Viscosity Estimation of Triacylglycerols and of Some Vegetable Oils, Based on Their Triacylglycerol Composition

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ABSTRACT: The experimentally determined kinematic viscosities of simple triacylglycerols [trilaurin, trimyristin (MMM), tripalmitin (PPP), tristearin (SSS), triolein (OOO), and trilinolein (LiLiLi) were correlated to a modified Andrade-type equation. The constants for the modified equation were derived for each simple triacylglycerol. The method was also used to estimate the viscosity of mixed triacylglycerols [1,2-dimyristoyl-3-palmitoyl (MMP), 1,2-dioleoyl-3-palmitoyl (OOP), 1,2-dimyristoyl-3-oleoyl (MMO), and 1,2-dipalmitoyl-3-oleoyl (PPO)], binary triacylglycerol mixtures (PPO/OOP, PPP/SSS, and OOO/SSS of different portions), and three types of vegetable oils [refined, bleached, and deodorized palm oil; cocoa butter; and canola oil] by applying modified Kay's rule utilizing the simple triacylglycerol constants derived earlier. In all cases, the estimated values for liquid viscosity were compared with experimental values determined in this work and with previous work from the literature. When applied to vegetable oils, the method requires knowledge of their triacylglycerol composition. Despite its simplicity, the method gives a reasonable estimate. The method may be used to predict the viscosity of different blends of vegetable oils, and the accuracy is expected to increase when more experimental data on simple triacylglycerols become available.

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KEY WORDS: Triacylglycerol, vegetable oil, viscosity estimation.

Viscosity is an important transport property of fluids, and it must be considered in chemical engineering design. Viscosity strongly affects flow behavior at different temperatures and significantly affects the design of pipelines and equipment.

Oils owe their relatively high viscosities to the intermolecular attractions of the long chains of the glyceride molecules. In general, viscosity increases with molecular weight but decreases with increases in unsaturation and temperature. Therefore, oils containing triacylglycerols of low molecular weight are slightly less viscous than oils of an equivalent degree of unsaturation containing only high molecular weight triacylglycerols (1).

A critical review of methods for determining viscosity suggests that most of the generalized methods, which are based on group contributions or which utilize critical properties and density, give large errors when applied to triacylglycerols and vegetable oils. This category includes the Orrick and Erbar and the Van Velzen, Cardozo, and Lagenkamp methods as reviewed by Reid *et al*. (2). The deviation of the calculated values, derived using these two methods, from the experimental values in this work approaches ± 100% (3). The generalized UNIMOD model for the estimation of viscosity for fatty mixtures gives high accuracy (4). This model is based on a group contribution method and requires a multitude of steps to calculate the parameters in the model. Andrade-type equations tend to give a better estimate since the constants are derived from experimental values; however, the constants are specific to the respective triacylglycerol or oil type, as shown previously (5,6).

A quick method for estimating viscosity of vegetable oil at varying temperatures with reasonable accuracy is the objective of this work. The constants for the modified Andrade-type equation were first derived from the experimental values for the range of triacylglycerols commonly found in vegetable oils. The method described below utilizes these constants to estimate viscosity of vegetable oil mixtures once their triacylglycerol composition is known.

The method established in this work is similar to the generalized method for estimating vegetable oil properties such as density (7) and specific heat capacity (8). However, for those two properties (density and specific heat capacity), the fatty acid compositions of the vegetable oil mixture were required, which therefore required inclusion of correction factors.

EXPERIMENTAL PROCEDURES

The kinematic viscosities of simple triacylglycerols [trilaurin (LLL), trimyristin (MMM), tripalmitin (PPP), and tristearin (SSS)], mixed triacylglycerols (MMP, MMO, PPO, and OOP), a binary triacylglycerol mixture (PPO/OOP, 55:45 w/w), and refined, bleached, deodorized palm oil (RBDPO) were determined in this laboratory (3). The kinematic viscosity of cocoa butter was determined in this laboratory (9). Pure triacylglycerols obtained from Sigma Chemical Co. Ltd., (Poole, United Kingdom) had a nominal purity of >99%; the binary triacylglycerol PPO/OOP was made up from the pure triacylglycerols. The RBDPO was obtained from Pandamaran Oil Product (Felda Refinery Corp., Port Klang, Malaysia). Cocoa butter was obtained from Malaysia Cocoa Manufacturing, Sdn. Bhd. (Petaling Jaya, Malaysia).

