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Published in:
Fluid Phase Equilibria

Link to article, DOI:
10.1016/j.fluid.2017.12.009

Publication date:
2018

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Damaceno, D. S., Perederic, O. A., Ceriani, R., Kontogeorgis, G. M., & Gani, R. (2018). Improvement of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to lipid technology. *Fluid Phase Equilibria*, *470*, 249-258. https://doi.org/10.1016/j.fluid.2017.12.009

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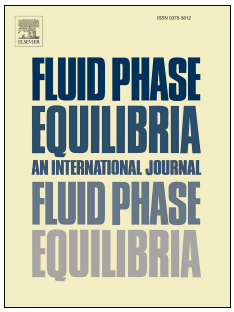

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PII: S0378-3812(17)30485-5

DOI: 10.1016/j.fluid.2017.12.009

Reference: FLUID 11682

To appear in: *Fluid Phase Equilibria*

Received Date: 9 September 2017

Revised Date: 2 December 2017

Accepted Date: 4 December 2017

Please cite this article as: D.S. Damaceno, O.A. Perederic, R. Ceriani, G.M. Kontogeorgis, R. Gani, Improvement of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to lipid technology, *Fluid Phase Equilibria* (2018), doi: 10.1016/j.fluid.2017.12.009.

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Improvement of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to lipid technology

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Abstract

Predictive methodologies based on group contribution methods, such as UNIFAC, play a very important role in the design, analysis and optimization of separation processes found in oils, fats and biodiesel industries. However, the UNIFAC model has well-known limitations for complex molecular structures that the first-order functional groups are unable to handle. In the particular case of fatty systems these models are not able to adequately predict the non-ideality in the liquid phase. Consequently, a new set of functional groups is proposed to represent the lipid compounds, requiring thereby, new group interaction parameters. In this work, the performance of several UNIFAC variants, the Original-UNIFAC, the Linear-UNIFAC, Modified-UNIFAC and the Dortmund-UNIFAC is compared. The same set of experimental data and the parameter estimation method developed by Perederic et al. (2017) have been used. The database of measured data comes from a special lipids database developed in-house (SPEED Lipids database

at KT-consortium, DTU, Denmark). All UNIFAC models using the new lipid-based parameters show, on average, improvements compared to the same models with their published parameters. There are rather small differences between the models and no single model is the best in all cases.

Keywords: Lipids, activity coefficient models, UNIFAC, Original, Linear, Modified, Dortmund

1. Introduction

In the recent years, the oil and fat industry has grown significantly, mainly as a result of increased production of biofuels, such as biodiesel. Among the unit operations required for biodiesel/biofuels production, those involving mass transfer, such as distillation and stripping, are among the most important steps in the separation and purification process. In these cases, the vapor-liquid equilibrium (VLE) description of the multicomponent mixture is essential to map the behavior of the different compounds under process conditions. As a consequence, the availability of predictive tools with acceptable accuracy and wide application for engineering design of oil/fat and biodiesel processes is underlined.

Predictive tools based on the group contribution method consider a mixture or any substance as an aggregate of functional groups present in the molecules that constitute it. Therefore, the mixture properties are the result of the sum of contributions of each of these groups, which are predicted through adjustable group interaction parameters. These group interaction-parameters are estimated through regression with carefully selected experimentally measured data. In the case of pure component properties, the contributions of the groups representing the compounds are used to estimate the corresponding property. Like the mixture properties, measured pure

component property data are used to estimate the group parameters. The advantage of this type of property estimation method is to allow the calculation of thermophysical properties (e.g. boiling points, heat capacity, critical point, densities) of pure compounds or multicomponent mixtures, for example, phase equilibria (activity coefficients of compounds in liquid phase in equilibrium with a vapor phase) of oil and fats. Thus, the use of predictive models based on group contribution methods in design, analysis and optimization of separation processes of oils, fats and biodiesel industries is very important. In particular, those group contribution methods associated with phase equilibrium are among the most important. Group contribution methods for activity coefficients are a valuable tool for process design in the absence of data or when insufficient or inaccurate data are available [1].

Original UNIFAC (UNIQUAC Functional-group Activity Coefficients) [2] and its variants [3-9] has limitations that are intrinsic to their generality, especially the so-called proximity effects. Other methods based on the group contribution approach share this limitation [10]. These proximity effects are particularly important when two or more functional groups are situated at equal or adjacent positions of the carbon atom. Recent works have indicated that these limitations of the UNIFAC method also affect the predictions involving fatty systems. Cunico et al. [11] and Belting et al. [12], evaluating the Original-UNIFAC and UNIFAC-Dortmund, observed that they were not able to adequately predict the non-ideality of the liquid phase of fatty systems, and they proposed changes in the division and/or interaction parameters of the functional groups.

Considering the limitations due to proximity effects and trying to enhance the accuracy of group contribution methods for estimation of activity coefficients related to applications in lipids technology, this work presents a new matrix of Linear-UNIFAC [5], Modified-UNIFAC [3] and

Dortmund-UNIFAC [4] models, especially suited for the estimation of VLE of mixture with lipids compounds, as well as an evaluation of the performance of the published [3-5] and the new lipid-based model-parameters. For purposes of completion purposes, the performance of the Original-UNIFAC model with its published and lipid-based parameters [13] is also included in the study. The same database and parameter estimation method developed [13] are applied to all UNIFAC-based models.

2 Models Description

In group contribution methods, the activity coefficient of compound *i* in liquid solution is calculated from the sum of the entropic contributions, related to the size and shape differences between molecules, and the residual contribution, which accounts for the intermolecular interactions of functional groups of multicomponent mixtures, as represented by Eq. 1 [10].

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

The general form of the combinatorial-term equation applied to all the UNIFAC models studied in this manuscript is described by Eq. 2. Original-UNIFAC and Linear-UNIFAC models have the same form for the combinatorial part. Modified-UNIFAC and Dortmund-UNIFAC models on the other hand have different volume fractions terms within the combinatorial part, as listed in Table 1. The Modified-UNIFAC [3] model uses a modified volume fraction of $r^{2/3}$, as suggested by Kikic et al. [14], while the Dortmund-UNIFAC model is based on volume fraction of $r^{3/4}$. Both modified volume fractions are of semi-empirical basis and they are shown to work well for mixtures of compounds with very different sizes [4] but they nevertheless fail for polymer solutions. The Modified-UNIFAC model is the only model that does not have the Staverman-

Guggenheim correction term in the combinatorial part [3]. The surface and volume parameters used for the Original-, Linear- and Modified-UNIFAC models are determined through Bondi's method [15], while for the Dortmund-UNIFAC model they are fitted from experimental data together with group interaction-parameters [4]. This poses a problem for extension of the Dortmund-UNIFAC model for the lipid-compounds and regression of the group-interaction parameters.

The residual term of Eq. 1 has the same expression for all models (Eq. 3). The difference between the models is represented by the group-group interaction parameter expression (a_{mn}), as represented by Eq.6 and given in Table 2. For Original-UNIFAC model the binary group-interaction parameters are temperature independent. In Linear- and Modified-UNIFAC models the group-interaction parameters are temperature dependent. In Dortmund-UNIFAC model the group-interaction parameters are temperature dependent but a different function is employed.

$$\ln \gamma_i^C = \ln \frac{r_i^{C_0}}{\sum_j x_j r_j^{C_0}} + 1 - \frac{r_i^{C_0}}{\sum_j x_j r_j^{C_0}} - C_1 \left(\ln \left(\frac{\Phi_i}{\theta_i} \right) + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (2)$$

$$\Phi_i = \frac{r_i}{\sum_j x_j r_j} \quad (3)$$

$$\theta_i = \frac{q_i}{\sum_j x_j q_j} \quad (4)$$

Table 1. C_0 and C_1 of Eq. 2

Model	C_0	C_1
Original-UNIFAC	1	$5q_i$
Linear-UNIFAC	1	$5\ q_i$
Modified-UNIFAC	$^2/_3$	0
Dortmund-UNIFAC	¾	$5\ q_i$

$$\ln \gamma_i^R = \sum_K^{groups} v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (3)$$

$$ln\Gamma_k = Q_k \cdot \left[1 - ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left(\theta_m \Psi_{mk} \Big/ \sum_n \Theta_n \Psi_{nm} \right) \right] \quad (4)$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (5)$$

$$X_m = \frac{\sum_i^M v_m^{(i)} x_i}{\sum_i^M \sum_j^N v_j^{(i)} x_i} \quad (6)$$

$$\Psi_{mn} = \exp\left(\frac{-a_{m,n}}{T} \right) \quad (7)$$

$$a_{m,n} = A_0 a_{mn,0} + A_1 a_{mn,1} + A_2 a_{mn,2} \quad (8)$$

Table 2. A_0, A_1 and A_2 of Eq. 6

Model	A_0	A_1	A_2
Original-UNIFAC	1	0	0
Linear-UNIFAC	1	T-T_0	0
Modified-UNIFAC	1	T-T_0	$T\ln(T_0/T) + T - T_0$
Dortmund-UNIFAC	1	T	T^2

