Group Contribution Model for Predicting Viscosity of Fatty Compounds

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In the present work, a group contribution model is proposed for estimating the dynamic viscosity of fatty compounds. For the major components involved in the vegetable oil industry (such as fatty acids, esters and alcohols, triacylglycerols, and partial acylglycerols), the optimized parameters are reported. In order to improve the data bank gathered from the literature, viscosity data were measured as a function of temperature for three saturated and three unsaturated fatty esters, one unsaturated fatty acid, and one unsaturated triacylglycerol. These last two are unavailable data in the literature (linolenic acid and trilinolenin). A simple method of calculation is also proposed to predict the dynamic viscosity of vegetable oils as an extended applicability of our equation. The model can be a valuable tool for designing processes and equipment for the oil industry, including edible and non-edible compounds, such as biodiesel.

Introduction

Information about transport properties such as the viscosity of liquids is essential for the design of pipes, accessories, and equipment utilized in the oil and fat industry as well as for process simulation and optimization, seeing that these properties affect flow characteristics, loss of energy due to friction, mass, and heat transfer coefficients among other important variables.[1−3]

Much work has been done on measuring and estimating transport properties of fatty compounds and vegetable oils as a function of temperature.[4−10] In most cases, specific equations were generated by adjusting each set of experimental data to a specific compound or to a class of compounds. More generalized models were developed for fatty acids,[5,9] triacylglycerols,[5] fatty esters,[9] and edible oils.[4−6,8] None of these works used the widely known concept of group contribution, in which a compound or a mixture of compounds is considered as a solution of groups and its properties are the sum of the contributions of each group.

Nowadays, the interest in biodiesel and other biofuels due to environmental concerns, energy prices, and government incentives around the world is increasing the demand for vegetable oils in global markets. As a consequence, the necessity of reliable data for a variety of fatty compounds over a large range of process conditions is required. Since it is not viable to measure the viscosities at all conditions of interest, methods for its estimation are of great practical interest. This fact encouraged us to develop a user-friendly method for the prediction of dynamic viscosity with an accuracy adequate for engineering applications.

Experimental Section

Materials. All methyl esters of fatty acids (methyl laurate, CASRN 111-82-0; methyl myristate, CASRN 124-10-7; methyl palmitate, CASRN 112-39-0; methyl oleate, CASRN 112-62-9; methyl linoleate, CASRN 112-63-0; and methyl linolenate, CASRN 301-00-8) and the linolenic acid (CASRN 463-40-1) were obtained from Sigma (St. Louis, MO), while trilinolenin (CASRN 463-40-1) was purchased from Nu-Chek-Prep (Elysian, MN). All fatty compounds had high purity (> 99 %) and were used without further purification. Trilinolenin was analyzed by gas chromatography of the fatty acid methyl esters according to the procedure described in Rabelo et al.[5] The chromatographic analyses confirmed its purity as 99.29 %. For the other compounds, we relied on the information given by the suppliers.

Apparatus and Procedure. A set of experimental dynamic viscosity data (η) was determined for each fatty ester in an automatic viscosimeter AMV 200 (Anton Paar), connected to a thermostatic bath (Paar Physica model Viscotherm VT2) at different temperatures. The principle of the measuring is the efflux time of a ball immersed in the sample inside a glass capillary for different inclination angles. The experimental data were measured at temperatures from 20 °C up to 70 °C at 10 °C intervals, totaling 34 data points. Each record was replicated at least four times with nine different inclination angles (30° to 70°). The standard deviations of the determinations in the Anton Paar viscosimeter varied within the range of 0.007 mPa·s (methyl myristate at 20 °C) and 0.065 mPa·s (methyl oleate at 70 °C), being more important at high temperatures. The variation coefficient ranged from 0.15 % to 3.3 %, so that the uncertainty of the experimental measurements, especially at high temperatures, can be estimated as being not higher than 3.3 %. Apparatus calibration (measuring system 1.6) was made periodically, using distilled water, in accordance with the user instructions. Twelve values of kinematic viscosities of linolenic acid and trilinolenin (ν) were measured for the same range of temperatures in glass capillary kinematic viscosimeters (sizes 75, 100, and 150) from Cannon Fenske (Cannon Instrument Co.), immersed in a constant-temperature bath (Cole-Parmer Instrument Co.). A thermometer (Cole-Parmer Instrument Co.) with subdivisions of 0.1 °C was used for monitoring bath temperature. Values of ν were calculated as a product of the efflux time and the instrument constant. An electronic timer accurate to 0.01 s was used for measuring the efflux time. The

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Table 1. Experimental Viscosity Data Bank of Fatty Compounds

		class of compounds			
		fatty acids	fatty alcohols	fatty esters	triacylglycerols
reference		4, 5, 14−24	16, 18, 25, 26	7, 24, 27−31	5, 6, 14, 19, 24, 32
temperature range/°C		20−121,1	15−100	10−98,9	20−170
no. of types of compounds	satd[a]	9 (C6 to C18)[c]	7 (C6 to C14)	24 (C7 to C21)	7 (C21 to C57)
	unsatd[b]	4 (C18 to C22)	none	5 (C19 to C20)	3 (C57)
no. of experimental points		284	97	264	118

[a] Saturated compounds. [b] Unsaturated compounds. [c] Range of the number of carbons in the chain.

