

Thermodynamic Modeling of Multi-phase Solid–Liquid Equilibria in Industrial-Grade Oils and Fats

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Abstract Compositional thermodynamic phase separation is investigated for industrial-grade vegetable oils with complex compositions. Solid–liquid equilibria have been calculated by utilizing the Margules 2-suffix activity-coefficient model in combination with minimization of the Gibb’s free energy of the system. On the basis of quasi-equilibrium solid-fat content (SFC) measurements, a new approach to the estimation of the interaction parameters, needed for the activity-coefficient model, has been developed. The parameters are fitted by matching the SFC of two oils at various degrees of dilution and isothermal temperatures. Subsequently, the parameters are successfully validated against three oils, rich in asymmetric and symmetric triacylglycerols (TAG), respectively. The new approach developed is shown to be very flexible, allowing incorporation of additional TAG and polymorphic states. It thereby provides a simple way to dealing with multi-component, multi-phase TAG mixtures without having the required binary interaction parameters at hand a priori. This ultimately provides a powerful, predictive tool which may serve as a starting point for laboratory screening and creation of tailor-made products because many different oil mixtures can be evaluated quickly with respect to specific properties, prior to more time-consuming experimental evaluation.

Keywords Triacylglycerols (TAG) · Solid-fat content (SFC) · Solid–liquid equilibrium (SLE) · Interaction parameters · Vegetable oil · Activity coefficients · Multi phase · Mathematical modeling

Abbreviations

List of Symbols

α	Polymorphic form, least stable
β	Polymorphic form, most stable
β'	Polymorphic form, intermediate stability
γ_i^j	Activity coefficient of TAG i in the solid phase, j
γ_i^l	Activity coefficient of TAG i in the liquid phase, l
μ_i^j (J/mol)	Chemical potential of component in the solid phase, j
μ_i^l (J/mol)	Chemical potential of component i in the liquid phase, l
θ	Interaction parameter matrix
A_{ik}	Interaction parameter between TAG i and k
G (J/mol)	Gibb’s free energy of the system
g^E (J/mol)	Gibb’s excess energy
ΔH_i^{sl} (J/mol)	Heat of fusion of TAG i
M_i (g/mol)	Molar mass of TAG i
m	Number of evaluated data points
N	Number of components in the system
n_i^j (mol)	Number of moles of TAG i in the solid phase, j
n^j (mol)	Number of moles in the solid phase, j
n^l (mol)	Number of moles in the liquid phase, l
n_i^l (mol)	Number of moles of TAG i in the liquid phase, l (mol)
$n_i^{l,eq}$	Number of moles of TAG i in the liquid phase at equilibrium

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$n_{i,\text{tot}}$ (mol)	Total amount of component i in the system
P	Number of phases in the system
R [J/(mol K)]	Gas constant (8.314)
T (K)	Temperature
$T_{m,i}$ (K)	Melting temperature of TAG i
x_i	Mole fraction of TAG i in the liquid phase, l
y_i	Mole fraction of component i in the trial phase
Y_i	Phase stability evaluation parameter
z_i^j	Mole fraction of TAG i in the solid phase, j

Sub/superscripts

d	d th adjustable parameter
i	i th triacylglycerol
j	j th solid phase
k	k th triacylglycerol
l	Liquid phase
s	s th data point
y	Trial phase

Introduction

Vegetable oils and fats constitute a considerable part of many food products such as chocolate, margarine, bread and spreads. Several attractive properties found in these products, including flavor release, melting profile and appearance, are governed by the oils and fats added [1]. Consequently, altering the fat phase may lead to enhanced properties of the products. To date such improvements have largely been based on empirical laboratory tests designed by skilled experts and specialists drawing on many years of experience and knowledge. Nonetheless, unexpected outcomes are quite often observed when mixing various oil fractions. For example, mixing cocoa butter substitutes (CBS) with cocoa butter leads to a strong incompatibility in the solid phase, rendering a product softer than expected. Furthermore, some fats used for chocolate fillings are seen to cause oil migration bloom much faster than others [2]. Mapping the behavior of oils and fats in a physiochemical context may improve understanding and predictability of the outcome when different oils and fats are mixed.

The primary focus of the present work is vegetable oils and fats originating from palm fruits, palm and shea kernels. Natural and interesterified oils are used to accommodate both symmetric and asymmetric triacylglycerols (TAG).

