Viscosities of Fatty Mixtures: Experimental Data and Prediction

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Viscosity data of fatty compounds and their mixtures are important for designing equipment for the oil industry, including edible, as some vegetable oils, and nonedible purposes, as biodiesel. To expand the data bank gathered from the literature, the present work reports viscosity data of fatty mixtures found in the oil and fat industry, such as mixtures of fatty acids, methyl esters, and triacylglycerols, over a large range of temperatures. Viscosities of these fatty mixtures as well as viscosity data taken from the literature were predicted by known methods, such as the modified Kay's rule, the Kendall and Moore model, and GC-UNIMOD. In general, the three models presented a good representation of the kinematic viscosity of fatty mixtures. For the majority of cases (or 77.1 %), the average relative deviations (ARD) obtained were not higher than 10 %.

Introduction

Viscosity information for fatty compounds and their mixtures is essential for the design of heat-transfer equipment, process piping, reactors, stripping columns, deodorizers, liquid−liquid extractors, distillation columns, crystallization equipment, and other units found in the oil and fat industry. Because viscosity strongly affects flow behavior, this transport property must be considered in engineering design, being also an input for process simulation and optimization.[1−5]

Viscosity data for fatty compounds [such as fatty acids (FAs), triacylglycerols (TAGs), and fatty esters], their mixtures, and vegetable oils are reported in the literature as a function of temperature.[2−4,6−24] The majority of these works developed specific equations for viscosity estimation of a specific compound or a class of compounds.[3,4,6,8,9] Recently, Ceriani et al.,[25] gathering a data bank of 763 experimental viscosity values,[2−4,6,7,11−24,26−28] used the widely known concept of group contribution to develop a user-friendly method for the prediction of the dynamic viscosity of a variety of fatty compounds, with an accuracy adequate for engineering applications. In this concept, a compound is considered as a solution of groups and its properties are the sum of the contributions of each group.[25] This idea can be applied also to mixtures of compounds, and some works in the literature put forth equations based on the group contribution concept for viscosity prediction of mixtures.[4,29−32] It is interesting to note that all of these equations require kinematic viscosities of the pure compounds that compose the mixtures as an input. It should be emphasized that this information can be a problem especially in the case of multicomponent mixtures, such as fats and oils, for which experimental data are not available for all pure components. Note also that, in some cases, the compound (saturated triacylglycerol, as an example) is solid at a given temperature when it is pure liquid as a component of the oil or fat.

To expand the available viscosity data bank in the literature, the present work reports viscosity data for 10 different mixtures, involving fatty acids, triacylglycerols, methyl esters, and vegetable oils, as a function of temperature. Because it is not viable to measure viscosity data at all conditions of interest, methods for its estimation are of great practical interest. With this in consideration, this work also tested three models from the literature for predicting viscosities of fatty mixtures and compared the results with experimental data: Kay's rule,[4] the Kendall and Monroe model,[31] and GC-UNIMOD.[32] The necessary viscosities of pure fatty compounds were also predicted by a generalized equation obtained in our previous work.[25]

Experimental Section

Materials. All pure chemicals used in this work [capric acid, $C_{10}H_{20}O_2$, CAS Registry No. (CASRN) 334-48-5; oleic acid, $C_{18}H_{34}O_2$, CASRN 112-80-1; tricaprylin, $C_{27}H_{50}O_6$, CASRN 538-23-8; tripalmitin, $C_{51}H_{98}O_6$, CASRN 555-44-2; triolein, $C_{57}H_{104}O_6$, CASRN 122-32-7; methyl myristate, $C_{15}H_{30}O_2$, CASRN 124-10-7; methyl palmitate, $C_{17}H_{34}O_2$, CASRN 112-39-0; methyl oleate, $C_{19}H_{36}O_2$, CASRN 112-62-9] were obtained from Sigma (St. Louis, MO), except for linoleic acid ($C_{18}H_{32}O_2$, CASRN 60-33-3) and trilinolein ($C_{57}H_{98}O_6$, CASRN 537-40-6), which were purchased from Nu-Chek-Prep (Elysian, MN). All fatty compounds had high purity (> 99 %) and were used without further purification. Trilinolein was analyzed by gas chromatography of the fatty acid methyl esters according to the procedure described by Rabelo et al.[6] The chromatographic analyses confirmed its purity as higher than 99 %. For the other compounds, we relied on the information given by the suppliers.

