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Predicting the Viscosity of Ester Biolubricants by the Functional Groups of Their Compounds Using a Sensitivity Parameter Model

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Abstract: Oleic-based trimethylolpropane (TMP) ester mixtures can be produced via esterification reaction between oleic acid (OA) and TMP, presenting important application as biobased lubricants. In this study, a new mathematical model that allows us to predict kinematic viscosities of such mixtures based on kinematic viscosity sensitivity parameters from product functional groups was developed, and it was also checked by fitting the experimental kinematic viscosities of the biolubricant products at 40 and 100 °C. This way, it is possible to predict kinematic viscosities and the viscosity index of these biolubricant mixtures and even pure TMP-esters without the availability to measure purified compounds. Moreover, the influence on the viscosity properties of the different chemical functional groups can be assessed with this physical model. So, the deleterious or beneficial effects of intermediate products and unreacted OA on the biolubricant viscosity index (VI) were quantified, showing that Trioletate and also Dioleate TMP-ester and their mixtures meet very interesting lubricant properties (VI up to 218), whereas the Monooleate TMP-ester and the unreacted OA decrease dramatically the viscosity properties. We believe that these findings can pave the way for the improvement and development of bio-based lubricant formulations towards effective industrial development.

Keywords: viscosity index; viscosity modeling; sensitivity parameters; kinematic viscosity; functional groups; biolubricant; TMP-oleates; TMP-ester

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1. Introduction

Nowadays, the production of environmentally friendly materials and processes is one of the main focuses of the scientific community. In particular, the search for novel lubricants that not only reduce friction and avoid corrosion but also decrease the environmental impact and pollution caused by their widespread use remains a challenge that needs to be explored in depth [1]. Thus, the introduction of biodegradable lubricants, obtained from natural sources, which are easily biodegradable, greener, and non-toxic, could mitigate the vast environmental impact driven by oil-based lubricants [1,2]. Among those biolubricants, vegetable oils and animal fats were originally conceived as biolubricants due to their high fatty acid (FA) content [3,4]. Unfortunately, these abundant and readily available

biolubricants present important drawbacks for large-scale implementation, as they can be oxidized under high temperatures or even degraded by thermolysis [5]. In this regard, the elimination of double bonds in the structure of such molecules reduces the oxidation issues, but at the expense of a loss of fluidity, especially at low temperatures. Therefore, the employment of lubricity additives [6] or the chemical transformation of these bio-based lubricants becomes essential [7].

In order to improve the lubricant properties of vegetable oils, many routes have been exploited [8–12]. In contrast, other routes employing trimethylolpropane (TMP) meet interesting advantages, such as avoiding the presence of β-hydrogens to form ester bonds [13]. Hence, the synthesis of TMP-esters by esterification with easily available fatty acids such as oleic acid (OA) has emerged as an important solution to produce biobased lubricant products [14–17]. So, in a previous study, we demonstrated the effective synthesis of TMP-oleates employing methanesulfonic acid as an environmentally friendly catalyst by varying the OA/TMP molar ratio [17]. The chemical products involved in such a reaction scheme are included in Figure 1, and the chemical reaction procedure is detailed in Equations (1)–(3).

$$\mathrm{TMP} + \mathrm{OA} \overset{\mathrm{H^+}}{\leftrightarrow} \mathrm{TMPMO} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{TMPMO} + \mathrm{OA} \overset{\mathrm{H^+}}{\leftrightarrow} \mathrm{TMPDO} + \mathrm{H_2O} \quad (2)$$

$$\mathrm{TMPDO} + \mathrm{OA} \overset{\mathrm{H^+}}{\leftrightarrow} \mathrm{TMPTO} + \mathrm{H_2O} \quad (3)$$

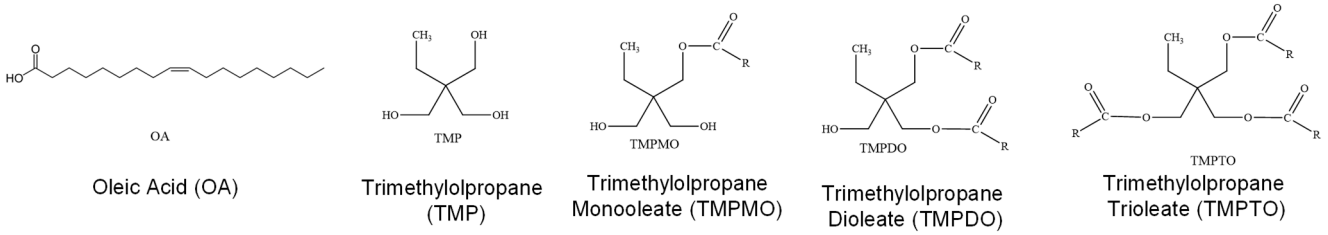


Figure 1. Chemical substances involved in the reaction of TMP with OA.