Vegetable oils usually contain more than 95 % TAG, a family of molecules which is shown to govern many of the aforementioned properties of oils and fats. Consequently, this family of compounds is the focus of the experiments and simulations conducted in this manuscript.

The incentive for the present work is to obtain a predictive tool, capable of describing solid–liquid phase equilibria (SLE) for several oils, with the ability to accommodate the oil complexity usually encountered in the industrial sector, with regard to composition and purity. Furthermore, the aim is to develop a simple and quick method to obtain the required TAG interaction parameters, without the need for excessive experiments with analytically pure, binary TAG mixtures.

The calculated equilibria can be used to determine the solid-fat content (SFC) of the oil-fat mixtures together with the number of phases and the TAG composition for each of these. Furthermore, it may shed light on solid–solid phase splits, which may be impossible to determine experimentally, but can be a primary driver for some of the phenomena, e.g., oil migration and rate of crystallization, observed when oils crystallize.

Previous Models Describing Thermodynamic Solid–Liquid Equilibria

The approach suggested in this work concerns calculation of the thermodynamic equilibrium for a given oil at a given temperature by minimizing the Gibbs free energy of the system. Simpler approaches for calculating the equilibrium in terms of solubility of given components were used previously [3–5], but these approaches proved inadequate when dealing with multi-component systems, involving solid–solid interactions.

The method of calculating multi-phase SLE for TAG mixtures by minimizing the Gibbs free energy of the system has been well documented by Wesdorp [6, 7] who built his minimization calculations on the work of Michelsen [8–10]. Using the Margules 2 and 3-suffix activity-coefficient models, Wesdorp did a comprehensive experimental study on binary interaction parameters for a fairly large number of TAG molecules, ultimately suggesting a correlation between the symmetric interaction parameter and the geometrical differences between TAG. A similar approach was used by Rousset *et al.* [11] for a binary TAG system.

The interaction correlation suggested by Wesdorp was later used by Santos and Los *et al.* [12–14] to calculate SLE for complex oil blends with up to 17 different TAG. The correlation was based solely on the chain-length differences between the fatty-acid moieties attached to the glycerol backbones of the mixed TAG and disregarded any degree of unsaturation, decreasing the predictive power of the correlated interaction parameters substantially [5].

Present Approach to Obtaining Interaction Parameters

To overcome the potential pitfalls, described above, involved when using the interaction parameter correlation

developed and at the same time accommodate the complexity of industrial-grade oils with respect to impurities and minor components, a new approach to estimation of interaction parameters is proposed and evaluated here. The interaction parameters required are fitted so that the total SFC of a given oil at a given temperature matches the experimentally obtained value. In this way, pure binary mixtures for each pair of TAG are not required to obtain the corresponding binary interaction parameters. Nonetheless, the immediate disadvantage of this approach is that the experimental SFC for a single experiment can be fitted using different combinations of interaction parameters, meaning the estimated parameters would be purely empirical lacking predictive power. However, if the parameters are fitted to a large array of experiments, where oils are mixed in different ratios and evaluated at different temperatures, it is likely that a unique set of parameters can be obtained.

Methodology for Solid–Liquid Equilibria Calculations

Solid–liquid equilibria calculations can be very complex when non-ideal mixing is taken into account [15–17]. Non-ideal behavior occurs as a consequence of different TAG having different interactions with each other and is responsible for multiple co-existing solid phases [6, 10, 18, 19].

Conditions for Solid–Liquid Equilibria

For solid–liquid systems, activity-coefficient models are generally used to describe non-ideal interactions [18, 20]. At equilibrium, it is required that the chemical potential for a given component should be the same in all phases present [17]:

$$\mu_i^l = \mu_i^j \tag{1}$$

where i and j refer to the i th component and j th solid phase, respectively.

Often, change in heat capacity is disregarded and ideal liquid behavior is assumed (i.e., $\gamma_i^l = 1$) [17, 20]. This approach has been well described in the literature and leads to the following equations [5, 6]:

$$\mu_i^l = RT \ln(x_i) \tag{2}$$

$$\mu_i^j = RT \left[\frac{\Delta H_i^{sl}}{RT_{m,i}} \left(\frac{T_{m,i} - T}{T} \right) + \ln(\gamma_i^j z_i) \right] \tag{3}$$

where R is the gas constant, T the temperature, x_i and z_i the mole fraction of component i in the liquid and solid phase, ΔH_i^{sl} the heat of fusion, $T_{m,i}$ the melting point and γ_i^j the activity coefficient.