Apparatus and Procedure. A set of kinematic viscosities (ν) of eight different mixtures containing fatty acids and triacylglycerols were measured over a large range of temperature in glass capillary kinematic viscometers (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

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instrument constant. An electronic timer accurate to 0.01 s was used for measuring the efflux time. For this set of experimental data, the standard deviations observed were not higher than $0.097 \cdot 10^{-6}\ \mathrm{m^2 \cdot s^{-1}}$ and the highest coefficient of variation (calculated by the ratio of the standard deviation to the mean viscosity value) was 1.60 %, suggesting a good reproducibility for the measured efflux times. The Cannon Fenske viscometers were calibrated on the basis of the value of water viscosity at 20 °C ($1.0038 \cdot 10^{-6}\ \mathrm{m^2 \cdot s^{-1}}$) and credited by the company. An additional set of kinematic viscosity data was obtained for a complex system formed by canola oil (Purilev brand) and commercial grade oleic acid (Riedel de-Häen). The fatty acid composition of the canola oil and of the commercial grade oleic acid can be found by referring to Rabelo et al.[6] Six values of dynamic viscosities (η) for a mixture containing methyl fatty esters were also determined in an automatic viscometer 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 to 70 °C at 10 °C intervals. 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 viscometer were not higher than 0.023 mPa·s, and the coefficient of variation ranged from 0.31 % to 0.45 %, indicating a very good reproducibility of the experimental measurements. The measuring system calibration was made periodically, using distilled water, in accordance with the user instructions. All of the fatty systems were prepared on a mass basis using an analytical balance (ADAM, model AAA 250 L) with an uncertainty of less than 0.0001 g.

Prediction

The experimental viscosity data were utilized for validating three selected viscosity predictive models: the modified Kay's rule, the Kendall and Moore model, and the GC-UNIMOD. In the modified Kay's rule, reported by Azian et al.,[4] the logarithm of the fatty mixture viscosity, ν_{mix}, is a function of the logarithmic viscosities of the individual fatty compounds. Eiteman and Goodrum[31] showed that kinematic viscosities of triacylglycerol mixtures could be calculated by the empirical model proposed by Kendal and Moore.[33] The modified Kay's rule and the Kendall and Moore model are presented in eqs 1 and 2, respectively

$$\ln(\nu_{\mathrm{mix}}) = \sum_{i=1}^{n} x_i \cdot \ln(\nu_i) \tag{1}$$

$$(\nu_{\mathrm{mix}})^{1/3} = \sum_{i=1}^{n} [x_i \cdot (\nu_i)^{1/3}] \tag{2}$$

where x_i is the mole fraction of component i, ν_i is the kinematic viscosity of the pure fatty compound, and n is the number of components in the mixture.

On the basis of the group contribution concept, Cao et al.[32] developed the group contribution thermodynamics–viscosity model (GC-UNIMOD) for predicting the viscosities of multicomponent mixtures. In a similar way to the UNIFAC method,[34] proposed for phase equilibrium prediction, the GC-UNIMOD equation takes into account two contributions for the mixture viscosity (ν_{mix}), *combinatorial* and *residual parts*, as follows:

$$\ln(\nu_{\mathrm{mix}}) = \sum_{i=1}^{n} [\xi_i^{\mathrm{C}} + \xi_i^{\mathrm{R}}] \tag{3}$$

The combinatorial part, ξ_i^{C} (see eqs 4, 5, and 6), is related to the differences in size of the molecules present in the mixture, so that only properties for pure substances are considered in this contribution.

$$\xi_i^{\mathrm{C}} = \phi_i \cdot \ln\left(\nu_i \cdot \frac{M_i}{M}\right) + 2\phi_i \cdot \ln\left(\frac{x_i}{\phi_i}\right) \tag{4}$$

$$r_i = \sum_{\substack{\text{all} \\ \text{groups } k}} \nu_k^{(i)} \cdot R_k \tag{5}$$

$$\phi_i = \frac{x_i \cdot r_i}{\sum_{j=1}^{n} x_j \cdot r_j} \tag{6}$$

where M_i, M, r_i, R_k, $\nu_k^{(i)}$, and ϕ_i are the molecular weight of component i, the molecular weight of the fatty mixture, the volume parameter for molecule i, the volume parameter of group k, the number of groups of type k in molecule i, and the volume fraction of component i, respectively. The values for R_k, were taken from Fredenslund and Sorensen.[35] Viscosities of pure fatty compounds, ν_i, also necessary in eqs 1 and 2, were estimated by the correlation proposed in our previous work.[25]