As it is detailed in Equations (1)–(3), the production of TMP-based esters from OA involves three consecutive esterification reactions. Initially, trimethylolpropane monooleate (TMPMO) is formed, followed by trimethylolpropane dioleate (TMPDO), and finally, the desired trimethylolpropane trioleate (TMPTO) is obtained. In this procedure, each mole of TMP consumes three moles of OA, resulting in the generation of three moles of water that should be removed. The different TMP-ester products obtained can be fruitful materials to produce biobased lubricants. However, to implement those products into biolubricant formulations, their lubricant properties must satisfy certain requirements, such as a high viscosity index or adequate pour point. In this sense, the characterization of the final kinematic viscosity properties needed to assess the VI of those mixtures results in relative ease, but, unfortunately, the measurement or estimation of lubricant properties of the pure substances that form the final mixture is not trivial and is normally discarded, losing valuable scientific information.

Generally speaking, the predictions of viscosity properties in organic compounds have been normally based on the direct estimation from a particular pure compound [18,19], finding very few studies focused on the impact of particular functional groups on the overall viscosity [20,21], and normally avoiding the direct quantification of viscosity properties in mixtures. The advantage of the method proposed by Rothfuss and Petters consists in the definition of the viscosity sensitivity parameter ($S_{\mu,i}$) for each functional group that allows quantifying how it varies the dynamic viscosity of a reference compound with the

number and location of functional groups added/eliminated [20]. However, these models only estimate dynamic viscosity (μ) instead of the kinematic one (ν) [18–21], which is the one needed for the calculation of VI, according to ASTM D2270 [22], and the most relevant in lubricant science. So, to our knowledge, a group contribution model permitting the quantification of the influence of functional groups upon kinematic viscosity and VI has neither been reported nor been applied to biolubricants to date.

Consequently, in this study a model based on kinematic viscosity sensitivity parameters analyzing the influence of the different functional groups formed during the TMP reaction with OA has been carried out, allowing us to predict the effect of the content of reagents and intermediates such as OA, TMPMO, TMPDO, and TMPTO upon the final biolubricant viscosity index. Moreover, the presence of different functional groups has been discussed, permitting the identification of the critical chemicals affecting the final viscosity properties of TMP-ester biolubricant products. The viscosity properties of all the pure compounds can also be estimated employing only a known pure compound used as a referential one, permitting the plotting of a 3D model predicting the viscosity properties (kinematic viscosity at 40 and 100 °C and VI) of any mixture, including such TMP-oleate bioproducts with lubricant interest.

2. Experimental Section and Methods

In this section, the methodology for modeling the kinematic viscosity properties in lubricant mixtures through a sensitivity parameters procedure based on functional groups is explained.

The main factors influencing the viscosity of substances are temperature, molecular weight, and the presence of different functional groups, as the latter can even modify the structure of the material by changing the intramolecular forces.

Regarding the variation in viscosity with the nature of the compounds, Rothfuss and Petters published a detailed study about the influence of several functional groups on the dynamic viscosity of different C3–C20 organic compounds [20]. The main advance of that study lies in the fact that the variation in dynamic viscosity per each change (ΔN) of a specific functional group (i) at a fixed temperature in an organic chain is summarized by means of a viscosity sensitivity parameter ($S_{\mu,i}$), according to Equation (4) as follows:

$$S_{\mu,i} = \frac{\Delta log_{10}\mu}{\Delta N_i} \tag{4}$$

Therefore, $S_{\mu,i}$ indicates the dynamic viscosity sensitivity parameter for one functional group (i) at a fixed temperature, where a positive value means an increase in viscosity when a new functional group is introduced and vice versa. So, the absolute value of the sensitivity parameter is proportional to its influence (being 0 in the case of null impact). ΔN_i represents the molar change as the variation in the number of functional groups. By using the logarithm properties, Equation (4) can be rewritten in terms of the dynamic viscosity of a non-functionalized base compound (μ_{nf}) and the functionalized one (μ_f) (Equations (5) and (6)), as follows:

$$S_{\mu,i} = \frac{log_{10}(\mu_i) - log_{10}(\mu_{nf})}{\Delta N_i} \tag{5}$$

$$\mu_i = \mu_{nf} \cdot 10^{S_{\mu,i} \cdot \Delta N_i} \tag{6}$$

Moreover, in fluid dynamics, kinematic viscosity (ν) is defined as the ratio of the dynamic viscosity divided by the density of the fluid. As the density of organic compounds from the same family (i.e., containing the same functional groups) is practically constant