The kinematic viscosity of the above-mentioned triacylglyc-

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erols and the binary triacylglycerols was measured using the suspended level capillary-type viscometer (Setavis, Stanhope-Seta, Surrey, England), whereas the RBDPO used the reversed flow–type Cannon-Fenske viscometer (Cannon Instrument Co., State College, PA). A Ubbelohde viscometer (Cannon Instrument Co.) was used to measure the kinematic viscosity of standards cocoa butter. The experiments conformed to the standards ASTM D 445–83 and ASTM D 446–83 (11).

The Setavis viscometer tubings come with "certificates of calibration" from Polten Selfe & Lee Ltd. (PSL Laboratory, Wiekford, Essex, England). The manufacturer and issuer of "certificates of calibration" for the Cannon-Fenske and the Ubbelohde viscometers was Cannon Instrument Co. (State College, PA).

The experimental results from this work for pure triacylglycerols, when compared to other documented experimental data from various sources, were in good agreement; deviations did not exceed ±2% (3).

The experimentally determined kinematic viscosity values of the simple triacylglycerol triolein (OOO) and the binary triacylglycerol mixtures (PPP/SSS in three different mixtures of 0.2688:0.7312, 0.5246:0.4754, and 0.7638:0.2362 mol/mol, and OOO/SSS in three different mixtures of 0.2509:0.7491, 0.5045:0.4955, and 0.7498:0.2502 mol/mol) were obtained from Valeri and Meirelles (6). The kinematic viscosity values of the simple triacylglycerol trilinolein (LiLiLi) and canola oil were obtained from Rabelo *et. al.* (4).

Estimation of viscosity. The experimental values of the six simple triacylglycerols (LLL, MMM, PPP, SSS, OOO, and LiLiLi) were fitted to the modified Andrade-type equation:

$$\ln \nu = A + B/T + C/T^2 \qquad [1]$$

where ν is the kinematic viscosity (cSt), T is the temperature (K), and A, B, and C are constants for the respective triacylglycerols. The temperature range where these constants are valid is the experimental temperature range. The plots of ln ν against 1/T (K) for the six simple triacylglycerols are given in Figure 1, and the constants A, B, and C derived from these plots are given in Table 1. These constants form the basis for estimating kinematic viscosity for mixed triacylglycerols and vegetable oil.

TABLE 1
Constants *A, B,* and *C* in the Modified Andrade Equation for Simple Triacylglycerols

Triacylglycerols	*A*	*B*	*C*	Temp. range (°C)
Trilaurin, LLL	1.57	−2425.24	928573.57	50–170
Trimyristin, MMM	0.84	−1858.44	853674.42	60–150
Tripalmitin, PPP	0.27	−1354.46	775552.72	80–150
Tristearin, SSS	−0.99	−89.44	504190.29	80–150
Triolein, OOO	−1.58	−2204.80	893707.14	20–100
Trilinolein, LiLiLi	−9.44	4740.04	−242201.06	30–100

Application of the method to mixed triacylglycerols. Kay's rule, to be applied to estimate the viscosity of mixed triacylglycerol, was modified. The logarithm of the viscosity of a mixed triacylglycerol is a function of the logarithmic viscosities of simple triacylglycerols:

$$\ln \nu_{(\text{mix})} = \Sigma\, x_i \ln \nu_i \qquad [2]$$

where x_i is the mole fraction and ν_i is the kinematic viscosity of the simple triacylglycerol. For example, for OOP, ln ν_i is a function of OOO and PPP. Hence,

$$\ln \nu_{(\text{OOP})} = 2/3 \ln \nu_{(\text{OOO})} + 1/3 \ln \nu_{(\text{PPP})} \qquad [3]$$

Figures 2 and 3 show the kinematic viscosities of the mixed triacylglycerols.