The residual part, ξ_i^{R} (eqs 7 to 14), takes into consideration the energy of interaction between the different groups present in the mixture.

$$\xi_i^{\mathrm{R}} = \sum_{\substack{\text{all} \\ \text{groups } k}} \nu_k^{(i)} \cdot [\Xi_{ki} - \Xi_{ki}^{(i)}] \tag{7}$$

$$\Xi_{mi} = -\frac{Q_m}{R_m} \cdot N_{mi}^{\mathrm{vis}} \cdot \phi_i \cdot \sum_{\substack{\text{all} \\ \text{groups } k}} \theta_{km} \cdot \ln(\Psi_{km}) \tag{8}$$

Ξ_{ki} and $\Xi_{ki}^{(i)}$ are, respectively, the group residual viscosity of group k for component i in the mixture and the group residual viscosity of group k for component i in a reference solution that contains only molecules of type i. The last term, $\Xi_{ki}^{(i)}$, is necessary to attain the normalization that the viscosity for the mixture, ν_{mix}, becomes the viscosity of the pure compound i as $x_i \rightarrow 1$. Both terms, Ξ_{ki} and $\Xi_{ki}^{(i)}$, can be calculated by eq 8, in which the other terms are defined by the following set of expressions:

$$\Psi_{mn} = \exp(a_{mn}/T) \tag{9}$$

$$\theta_m = \frac{X_m \cdot Q_m}{\sum_{\substack{\text{all} \\ \text{groups } k}} X_k \cdot Q_k} \tag{10}$$

$$\theta_{mn} = \frac{\theta_m \cdot \Psi_{mn}}{\sum_{\substack{\text{all} \\ \text{groups } k}} \theta_k \cdot \Psi_{kn}} \tag{11}$$

$$X_m = \frac{\sum_i^n \nu_m^{(i)} \cdot x_i}{\sum_i^n \sum_{\substack{\text{all} \\ \text{groups } k}} \nu_k^{(i)} \cdot x_i} \tag{12}$$

$$q_i = \sum_{\substack{\text{all} \\ \text{groups } k}} \nu_k^{(i)} \cdot Q_k \tag{13}$$

$$N_{ki}^{\text{vis}} = Q_k \left(\frac{q_i - r_i}{2} - \frac{1 - r_i}{z} \right) \tag{14}$$

X_k, Q_k, θ_k, q_i, and z are the mole fraction of group k, the surface area parameter for group k, the area fraction of group k, the measure of the molecular surface area of component i, and the coordination number (equal to 10), respectively. The term a_{mn} is the interaction parameter between groups m and n, being that there are two of them ($a_{mn} \neq a_{nm}$) for each pair of groups. For the fatty compounds used in this work, the following groups should be considered: CH_2 (with subgroups CH, CH_2, and CH_3), CH=CH (double bond), COOH (acid), and CH_2COO (ester). As suggested by Rabelo et al.,[6] the interaction parameters for this work were taken from Frendenslund and Sorensen.[35]

Looking at eqs 1 to 14, it should be noted that the modified Kay's rule and the Kendall and Moore model are much easier to use than the GC-UNIMOD, but the last one is supposed to be capable of describing differences between molecules in a mixture in a better way, given that it considers differences in size of the molecules and the interaction between the different groups in the mixture.

