)	$1/t_{F=0.50}$[a] (min^{-1})	E_a (Kcal/mol)	n	z (min^{-1})	E_a (Kcal/mol)
287.0	0.98	0.04854	46.07	4.14	0.04420	45.97
289.0		0.03759		3.28	0.03367	
291.0		0.02890		3.23	0.02578	
293.0		0.01232		3.35	0.01104	
294.0		0.00790		3.39	0.00706	
295.0		0.00598		3.12	0.00552	
294.0	1.80	0.03012	35.59	2.79	0.02638	34.75
295.0		0.02604		2.46	0.02248	
296.0		0.02155		3.39	0.01935	
297.0		0.01548		2.83	0.01349	
298.0		0.01244		3.37	0.01122	
299.0		0.01205		2.49	0.01069	
294.5	2.62	0.07813	48.55	3.57	0.07065	48.81
295.5		0.05556		3.38	0.04954	
296.0		0.03497		2.46	0.02993	
297.5		0.03067		2.67	0.02678	
298.5		0.02155		2.64	0.01910	
299.0		0.02203		3.03	0.01964	

[a]Reciprocal time for $F = 0.50$; z, crystallization rate constant; E_a, energy of activation.

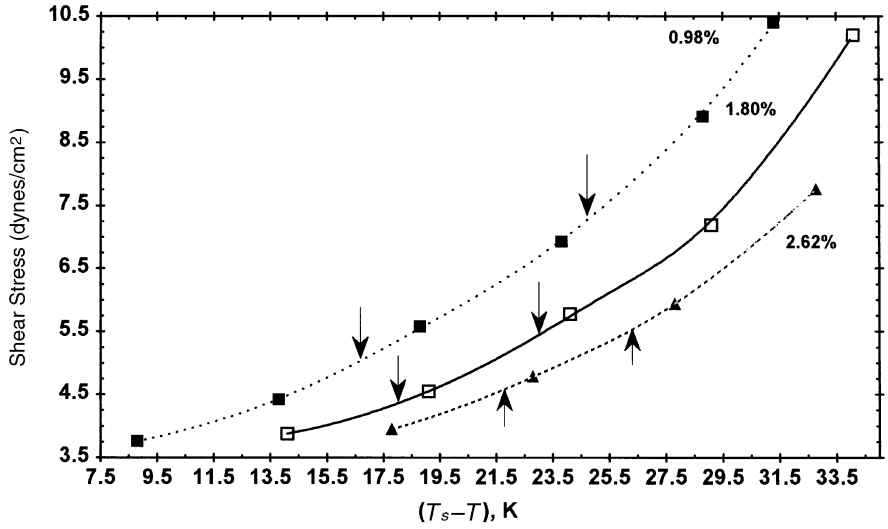

FIG. 1. Shear stress of tripalmitin sesame oil solutions at 7.92 s^{-1}: 0.98% (■), 1.80% (□), and 2.62% (▲) (wt/vol). The arrows indicate the supercooling interval corresponding to the crystallization temperatures utilized for each tripalmitin solution.

temperature utilized, and T_s is the maximum temperature in the melting peak of TP in sesame oil (e.g., 311.8 K for 0.98% TP solution, 317.1 K for 1.80% TP solution, and 320.8 K for 2.62% TP solution, which were determined previously by dynamic differential scanning calorimetry measurements and reported in Ref. 6).

RESULTS AND DISCUSSION

The fatty acid profile of the sesame oil utilized (palmitic acid 10.0% ±0.2, stearic acid 5.7% ±0.0, palmitoleic acid 0.3% ±0.0, oleic acid 40.1% ±0.2, linoleic acid 42.7% ±0.1, linolenic acid 0.6% ±0.2, unidentified fatty acids 0.6% ±0.2, wt/vol) was practically the same as reported previously (6) and in close agreement with the results obtained by Toro-Vazquez and Gallegos-Infante (5) and Kamal-Eldin and Appelqvist (9).