Table 2. Linear Coefficients Correlating Density with Temperature for Methyl and Propyl Fatty Esters[a,b]

carbon number[c]	*a*	*b*	R^2
	Methyl Esters		
6	0.903	−0.00096	0.9(5,7)[d]
8	0.895	−0.00089	0.9(4,6)
10	0.890	−0.00084	0.9(4,4)
12	0.885	−0.00079	0.9(4,8)
14	0.882	−0.00076	0.9(4,4)
16	0.880	−0.00074	0.9(4,6)
18	0.880	−0.00073	0.9(3,8)
	Propyl Esters		
6	0.886	−0.00090	0.9(4,7)
8	0.884	−0.00088	0.9(2,6)
10	0.878	−0.00080	0.9(4,8)
12	0.875	−0.00076	0.9(4,8)
14	0.874	−0.00074	0.9(5,3)
16	0.873	−0.00072	0.9(4,8)
18	0.872	-0.000718	0.9(5,8)

[a] Experimental data from ref 28. [b] Linear equation: $\rho/\text{g·cm}^{-3} = a + b(t/°\text{C})$. [c] Number of carbons excluding the alcoholic part (i.e., 1 for methyl esters and 3 for propyl esters). [d] Simple notation for the coefficient of determination R^2. For example, $R^2 = 0.9(5,7)$ is the same as $R^2 = 0.999997$.

mean standard deviation observed was 0.13×10^{-6} m²·s⁻¹ for the set of experimental data measured in the Cannon Fenske viscosimeter. The highest variation coefficient was 0.69 %, suggesting a good reproducibility for the measured efflux times. The Cannon Fenske viscosimeters were calibrated based on the value of water viscosity at 20 °C (1.0038×10^{-6} $\text{m}^2\text{·s}^{-1}$) and credited by the company.

Inspired by a previous work of Ceriani and Meirelles,[11] in which a group contribution method was proposed for the estimation of vapor pressure of pure fatty compounds, this paper proposes a new model to predict their dynamic viscosities as a function of temperature and of the compound chemical formula. In fact, there is a relation between these two properties, as already stated by Sastri and Rao.[12] These authors developed a predictive model for dynamic viscosity of pure compounds based in the linear dependence between its natural logarithm ($\ln \eta$) and the natural logarithm of vapor pressure ($\ln P^{\text{sat}}$) at that temperature. This hypothesis was confirmed in this work by plotting predicted values of $\ln P^{\text{sat}}$ (from Ceriani and Meirelles[11]) versus predicted values of $\ln \eta$, as will be shown latter in this paper, for some fatty compounds.

The first step to develop the dynamic viscosity model was to collect a representative data bank for the whole class of fatty compounds, including acids, alcohols, esters, and triacylglycerols. The last class of compounds is of major interest in the edible oil industry, given that TAG often represents between 94.4 % and 99.1 % of the mass of oil.[13] Fatty esters are also of importance due to their presence in biodiesel.

After a careful search in the literature, 717 experimental values of dynamic and kinematic viscosities of 59 compounds were found. In conjunction with the 46 experimental points measured specifically for this work, we came up with a data bank of 763 points distributed as given in Table 1. All the experimental data were taken from refs 4 to 7 and from refs 14 to 32. Some of these references[15,27] reported two experimental values of dynamic viscosity at one temperature. In such cases, it was assumed that both appeared equally creditable and were included in the parameter adjustment procedure. These circumstances occurred for 32 experimental points in the classes of fatty acids and fatty esters.

Some of the experimental data for fatty acids, fatty esters, and triacylglycerols extracted from refs 5, 6, 19, 22−24, 27, and 28 and also the measured data for linolenic acid and trilinolenin were given as kinematic viscosities (ν) and had to be converted to dynamic viscosities (η) by means of the following equation:

$$\eta = \rho\cdot\nu \tag{1}$$

where ρ is the density.

Necessary values of density for fatty acids and triacylglycerols at different temperatures were calculated using the predictive method described by Halvorsen et al.;[33] high-quality accuracy was already demonstrated by Rabelo et al.[5] for these two classes of fatty compounds. Density data for fatty esters, as a function of temperature, are available in the literature.[15,28,34] Considering that there is generally a linear relationship between density and temperature, over a limited temperature range,[5,19] linear correlations were adjusted using the toolbox *curve fitting* from MatLab (Mathworks 7.1). Table 2 gives the coefficients. It should be mentioned that from the 32 experimental kinematic viscosity values given by Knothe and Steidley,[24] 22 values were used in this work because of the lack of density values at 40 °C or predictive models in the literature for the other 10 compounds.

In the development of a model to predict vapor pressure of fatty acids, fatty alcohols, and sitosterols, Bokis et al.[35] included a "perturbation term" in a Clausius−Clapeyron type equation to augment the size dependence of the physical property and describe the influence of the compound chain length on its vapor pressure. Tu,[36] on the other hand, proposed that some molecular structures (double bounds, side chains) and functional groups (-OH, -COOH) may have a significant effect on the vapor pressure and had grouped then in a "correction term". These two ideas were followed by Ceriani and Meirelles[11] to develop their equation for vapor pressure prediction.