After a careful search of the literature, 211 experimental values of dynamic and kinematic viscosities of 25 different mixtures were found (see refs 2, 6, 9, 17, and 30), as given in Table 1. In conjunction with the 84 experimental points measured specifically for this work, we came up with a data bank of 295 points. Some of the experimental data extracted from the literature (refs 17 and 30) and the measured data for methyl ester mixtures were given as dynamic viscosities (η) and had to be converted to kinematic viscosities (ν) by means of the equation

$$\nu = \frac{\eta}{\rho} \tag{15}$$

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.,[36] whose high-quality accuracy has been demonstrated by Rabelo et al.[6] for these two classes of fatty compounds. For fatty esters, linear correlations for densities and temperatures were adjusted in our previous work[25] using data reported elsewhere.[21]

Results

Table 2 presents the kinematic viscosities for the following binary mixtures: capric acid + oleic acid, oleic acid + triolein, oleic acid + trilinolein, linoleic acid + triolein, linoleic acid + trilinolein, and capric acid + tricaprylin. Tables 3 and 4 present kinematic viscosities for the mixtures capric acid + oleic acid + tricaprylin + tripalmitin and commercial grade oleic acid + canola oil, respectively. Note that the mixtures and their compositions were not selected arbitrarily, but aimed at determining the effects of some characteristics of the compounds on the viscosities of the mixtures, such as the presence (or the degree) of unsaturations, the molecular weight of the compounds, and the differences in the class of compounds. Dynamic viscosities for the ternary mixture composed of methyl myristate + methyl palmitate + methyl oleate are shown in Table 5.

Table 1. Experimental Viscosity Data Bank of Fatty Mixtures

fatty mixture	ref	*t* range °C	no. of exptl points
fatty acids[a]	2, 17	40 to 90	114
triacylglycerols[a]	2	70 to 90	51
fatty acids[b]	17	70 to 90	16
fatty acids + triacylglycerol[b]	6	30 to 90	7
fatty acids[c]	6, 17	45 to 90	14
methyl esters[d]	9, 30	25 to 50	9

[a] Binary mixture. [b] Ternary mixture. [c] Quaternary mixture. [d] Multicomponent mixture (with more than four compounds).

In Tables 2 to 5, it can be seen that an increase in the temperature reduces the viscosity of the fatty mixtures. In fact, such behavior was already expected, given that higher temperatures enhance the average kinetic energy of molecules, reducing (on average) the time interval that the molecules remain next to the others. Thus, attractive intermolecular forces become less effective, decreasing the viscosity. Table 2 also allows us to conclude that viscosity is related to the unsaturation of the mixture. Note that for the mixtures of capric acid (1) + oleic acid (2), viscosity values always increased when the mole fraction of compound 1 (saturated fatty acid) was reduced (from $x_1 = 0.6211$ to 0.3533). On the other hand, viscosity data measured for mixtures involving one fatty acid and one triacylglycerol showed that changing the fatty acid (compound 1) or the triacylglycerol (compound 2) of the mixtures, from oleic acid to linoleic acid or from triolein to trilinolein, increasing the unsaturation of the mixture, generated a decrease in its viscosity. Looking at the data obtained for the mixtures of capric acid (1) and tricaprylin (2), one can see that the viscosity decreased when the mole fraction of the compound with lower carbon chain and, consequently, lower molecular weight (capric acid) increased. The same observation rises from the results for the mixtures involving oleic acid (1) and triolein (2) or trilinolein (2) and linoleic acid (1) and triolein (2) or trilinolein (2). Changing the fatty acid (compound 1) or the triacylglycerol (compound 2) of the mixtures, from oleic acid to linoleic acid or from triolein to trilinolein, decreasing the molecular weight of the mixture, generated a decrease in its viscosity.

The predictive capability of the three models (eqs 1, 2, and 3) was investigated by calculating the average relative deviation (ARD), according to eq 16. The ADR values for the viscosity data measured in this work and for the ones taken from the literature are shown in Table 6 for each model.

$$\text{ARD} = 100 \cdot \frac{\sum_n \frac{|\nu_{\text{exptl}} - \nu_{\text{calcd}}|}{\nu_{\text{exptl}}}}{N} \tag{16}$$

In eq 16, N is the number of experimental data considered, exptl refers to experimental data, and calcd represents the predicted viscosity values.