The corrected overall z for crystallization (Equation 2) of TP in sesame oil at different temperatures is shown in Table 1, along with the reciprocal of the time required to achieve F = 0.50 (i.e., 50% of crystallization). This time, $t_{F=0.50}^{-1}$, is an appropriate measurement of the rate of the crystallization reaction (8). Thus, Arrhenius plots of $t_{F=0.50}^{-1}$ would provide values of E_a that are nearly equal to those obtained with authentic values of the z. In fact, for the same TP concentration, quite similar values of E_a were obtained by using either z or $t_{F=0.50}^{-1}$ (Table 1). The Arrhenius plots obtained with z or $t_{F=0.50}^{-1}$ always provided regression coefficients greater than 0.95 ($P < 0.0030$). However, E_a values calculated with z obtained with Avrami's original equation [i.e., $-\ln(1 - F) = zt^n$] were quite different from those obtained with $t_{F=0.50}^{-1}$ (i.e., 104.4, 110.6, and 75.1 Kcal/mol for TP solutions at concentrations of 0.98, 1.80, and 2.62%, respectively); additionally, the regression coefficients for the Arrhenius plots were lower than 0.80 with limited statistical significance (e.g., $P \approx 0.04$, $P \approx 0.11$, and $P \approx 0.22$, respectively). Thus, z and E_a values, obtained through the unmodified Avrami equation, yield erroneous results (8), especially when comparing crystallization processes at different magnitudes of n, as in this particular study.

The z is a composite rate constant that incorporates nucleation and growth rate characteristics (7,8). Nucleation mainly depends on the extent of supercooling, the thermodynamic driving force for crystallization. In contrast, crystal growth is affected by several factors, the more important being diffusion of molecules to the surface of growing crystals and incorporation of molecules onto the crystal surface (10). Therefore, the E_a associated with z (Table 1) represents the energy involved in the overall reaction for TP crystallization in sesame oil as affected by supercooling, molecular diffusion, or incorporation of TP molecules on the crystal surface. In general, for a particular crystallization reaction, one of these factors predominates and limits or favors the nucleation rate or crystal growth rate. For the system studied, Figure 1 shows the magnitude of oil phase viscosity (e.g., shear stress at 7.92 s^{-1}), which is inversely associated with molecular diffusion (10), as a function of supercooling for the TP solutions in sesame oil. At the supercooling achieved with the temperature interval utilized, the system with the lowest values of z (or $t_{F=0.50}^{-1}$, Table 1) showed the highest value of viscosity (i.e., 0.98% TP solution, Fig. 1). Additionally, at the same supercooling, the TP solution with the lowest viscosity (i.e., 2.62% TP solution) had the highest magnitude of z (Table 1 and Fig. 1). Under high-viscosity conditions, molecular diffusion is limited, and so is crystal growth. Thus, the size of TP crystals would follow an inverse relationship with oil phase viscosity, independent of TP concentration. This is true, provided similar supercooling conditions (e.g., 22.0–22.5,

Fig. 1) and equivalent time for crystallization (i.e., 30 min after induction time for nucleation) were utilized. In contrast, at constant viscosity of the oil phase (e.g., 5.25–5.5 dynes/cm^2) and crystallization time, nucleation would follow a direct relationship with the degree of supercooling achieved for the TP solutions (i.e., nucleation mainly depends on the extent of supercooling). Photographs of TP crystals, obtained under the conditions described above (data not shown), appear to support these conclusions. However, few crystals were obtained under such conditions and establishment of the actual crystal size as affected by viscosity and supercooling is difficult.

The results obtained indicate that, to obtain meaningful values of z and associated E_a, the z obtained from the Avrami equation has to be corrected as proposed by Khanna and Taylor (8). To investigate the effect of supercooling, molecular diffusion (i.e., viscosity), and TP concentration (i.e., high melting temperature component) on the magnitude of z and E_a during TP crystallization in sesame oil, a multiple variable approach is advisable (e.g., multivariate statistical analysis). This approach is now being utilized to describe the crystallization process in palm stearin/sesame oil solutions.

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