Based in the work of Ceriani and Meirelles,[11] a new equation correlating dynamic viscosity (η) and absolute temperature (T) is proposed here:

$$\ln(\eta_i/\text{mPa·s}) = \sum_k N_k\left(A_{1k} + \frac{B_{1k}}{T/\text{K}} - C_{1k}\ln T/\text{K} - D_{1k}T/\text{K}\right) + \left[M_i \sum_k N_k\left(A_{2k} + \frac{B_{2k}}{T/\text{K}} - C_{2k}\ln T/\text{K} - D_{2k}T/\text{K}\right)\right] + Q \tag{2}$$

where N_k is the number of groups k in the molecule i; M is the component molecular weight that multiplies the "perturbation

Table 3. Dynamic Viscosities η of Methyl Esters as a Function of Temperature t

t	η/mPa·s											
	laurate CH_3-$C_{12}H_{23}O_2$		myristate CH_3-$C_{14}H_{27}O_2$		palmitate CH_3-$C_{16}H_{31}O_2$		oleate CH_3-$C_{18}H_{33}O_2$		linoleate CH_3-$C_{18}H_{31}O_2$		linolenate CH_3-$C_{18}H_{29}O_2$	
°C	this work	lit (ref)	this work	lit (ref)	this work	lit (ref)	this work	lit (ref)	this work	lit (ref)	this work	lit (ref)
20	3.096	3.08−3.15[a] (7, 27, 28)	4.442	4.430−4.509 (27, 28)			6.370	na[b]	4.798	na	4.022	na
30	2.475	2.491 (7)	3.496	na			4.922	na	3.822	na	3.301	na
40	2.044	2.031−2.074 (24, 27, 28)	2.841	2.751−2.811 (24, 27)	3.764	3.724 (24)	3.939	3.877 (24)	3.166	3.183 (24)	2.790	2.774 (24)
50	1.643	1.702 (7)	2.252	na	2.931	na	3.097	na	2.550	na	2.299	na
60	1.383	1.444−1.451 (7, 28)	1.819	1.943 (28)	2.336	2.505 (28)	2.472	na	2.078	na	1.862	na
70	1.173	1.236−1.245 (7, 27, 28)	1.521	1.616−1.649 (27)	1.946	na	2.054	na	1.755	na	1.596	na

[a] Range of values found in the literature. [b] Not available.

term"; A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, and D_{2k} are parameters obtained from the regression of the experimental data; k represents the groups of component i; Q is a correction term expressed as[11]

$$Q = \xi_1 q + \xi_2 \tag{3}$$

where ξ_1 and ξ_2 are related to each class of compounds.

In eq 3, q is a function of the absolute temperature:[11]

$$q = \alpha + \frac{\beta}{T/\mathrm{K}} - \gamma \ln(T/\mathrm{K}) - \delta T/\mathrm{K} \tag{4}$$

where α, β, γ, and δ are optimized parameters obtained by regression of the data bank as a whole. The effect of functional groups on the dynamic viscosity is corrected by the term Q according to the total number of carbon atoms N_c in the molecules, as in eq 5. ξ_1 is a function of N_c applicable to all compounds and stated as follows:[11]

$$\xi_1 = f_0 + N_c f_1 \tag{5}$$

where f_0 and f_1 are optimized constants.

The term ξ_2 describes the differences between the vapor pressures of isomer esters at the same temperature and is related to the number of carbons of the substitute fraction (N_{cs}) as follows:[11]

$$\xi_2 = s_0 + N_{cs} s_1 \tag{6}$$

where s_0 and s_1 are optimized constants. Equation 6 is mainly used to account for the effect of the alcoholic portion of fatty esters. Since they are obtained from the reaction of fatty acids and short-chain alcohols (C_1 to C_4),[37] the molecule can be split in two parts: N_{cs} represents the number of carbons of the alcoholic part.

All the fatty compounds gathered in the experimental data bank were split into seven functional groups: CH_3, CH_2, COOH, CH=, OH, COO, and CH_2−CH−CH_2. This last group describes the glycerol portion of acylglycerols.[11] It should be noted that each double bond corresponds to two CH= groups.[11]

Results

The dynamic viscosities for methyl laurate (or methyl dodecanoate), methyl myristate (or methyl tetradecanoate), methyl palmitate (or methyl hexadecanoate), methyl oleate (or methyl 9-*cis*-octadecenoate), methyl linoleate (methyl 9-*cis*,12-*cis*-octadecadienoate), and methyl linolenate (or methyl 9-*cis*,12-*cis*,15-*cis*-octadecatrienoate) are given in Table 3. Kinematic viscosities of linolenic acid (or 9-*cis*,12-*cis*,15-*cis*-octadecatrienoic acid) and trilinolenin (or 9-*cis*,12-*cis*,15-*cis*-octadecatrienoic acid, 1,2,3-propanetriyl ester) are given in Table 4. For comparison purposes, Table 3 also shows dynamic viscosities values found in the literature[7,24,27,28] for the measured methyl esters. As one can see, they were in a fairly good agreement with our experimental data. The highest difference between these data and those published in the literature was 0.169 mPa·s (methyl palmitate at 60 °C),[28] which is reasonable in comparison with differences that we found among data from the references that were used in this work.