T_0 is reference temperature (T_0 = 298.15 K)

3. Parameter Estimation Method

The estimation of a new set of group-interaction parameters for Linear-UNIFAC, Modified-UNIFAC and Dortmund-UNIFAC models dedicated to systems with lipid compounds was performed using the systematic parameter estimation method of Perederic et al. [13] and employing an in-house database, SPEED Lipids Database, also used by Perederic et al. [13]. The method is divided into three hierarchical parts: a) data collection and analysis; b) data

125 organization and selection; and finally c) parameter estimation according to an estimation order
126 and validation. All parts are hereafter briefly described.
127
128 *3.1. Data Collection and Analysis*
129 Considering the SPEED Lipids Database [13] is already available, according to the employed
130 method [13], the next step is to analyze the collected experimental data. Thus, pure compound
131 data availability (e.g.: vapor pressure) and transcript errors (outlier points) are checked. Also,
132 thermodynamic consistency tests [16] are applied to all collected data sets. The TDE
133 (ThermoData Engine) software from NIST is used to calculate the quality factor (Q_{VLE}) for all
134 binary systems. Note that the same data and analysis are also used by Perederic et al. [13].
135
136 *3.2. Data Organization and Selection*
137 The first step of the data organization and selection is the compound group definition and
138 assignment. In this step the main groups and subgroups of the mixtures are defined and identified
139 (see Table 3). The main groups and subgroups of the UNIFAC models are listed and assigned to
140 represent the compounds found in the VLE datasets, in this case the SPEED Lipids database. The
141 group selection was based on the Original-UNIFAC model division/assignment [13]. All the
142 compounds found in this database are represented by the selected model groups and subgroups.
143 Also, the two new functional groups proposed by Perederic et al [13] to better describe systems
144 containing glycerol [13,17-18] and acylglycerols [13,17], are used in this work, which are GLY
145 and OH_{acyl} groups. In this work, all UNIFAC models have the same groups division, however,
146 the subgroups of Dortmund-UNIFAC has an exception [6], as this UNIFAC-based model has
147 two OH subgroups divisions for R_k and Q_k parameters (see Table 3), the OH primary (OH_p) and

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148 secondary (OH_s). It is important to underline that, the same OH_p and OH_s division was applied to
149 the OH_{acyl} group for Dortmund-UNIFAC (see Table 3). For this case, the monoacylglycerols,
150 which have two OH_{acyl} groups, where described with one $OH_{acyl,p}$ and one $OH_{acyl,s}$. For example,
151 the system oleic acid + ethanol is represented by the following main groups: CH_2, CH=CH, OH
152 and COOH. In this example, the OH subgroup is OH for Linear- and Modified-UNIFACs, and
153 OHp (primary) for Dortmund-UNIFAC. The surface and volume parameters for the functional
154 groups used are given in Table 3.

155

156 Table 3. Area (Q_k) and volume (R_k) parameters for the groups used for the UNIFAC models.

Main Group	Sub group	Original-, Linear- and Modified-UNIFAC [10]		Dortmund-UNIFAC [6]	
		R_k	Q_k	R_k	Q_k
	CH3	0.9011	0.8480	0.6325	1.0608
CH_2	CH2	0.6744	0.5400	0.6325	0.7081
	CH	0.4469	0.2280	0.6325	0.3554
C=C	CH=CH	1.1167	0.8670	1.2832	1.2489
	OH	1.0000	1.2000	-	-
OH	OHp[*a]	-	-	1.2302	0.8927
	OHs[*a]	-	-	1.0630	0.8663
CH_3OH	CH3OH	1.4311	1.4320	0.8585	0.9938
H_2O	H2O	0.9200	1.4000	1.7334	2.4561
CH_3CO	CH3CO	1.6724	1.4480	1.7048	1.6700
CCOO	CH2COO	1.6764	1.4200	1.2700	1.4228
COOH	COOH	1.3013	1.2240	0.8000	0.9215
	OH_{acyl}	1.0000	1.2000	-	-
OH_{acyl}[*b]	$OH_{acyl,p}$[*c]	-	-	1.2302	0.8927
	$OH_{acyl,s}$[*c]	-	-	1.0630	0.8663
GLY[*d]	GLY[*e]	4.7957	4.9080	-	-
	GLY[*f]	-	-	5.4209	4.4233

157 [*a] OHp and OHs subgroups are used only for Dortmund UNIFAC

158 [*b] OHacyl describes mono- and diacylglycerols molecules and uses same R and Q as OH group

159 [*c] For Dortmund UNIFAC monoacylglycerols are described with one $OH_{acyl,p}$ and one $OH_{acyl,s}$, while diacyglycerols
160 are described with one $OH_{acyl,p}$

161 [*d] GLY represents the glycerol molecule. R and Q parameters are calculated from contribution of constitutive groups

[*e] For all UNIFAC models except Dortmund GLY is considered as 2 CH_2, 1 CH, 3 OH

[*f] For Dortmund UNIFAC GLY is considered as 2 CH_2, 1 CH, 2 OHp, 1 OHs

The second step of the data organization and selection is data category assignment and quality sorting. The data organization algorithm of Perederic et al. [13] is used to assign the data in different category-groups according to binary-interaction provided. A category-group contains VLE data sets that involve the same binary group interaction parameters. The Algorithm A provides the following notation for the category-groups: X.M.N, where: X is the number of group-interaction parameters involved within a category-group, M is the number of binary pairs that need to be estimated, and N is the type of involved pairs of the mixture (the user can select the order of parameter estimation and this will not affect the final result). Examples are presented in Table 4. The Algorithm A and more details of the method are presented by Perederic et al. [13].

Table 4. Data organization through Algorithm A

Binary systems	Interaction pars	X	M	N	Category -groups: X.M.N
octanoic acid + hexanoic acid	CH_2-COOH	X=1, one pair of interaction parameter	M=1, one pair of interaction parameter to be estimated	M=1, the user can select the order to estimate, this order will not affect the next step.	1.1.1
ethyl myristate + ethyl palmitate	CH2-CCOO	X=1, one pair of interaction parameter	M=1, one pair of interaction parameter to be estimated	M=2, the user can select the order to estimate, this order will not affect the next step.	1.1.2
methyl dodecanoate + methanol	CH_2-CCOO; CH_2-CH_3OH; CCOO-CH_3OH	X=3, three pairs of interaction parameters	M=2, two pairs of interaction parameter to be estimated, because CH2-CCOO was estimated in step 1.1.2	M=1, the user can select the order to estimate, this order will not affect the next step.	3.2.1

methyl dodecanoate + ethanol	CH_2-CCOO; CH_2-OH; CCOO-OH	X=3, three pairs of interaction parameters	M=2, two pairs of interaction parameter to be estimated, because CH2-CCOO was estimated in step 1.1.2	M=2, the user can select the order to estimate, this order will not affect the next step	3.2.2

The third step of data organization and selection is the data selection. The best data is chosen by using a selection algorithm, Algorithm B. The foundation of this step is the quality factor and the data availability. Each category-group is independently evaluated with this algorithm. If there are data sets with quality value equal or higher than 0.5 those come first in the evaluation list (descending order). Then, if a binary system has quality factor below 0.5, the next step is to evaluate if, in this category-groups, there are other systems with quality factor above 0.5. If there are indeed other systems, the data set is not selected, but if there are no other systems available, the data set is selected. For example: the system octanoic acid + hexanoic acid, from the category-group: 1.1.1, has a quality factor equal to 0.650, which means, that this system will be used for parameter estimation. Another example, the system methyl dodecanoate + ethanol, from the category-group 3.2.2, has quality factor equal to 0.250, and the only other available system in this category-group has also quality factor equal to 0.250. According to the algorithm, both systems will be used for the estimation. The Algorithm B and more details are given in [13].