According to the ARD values shown in Table 6, the three predictive models presented similar performances for the majority of mixtures. The worse values (> 10 %) occurred

Table 2. Experimental Kinematic Viscosities ν of Binary Fatty Mixtures as a Function of Temperature

	$\nu/10^{-6}$ m^2·s^{-1}								
	capric acid (1) + oleic acid (2)		oleic acid (1) + triolein (2)	oleic acid (1) + trilinolein (2)	linoleic acid (1) + triolein (2)	linoleic acid (1) + trilinolein (2)	capric acid (1) + tricaprylin (2)		
t/°C	$x_1 = 0.6211$	$x_1 = 0.3533$	$x_1 = 0.7580$	$x_1 = 0.7564$	$x_1 = 0.7576$	$x_1 = 0.7536$	$x_1 = 0.4763$	$x_1 = 0.7423$	$x_1 = 0.8902$
20			67.77	41.39					
30	14.51	19.90	44.87	28.18	29.60	25.52	14.77	12.91	8.98
40	10.75	14.46	31.30	20.65	21.25	18.50	10.54	9.46	7.83
50	8.25	10.94	22.78	14.78	15.88	13.15	7.89	7.16	6.09
60	6.39	8.52	16.18	11.48	12.29	9.96	6.15	5.66	4.90
70	5.17	6.83	12.61	9.32	9.76	7.98	5.12	4.57	3.99
80	4.27	5.63	10.01	7.62	7.91	6.83	4.13	3.88	3.24
90	3.36	4.69	8.22	6.38	6.52	5.69	3.53	3.18	2.58

Table 3. Experimental Kinematic Viscosities ν of a Quaternary Fatty Mixture as a Function of Temperature

	$\nu/10^{-6}$ m^2·s^{-1}
t/°C	capric acid (1) + oleic acid (2) + tricaprylin (3) + tripalmitin (4) $x_1 = 0.4568$; $x_2 = 0.2786$; $x_3 = 0.1674$
70	7.37
75	6.64
80	6.00
85	5.52
90	5.12

Table 4. Experimental Kinematic Viscosities ν of a Multicomponent Fatty Mixture as a Function of Temperature

	$\nu/10^{-6}$ m^2·s^{-1}
t/°C	commercial grade oleic acid[a] + canola oil[b]
20	49.64
30	33.44
40	23.77
50	20.58
60	15.52
70	12.12
80	9.70
90	7.92

[a] Commercial oleic acid composition was taken by ref 6: myristic ($x_1 = 0.0056$), palmitic ($x_2 = 0.0128$), palmitoleic ($x_3 = 0.0184$), stearic ($x_4 = 0.0037$), oleic ($x_5 = 0.1935$), linoleic ($x_6 = 0.0106$), and linolenic ($x_7 = 0.0011$). [b] Canola oil ($x_9 = 0.7543$) was represented by an equivalent triacylglycerol of molecular weight equal to 829.35, calculated according to methodology described in our previous work.[25]

Table 5. Experimental Dynamic Viscosities η of a Ternary Methyl Esters Mixture as a Function of Temperature

	η/mPa·s
t/°C	methyl myristate (1) + methyl palmitate (2) + methyl oleate (3) $x_1 = 0.3657$; $x_2 = 0.3324$
20	5.69
30	4.41
40	3.41
50	2.78
60	2.32
70	1.97

always for complex mixtures composed by fatty acids (FA) and triacylglycerols (TAG), compounds with very different molecular weights. For the system of commercial grade oleic acid + canola oil, the ARD values of around 15 % can be considered satisfactory, because of the complexity and the large number of components involved in this mixture. A comparison of the predictions using the two simplest models, Kay' rule and the Kendall and Moore model, showed that the latter provided slightly better results for almost all kinds of systems studied. Kay's rule provided lower ARD values for only three of a total of four methyl esters mixtures (including the one measured in this work) and for the complex mixture composed by commercial oleic acid and canola oil.