Table 4. Kinematic Viscosities ν of Linolenic Acid and Trilinolenin as a Function of Temperature t

t/°C	$\nu/10^{-6}$ m²·s⁻¹ $C_{18}H_{30}O_2$	$\nu/10^{-6}$ m²·s⁻¹ $C_{57}H_{92}O_6$
20	15.46	23.70
30	12.42	17.58
40	8.905	13.55
50	7.262	10.70
60	5.962	8.68
70	5.13	7.18

Table 5 shows the adjusted values of the parameters that appear in eqs 2 to 6. They were fitted using the Statistical Analysis System package (SAS, Cary, NC) with the regression method suggested by Marquardt.[38] The following objective function[11] was used:

$$f = \sum_{j=1}^{n} \left[\frac{|\ln(\eta_{\mathrm{expt}}) - \ln(\eta_{\mathrm{calc}})|}{\ln(\eta_{\mathrm{expt}})} \right]_j \tag{7}$$

where n is the number of experimental data considered; $\ln(\eta_{\mathrm{expt}})$ and $\ln(\eta_{\mathrm{calc}})$ are respectively the logarithm of the experimental and calculated dynamic viscosities. It should be noted that 68.9 % of the data bank is composed by viscosity values measured at high temperatures (over 40 °C), and eq 7 was chosen as the objective function to emphasize the weight of low viscosities at high temperatures in the parameter fitting. The analysis of the results show that 40 % and 38 % of the predicted values were overestimated, respectively, for temperatures up to 40 °C and over 40 °C, indicating a well-balanced fitting. We started by adjusting A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, and D_{2k} for TAG and their groups, followed by the addition of other classes and their representative groups. The Q term was adjusted as a final trial. An example of calculation of dynamic viscosity using eqs 2 to 6 is shown in Appendix A.

To test the predictive capability of the model generated by this investigation, we calculated the average relative deviation (ARD) according to the relation below:

$$\mathrm{ARD} = 100 \frac{\sum_{n} \frac{|\eta_{\mathrm{expt}} - \eta_{\mathrm{calc}}|}{\eta_{\mathrm{expt}}}}{N} \tag{8}$$

Table 5. Adjusted Parameters for Equations 2 to 6

group	A_1k	B_1k	C_1k	D_1k	A_2k	B_2k	C_2k	D_2k
CH_3	−0.2579	210.6	0.2275	−0.00389	0.000423	−0.0466	−0.00037	0.00000624
CH_2	−0.13	70.688	−0.0271	0.000449	0.000018	−0.0175	0.000038	−0.000000636
COOH	14.017	−2477.4	−0.8944	0.0375	−0.0435	17.2293	0.0108	−0.00018
CH=	49.8378	−1759.1	8.1803	−0.00867	0.000307	0.1681	0.000247	−0.00000206
OH	−8.6357	2483.6	0.0092	−0.00012	0.00856	0.0317	−0.00023	0.000004028
COO	−828.4	25192.6	−140.8	0.2041	1.0924	−32.5558	0.1852	−0.00026324
$CH_2-CH-CH_2$	1997.2	−56987.6	343.1	−0.5253	−2.8043	81.0608	−0.47675	0.000687

compound	f_0	f_1	s_0	s_1
fatty acids	−11.1293	−21.1798	0	0
alcohols	−4196.4	516.7	0	0
esters	−5291.2	354	0.1984	−0.0512
acylglycerols	−236.9	2.4799	0	0

q	α	β	γ	δ
	−0.3157	9.324	−0.054	0.00007812

Table 6. Average Relative Deviation (ARD) for Dynamic Viscosity of Fatty Compounds

	ARD		
class of compounds	this work	ref 5	ref 9
saturated fatty acids	5.71	2.64	10.05
unsaturated fatty acids	4.99	4.40	na[a]
fatty esters	4.50	na	8.88[b]
methyl	3.71	na	8.88[b]
ethyl	5.66	na	na
propyl	6.86	na	na
fatty alcohols	3.98	na	na
triacylglycerols	4.85	20.43	na
total	4.86	8.14	9.56

[a] na, not applicable. [b] Only saturated fatty esters.

where N is the number of experimental data considered. After the optimization of the adjusted parameters, a sensitivity analysis of the dynamic viscosity model was performed. Even though most of the data was extracted from different and, in some cases, old data banks, our model behaved stable, generating oscillations between 0.3 % and 1.8 % under application of ± 1 °C variations on the experimental temperature values. The final results are presented in Table 6. As one can see, a good representation of the dynamic viscosity of fatty compounds was achieved. For the whole data bank (763 experimental points), the proposed model overestimated 365 points or 47.8 % (131 of fatty acids, 44 of alcohols, 131 of esters and 59 of triacylglycerols) and underestimated 398 points or 52.2 % (153 of fatty acids, 53 of alcohols, 133 of esters and 59 of triacylglycerols).

For comparison purposes, Table 6 also shows the ARD values obtained under the application of the models proposed by Rabelo et al.[5] for fatty acids and triacylglycerols and by Krisnangkura et al.[9] for saturated fatty acids and esters. As one can see, the proposed equation gave lower deviations for fatty esters and triacylglycerols as well as allowed the prediction of viscosities for an extended range of compounds. It is of note that the model developed by Rabelo et al.[5] had two different groups of parameters, one for fatty acids and other for triacylglycerols while our model uses one set of parameters for the whole data bank (i.e., it is more general). The same fact occurred for the models of Krisnangkura et al.,[9] who adjusted one equation for fatty acids and two equations for fatty esters, one specific to short-chain compounds and the other to long-chain compounds.