Table 5 gives the results of organization and selection part of the method. The same datasets are selected/used for parameter estimation as in Perederic et al. [13], ensuring thus a fair comparison between all UNIFAC-based models. Table 5 lists the order in which the data and corresponding groups are to be estimated, the number of available systems and the number of selected systems used for estimation of the interaction parameters in each category-group.

197 Table 5. Data organization and selection of binary mixtures database used for parameter estimation [13]

Category -group [a]	Binary system type		Available systems	Selected systems
	Compound I	Compound II		
1.1.1.	Saturated Fatty Acids	Saturated Fatty Acids	23	4
1.1.2.	Saturated Ester	Saturated Ester or Hydrocarbon	26	9
1.1.3.	Glycerol	Methanol	20	9
1.1.4.	Glycerol	Water	44	14
3.1.1.	Saturated Fatty Acids	Saturated Ester	1	1
3.2.1.	Saturated Ester	Methanol	5	5
3.2.2.	Saturated. Ester	Ethanol	2	2
3.2.3.	Saturated Monoacylglycerol	Saturated Ester	2	2
3.2.4.	Glycerol	Saturated Alcohol	34	11
3.2.5.	Unsaturated Fatty Acids	Saturated Fatty Acid or Hydrocarbon	3	1
3.2.6.	Unsaturated Ester or Triacylglycerol	Saturated Ester or Hydrocarbon	3	2
6.1.1.	Saturated Monoacylglycerol	Saturated Fatty Acids	2	2
6.1.2.	Unsaturated. Ester	Methanol	2	1
6.1.3.	Unsaturated Ester	Ethanol	2	2
6.1.4.	Unsaturated Fatty Acids	Methanol	1	1
6.1.5.	Saturated Fatty Acids	Saturated Alcohol	2	2
6.3.1.	Unsaturated Triacylglycerol	Acetone	1	1
6.3.2.	Saturated Fatty Acids	Acetone	1	1

198 [a] The category-group is described in Data Organization and Selection section [13]
199

200 *3.3. Parameter Estimation and Validation*

201 The parameter estimation task is performed by minimization of the summation of least squares of
202 the pressure, as the objective function (Eq. 9) shows. The optimization problem is solved with
203 the Harwell subroutine VA07AD [19]; in this way, the full set of parameters can be regressed
204 efficiently and quickly [13].

205 $$F_{obj} = \sum_i \left(\frac{P^{\exp erimental} - P^{calculated}}{P^{\text{experimental}}} \right)_i^2 + \frac{1}{\beta} \sum_m \sum_n \left(a_{mn} - a_{mn}^0 \right)^2 \quad (9)$$

206 where, F_{obj} is the objective function, $P^{experimental}$ is the experimental pressure, and $P^{calculated}$ is the
207 calculated pressure, a_{mn} is the estimated binary interaction parameter, and $a^0{}_{mn}$ is the initial value

of the binary interaction parameter. The initial values are in this work the Linear- [5], Modified- [3] and Dortmund- [4] UNIFAC model group-interaction parameter values, or zero for the GLY and OH_{acyl} interactions. β is an empirical term, that it can range from 10^3 up to 10^5, and in this work was set equal to 10^5 [13], based on trial and error from several regressions, and monitoring the first and second parts of Eq 9 [11,17,20]. So, the first part of Eq. 9 represents the residual pressure, and the second part is the regularization term, which only the most sensitive parameters are allowed to deviate from their nominal values (a^0_{mn}), avoiding unreliable values to the estimated parameters (a_{mn}) [11,17,20].

Finally, to evaluate the performance of the models, all data sets from the SPEED Lipids database are employed to compare them with those predicted with the new parameters and the published parameters. For this purpose, the average relative deviation (ARD, %), Eq. 10, is used.

$$ARD(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P^{experimental} - P^{calculated}}{P^{experimental}}\right|.100 \quad (10)$$

where, *ARD* is the average relative deviation in %, $P^{experimental}$ is the experimentally measured pressure, and $P^{calculated}$ is the calculated pressure.

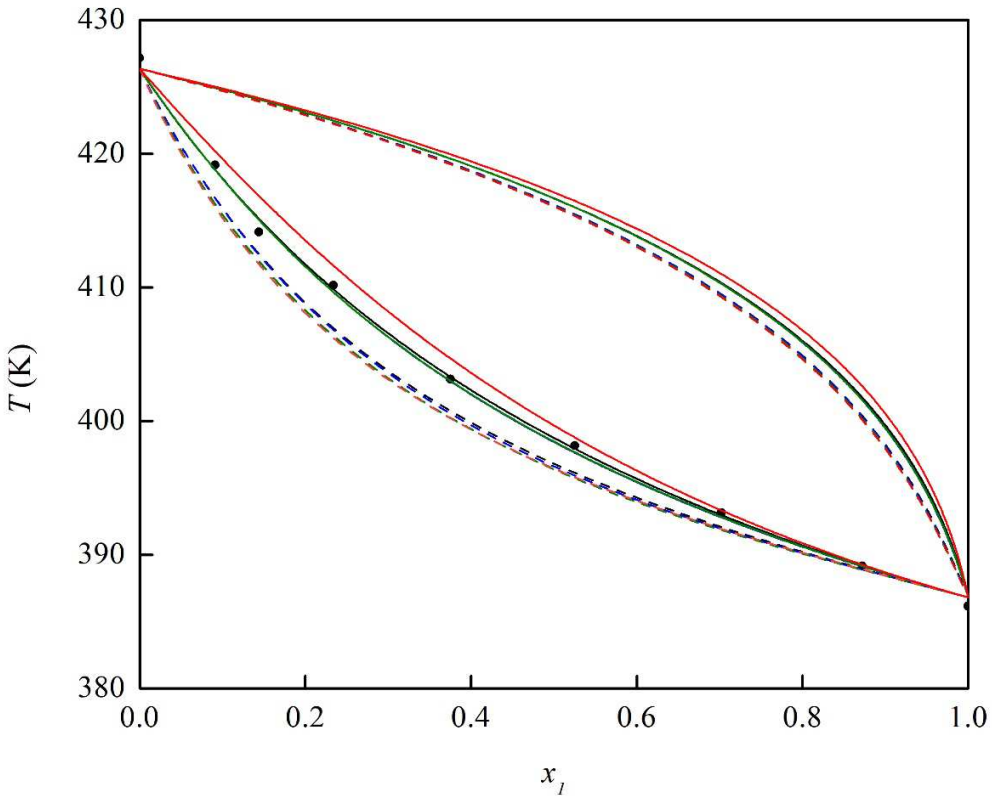
4. Results and Discussion

New binary interaction parameters for lipids systems were regressed for the Linear-, Modified- and Dortmund-UNIFAC models. All the new, lipids-based group-interaction parameters are given in Table 6, along with the parameters for Original-UNIFAC model [13]. The temperature ranges for the VLE data for each binary system is also given in Table 6.

Table 7 lists the ARD (%) for all VLE binary datasets retrieved from the SPEED lipids database in terms of category-group of the dataset for all the UNIFAC-based models with their published parameters and with the lipids-based group interaction parameters from this work. Furthermore, Table 7 gives the consistency test scores (Q_{VLE}) for each data-type (category-group) of the mixtures from the database, indicating the quality of the data.

In general, the Linear-UNIFAC model with lipids-based group-interaction parameters show the best performance as it has the lowest overall deviation of about 8.9%. This is about 1% better than the Dortmund-UNIFAC model, which is the second best model (also with lipids-based group-interaction parameters). The Modified-UNIFAC using lipids-based group interaction parameters show the lowest deviation for the category-group of saturated fatty acid + saturated ester mixtures (ARD = 1.5%). Also, lipids-based Dortmund-UNIFAC model gives the best performance for the category-group of saturated ester + saturated ester or hydrocarbon mixtures with ARD = 4.8%. Still, the general conclusion is that differences between the UNIFAC-based models with the lipids-based group-interaction parameters is rather small as all four models have deviations are around 8–14%. All four models perform far better than when the published parameters are used where the deviations are about or above 20%.

Figure 1 shows the performance of all models (using published and lipids-based group-interaction parameters) for the system dodecanoic acid + methyl dodecanoate at 0.5 kPa [21]. All models show similar behavior, and better prediction is achieved with the lipids-based group-interaction parameters (given in Table 6).