In general, the three models presented a good representation of the kinematic viscosity of systems composed of a mixture of compounds of the same class. The lowest ARD values (<1 %) were obtained for the mixture of triolein + triestearin[2] and for the palm methyl ester mixture.[9,30] From a comparison of Kay's rule and the Kendall and Moore model with the GC-UNIMOD, it can be observed that the last one gave slightly better results for 22 mixtures or 71.9 % of the calculations. This fact is more evident for the mixtures of tricaprylin + tripalmitin,[2] capric acid + oleic acid + tricaprylin,[6] and pelargonic acid + capric acid + lauric acid + oleic acid.[6] It is important to note that GC-UNIMOD presented the highest ARD values for some mixtures of different classes of compounds, such as the binary mixtures of fatty acid + triacylglycerol. This could be an indication that, although GC-UNIMOD is a more elaborate model, it still presents some fragility in the prediction of the viscosities of complex fatty systems. To visualize this fact, Figure 1 brings the difference between experimental and predicted kinematic viscosity values ($\nu_{\text{exptl}} - \nu_{\text{calcd}}$) for the binary mixtures of oleic acid + trilinolein and capric acid + oleic acid, as a function of temperature, using the three models tested in this work. In contrast, for the ternary mixture of capric acid + oleic acid + tricaprylin and for the quaternary mixture of capric acid + oleic acid + tricaprylin + tripalmitin, GC-UNIMOD provided better predictions, presenting the lowest values of $\nu_{\text{exptl}} - \nu_{\text{calcd}}$, as can be seen in Figure 2.

Because the viscosity of the pure compounds of the fatty mixtures is an input for the three predictive methods tested in this work, poor estimations could be a consequence of the prediction method selected[25] for pure compounds. To clarify this question, we adjusted Antoine type equations (η vs T) for experimental data of oleic acid,[2,3,6,18,19,27] linoleic acid,[2,27] triolein,[2,4,27] and trilinolein[2,4,27] (R^2 of 0.9989, 0.9953, 0.9974, and 0.9996, and ARD of 1.9 %, 4.1 %, 2.1 %, and 1.0 %, respectively) and estimated the viscosity of the pure component as input to the predictive methods for the mixtures of oleic acid + triolein, oleic acid + trilinolein, linoleic acid + triolein, and linoleic acid + trilinolein. The corresponding coefficients of these linear equations are shown in Table 7. It should be noted that the group contribution model developed by Ceriani et al.[25] gave ARD values of 3.3 %, 10.0 %, 7.0 %, and 4.7 % for oleic acid, linoleic acid, triolein, and trilinolein, respectively.

The new ARD values obtained for viscosity predictions of the mixtures oleic acid + triolein, oleic acid + trilinolein, linoleic acid + triolein, and linoleic acid + trilinolein were, respectively, 24.90 %, 3.75 %, 20.01 %, and 15.59 %, respectively, using Kay's rule; 23.89 %, 3.85 %, 17.54 %, and 13.78 %, using the Kendall and Moore model; and 26.97 %, 11.62 %, 15.57 %, and 17.15 %, using the GC-UNIMOD.

Table 6. Average Relative Deviation (ARD) for Kinematic Viscosity of Fatty Mixtures [Fatty Acids (FAs) and Triacylglycerols (TAGS)]

fatty mixture	Kay's rule	Kendall and Moore	GC-UNIMOD
binary: FAs			
capric acid + oleic acid[a]	7.17	3.96	3.16
capric acid + lauric acid[b]	5.99	5.67	5.25
pelargonic acid + capric acid[b]	4.63	4.54	4.42
stearic acid + oleic acid[b]	2.55	2.32	2.50
lauric acid + myristic acid[b,c]	9.53	9.33	9.15
myristic acid + palmitic acid[b,c]	6.92	6.67	6.43
palmitic acid+ stearic acid[b,c]	3.79	3.56	3.34
lauric acid + palmitic acid[c]	7.30	6.48	6.33
lauric acid + stearic acid[c]	6.26	5.00	5.38
myristic acid + stearic acid[c]	5.47	4.92	4.79
binary: TAGs			
tricaprylin + tripalmitin[b]	10.25	6.49	1.01
tricaprylin + tristearin[b]	16.29	11.45	2.79
tripalmitin + tristearin[b]	0.78	0.79	0.82
triolein + tristearin[b]	4.31	3.80	4.49
binary: FA + TAG			
oleic acid + triolein[a]	25.44	24.66	27.83
oleic acid + trilinolein[a]	4.44	4.41	13.64
linoleic acid+ triolein[a]	17.07	15.11	15.04
linoleic acid + trilinolein[a]	11.28	10.75	16.40
capric acid + tricaprylin[a]	12.63	9.73	10.73
ternary: FAs			
lauric acid + myristic acid + palmitic acid[c]	7.63	6.66	5.56
lauric acid + myristic acid + stearic acid[c]	6.06	3.49	2.38
lauric acid + palmitic acid + stearic acid[c]	4.62	3.27	1.97
myristic acid + palmitic acid + stearic acid[c]	3.61	3.13	2.67
ternary: FAs + TAGs			
capric acid + oleic acid + tricaprylin[d]	9.79	11.13	3.11
quaternary: FAs			
pelargonic acid + capric acid + lauric acid + oleic acid[d]	7.02	4.48	0.89
lauric acid + myristic acid + palmitic acid + stearic acid[c]	5.80	4.38	3.41
quaternary: FAs + TAGs			
capric acid + oleic acid + tricaprylin + tripalmitin[a]	22.26	18.55	16.89
methyl esters			
methyl myristate + methyl palmitate + methyl oleate[a]	2.13	2.36	2.67
coconut oil methyl esters[e,f]	6.27	4.90	4.02
palm oil methyl esters[e,f]	0.85	0.90	0.80
soybean methyl esters[e]	2.16	2.45	2.05
commercial fatty acid + vegetable oil			
commercial grade oleic acid + canola oil[a]	16.23	17.79	15.14