Figure 1a brings a comparison of experimental and predicted dynamic viscosity data for some saturated fatty acids, while Figure 1b shows the agreement achieved for unsaturated triacylglycerols. As expected, the viscosities decreased exponentially with increasing temperature, which is in accordance with the classical Andrade equation analogous to the Arrhenius law. As one can see, this variation increased with chain length and molecular weight (from C10 to C18, and from triolein to trilinolenin).

It is noteworthy that the model outlined in eqs 2 to 6 is capable of predicting also the viscosity of mixed triacylglycerols, for which few experimental data can be found in the literature. Although Noor Azian et al.[6] measured viscosities of mixed triacylglycerols, the numerical values were not given in their paper, and we were not able to test the predictive capacity of our model. Noor Azian et al.[6] reported ARD values, between their experimental data and the estimated results using their estimation method, that varied from 2.83 % to 6.14 % for four mixed triacylglycerols. It should be mentioned that for simple

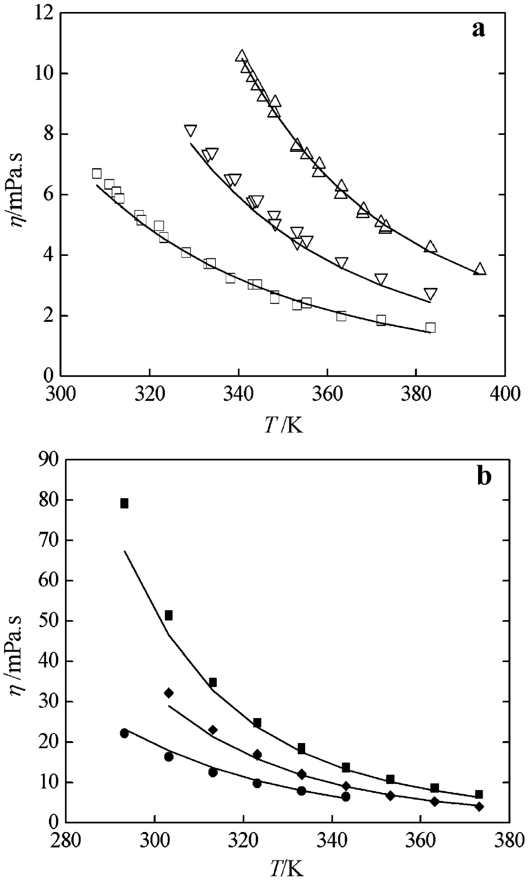

Figure 1. Comparative dynamic viscosities of fatty compounds: □, capric acid; ▽, myristic acid; Δ, stearic acid; ■, triolein; ◆, trilinolein; ●, trilinolenin. Calculated values by using eqs 2 to 6 are plotted as solid lines. (a) Saturated fatty acids. (b) Unsaturated triacylglycerols.