Stoichiometric Constraints

The solution to the solid–liquid equilibrium must also satisfy the overall mass-balance leading to the formulation of a few stoichiometric constraints. The mole fractions in each phase must sum to unity, and the sum of the moles of component i in all phases must be equal to the total number of moles of component i .

$$\sum_{i=1}^N x_i = \sum_{i=1}^N z_i^j = 1 \tag{4}$$

$$\sum_{j=1}^{P-1} z_i^j n^j + x_i n^l = n_{i,tot} \tag{5}$$

From Eqs. (3–5) it is evident that $P(N + 1)$ equations with $P(N + 1)$ unknowns arise. P and N are the number of phases and components, respectively. Once values of the activity coefficients are available, this non-linear set of equations can in principle be solved using an appropriate method.

Activity-Coefficient Model

Several activity-coefficient models of increasing complexity exist [20–22]. Based on Wesdorp’s suggestion, the simple Margules 2-suffix model has been chosen here since this model was shown to perform well in mixtures with components having similar molecular volumes, shapes and chemical compositions [6, 12]. Furthermore, advanced models require both precise and extensive amounts of pure-component data, which are not available for TAG. The Margules 2-suffix model assumes symmetric interactions between TAG and thus requires only one interaction parameter per binary pair of TAG. For a multi-component system, the activity coefficients are described as a function of mole fractions and binary-interaction parameters:

$$A_{ik} = A_{ki} \tag{6}$$

$$RT \ln \gamma_i = -g^E + \sum_{k=1, i \neq k}^N A_{ik} x_k \tag{7}$$

$$g^E = \sum_{i=1}^N \sum_{k=i+1}^N A_{ik} x_i x_k \tag{8}$$

Triacylglycerols have been shown to behave nearly athermally when mixed and thus temperature dependence of the interaction parameters is disregarded [6, 20].

Phase Splits

If the number of phases at equilibrium is known Eqs. (2–5) can be solved by successive substitution [10]. However, the number of phases at equilibrium is usually not known *a priori*, and a method is therefore needed to determine whether a potential phase split is feasible.

Michelsen [8] has developed a method (the tangent-plane criteria) to evaluate whether a given system is stable, or whether addition of a trial phase (y) would increase stability in terms of lowering the overall Gibbs free energy of the system. This method has successfully been applied to solid–liquid systems by rewriting the original equations [6]:

$$\ln(Y_i) = \frac{\mu_i^j - \mu_i^y}{RT} - \ln \gamma_i^y \quad (9)$$

$$y_i = \frac{Y_i}{\sum_i Y_i} \quad (10)$$

According to the tangent-plane criteria, Y_i must be less than unity for the system to be stable and therefore a value above unity suggests that a phase split would result in an overall decrease in Gibbs free energy. The methodology to ensure that the minimum Gibbs free energy is reached is well described by Michelsen [8].

Phase Coalescence

During the calculations it is possible that the overall Gibbs free energy can be decreased by reducing the number of phases on account of coalescence. Therefore, during the calculations, if one or more phases comprise less than 10 % of the overall system, coalescence of these qualifying phases with all other phases is evaluated.

Minimizing the Gibbs Free Energy

In general, the Gibbs free energy of the system should be at its minimum and the mass-balance constraints satisfied to ensure equilibrium conditions.

$$G = \sum_{j=1}^P \sum_{i=1}^N n_i^j \mu_i^j \quad (11)$$

Minimization can be solved by applying the Newton–Raphson method as described by Michelsen [10]. The iterative solving procedure, handling minimization of the Gibbs free energy has been adopted from Wesdorp [6].

When the Gibbs free energy of the system has been minimized, the SFC of the system can be calculated:

$$\text{SFC} = \frac{\sum_{j=1}^{P-1} \left[n^j \sum_{i=1}^N z_i^j M_i \right]}{\sum_{i=1}^N n_{i,\text{tot}} M_i} \quad (12)$$

All calculations and simulations were carried out on a standard PC and the minimization routine was written in C++.