[a] Experimental data measured in this work. [b] Data taken from ref 2. [c] Data taken from ref 17. [d] Data taken from ref 6. [e] Data taken from ref 30. [f] Data taken from ref 9.

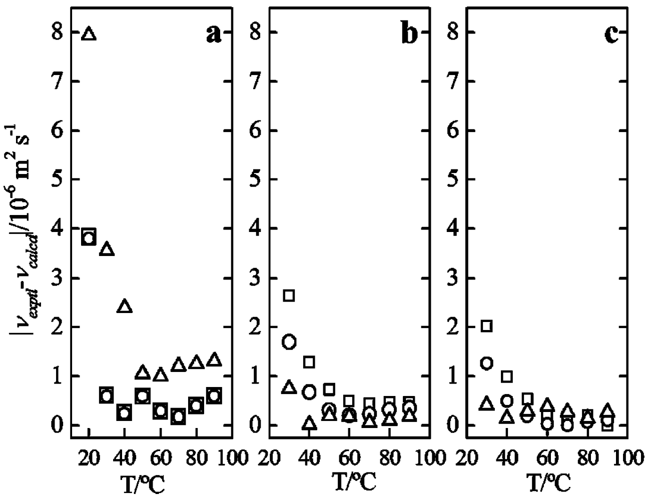

Figure 1. Difference between experimental and predicted kinematic viscosity of binary fatty mixtures: a, olein + trilinolein; b, capric acid + oleic acid, mass ratio 1:3; c, capric acid + oleic acid, mass ratio 1:1; □, Kay's rule; ○, Kendall and Moore model; △, UNIMOD.

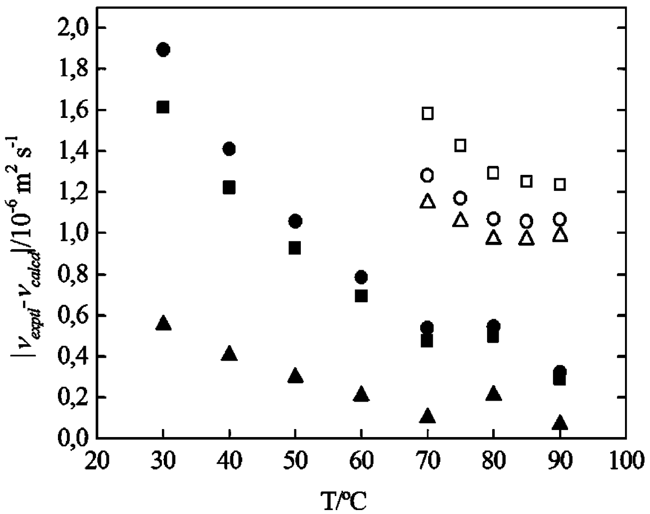

Figure 2. Difference between experimental and predicted kinematic viscosities of fatty mixtures: solid symbol, capric acid + oleic acid + tricaprylin;[6] open symbol, capric acid + oleic acid + tricaprylin + tripalmitin; ■/□, Kay's rule; ●/○, Kendall and Moore model; ▲/△, UNIMOD.