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251 Figure 1. Binary system methyl dodecanoate (x_1) + dodecanoic acid (x_2) at 0.5 kPa. Experimental data
252 [21] (●). Published parameters models: Original- (--), Linear- (--) Modified- (--) and Dortmund-UNIFAC
253 (--). Lipids-based group interaction parameters models: Original- (—), Linear- (—), Modified- (—) and
254 Dortmund-UNIFAC (—)
255

256 Figure 2 shows the performance of the new group GLY (glycerol group) for the binary system
257 glycerol + water at 14.19 kPa [22]. The Linear- and Modified-UNIFAC models with lipids-based
258 group-interaction parameters have the best predictions for this system, which is the most
259 complex among all systems considered (with deviations around 50% for the best performing
260 models). The ARD (%) for the group-categories: glycerol + methanol, glycerol + water and
261 glycerol + alcohols, show that all UNIFAC-based models with lipids-based group-interaction
262 parameters have similar performances, and lower deviations when compared with UNIFAC-

263 based models with published parameters (given in Table 7). The Dortmund-UNIFAC model with
264 published parameters give the highest deviation for the group-category glycerol + water, while
265 with the lipids-based group-interaction parameters the same model showed a significant
266 improvement, a reduction from an ARD of 198% [4] to 56% (this work). It is important to
267 highlight that for the calculations with the published UNIFAC parameters the glycerol compound
268 is considered as 2 CH_2, 1 CH and 3 OH, except for Dortmund-UNIFAC, where glycerol is
269 considered as 2 CH_2, 1 CH, 2 OH_p and 1 OH_s. The deviations for all glycerol-containing
270 mixtures (with water, methanol or other alcohols) are the highest among all systems considered.
271 These are cross-associating systems with very strong hydrogen bonding both self- and cross-
272 associations. The UNIFAC-models account for such effects only indirectly (interaction
273 parameters and local composition concept) and better performance for such complex mixtures
274 can be obtained with association equations of state like CPA [23] and SAFT [24], as shown in
275 literature by Tsivintzelis et al. [25]
276

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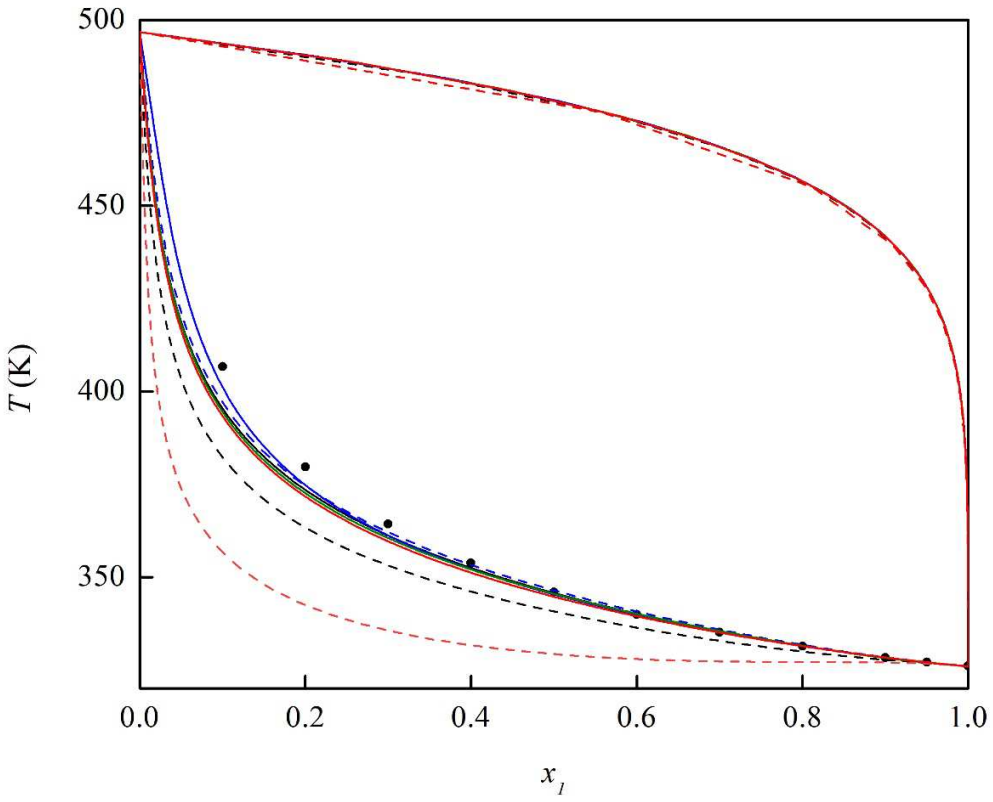
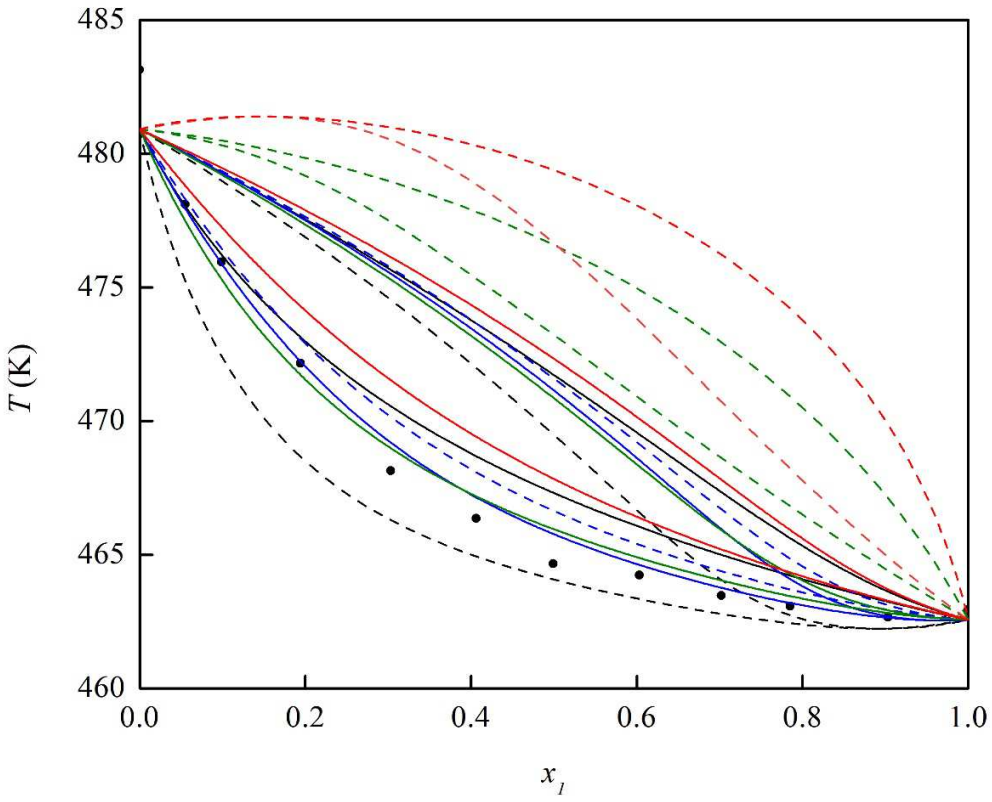


Figure 2. Binary system water (x_1) + glycerol (x_2) at 14.19 kPa. Experimental data [22] (●). Published parameters models: Original- (--), Linear- (--) Modified- (--) and Dortmund-UNIFAC (--). Lipids-based group interaction parameters models: Original- (—), Linear- (—), Modified- (—) and Dortmund-UNIFAC (—)

The new group OH_{acyl} introduced for the UNIFAC-based models with lipids-based group-interaction parameters, demonstrated improved predictions for mixtures with acylglycerols, such as monoacylglycerols, when compared with the UNIFAC-based models using the published parameters. Figure 3 shows a poor prediction of the Modified- and Dortmund-UNIFAC models using the published parameters. Both models with published parameters overestimate the temperature of monoacylglycerols + fatty acids systems.