Materials and Methods

Materials

Six industrial-grade oils, both asymmetric (interesterified) and symmetric, obtained from AAK Denmark A/S, were used in the present work. The TAG compositions of the oils are shown in Table 1. All oils were neutralized, bleached and deodorized prior to the experimental work. The compositions presented are simplified, following a lumping-procedure (to be explained later), to remove several minor TAG.

If the diacylglyceride (DAG) content in the oils was above 3 %, the oils were washed with ethanol, until the diacylglyceride content was brought beneath this threshold.

Analytical Equipment

SFC measurements were carried out using pulsed NMR on a Bruker Minispec SFC analyzer. Differential-scanning calorimetry (DSC) measurements were carried out on a Mettler Toledo DSC823°. Aluminum, 40 μl crucibles were used and all samples were analyzed using a heating-slope of 5 $^\circ\text{C}/\text{min}$. X-ray measurements were carried out using Siemens D500 equipment and 10 mg of the given oil sample.

For all analyses the samples were kept at 60 $^\circ\text{C}$ for 2 h and subsequently placed at the desired holding temperature (10–25 $^\circ\text{C}$) for 100 h before analyzing the samples.

Methodology for Obtaining Interaction Parameters

Lumping of Oil Compositions

The industrial-grade oils contained an abundant number of TAG of which a fairly large share were only present in low concentrations. To decrease the complexity of the oil (and thereby increase the calculation speed), the number of TAG was reduced by lumping them into groups, using two criteria: First, one TAG from every TAG-category (see Table 1) should be present in the composition. This was desirable in order to capture the specific features linked to the various TAG categories [23, 24]. Secondly, if a TAG comprised less than 1.5 % of the oil, the TAG was removed and the amount added to the most similar TAG included in the

Table 1 Triacylglycerol composition [% (w/w)] and pure-component data for the six used oils

TAG category	TAG	References	$T_m(\beta')$ (K)	$\Delta H^{sl}(\beta')$ (kJ/mol)	Oils					
					I	II	III	IV	V	VI
1–Trisat.	StStSt	[32]	336.6	149.7	–	–	2.5	0.5	1.0	2.4
	PPP	[32]	329.8	129.0	6	1.7	–	–	3.4	–
	PPSt	[6, 32]	331.3	124.0	4.2	3.3	–	–	–	–
2–Mono-unsat.	POP	[6]	303.6	104.0	13.4	4.8	–	–	60.6	0.8
	PPO	[32]	307.6	111.0	30.7	10.9	–	–	5.5	–
	POSt	[6]	306.0	114.0	5.6	10	2.1	–	13.6	7.7
	PStO	[32]	313.0	109.3	11.8	23.9	4.4	–	–	–
	StOSt	[6]	310.4	111.0	1.5	5.7	24.1	1.3	1.9	71.1
	StStO	[32]	315.9	138.3	1.9	15	51.2	–	–	–
3–Disat., di-unsat.	PLiP	[6]	300.1 (γ)	96.2 (γ)	12.8	13.3	–	–	8.0	–
	StLiSt	[49]	302.1 (γ)	137.4 (γ)	–	–	6.5	0.6	–	8.6
4–Di-unsat.	POO	[32]	275.5	93.3	8	3.9	–	11.9	4.1	1.0
	StOO	[32]	281.6	109.8	2.4	6.4	8.3	11.6	1.3	8.4
5–Tri-unsat.	OOO	[32]	264.0	79.0	1.7	1.1	0.9	74.1	1.4	1.4

The conventional nomenclature has been used: the three fatty acid moieties attached to the glycerol backbone is abbreviated using letters. The leftmost column denotes the category to which the TAG belong. *St* stearic, *P* palmitic, *O* oleic, *Li* linoleic

composition, having this TAG's pure-component properties. For example, PPS would be added to PPP (Having the pure-component properties of PPP), LiOO would be added to OOO and so on.

Although up to 3 % diacylglycerols were allowed in the oils, these were disregarded in the oil compositions.

Polymorphism

Generally, TAG are considered to exhibit monotropic polymorphism in terms of three major polymorphs together with a number of sub-modifications, more difficult to distinguish from one another [25–28]. The major polymorphs are named α , β' and β in order of increasing stability. The stability is linked to the order in the crystal structure, so that the α -phase can be regarded as behaving ideally, while the latter two modifications may show non-ideal behavior. The instability of the α -phase renders its presence improbable at equilibrium for all types of TAG considered in this work [11, 27, 29, 30]. Therefore this modification is left out of the calculations.