for hydrocarbon chains longer than 5 C atoms [20,21], the density of an organic fluid mixture made of compounds with similar functional groups and chains longer than C_5 is not significantly altered by its specific composition. This fact is essentially accurate for most of the lubricants in general and very precise for the TMP-based lubricants synthesized here in particular [23,24]. Thus, it can be assumed that $\rho_i \approx \rho_{nf} \approx \rho \approx$ constant, allowing Equation (6) to transform into Equation (7), where the variation in kinematic viscosity per each change of a specific functional group (ΔN_i) at a fixed temperature is modeled with a kinematic viscosity sensitivity parameter ($S_{\nu,i}$), results in more useful information from a lubricant science point of view:

$$\nu_i = \nu_{nf} \cdot 10^{S_{\nu,i} \cdot \Delta N_i} \tag{7}$$

At this point, to study mixtures of compounds, it is necessary to define a rule of mixture for viscosity. In this research, Kendall and Monroe's rule of mixture [25] has been introduced (Equation (8)), since it is relatively simple but capable of reproducing in an accurate way the dynamic viscosity of a mixture.

$$\mu_m = \left(\sum_{i=1}^{n} x_i \cdot \mu_i^{\frac{1}{3}}\right)^3 \tag{8}$$

where μ_m is the dynamic viscosity of the mixture, μ_i is the dynamic viscosity of each compound, and x_i is the molar fraction of each compound. Although Kendall and Monroe's rule of mixture was originally described for dynamic viscosities, with the constant density simplification previously defined for these lubricant mixtures, it can also be applied to kinematic viscosities, according to Equation (9) as follows:

$$\frac{\mu_m}{\rho_m} = \left(\sum_{i=1}^{n} x_i \cdot \left(\frac{\mu_i}{\rho_i}\right)^{\frac{1}{3}}\right)^3 \overset{\rho=\rho_m=\rho_i=constant}{\longrightarrow} \nu_m = \left(\sum_{i=1}^{n} x_i \cdot \nu_i^{\frac{1}{3}}\right)^3 \tag{9}$$

Consequently, the kinematic viscosity of a mixture (ν_m) can be expressed with the Kendall and Monroe's rule of mixture applied to kinematic viscosities and considering a non-functionalized pure compound (nf) as the reference one (Ref), according to Equation (10) as follows:

$$\nu_m = \nu_{Ref} \cdot \left[\sum_{i}^{n} \left(x_i \cdot \left(10^{S_{\nu,i} \cdot \Delta N_i}\right)^{\frac{1}{3}}\right)\right]^3 \tag{10}$$

So, according to this model, the kinematic viscosity of a mixture of organic compounds where only one type of functional group is changed (ν_m), can be easily calculated as a function of one pure compound employed as reference (ν_{Ref}). Its implementation requires to knowing the precise composition of the mixture (defined as the molar fraction of each pure compound in the mixture, x_i), and the sensitivity parameters ($S_{\nu,i}$) for each change (ΔN_i) of the modified functional group (i), where the kinematic viscosity of the reference pure compound (ν_{Ref}) at a given temperature can be either obtained from the literature or predicted by the Mark–Houwink equation as a function of its molecular weight [26–28]. If the kinematic viscosity sensitivity parameters ($S_{\nu,i}$) were unknown, they can be tuned by minimizing the error between the known and modeled kinematic viscosities of lubricant products made from a mixture of compounds from the same family. Moreover, this method not only circumvents the a priori issue regarding the quantification of the kinematic viscosities of the pure compounds found in the lubricant mixture, since it is often hard to find in the literature (being here only necessary to know the kinematic viscosity of the pure reference compound, ν_{Ref}), but also allows us to estimate those kinematic viscosities of the pure compounds in a mixture a posteriori, i.e., after the sensitivity parameter tuning step.