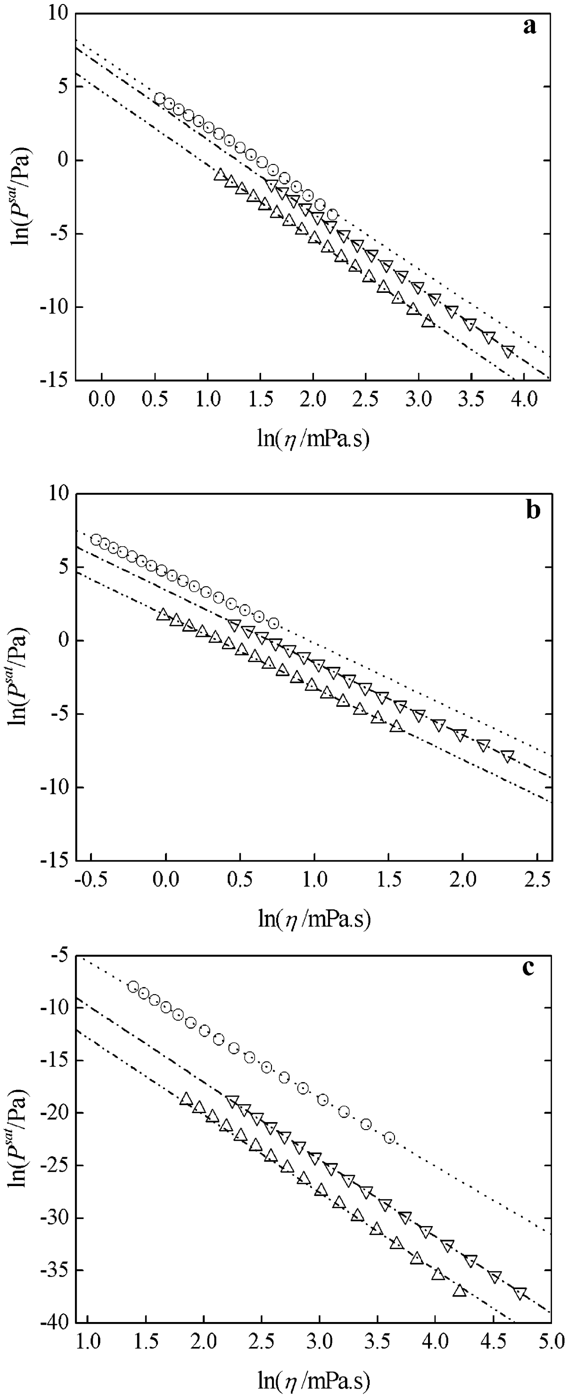

Figure 2. Linear relationship between predicted values of ln (P^{sat}/Pa), using the model of Ceriani and Meirelles,[11] and of ln(η/cP) using eqs 2 to 6: ○, capric acid, caprate methyl ester, and tricaprin; ▽, stearic acid, stearate methyl ester, and tristearin; Δ, linoleic acid, linoleate methyl ester, and triolein. Lines represent linear correlations adjusted to predicted values, whose coefficients are shown in Table 7. (a) Fatty acids. (b) Fatty esters. (c) Triacylglycerols.

triacylglycerols (not mixed), our model gave an ARD of 4.85 %.

Ceriani and Meirelles[11] worked with a data bank of 1220 points of vapor pressure distributed in five different classes of fatty compounds: 528 points for acids, 307 points for esters, 332 points for alcohols, 47 points for triacylglycerols, and 6 points for monoacylglycerols. Their equation has been used for the prediction of the vapor−liquid equilibria for fatty systems with success in the computational simulation of processes of the oil industry.[1,11] In order to further validate the model discussed in the present work, we tried to correlate some predicted values of dynamic viscosity with estimated values of vapor pressure calculated with the model of Ceriani and Meirelles.[11] In Figure 2, the linear dependence between the natural logarithm of dynamic viscosity (ln η) and the natural logarithm of vapor pressure (ln P^{sat}), assumed by Sastri and Rao,[12] is demonstrated for some fatty compounds by plotting predicted values of ln P^{sat} against predicted values of ln η for selected compounds at temperatures from 20 °C up to 100 °C. The lines in Figure 2 represent the linear correlations adjusted to these predicted values. The corresponding coefficients of these linear relations are shown in Table 7. As one can see, the predictive models for vapor pressure[11] and dynamic viscosity (this work) are in agreement with the assumption of Sastri and Rao.[12] We believe that these results are a good indicative that eqs 2 to 6 can be also used as a tool to estimate with good accuracy the viscosity of fatty compounds.

Table 7. Linear Coefficients for the Correlation of ln(P^{sat}/Pa) with ln(η/mPa·s)[a]

compound	c	d	R^2
capric acid	7.0127	−4.7967	0.9979
stearic acid	6.4181	−5.1432	0.99998
linoleic acid	4.6874	−5.0168	0.9992
caprate methyl ester	4.6247	−4.7989	0.99996
stearic methyl ester	3.4399	−4.9186	0.9997
linoleate methyl ester	1.7238	−4.9048	0.9994
tricaprin	0.9344	−6.4964	0.9997
tristearin	−2.4052	−7.3364	0.99995
triolein	−5.4660	−7.3658	0.9997

[a] Linear equation: $\ln(P^{sat}/\text{Pa}) = c + d \ln(\eta/\text{mPa·s})$ adjusted for temperatures over 20 °C up to 100 °C.

To finalize this work, a simple method of calculation is also proposed to predict the dynamic viscosity of vegetable oils as an extended applicability of our model. Considering that vegetable oil viscosity depends on fatty acid composition,[8,10] it was first necessary to compute an equivalent fatty acid (eqFA) to represent it, and then an equivalent triacylglycerol (eqTAG) that would represent the entire oil. An equivalent triacylglycerol could be sketched as

$$\begin{array}{lcl} CH_2-\text{COO}-\text{R}_{ll'} & & \text{CH}_2-\text{COO}-(\text{CH}_2)_l-(\text{CH}{=}\text{CH})_{l'}-\text{CH}_3 \\ | & & | \\ \text{CH}-\text{COO}-\text{R}_{mm'} & = & \text{CH}-\text{COO}-(\text{CH}_2)_m-(\text{CH}{=}\text{CH})_{m'}-\text{CH}_3 \\ | & & | \\ \text{CH}_2-\text{COO}-\text{R}_{nn'} & & \text{CH}_2-\text{COO}-(\text{CH}_2)_n-(\text{CH}{=}\text{CH})_{n'}-\text{CH}_3 \end{array} \tag{9}$$

where l, l', m, m', and n, n' are integers, and $\text{R}_{ll'}$, $\text{R}_{mm'}$, and $\text{R}_{nn'}$ stand for three different fatty acids.