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290 Figure 3. Binary system monocaprylin (x_1) + palmitic acid (x_2) at 1.20 kPa. Experimental data [11] (●).
291 Published parameters models: Original- (--), Linear- (--) Modified- (--) and Dortmund-UNIFAC (--).
292 Lipids-based group interaction parameters models: Original- (—), Linear- (—), Modified- (—) and
293 Dortmund-UNIFAC (—)
294

295 Figure 4 shows the total value of ARD (%) versus number of data points for the UNIFAC-based
296 models with lipids group-interaction parameters. It is possible to observe that the model with the
297 lowest deviation is the Linear-UNIFAC model, while Original-UNIFAC has the highest
298 deviation. Among all models, Original-UNIFAC is the only one with temperature-independent
299 parameters, and has thus fewer adjustable parameters compared to the other three UNIFAC
300 variant models. Figure 5 presents the total ARD (%) versus the number of data points for the

Linear-UNIFAC model with published and lipids group-interaction parameters, which shows an improvement for the lipids-based model.

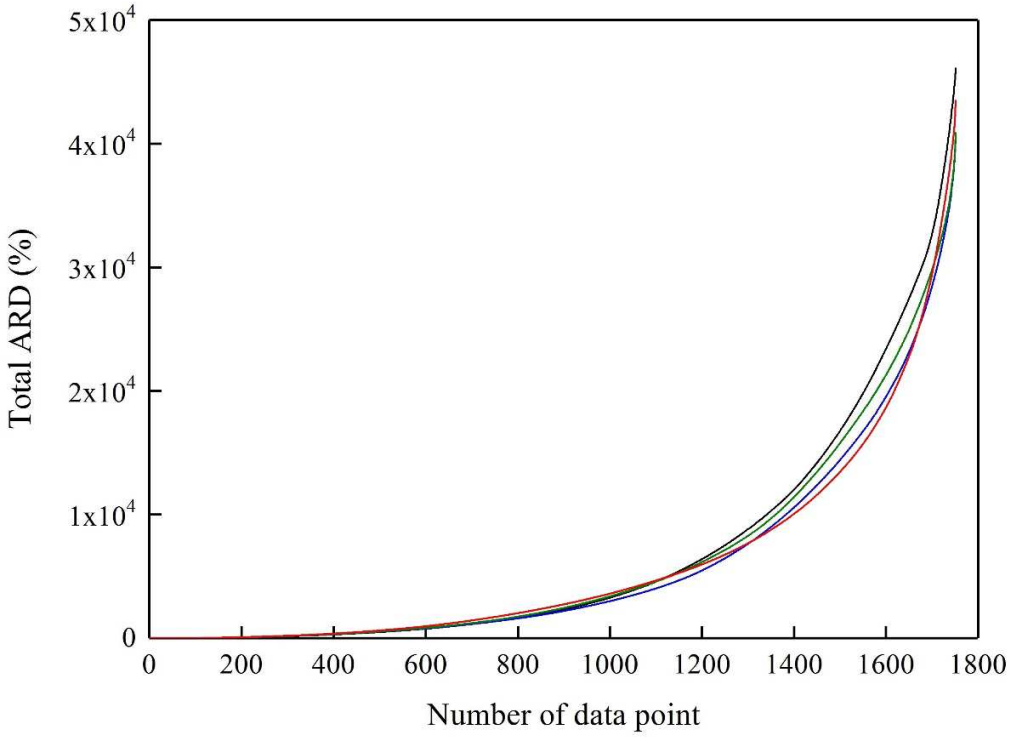

Figure 4. Total ARD (%) for the Original- (—), Linear- (—), Modified- (—) and Dortmund-UNIFAC (—) using the lipids-based group interaction parameters for the UNIFAC models versus the total number of data points

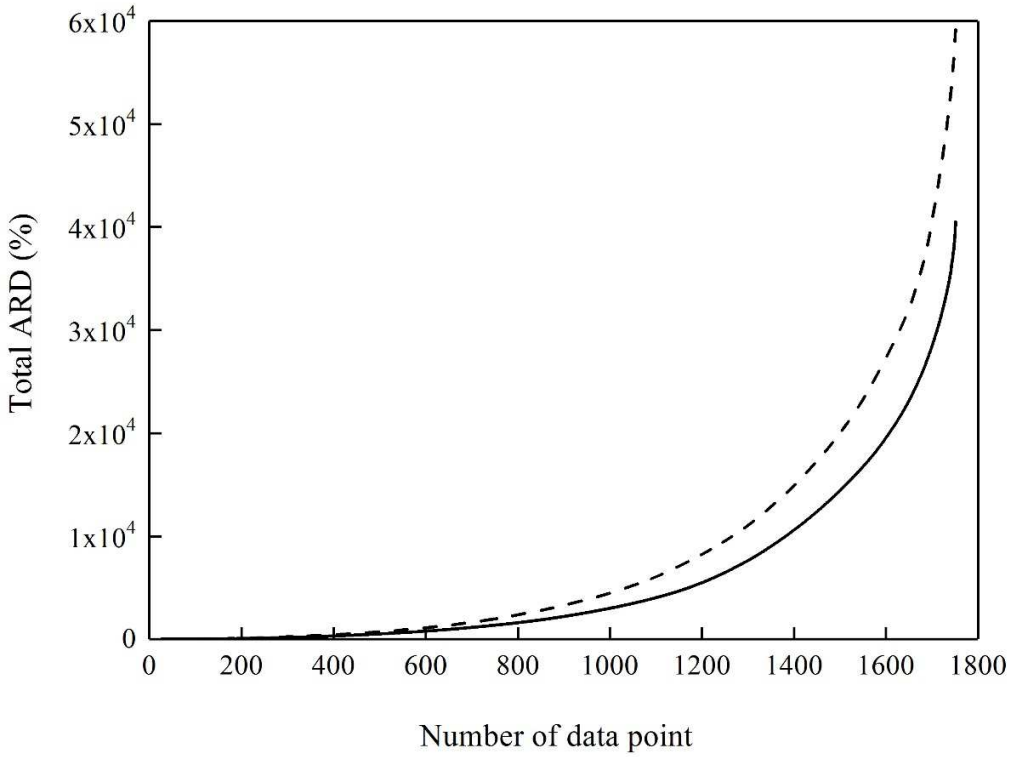

Figure 5. Total ARD (%) for the published parameters of the Original-UNIFAC (--), and the lipids group-interaction parameters for the Linear-UNIFAC (—) versus the total number of data points

The parity plots, experimental vs. calculated pressure for all data points, varying from sub-atmospheric pressure to ≈ 101 kPa (except for the glycerol systems), and for all UNIFAC-based models with published and lipids group-interaction parameters are presented in Figure 6. The glycerol systems were not included due to the large deviations for both sets of parameter values. Figure 6 (a) and (b) shows that Original- and Linear-UNIFAC models with published and lipids-based group-interaction parameters underestimate the pressure values for lipids systems. On the other hand, Figure 6 (c) for the Modified-UNIFAC model with both sets of parameters shows that this model tends to overestimate the pressure of the lipids systems. The Dortmund-UNIFAC model with published parameters underestimates the pressure, while using the lipids group-interaction parameters, an overestimation of the pressure is observed. For all models, published and lipids UNIFAC, a high deviation is observed, around 100 kPa, when compared with data at

lower pressures (e.g.: systems with alcohol compounds), though, with the lipids-based group-interaction parameters it is possible to observe a lower deviation.