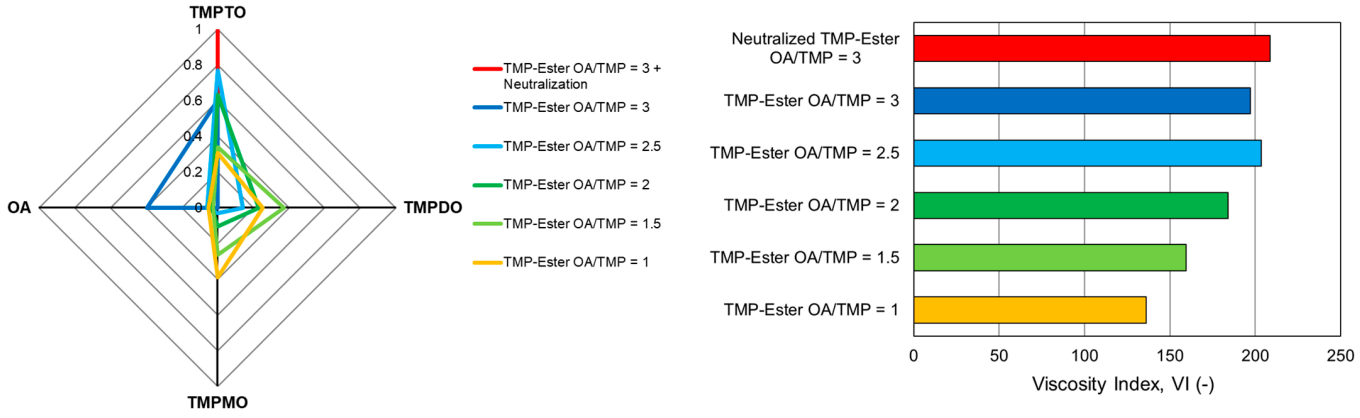
Finally, once the kinematic viscosities of the lubricant products have been determined both at 40 and 100 °C ($\nu_{i,40}$ and $\nu_{i,100}$), their viscosity index (VI) can be simply evaluated following the ASTM D2270 standard method [22]. With this method, this VI prediction is not only valid for any final lubricant mixture containing a combination of organic compounds of the same family but also for the estimation of the VI of the pure compounds present in such a mixture after the a posteriori analysis. For such predictions, this model only requires knowing the kinematic viscosity of one pure compound employed as a reference and data on the kinematic viscosities of mixtures with known molar compositions at both 40 and 100 °C, which are the most frequently reported temperatures for kinematic viscosity analysis.

Regarding the kinematic viscosity units, in spite of the fact that ASTM D2270-10 refers to the use of mm^2/s as the unit of kinematic viscosity, we have preferred to employ cSt, which is equivalent, as it is also present in the standard method tables (although between brackets), represents a unit of kinematic viscosity of great historical importance, and is still reported in several of the literature references consulted.

3. Results and Discussion

3.1. TMP-Ester Biolubricant Mixtures Analyzed

The experimental production of TMP-esters biolubricants by reacting TMP with oleic acid, varying the OA/TMP molar ratio, was carried out in previous research [17]. The molar distribution of TMP-ester products (TMPMO, TMPDO, and TMPTO) and unreacted OA obtained in such reactions by varying the OA/TMP molar ratio is shown in Figure 2, together with their respective VI. The product coded as "TMP-ester OA/TMP = 3 + Neutralization" consisted of a TMP-ester biolubricant product prepared under an OA/TMP molar ratio of 3 and subsequently neutralized with choline hydroxide to remove the leftovers of unreacted oleic acid, permitting the manufacture of pure TMPTO. Further details about the reaction protocols, purification step (neutralization), and viscosity measurements can be found in Ramos et al. [17].



(**a**) (**b**)

Figure 2. (**a**) Experimental product distribution and (**b**) experimental viscosity indices of TMP-ester biolubricants as a function of the OA/TMP molar ratio employed in their synthesis. The neutralization step consists in washing the TMP-ester product with choline hydroxide (ChOH) to remove the excess of unreacted OA. Source: adapted from Ramos et al. [17].

3.2. Development of a Model Based on Sensitivity Parameters for Kinematic Viscosity and Viscosity Index in TMP-Ester Biolubricants

According to the model previously explained in the experimental section, the kinematic viscosity of a mixture of organic compounds with carbon chains longer than 5 C

atoms at a given temperature can be easily described considering the detailed molar composition of the mixture, a rule of mixture (Kendall and Monroe, in this case) [25], and the known kinematic viscosity of one referential compound present in such a mixture at that study temperature (Equation (10)). This way, introducing the Neutralized TMP-ester-3 as the reference pure compound (pure TMPTO, since all the OA impurities were removed during its purification step), the modeled kinematic viscosities for the rest of the oleic-based TMP-ester biolubricant mixtures prepared under different OA/TMP molar ratios can be determined by tuning the kinematic viscosity sensitivity parameters ($S_{\nu,i}$). In this case, that optimization step was developed with an in-house spreadsheet implemented in Excel using the Levenberg–Marquardt algorithm programmed in Visual Basic. This procedure was carried out with experimental data both at 40 and 100 °C, permitting the tuning of the sensitivity parameter at each temperature by minimizing the error between experimental and modeled data. Once both the sensitivity parameter and modeled kinematic viscosities were tuned both at 40 and 100 °C, it was also possible to evaluate the modeled VI by following the ASTM standard method [22]. Therefore, Figure 3 shows the experimental and modeled kinematic viscosity at 40 and 100 °C, together with their corresponding experimental and modeled VI as a function of the OA/TMP molar ratio employed in the fabrication of the oleic-based TMP-ester biolubricants studied. In addition, Table 1 includes the values of kinematic viscosity sensitivity parameters ($S_{\nu,i}$) optimized by Levenberg–Marquardt at the two examined temperatures (40 and 100 °C) for the different functional group changes investigated in this study.