Application of the method to mixtures. This method, when applied to mixtures, the binary triacylglycerol mixtures, and vegetable oils (RBDPO, cocoa butter, and canola oil) required knowledge of triacylglycerol composition. The triacylglyc-

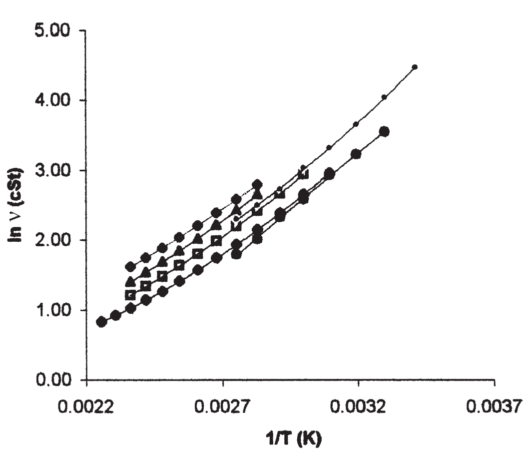

FIG. 1. The plot of ln ν (cSt) vs. 1/*T* (K) for simple triacylglycerols. The symbols are the experimental points from various sources. ◆, Trilaurin, LLL (3); □, trimyristin, MMM (3); ▲, tripalmitin, PPP (3); ◇, tristearin, SSS (3); •, triolein, OOO (6); ●, trilinolein, LiLiLi (4).

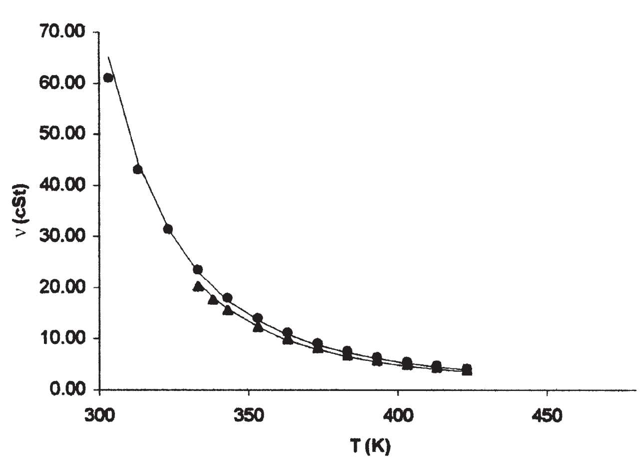

FIG. 2. Kinematic viscosities of mixed triacylglycerols (MMP and PPO). Symbols are experimental data points [▲, MMP (3); ●, PPO (3)]; continuous lines represent estimated functions.

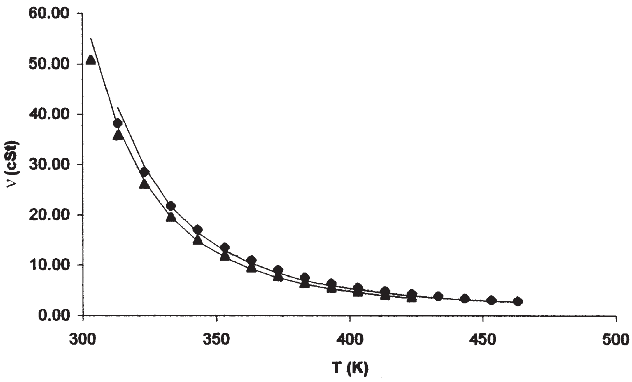

FIG. 3. Kinematic viscosities of mixed triacylglycerols (MMO and OOP). Symbols are experimental data points [◆, OOP (3); ▲, MMO (3)]; continuous lines represent estimated functions.

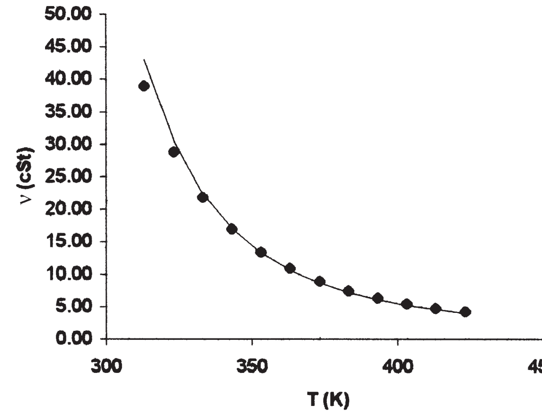

FIG. 4. Kinematic viscosity of binary triacylglycerol (PPO/OOP, 55:45 w/w). ◆, Experimental data (3); —, estimated function.

erol composition of RBDPO, cocoa butter, and canola oil are tabulated in Table 2. Kay's rule was applied throughout; it is assumed that the viscosity of a vegetable oil mixture is a function of the mole fractions of the respective triacylglycerols present in the oil.

For lack of experimental data for LeLeLe, the portions of triacylglycerol having linolenic acid (Le) were replaced by linoleic acid (Li) in canola oil, as shown in the revised triacylglycerol composition in Table 2. In cocoa butter, the portion containing arachidic acid in 1-stearoyl-2-oleoyl-3-arachidoyl, which accounts for 1.1%, was ignored since no experimental data were available.