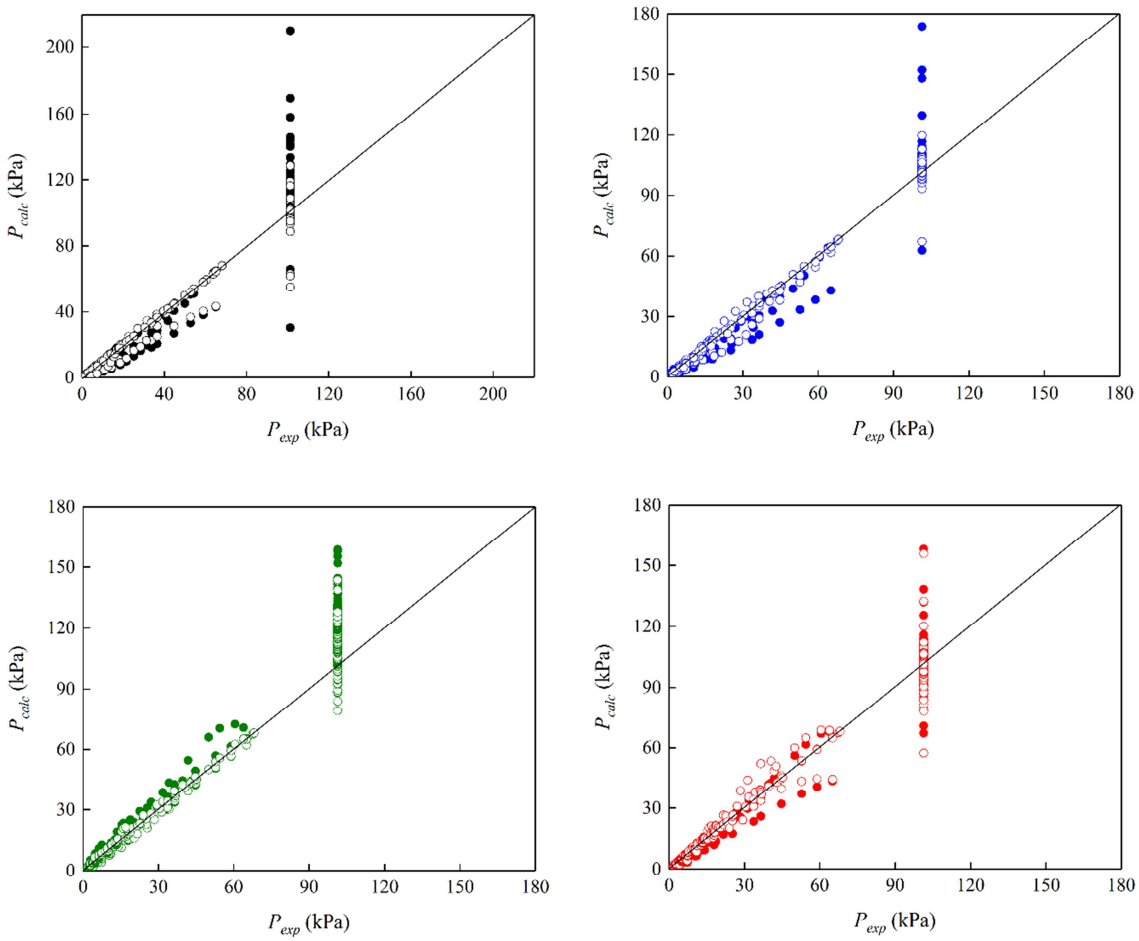

Figure 6. Experimental pressure (P_{exp}) versus calculate pressure (P_{calc}) of all data points (except for glycerol mixtures) using published parameters Original-UNIFAC (●), lipids group-interaction parameters Original-UNIFAC (○), published parameters Linear-UNIFAC (●), lipids group-interaction parameters Linear-UNIFAC (○), published parameters Modified-UNIFAC (●), lipids group-interaction parameters Modified-UNIFAC (○) and published parameters Dortmund-UNIFAC (●), lipids group-interaction parameters Dortmund-UNIFAC (○),

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337 Table 6. Group-interaction parameters a_{mn0}, a_{mn1} and a_{mn2} for the Original-, Linear-, Modified- and Dortmund-UNIFAC models fitted to lipid data

	Original Lipids	Linear Lipids		Modified Lipids			Dortmund Lipids			Temperature range	
Groups (*mn*)	a_{mn0}	a_{mn0}	a_{mn1}	a_{mn0}	a_{mn1}	a_{mn2}	a_{mn0}	a_{mn1}	a_{mn2}	T_{min} (K)	T_{max} (K)
CH_2/COOH	320.95	685.10	-2.0030	614.54	1.3170	-7.3900	1315.00	-5.0072	0.0088	371.65	524.25
COOH/CH_2	1337.28	64.02	-2.4591	151.63	-1.7430	4.0193	1970.40	-9.2756	0.0098		
CH_2/CCOO	459.02	277.81	0.0905	253.66	-0.0909	-3.7850	65.65	2.6493	-0.0008	327.37	535.50
CCOO/CH_2	395.55	76.42	-0.9890	149.49	-0.9999	0.5518	348.47	-2.2544	0.0011		
GLY/CH_3OH	159.53	86.31	0.0600	191.55	-1.5700	-8.3300	-96.34	0.0726	0.0005	282.55	561.18
CH_3OH/GLY	-7.24	49.44	0.0700	-53.90	0.0220	0.25	-73.29	0.6586	0.0001		
GLY/H_2O	138.70	258.23	-1.8800	-268.78	1.1600	-6.8700	-12.62	-0.5880	-0.0001	153.15	563.18
H_2O/GLY	140.77	-232.25	1.3010	491.57	-5.1800	-5.2400	-15.60	-0.0260	0.0001		
COOH/CCOO	-256.39	-280.38	0.0599	-211.13	-0.5032	-1.1867	18.58	-0.7700	0.0003	386.15	427.15
CCOO/COOH	660.60	610.73	-2.0130	244.68	0.0180	3.6303	57.89	0.6900	-0.0005		
CH_2/CH_3OH	515.53	757.92	0.3612	1321.00	-0.0126	9.0000	2791.12	-2.0988	-0.0013		
CH_3OH/CH_2	41.86	21.55	-0.4125	15.50	-0.7456	0.6924	82.61	-0.4901	-0.0002	337.63	617.50
CCOO/CH_3OH	421.58	369.86	0.1220	395.10	-0.5610	-0.1005	294.76	0.2493	0.0010		
CH_3OH/CCOO	229.89	5.45	-3.6900	-49.46	-0.7764	0.4687	299.76	-1.2700	-0.0001		
CH_2/OH	613.72	874.14	-0.8130	629.70	0.5774	8.7730	2159.41	-4.4226	0.0005		
OH/CH_2	35.84	35.59	-1.4292	405.36	-3.4830	-2.7090	1946.97	-3.2692	0.0001	351.46	617.50
CCOO/OH	406.11	427.70	-0.8859	266.90	-0.9990	0.6670	788.63	3.5416	-0.0002		
OH/CCOO	555.63	212.89	-0.0080	169.10	0.3607	0.1110	1176.55	-5.2856	0.0080		
CH_2/OH_{acyl}	50.30	1264.6	-6.6027	645.14	0.6569	8.4845	2252.43	-4.3074	0.0007		
OH_{acyl}/CH_2	499.23	297.02	0.5200	418.85	-3.4137	-2.9607	1860.42	-3.6451	-0.0008	461.24	493.38
CCOO/OH_{acyl}	253.23	242.30	-0.4278	-632.85	3.3000	7.2200	788.73	9.4865	0.0384		
OH_{acyl}/CCOO	124.02	104.60	-0.7800	83.48	-0.0870	1.3875	799.93	-4.8488	0.0080		
GLY/OH	120.90	41.27	-1.1893	478.6	-1.3700	-8.4900	327.01	0.2139	0.0006		
OH/GLY	128.76	-18.85	-1.5900	-217.53	-2.411	-2.1300	-287.98	-0.0030	-0.0001	232.15	561.18
GLY/CH_2	45.83	198.50	0.8480	86.36	2.3100	1.9990	18.58	0.2598	0.0006		
CH_2/GLY	137.56	232.00	1.2269	966.13	-3.5631	5. 9958	525.55	-0.4333	-0.0018		

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341 Table 6. (continuation.). Group-interaction parameters a_{mn0}, a_{mn1} and a_{mn2} for the Original-, Linear-, Modified- and Dortmund-UNIFAC models fitted to lipid data