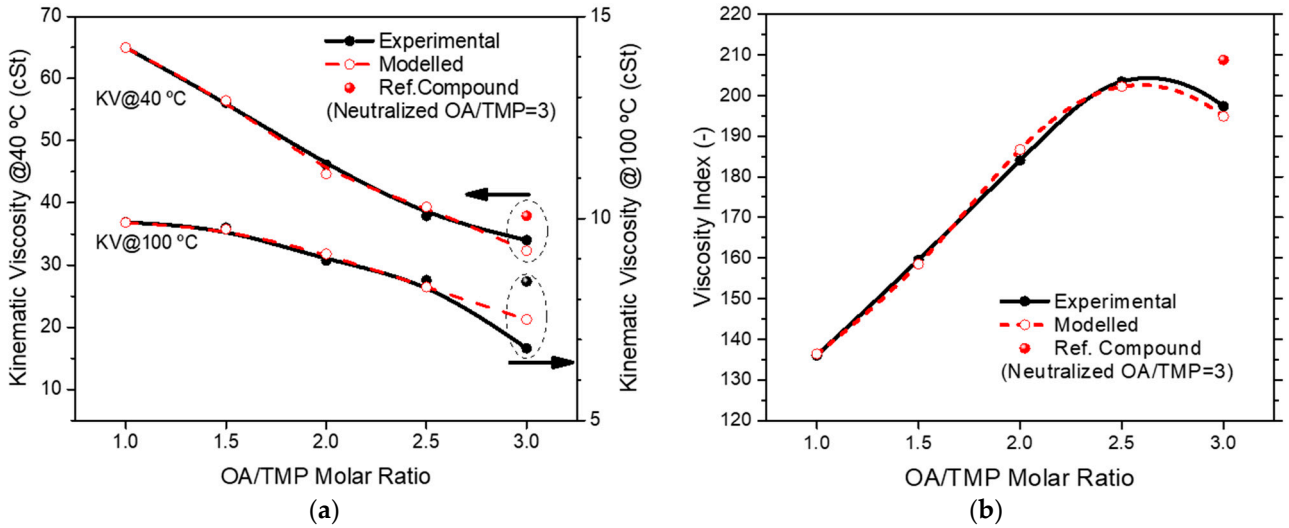


Figure 3. (**a**) Experimental and modeled kinematic viscosities at 40 and 100 °C. (**b**) Viscosity index (VI) for the synthesized TMP-ester biolubricants as a function of the OA/TMP molar ratio. Experimental data taken from Ramos et al. [17].

Table 1. Values of kinematic viscosity sensitivity parameters ($S_{\nu,i}$) at 40 and 100 °C obtained by the modeling for the oleic-based TMP-ester biolubricants analyzed in this study.

Process	Functional Group Change, *i*	Change Made	Δ*N*	Sensitivity Parameter, $S_{v,i}$@40 °C (-)	Sensitivity Parameter, $S_{v,i}$@100 °C (-)
TMPTO → OA	TMP-(R-COO)$_3$ → R-COOH	3 -COO → pure OA	3	−0.0614	−0.0848
TMPDO → TMPMO	TMP-(R-COO)$_3$ → (R-COO)-TMP-(OH)$_2$	3 -COO → 1 -COO + 2 -OH	2	0.2633	0.0796
TMPTO → TMPDO	TMP-(R-COO)$_3$ → (R-COO)$_2$-TMP-OH	3 -COO → 2 -COO + 1 -OH	1	0.0476	0.0680
Ref: TMPTO → TMPTO	*Ref*: TMP-(R-COO)$_3$ → TMP-(R-COO)$_3$	N/A	0	0	0
			r^2	0.9931	0.9667

R = $(CH_2)_7$-CH=CH-$(CH_2)_7$-CH_3.