Following the group contribution concept, η_{eqTAG} could be computed as the sum of the contributions, [η], of groups CH_3, CH_2, CH═, COO, and $\text{CH}_2-\text{CH}-\text{CH}_2$, explicitly:

$$\eta_{\text{eqTAG}} = [\eta]_{\text{CH}_2-\text{CH}-\text{CH}_2} + 3[\eta]_{\text{COO}} + 3[\eta]_{\text{CH}_3} + (l + m + n)[\eta]_{\text{CH}_2} + 2(l' + m' + n')[\eta]_{\text{CH}=} \tag{10}$$

which, in terms of an equivalent fatty acid that represents fatty acids ll', mm', and nn', becomes

$$\eta_{\text{eqTAG}} = [\eta]_{\text{CH}_2-\text{CH}-\text{CH}_2} + 3[\eta]_{\text{COO}} - 3[\eta]_{\text{COOH}} + 3\eta_{\text{eqFA}} \tag{11}$$

Assuming that

$$\eta_{\text{eqFA}} = [\eta]_{\text{CH}_3} + p[\eta]_{\text{CH}_2} + 2p'[\eta]_{\text{CH}=} + [\eta]_{\text{COOH}} \tag{12}$$

Table 8. ARD for Viscosities of Vegetable Oils

						ARD			
								ref 8[d]	
oil	ref	MUFA[a]	PUFA[b]	p	p'	this work	ref 5[c]	monounsaturated	polyunsaturated
almond	8	65.64	25.52	14	1	15.5		16.1	10.8
canola/ rapeseed	5	61.47	29.49	13	1	6.8	9.6	5.9	10.0
	8	52.98	35.49	13	1	17.1		17.8	10.0
	10	65.20	29.30	13	1	9.1		6.2	10.9
coconut	4	5.00	1.00	10	0	3.4	1.6	19.9	23.3
corn	4	21.40	64.30	13	1	5.7	10.1	20.7	19.1
	8	25.60	59.47	13	1	8.1		20.7	15.4
	10	33.50	51.00	13	1	2.8		14.2	18.1
crambe	4	77.80	17.00	16	1	5.5		23.8	27.0
grapeseed	8	18.58	70.14	16	2	28.6		27.7	10.0
hazelnut	8	77.63	13.45	14	1	11.3		14.1	12.1
milkweed	4	41.60	50.00	13	1	5.7		13.1	16.0
olive	8	76.06	7.06	14	1	12.1		15.5	13.3
	10	71.30	12.70	14	1	5.9		9.3	5.6
peanut	8	56.66	28.79	14	1	11.6		15.5	13.3
rice	10	40.80	40.10	13	1	22.0		23.7	9.8
safflower	8	13.52	78.20	13	2	19.2		24.0	21.4
soybean	4	25.40	58.00	13	1	5.8		19.4	17.2
	8	22.41	61.35	13	2	24.1		22.5	14.0
	10	24.30	60.00	13	1	2.9		15.3	18.9
sesame	8	36.07	52.50	13	1	14.6		21.0	11.8
sunflower	8	52.53	39.32	13	1	14.9		15.7	11.9
	10	22.80	65.20	13	2	9.0		17.0	21.5
walnut	8	15.71	72.70	13	2	15.6		23.5	24.9

[a] MUFA, monounsaturated fatty acid level. [b] PUFA, polyunsaturated fatty acid level. [c] Values reported by Rabelo et al.[5] [d] Values obtained by using the equations of Fasina et al.[8]

the dynamic viscosity of the oil could be calculated considering the following equation:

$$\eta_{\mathrm{eqTAG}} = [\eta]_{\mathrm{CH_2-CH-CH_2}} + 3[\eta]_{\mathrm{COO}} + 3[\eta]_{\mathrm{CH_3}} + 3p[\eta]_{\mathrm{CH_2}} + 6\cdot p'\cdot[\eta]_{\mathrm{CH=}} \quad (13)$$

where $[\eta]$ is the contribution of a group to dynamic viscosity of a compound.

To calculate p, the number of CH_2 group in the equivalent fatty acid and p', the number of CH═CH group in the equivalent fatty acid, the fatty acid composition of the oil is used (see Appendix B for an example of calculation):

$$p = \sum_j x_j(\mathrm{NC}_j - 2 - 2\mathrm{ND}_j) \quad (14)$$

$$p' = \sum_j x_j ND_j \quad (15)$$

where NC is the number of carbons and ND is the number of double bounds in the fatty acid of type j. Note that p and p' are necessarily integers to have a physical meaning. In this way, the values calculated with eqs 14 and 15 should be rounded to the closest integer.

The methodology outlined in eqs 9 to 15 was tested by predicting some of the viscosity data determined by Noureddini et al.,[4] Rabelo et al.,[5] Fasina et al.,[8] and Santos et al.[10] Rabelo et al.[5] gave the complete fatty acid composition of canola oil, which is used in Appendix B. The other authors gave the composition of vegetable oils in terms of saturated, monounsaturated, and polyunsaturated fatty acids. Combining this information and the detailed fatty acid composition given by Firestone,[39] we were capable of estimating one fatty acid composition for each oil. In the total, 16 types of oils were studied; for 5 types, experimental data were obtained for more than one author, each one corresponding to a different fatty acid composition. This fact occurred for canola oil;[5,8,10] corn oil;[4,8,10] olive, sunflower, and soybean oils.[8,10] In total, 156 experimental values of dynamic viscosities were predicted for 24 different fatty acid compositions of the 16 types of oils. Table 8 presents the ARD values together with the calculated values of p and p', after rounding them, as mentioned above in eqs 14 and 15. For comparison purposes, Table 8 also shows the ARD values obtained by using the mathematical relationships for viscosity prediction developed by Fasina et al.:[8] one based in the monounsaturated fatty acid content and the other based in the polyunsaturated fatty acid content. As one can see, for 14 fatty acid compositions (58.3 %) our methodology generated lower ARD values in comparison to the equations of Fasina et al.[8] Among all 24 fatty acid compositions, only one, from Rabelo et al.,[5] was not estimated because the authors informed the complete fatty acid composition. Consequently, p and p' values were more accurately calculated. In this case, our model gave a ARD value (6.84 %) lower than the one obtained by Rabelo et al.[5] (9.60 %) using the UNIMOD, an UNIFAC-based model, to predict the viscosity of canola oil as mixture of triacylglycerols, which is certainly a much more complicated procedure of calculation.