RESULTS AND DISCUSSION

The estimated and the experimental values of viscosity for the mixed triacylglycerols (MMP, MMO, PPO, and OOP), the binary triacylglycerol mixtures (PPO/OOP, PPP/SSS, and OOO/SSS), and vegetable oils (RBDPO, cocoa butter, and canola oil) were compared, and the average absolute deviations (AAD) were tabulated (Table 3). The AAD were calculated as

$$\mathrm{AAD} = \sum_{i=1}^{p}[(|\nu_{i,\mathrm{exp}} - \nu_{i,\mathrm{est}}|/\nu_{i,\mathrm{exp}})/p] \times 100 \qquad [4]$$

where $\nu_{i,\mathrm{exp}}$ and $\nu_{i,\mathrm{est}}$ are the experimental and estimated viscosities, respectively, and p is the number of times the experiment was performed.

The relationships between the estimated viscosities and experimental data are shown in Figures 2 and 3 for the mixed triacylglycerols, in Figure 4 for the binary triacylglycerol, and in Figures 5–7 for the vegetable oils (RBDPO, cocoa butter, and canola oil, respectively). In all cases, comparisons were made in

TABLE 2
Triacylglycerol Composition[a] of Refined, Bleached, Deodorized Palm Oil (RBDPO), Cocoa Butter, and Canola Oil

RBDPO		Cocoa butter		Canola oil		Revised	
Triacylglycerol	Mole fraction (10)[b]	Triacylglycerol	Mole fraction (9)[b]	Triacylglycerol	Mole fraction (4)[b]	Triacylglycerol	Mole fraction
PMP	0.004	PPS	0.006	POP	0.0090	POP	0.0090
PPP	0.067	PSS	0.023	PLiP	0.0057	PLiP	0.0057
PPO	0.294	POP	0.158	POO	0.0909	POO	0.0909
SPO	0.050	POS	0.401	POLi	0.0668	POLi	0.1058
OOS	0.026	SOS	0.275	POLe	0.0390		
PPLi	0.084	POO	0.027	PLiLe	0.0105	PLiLi	0.0105
POO	0.239	PLiP	0.016	SOO	0.0214	SOO	0.0214
		PLiS	0.023	OOO	0.2376	OOO	0.2376
POLi	0.118						
PLiLi	0.014	SOO	0.026	OOLi	0.2409	OOLi	0.4185
OOO	0.061	SLiS	0.022	OOLe	0.1776		
OOLi	0.043						
		SLiO	0.007	OLiLe	0.0756	OLiLi	0.1005
		OOO	0.004	OLeLe	0.0249		
		SOA	0.011				
Total	1.000		0.999		0.9999		0.9999

[a]Li, linoleic acid; M, myristic acid; O, oleic acid; P, palmitic acid; S, stearic acid; Le, linolenic acid. Therefore, for example, PMP = 1-palmitoyl-2-myristoyl-3-palmitoyl (triacylglycerol).
[b]Reference number is in parentheses.

TABLE 3
Average Absolute Deviation (AAD) for Viscosities of Mixed Triacylglycerols, Binary Triacylglycerols, and Vegetable Oils [a]

Mixed triacylglycerol (3)[b]	AAD (%)	Binary triacylglycerol[b]	AAD (%)
MMP	3.30	PPO/OOP (0.558:0.442) (3)	3.56
MMO	2.83	PPP/SSS (0.2688:0.7312) (6)	0.84
PPO	6.14	PPP/SSS (0.5246:0.4754) (6)	1.71
OOP	3.20	PPP/SSS (0.7638:0.2362) (6)	1.21
		OOO/SSS (0.2509:0.7491) (6)	3.11
		OOO/SSS (0.5045:0.4955) (6)	3.95
		OOO/SSS (0.7498:0.2502) (6)	1.61
Vegetable oil			
RBDPO (3)	7.46		
Cocoa butter (9)	4.18		
Canola oil (4)	4.58		

[a]The source of the experimental data is indicated in parentheses following the respective triacylglycerols and mixtures.
[b]Mixtures shown in parentheses are in mol/mol; for example, PPO:OOP is 0.558 mol PPO and 0.442 mol OOP. For abbreviations see Table 2.

the experimental temperature range only. The results are encouraging since the viscosity of the three vegetable oils—RBDPO, cocoa butter, and canola oil—can be reasonably estimated from the six simple triacylglycerol types shown in Table 1.