In Figure 3a, an excellent agreement was found for the modeling of kinematic viscosity of TMP-esters from OA for all OA/TMP molar ratios, with an average relative error lower than 3% at both temperatures, confirming the reliability of the current model for estimating the kinematic viscosity of biolubricants constituted by organic mixtures. In detail, the absolute error between experimental and modeled data never exceeded 2 cSt at 40 °C and never reached 1 cSt at 100 °C, being the only data point with a relative error of >5% in the kinematic viscosity at 100 °C for OA/TMP = 3 (9.53% relative error), presumably due to the important quantity of OA in such a sample. Moreover, the coefficient of determination (r^2) was 0.9931, with an average error of 2.54% for the data at 40 °C, whereas the coefficient of determination for the data at 100 °C was 0.9667, with an average error of 2.76%, revealing an excellent fitting of the model here developed. Regarding the viscosity index modeling (Figure 3b), the model is even more precise, since all the absolute errors were below 1.5%, with a maximum absolute error of 2.46 arbitrary units of viscosity in the case of TMP-ester-3. Anyway, the influence of the different TMP-oleates (TMPMO, TMPDO, and TMPTO) is perfectly described with this model, both for kinematic viscosities and VI, independently of the distribution of those species, corroborating the accuracy of the proposed model for predicting viscosity properties.

Once this model is validated, the real influence of the different functional groups on the viscosity properties of the TMP-ester lubricants can be estimated. Therefore, the introduction of hydroxyl functional groups (-OH) always revealed an increase in kinematic viscosity due to the positive value of $S_{\nu,i}$, both when passing from no -OH groups (TMPTO) to one hydroxyl group and from 1 -OH to 2 hydroxyl groups at both temperatures. This effect of hydroxyl groups enlarging viscosity has been widely reported in the literature, being attributed to the capability of forming more stable hydrogen bonds, which reduce the fluidity of the compound [20,23,29]. However, at 40 °C, the introduction of the second hydroxyl group showed a much larger kinematic viscosity increment ($S_{\nu,i}$ = 0.2633) than the first one ($S_{\nu,i}$ = 0.0476), probably due to a cooperative effect promoted by the creation of hydrogen bonds among both -OH groups. In contrast, at 100 °C, both hydroxyl insertions revealed a similar influence (first one: 0.0680 and second one: 0.0796), possibly associated with the fact that the temperature-driven viscosity reduction softens the rise of kinematic viscosity linked to the -OH functional group. Anyway, the second addition of hydroxyl groups showed a higher increase in kinematic viscosity than the first one, which was also evidenced before by Rothfuss and Petters in their model applied to dynamic viscosities [20]. For modeling the kinematic viscosity in OA from referential TMPTO, the following two counterpart effects seem to take place: the increase in viscosity driven by the presence of -COOH groups and the decrease in the viscosity attending to the reduction in the molecular weight (Mark–Houwink effect) when the TMPTO molecule is split into three molecules of OA and TMP. Then, the overall effect is negative but much less important than the presence of -OH groups and poorly dependent on temperature (−0.0614 at 40 °C and −0.0848 at 100 °C).

To conclude this section, the modeled viscosity indices obtained for the TMP-oleate biolubricant products make them very interesting candidates to be considered for the lubricant industry due to their interesting values of VI.

3.3. Influence of the Composition of a Biolubricant Made with Neutralized TMP-Ester Biolubricants on the Viscosity Index

As the purification step consisting of the neutralization of unreacted OA with choline hydroxide (ChOH) has been successfully reported not only in terms of vanishing the acidity of the biolubricant but also avoiding the undesirable generation of other TMP-oleate hydrolysis by-products [17], it is possible to assume that all the TMP-ester products here analyzed from different OA/TMP molar ratios can be effectively neutralized using

that process as well. Accordingly, the product distribution of the synthesized TMP-ester lubricants was theoretically re-evaluated based on a theoretical complete removal of OA by ChOH (except Neutralized OA/TMP = 3, that is, the previous referential one), and, therefore, their modeled kinematic viscosities and their theoretical viscosity indices were also calculated employing the tuned kinematic viscosity sensitivity parameter method previously described (Table 2).

Table 2. Product distribution expressed as molar fraction and modeled kinematic viscosities at 40 and 100 °C, and modeled VI of the TMP-ester biolubricant products theoretically neutralized with ChOH (except Neutralized OA/TMP = 3, which is the previous referential one).

Product	OA/TMP	Molar Fraction				Modeled ν @40 °C (cSt)	Modeled ν @100 °C (cSt)	Modeled VI (-)
		TMPTO	TMPDO	TMPMO	OA			
Neutralized TMP-ester	1	0.323	0.266	0.412	-	68.0	10.3	137
	1.5	0.350	0.380	0.270	-	57.5	9.9	160
	2	0.653	0.239	0.107	-	45.5	9.1	188
	2.5	0.819	0.150	0.031	-	40.4	8.7	204
	3 *	1.000	0.000	0.000	-	37.9 *	8.4 *	209 *

* Neutralized TMP-Ester with OA/TMP = 3 (pure TMPTO) values were the experimental data to be used as reference and not modeled ones [17].