	Original Lipids	Linear Lipids		Modified Lipids			Dortmund Lipids			Temperature range	
Groups (*mn*)	a_{mn0}	$a_{mn\,0}$	$a_{mn\,1}$	$a_{mn\,0}$	$a_{mn\,1}$	$a_{mn\,2}$	$a_{mn\,0}$	$a_{mn\,1}$	$a_{mn\,2}$	T_{min} (K)	T_{max} (K)
COOH/CH=CH	1318.50	-647.09	-5.0780	227.30	-9.1300	7.2000	-347.50	0.4466	-0.0026		
CH=CH/COOH	998.30	4334.00	0.1008	143.39	-0.8700	-0.1777	-2026.10	6.7093	-0.0046	318.14	481.08
CH_2/CH=CH	125.74	-102.30	0.1679	245.29	-0.1834	-0.3660	518.75	-0.2723	0.0033		
CH=CH/CH_2	555.93	144.80	-0.2720	-46.45	-0.1817	-1.4700	-29.00	0.0803	0.0004		
CCOO/CH=CH	135.28	200.62	7.0201	524.35	1.2210	4.7700	-546.07	-0.7768	-0.0011	318.14	514.61
CH=CH/CCOO	54.61	-153.14	4.7899	-24.00	0.6530	0.0700	981.10	-0.9514	-0.0015		
COOH/OH_{acyl}	-129.89	-39.43	2.5500	-15.76	-1.0721	0.3364	2654.44	-4.8021	0.0004	462.67	498.35
OH_{acyl}/COOH	222.89	872.19	-5.7000	213.59	0.6206	-0.9373	918.67	4.9300	-0.008		
CH=CH/CH_3OH	1424.55	875.80	-7.5100	3056.13	3.0000	1.9600	-726.27	9.6322	-0.0163	338.28	387.11
CH_3OH/CH=CH	64.65	-110.20	2.9200	-102.00	0.2710	0.8500	-103.71	0.6024	-0.0019		
CH=CH/OH	384.72	984.73	-4.1293	1192.06	3.4403	-1.4330	2903.73	-5.9300	0.0048	318.15	617.42
OH/CH=CH	407.71	215.88	-5.9670	800.02	-8.1016	0.0320	1281.84	-6.5900	0.0052		
COOH/CH_3OH	2981.07	-63.07	9.7476	714.07	9.6100	3.6990	1077.72	-3.4269	0.0001	318.15	
CH_3OH/COOH	-272.84	52.19	-5.7800	-321.10	-7.1201	3.0110	-761.76	2.2449	-0.0003		
COOH/OH	37.73	-267.59	1.8507	-75.83	0.8131	0.6300	1531.83	-4.8965	0.0007	318.15	
OH/COOH	294.83	513.52	-4.9999	35.55	-1.3114	0.3400	-1323.86	4.2727	-0.0002		
CCOO/CH_2CO	778.64	327.78	0.2500	43.65	0.1905	0.0030	113.15	0.4210	-0.0001		
CH_2CO/CCOO	44.62	33.37	-2.4311	-11.93	-0.0406	0.0010	-4.61	-0.2792	0.0001		
CH=CH/CH_2CO	528.31	607.86	7.0965	1217.00	9.7600	1.0080	485.78	0.6991	-0.0001	318.15	
CH_2CO/CH=CH	-153.42	-176.49	-9.6200	-72.75	3.5800	-0.1090	107.82	-1.5500	-0.0001		
CH_2/CH_2CO	529.15	525.94	4.4100	476.78	-5.2902	1.8030	568.85	0.1403	-0.0001		
CH2CO/CH_2	13.51	13.24	-2.8907	71.93	-9.2220	-2.9160	150.59	-0.8800	-0.0001		
COOH/CH_2CO	39.48	-17.25	5.5567	-183.43	9.2540	-6.0396	356.88	-0.8000	0.0001	303.13	318.15
CH_2CO/COOH	247.02	24.81	-0.6438	282.94	0.7244	1.0960	-156.75	0.8200	-0.0001		

Table 7. ARD (%) between experimental and predicted bubble-point pressured using UNIFAC models with the published and lipids-based group interaction parameters. The lipids-based group interaction parameters for Linear-, Modified- and Dortmund-UNIFAC are from this work.

Binary system type[a]		Original		Linear		Modified		Dortmund		Consistency score (Q_{VLE})		
		Published [2]	Lipids [13]	Published [5]	Lipids	Published [3]	Lipids	Published [4]	Lipids			
Compound I	Compound II	ARD %								$Q_{VLE,\ minimum}$	$Q_{VLE,\ maximum}$	$Q_{VLE,\ average}$
Saturated Fatty Acids	Saturated Fatty Acids	2.67	2.63	2.22	2.15	2.27	2.24	2.26	2.20	0.000	0.650	0.137
Saturated Ester	Saturated Ester or Hydrocarbon	6.18	5.71	5.16	5.12	5.00	4.85	5.06	4.84	0.001	0.760	0.258
Glycerol	Methanol	20.76	12.50	19.14	9.31	17.14	11.11	19.39	10.26	0.063	0.500	0.243
Glycerol	Water	91.50	88.50	68.81	48.67	78.87	50.98	198.01	56.83	0.005	0.500	0.172
Saturated Fatty Acids	Saturated Ester	24.39	1.65	8.34	1.58	9.76	1.53	10.06	4.25	0.027	0.027	0.027
Saturated Ester	Methanol	15.14	10.89	9.44	5.05	17.64	14.66	9.04	8.29	0.250	0.500	0.400
Saturated. Ester	Ethanol	11.69	2.58	2.55	2.23	9.63	4.25	6.58	5.27	0.250	0.250	0.250
Saturated Monoacylglycerol	Saturated Ester	11.63	5.45	24.07	3.76	9.17	4.38	3.91	3.84	0.009	0.009	0.009
Glycerol	Saturated Alcohol	27.99	24.63	22.76	21.87	21.90	20.56	17.27	15.91	0.000	0.460	0.188
Unsaturated Fatty Acids	Saturated Fatty Acid or Hydrocarbon	30.76	28.56	23.15	21.78	20.56	19.64	18.41	14.49	0.007	0.500	0.183
Unsaturated Ester or Triacylglycerol	Saturated Ester or Hydrocarbon	17.88	15.48	9.28	9.15	4.58	4.51	7.55	7.48	0.097	0.377	0.248
Saturated Monoacylglycerol	Saturated Fatty Acids	17.26	3.62	3.91	1.40	17.14	1.92	22.21	5.93	0.008	0.011	0.009
Unsaturated Ester	Methanol	22.25	2.94	4.31	4.03	24.66	15.39	9.53	4.94	0.250	0.250	0.250
Unsaturated Ester	Ethanol	33.87	32.07	13.47	6.88	23.77	12.10	10.68	10.55	0.001	0.250	0.125
Unsaturated Fatty Acids	Methanol	10.12	5.91	18.20	8.06	33.94	8.69	8.56	6.28	0.500	0.500	0.500
Saturated Fatty Acids	Saturated Alcohol	4.68	4.07	11.40	6.70	13.19	6.60	7.77	5.31	0.008	0.500	0.254
Unsaturated Triacylglycerol	Acetone	21.30	1.99	21.49	1.19	16.80	11.21	8.72	8.53	0.476	0.476	0.476
Saturated Fatty Acids	Acetone	20.68	2.10	18.68	0.95	4.55	2.97	6.76	2.40	0.500	0.500	0.500

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ARD (%) for all model (Published and lipids)	21.71	13.96	15.91	8.88	18.36	10.98	20.65	9.87

[a] The binary systems tested are from the SPEED Lipids database.

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5. Model extrapolation capability for SLE prediction

The parameters obtained for each UNIFAC model are further validated by checking their prediction capability for lipids SLE data. As mentioned previously, SLE data is not used for the regression of the parameters. The SLE data is extracted from the SPEED Lipids Database [13]. The SLE data is organized in category-groups in the same way as the VLE data, by applying the data organization algorithm (Algorithm A). For consistency, the same name category-groups are used for describing the SLE data sets. A new category-group is defined for SLE, named "Others". This category-group contains unsaturated triacylglycerols – saturated fatty acids and saturated triacylglycerols – unsaturated fatty acids type of systems. Available SLE data used in this study is given in Table 8.

All the SLE calculations are performed with ICAS-MoT [26]. SLE is calculated using Eq. 11. The melting temperature (T_m) is taken from literature when data is available; otherwise values from SPEED Lipids Database [13] are used. The heat of fusion (H_f) values are taken from SPEED Lipids Database.

$$\ln(x_i) = \ln \gamma_i + H_f \left(\frac{1}{T_{m,i}} - \frac{1}{T} \right) \tag{11}$$

where x_i is the mole fraction of the compound with higher melting point, γ_i is the activity coefficient of compound i, H_f is the fusion enthalpy of compound i, $T_{m,i}$ is the melting point of compound i, and T is the mixture melting temperature.