Table 7. Linear Coefficients for the Correlation of η versus T[a]

compound	t range/°C	a	b	c	R^2	ARD
oleic acid	20 to 110	−3.685	1320	162.5	0.9989	1.90
linoleic acid	30 to 90	−14.07	10450	592	0.9953	4.10
triolein	20 to 100	−1.963	824.4	110.1	0.9974	2.10
trilinolein	30 to 100	−12.49	7407	433.9	0.9996	1.00

[a] Linear equation: $\ln(\eta/\mathrm{mPa{\cdot}s}) = a + b/c + T/°\mathrm{C}$.

Comparing these results with ARD values shown in Table 6 for the same mixtures, it can be observed that the insertion of the new viscosities of pure components (estimated by the adjusted linear equations presented in Table 7) on the predictive methods slightly improved viscosity predictions of the two first mixtures. Note that, even for the systems in which prediction was worse, such differences were very small, indicating that the generalized equation developed by Ceriani et al.[25] had little effect on the high ARD values obtained.

For further analyses, we also tested the predictive capacity of GC-UNIMOD for the same mixtures of FA + TAG mentioned above, now excluding the residual term. Note that the combinatorial term takes into account the differences in size of the molecules (fatty acid and triacylglycerol) present in the mixture. Such calculations gave ARD values of 25.83 %, 13.02 %, 11.53 %, and 15.02 % for the mixtures of oleic acid + triolein, oleic acid + trilinolein, linoleic acid + triolein, and

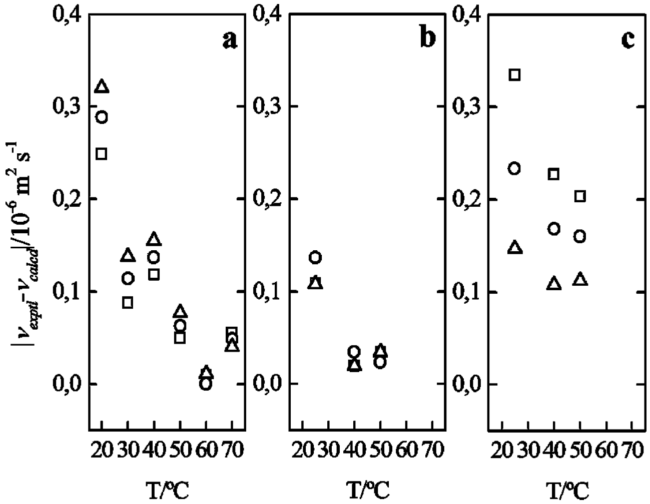

Figure 3. Difference between experimental and predicted kinematic viscosities of methyl esters mixtures: a, methyl myristate + methyl palmitate + methyl oleate; b, palm oil methyl esters;[9] □, Kay's rule; ○, Kendall and Moore model; △, Moore model; △, UNIMOD.

linoleic acid + trilinolein, respectively. In this case, the ARD values were lower than the ones shown in Table 6, but such improvement was not higher than 3.5 % (mixture of linoleic acid + triolein). Similar results were found by Rabelo et al.[6] for binary, ternary, and quaternary mixtures of fatty acids and/or triacylglycerols and also vegetable oils (treated as multicomponent mixtures).

For the three mixtures of methyl esters investigated in this work, the ARD values given by GC-UNIMOD were always the lowest ones, but the other two methods also gave good predictions. Figure 3 provides a comparison of experimental and predicted dynamic viscosities data of the methyl esters mixtures studied. Such data are of great interest due to their presence in biodiesel, and the good results obtained by the predictions show that the three models tested in this work can be useful tools for biofuels production.

Conclusion

This work presents viscosity experimental data of several fatty mixtures as a function of temperature. In conjunction with a data bank obtained from the literature, those data were predicted by known group contribution methods: Kay's rule, the Kendall and Moore model, and GC-UNIMOD. In most cases, good agreement between experimental and calculated values was obtained. These indicate that the three models tested in this work can be applied as a first approximation for the viscosity estimation for fatty mixtures, including fatty acids, triacylglycerols, and methyl esters, being useful tools for the oil industry and for biodiesel producers.

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