In detail, the viscosity indices of theoretically neutralized products were 137, 160, 188, 204, and 209 for the TMP-oleate esters from OA/TMP molar ratios of 1, 1.5, 2, 2.5, and 3, respectively. It is worthy to mention that except for Neutralized TMP-ester-3, which has been deeply discussed before and is not really a theoretical product but a previously manufactured biolubricant, the rest of the theoretically neutralized products did not show important variations either in composition or in VI due to the relatively low content of unreacted OA in experimental samples. Additionally, it is worthy to remark that in the absence of OA, the optimized value of $S_{\nu,i}$ the theoretical kinematic viscosities can be estimated not only for mixtures but also for pure TMP-oleate biolubricants. Hence, the theoretical kinematic viscosities at 40 and 100 °C reach values of 42.3 and 9.9 cSt for pure TMPDO and 127.5 and 12.2 cSt in the case of TMPMO, respectively. Accordingly, VIs values of 230 and 82 are obtained for pure theoretical TMPDO and TMPMO, respectively (Table 3).

Table 3. Modeled kinematic viscosities at 40 °C and 100 °C together with their corresponding viscosity indices for the pure TMP-oleates studied in this study. TMPTO values were experimental data and not modeled ones obtained from Ramos et al. [17].

Compound	Modeled ν @40 °C (cSt)	Modeled ν @100 °C (cSt)	Modeled VI (-)	Molecular Weight (g·mol^{-1})
TMPMO	127.5	12.2	82	398
TMPDO	42.3	9.9	230	662
TMPTO *	37.9 *	8.4 *	209 *	926

* TMPTO values were experimental data and not modeled ones [17].

Following the same procedure but sweeping all possible molar compositions of neutralized TMP-oleate esters (without OA), 3D graphs can be represented, showing the VI of the final Neutralized TMP-oleate-based biolubricant as a function of the molar composition of TMPMO-TMPDO-TMPTO (Figure 4). For improving visualization, molar ratios of TMPMO and TMPDO were limited between 0 and 0.4 in graphs, considering the real experimental concentration intervals at which the kinematic viscosity sensitivity parameters were obtained. In addition, the viscosity indices for the neutralized TMP-ester compounds for the different OA/TMP molar ratios were depicted as black spheres as well.