The results obtained for each category-group, with all UNIFAC-based models, using both published and lipids-based group-interaction parameters are given in Table 9. A slight improvement is noticed for Modified-UNIFAC model using the lipids-based group-interaction parameters compared to the published parameters, except for Linear- and Dortmund-UNIFAC

367 model. This bigger deviation for Dortmund-UNIFAC with lipids group-interaction parameters
368 could be due to the R_k and Q_k parameters, which are not regressed for lipids systems in this work.
369 Also, the extrapolation of the parameters to outside the range of temperatures and phase
370 equilibria type could affect the prediction of this models. From all UNIFAC-based models using
371 published parameters, the best performance is obtained with Dortmund-UNIFAC model (ARD =
372 1.34%) followed by Linear-UNIFAC model (ARD = 1.35%). Using the lipids group-interaction
373 parameters, again the best overall results is provided Linear-UNIFAC model (ARD = 1.43%).
374 Analyzing the deviations for each-category group, the best performances are in general when
375 lipids group-interaction parameters are used. It is important to emphasize, that for the SLE
376 prediction, the parameters are not only extrapolated to another type of phase equilibria, but also
377 to another range of temperatures (see also Table 6 and Table 8), so unexpected behavior may
378 occur.
379 An example of SLE prediction is presented in Figure 7, where the best performances are shown
380 for different UNIFAC-based models (see also Table 9). In Figure 7, the prediction for system
381 ethyl linoleate + ethyl stearate [27] is presented for Linear, Modified and Dortmund UNIFAC
382 models using lipids-based group-interaction parameters, all models presented analogous
383 behavior.
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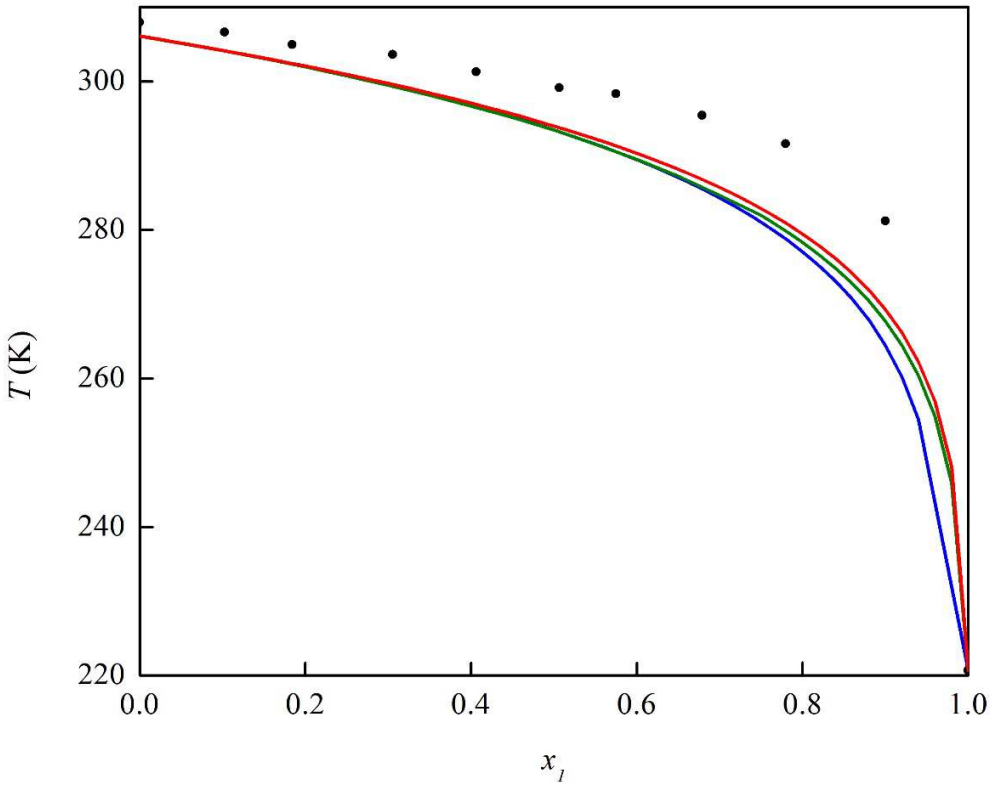

Figure 7. SLE system ethyl linoleate (x_1) + ethyl stearate (x_2). Experimental data [27] (●). Lipids-based group interaction parameters UNIFAC models: Linear (—), Modified (—) and Dortmund (—)

The extrapolation results do show that in general the lipids group-interaction parameters can be used for SLE predictions, nonetheless one should use them with some care since different temperature ranges and behaviors are encountered for this type of systems and this form of phase equilibria. It cannot be concluded that one model works best for all type of SLE systems, but the selection of a model for performing SLE prediction should be done according to the type of SLE systems involved.

Table 8. Database used for the SLE predictions with UNIFAC models.

Category-group	System type		Constitutive groups	SLE datasets	Temperature range $T_{minimum}$ (K)	Temperature range $T_{maximum}$ (K)
1.1.1.	Saturated Fatty Acids	Saturated Fatty Acids	CH_2 COOH	12	278.36	343.98
1.1.2.	Saturated Ester	Saturated Ester	CH_2 CCOO	9	272.51	314.07
3.2.5.	Unsaturated Fatty Acids	Sat. FA	CH_2 COOH CH=CH	5	264.99	342.25
3.2.6.	Unsaturated Ester Saturated Triacylglycerol	Saturated Ester Unsaturated Triacylglycerol	CH_2 CH=CH CCOO	8	220.68	338.79
6.3.2.	Saturated Fatty Acids	Acetone	CH_2 CH=CH CH_2CO COOH	1	333.71	329.95
Other *	Unsaturated Triacylglycerol Saturated Triacylglycerol	Saturated Fatty Acids Unsaturated Fatty Acids	CH_2 CH=CH CH_2COO COOH	9	258.62	342.25
Total				44	220.68	343.98

*Other category-group contains constitutive groups that were not in any of the VLE identified category-groups

Table 9. SLE prediction for Linear, Modified and Dortmund-UNIFAC using published and lipids-based group interaction parameters.

Category-Group	Linear		Modified		Dortmund	
	Published [5]	Lipids	Published [3]	Lipids	Published [5]	Lipids
	ARD (%)					
1.1.1	0.94	0.94	0.92	0.92	0.92	0.92
1.1.2	1.25	1.25	1.15	1.33	1.16	1.15
3.2.5	0.36	1.66	0.38	0.42	0.43	0.56
3.2.6	2.33	2.37	2.35	2.33	2.32	2.32
6.3.2	0.35	0.19	2.21	2.18	1.43	1.43
Other	2.88	2.20	4.76	3.51	1.78	3.77
Total ARD (%)[b]	1.35	1.43	1.96	1.78	1.34	1.69

[a] $ARD(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{T^{experimental} - T^{calculated}}{T^{experimental}}\right|.100$, [b] $TotalARD(\%) = \frac{1}{M}\, X.M.N$

6. Conclusions

The method of Perederic et al. [2017] was successfully applied for the binary interaction parameter estimation for three UNIFAC-based models: Linear, Modified and Dortmund. For the estimation of the binary group interaction parameters, the SPEED Lipids Database was used for VLE data collection, and the same data sets were used as in Perederic et al. [2017]. Two new functional groups were added for the description of acylglycerols (OH_{acyl}) and glycerol (GLY) compounds for all models for improving their prediction capabilities for lipids, as was also done for Original-UNIFAC [13].

The estimated group-interaction parameters have been validated by checking their performances on all VLE data sets available in the SPEED Lipids Database. All UNIFAC-based models present better performances with the new sets of binary group-interaction parameters compared to the original published parameters. Among all the models, the Linear-UNIFAC model has been found to give the best overall performance for VLE predictions. Addition of the OH_{acyl} improves qualitatively and quantitatively the VLE prediction of acylglycerol systems. For the glycerol systems, introduction of the GLY group results in a significant improvement in the VLE prediction, but the deviations remain quite high for all models considered. This is a limitation of the group contribution concept for the description of systems containing compounds with many OH groups attached to the adjacent carbon atoms, such as glycerol, that has three OH groups. For strongly hydrogen bonding systems, the group contribution concept does not work very well and more advanced models are needed e.g. association equations of state like CPA [23] and SAFT [24].

The parameters are also tested for SLE predictions for lipids systems. All the SLE datasets are collected from the SPEED Lipids Database. For the UNIFAC with lipids group-interaction parameters, a slight improvement in SLE prediction is observed for Modified-UNIFAC model when compared to the published parameters are used.

The main drawback in developing and extending the predictive capabilities of the group contribution concept remains the accuracy and availability of experimental data used for parameter estimation. Attention should be taken when using the parameters for other types of systems and other range of temperatures than the ones used in the parameter estimation as well as for strongly polar and hydrogen bonding systems for which the group contribution and local composition concepts deteriorate.

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