The estimation method does not distinguish between triacylglycerols of the same fatty acid composition, but it does for ones of different orientation, such as between 1,2-dipalmitoyl-3-oleoyl, PPO and 1,3-dipalmitoyl-2-oleoyl, POP. However, the variations in the kinematic viscosities for triacylglycerols of these types were found to be insignificant (3). This factor may not significantly affect the accuracy of this estimation method.

This method is in error mainly when it is applied beyond the valid temperature range of the simple triacylglycerols. However, this is sometimes unavoidable since generally the mixed triacylglycerols are in the liquid form even as low as 30°C. In contrast, the melting point of the simple triacylglycerols are high, especially for PPP and SSS (above 70°C). This problem can be illustrated for the mixed triacylglycerol, OOP, in the estimation of viscosity from the constant values derived from the experimental values for two simple triacylglycerols PPP and OOO. The estimation of liquid viscosity of OOP at, say, 40°C has already extended the validity of the temperature range of PPP (a solid at this temperature); therefore, this is bound to introduce significant error even though OOP is a liquid at this condition. The same problem arises with the estimation of vegetable oil viscosity since it is calculated from the summation of the viscosities of triacylglycerols.

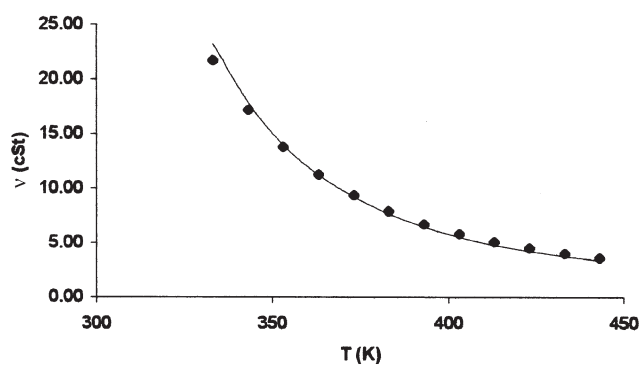

FIG. 6. Kinematic viscosity of cocoa butter. ◆, Experimental data (9); —, estimated function.

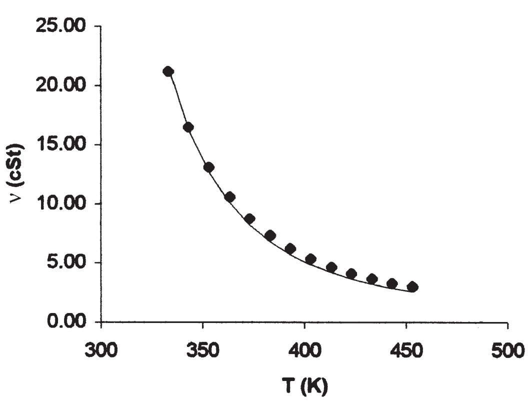

FIG. 5. Kinematic viscosity of refined, bleached deodorized palm oil. ◆, Experimental points (3); —, estimated function.

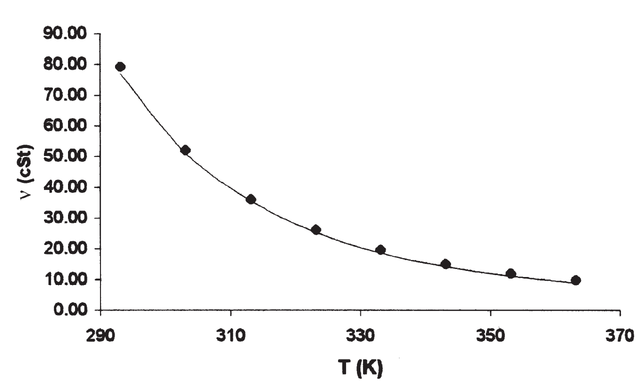

FIG. 7. Kinematic viscosity of canola oil. ◆, Experimental data (4); —, estimated function.

Despite this problem, the method is simple and gives a reasonable estimate of the viscosity of mixed triacylglycerols and vegetable oils. The method could be extended to other vegetable oils if all of the simple triacylglycerols constants were available and the triacylglycerol composition were known. Accuracy of the method is expected to increase if the experimental temperature range of the simple triacylglycerols can be expanded.

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