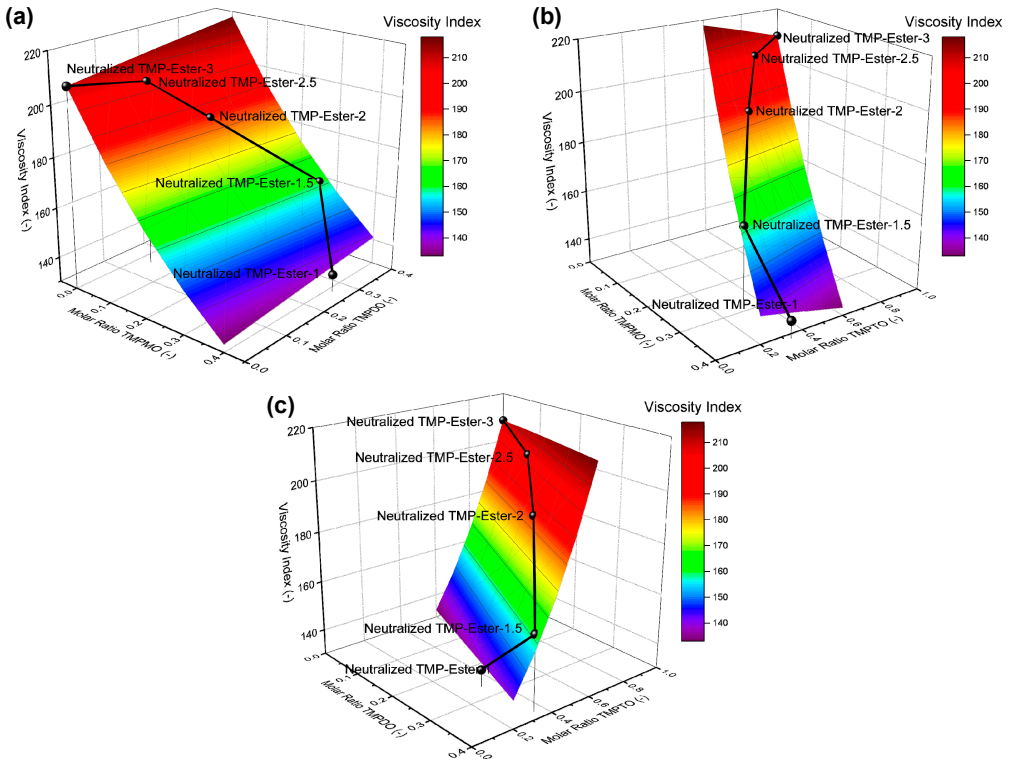


Figure 4. Modeled VI of the final Neutralized TMP-oleate-based biolubricant as a function of the OA/TMP molar ratio of (**a**) TMPMO-TMPDO, (**b**) TMPMO-TMPTO, and (**c**) TMPDO-TMPTO. VI of the Neutralized TMP-esters for the different OA/TMP molar ratios under study are represented as black spheres connected between them.

For neutralized TMP-esters, a clear trend in viscosity index is observed; although the presence of TMPMO increases the kinematic viscosity values regarding TMPDO and TMPTO, it dramatically reduces the VI, even for molar ratios < 0.4, leading to a product with more viscosity changes with temperature. Nevertheless, both TMPDO and TMPTO notably increase the behavior of the TMP-ester biolubricants with temperature, obtaining viscosity indices higher than 200 a.u. when TMPMO is properly removed. Despite increasing the OA/TMP molar ratio up to 3 permitted to attain final products with higher VI, it is only correlated with the disappearance of TMPMO (and OA by neutralization), since the presence of TMPDO in the biolubricant ester mixture not only does not reduce the VI but even raises it for the interval studied (x_{TMPDO} < 0.4). In detail, a biolubricant TMP-ester mixture with molar ratios x_{TMPTO} = 0.6 and x_{TMPDO} = 0.4 leads to a VI = 218, even higher than for pure TMPTO. These findings obtained through modeling of the viscosity properties may allow one to adjust the final VI of a TMP-oleate biolubricant by adding to a neutralized biolubricant mixture other potentially cheaper by-products (TMPDO), which are normally discarded or not completely considered.

4. Conclusions

The present study demonstrates that the proposed model based on kinematic viscosity sensitivity parameters was able to predict perfectly kinematic viscosities of biolubricants based on TMP-oleate mixtures and their corresponding viscosity indices. This prediction model requires knowing the composition of such mixtures, the molar change as the variation in the number of functional groups (ΔN_i), and just the kinematic viscosity properties of one pure compound of the mixture employed as a reference (TMPTO in this case), permitting the tuning of the kinematic viscosity sensitivity parameter and thus predicting the kinematic viscosities (both at 40 and 100 °C) of any mixture of those

compounds and its corresponding VI. These sensitivity parameters present a physical meaning, where a positive value means that the variation in such a functional group increases the kinematic viscosity and vice versa, their absolute value being proportional to their effect. So, the introduction of one hydroxyl group (-OH) in replacement of the ester one increases the kinematic viscosity of TMP-oleate biolubricants ($S_{\nu,i}$@40 °C = 0.0476 and $S_{\nu,i}$@100 °C = 0.0680), but the second one still showed a more important effect ($S_{\nu,i}$@40 °C = 0.2633 and $S_{\nu,i}$@100 °C = 0.0796), even when the molecular weight decreases. In contrast, passing from TMPTO to OA resulted in a reduction in kinematic viscosity ($S_{\nu,i}$@40 °C = −0.0614 and $S_{\nu,i}$@100 °C = −0.0848). Additionally, the model established that the presence of unreacted OA and particularly TMPMO are undesirable; however, the introduction of the TMP-oleate diester (TMPDO), normally discarded or not completely considered, can be even more beneficial in order to push the final VI of the biolubricant product. Then, the model was extended to a 3D representation to predict the VI of any TMPMO-TMPDO-TMPTO mixture. Therefore, by means of this model, it was possible to estimate that a biolubricant mixture combining TMPDO and TMPTO could lead to a higher viscosity index even than pure TMPTO, since, according to our model, a 40%/60% molar mixture of TMPDO and TMPTO, respectively, led to attaining a theoretical VI = 218. We believe that these findings could pave the way for estimating the viscosity and lubricating properties of complex mixtures when the composition of the mixture is well defined, but the specific kinematic viscosities of its components are unknown.

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Abbreviations

The following abbreviations are used in this manuscript:

TMP	trimethylolpropane
OA	oleic acid
TMPMO	trimethylolpropane monooleate
TMPDO	trimethylolpropane dioleate
TMPTO	trimethylolpropane trioleate
VI	viscosity index

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