Conclusion

A group contribution method is presented for predicting dynamic/kinematic viscosity of major fatty compounds found in the vegetable oil industry as a function of temperature. A calculation procedure was developed to estimate the viscosity of vegetable oils with accuracy sufficient for engineering applications. In general, the ARD values were at least in the same range of other methods presented in the literature, besides being more general. The predictive tool developed in this work provides a good first guess for the viscosity of fatty compounds, especially for the cases where no published data are available.

Appendix A: Calculation of Dynamic Viscosity of Methyl Oleate Ester at 313.15 K

Methyl oleate ester has the following structure:

$$\mathrm{CH_3{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}COO{-}}\mathbf{CH_3}$$

where the boldfaced chain comes from the alcohol. Thus, according to the group contribution method described above, the group count is as follows:

CH_3	2
CH_2	14
CH	2
COO	1

$N_c = 19$; $N_{cs} = 1$; M_i =296.49 g/gmol. From eq 2, using the adjusted parameters from Table 5: $\ln \eta(\text{mPa}\cdot\text{s}) = \{[2(-0.2579) + 14(-0.13) + 2(49.8378) + 1(-828.4)] + 296.49[2(4.23\cdot 10^{-4}) + 14(1.8\cdot 10^{-5}) + 2(3.07\cdot 10^{-4}) + 1(1.0924)]\} + \{[2(210.6) + 14(70.688) + 2(-1759.1) + 1(25192.6)] + 296.49[2(-4.66\cdot 10^{-2}) + 14(-1.75\cdot 10^{-2}) + 2(0.1681) + 1(-32.5558)]\}/313.15 - \{[2(0.2275) + 14(-2.71\cdot 10^{-2}) + 2(8.1803) + 1(-140.8)] + 296.49[2(-3.7\cdot 10^{-4}) + 14(3.8\cdot 10^{-5}) + 2(2.47\cdot 10^{-4}) + 1(0.1852)]\} \ln(313.15) - \{[2(-3.89\cdot 10^{-3}) + 14(4.49\cdot 10^{-4}) + 2(-8.67\cdot 10^{-3}) + 1(0.2041)] + 296.49[2(6.24\cdot 10^{-6}) + 14(-6.36\cdot 10^{-7}) + 2(-2.06\cdot 10^{-6}) + 1(-2.6324\cdot 10^{-4})]\}\cdot 313.15 + (-5291.2 + 19\cdot 354)[-0.3157 + 9.324/313.15 + 5.40\cdot 10^{-2} \ln(313.15) - 7.812\cdot 10^{-5}\cdot 313.15] + (0.1984 - 5.12\cdot 10^{-2}\cdot 1)$. $\eta(313.15\ \text{K}) = 4.0317$ mPa·s. The experimental value is 3.9389 mPa·s, corresponding to an ARD of 2.4 %.

Appendix B: Calculation of the Equivalent Fatty Acid of Canola Oil

Fatty acid composition (mole fraction) of canola oil analyzed by Rabelo et al.:[5] 0.1 % of myristic acid (NC = 14, ND = 0), 7.4 % of palmitic acid (NC = 16, ND = 0), 0.4 % of palmitoleic acid (NC = 16, ND = 1), 1.8 % of stearic acid (NC = 18, ND = 0), 60.4 % of oleic acid (NC = 18, ND = 1), 21.0 % of linoleic acid (NC = 18, ND = 2), 8.5 % of linolenic acid (NC = 18, ND = 3), 0.3 % of arachidic acid (NC = 20, ND = 0), 0.1 % of erucic acid (NC = 22, ND = 1).

From eqs 14 and 15:

$$\begin{aligned} p = \frac{1}{100}[&0.1(14 - 2 - 2\cdot 0) + 7.4(16 - 2 - 2\cdot 0) + \\ &0.4(16 - 2 - 2\cdot 1) + 1.8(18 - 2 - 2\cdot 0) + \\ &60.4(18 - 2 - 2\cdot 1) + 21.0(18 - 2 - 2\cdot 2) + \\ &8.5(18 - 2 - 2\cdot 3) + 0.3(20 - 2 - 2\cdot 0) + \\ &0.1(22 - 2 - 2\cdot 1)] = 13.3 \Rightarrow p = 13 \text{ (rounded value)} \end{aligned}$$

$$\begin{aligned} p' = \frac{1}{100}[&0.1\cdot 0 + 7.4\cdot 0 + 0.4\cdot 1 + 1.8\cdot 0 + 60.4\cdot 1 + 21.0\cdot 2 + \\ &8.5\cdot 3 + 0.3\cdot 0 + 0.1\cdot 1] = 1.3 \Rightarrow p' = 1 \text{ (rounded value)} \end{aligned}$$

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