Generally, β' polymorphism is promoted by interesterification of oils by increasing the amount of asymmetric TAG [31, 32] and palm oil based blends are often shown to be β' tending [33–35]. Furthermore, double chain-length packing of the TAG is common for many natural oil systems, comprising a wide array of different TAG [25, 32, 36, 37]. Although mono-acid saturated TAG generally exhibit β polymorphism, this group only comprises a few percent

of the investigated oils, and are assumed to exhibit β' polymorphism. Symmetric, mono-unsaturated TAG also exhibit β conformation in their most stable state. However none of the oils have been tempered and therefore it is assumed that the symmetric oils are β' tending under the conditions used in this work [27, 32].

Finally, the potential presence of molecular compounds has been disregarded [38–40].

Obtaining Interaction Parameters from SFC Measurements

A new approach to estimating interaction parameters is proposed in this work. In complex systems, several TAG exist and it would be prohibitively time-consuming to estimate the required interaction parameters from binary mixtures of the complete TAG combination matrix. In addition, not all TAG needed may be commercially available in pure form. Hence, a new approach to estimating interaction parameters, based on SFC, has been developed. This method essentially estimates the interaction parameters from the best match between simulated and experimental SFC at quasi-equilibrium.

Undoubtedly, for a single experiment it would be possible to arrive at the correct SFC value using several combinations of the interaction parameters. Therefore, a large array of experimental SFC data points are needed to ensure semi-universal values of the estimated interaction parameters. To form this array of experimental data, oils I and II were used and diluted with liquid oil (oil IV) in different

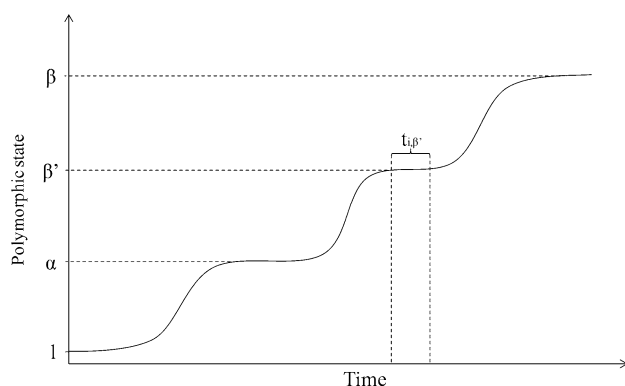


Fig. 1 Schematic representation of the quasi-equilibrium states at which data for parameter estimation can be obtained. $t_{i,\beta'}$ represents the interval during which data for the β' polymorph can be obtained

ratios. The isothermal holding temperature was varied between 10 and 25 °C to obtain different concentrations of TAG in the liquid and solid phases. In total, 80 experimental SFC points served as the foundation for the following parameter estimation.

The Concept of Quasi-Equilibria

The term “quasi-equilibrium” describes an apparent steady state, or time span, during which no changes are observed in the system. The concept behind the quasi-equilibrium state, shaping the foundation of the following parameter estimation, was that no significant changes would occur in the crystallized oils around the time of SFC measurement—the system need not be in its final equilibrium state, but it should be possible to relate the SFC measurement to specific polymorphic states of the involved TAG. Consequently, interaction parameters for different polymorphic states could then be obtained by “trapping” the system in the desired polymorphic form and measuring the SFC under these conditions. This principle is schematically shown in Fig. 1.

The quasi-equilibrium SFC of the oils were obtained by leaving the oils at a specified temperature for a given time. Whether quasi-equilibrium was reached was evaluated by changes in SFC over time, coupled with DSC and X-ray measurements. The oils were thus evaluated isothermally over a certain time span until a quasi-equilibrium state was evident from the given measurements, keeping in mind that dilution and temperature may alter the crystallization kinetics [11, 41, 42].

Methodology of Parameter Fitting

The interaction parameters were fitted by minimization of a defined objective function. The non-linear least squares

method objective function was applied [43, 44]. The sum of squares of the residuals (SSR) is calculated as shown in Eq. (13). Using this method, all adjustable parameters are fitted to all datasets at once.

$$SSR = \sum_{s=1}^m [\text{SFC}_{\text{exp},s} - \text{SFC}(\theta)_s]^2 \quad (13)$$

where s is the current data point, m is the number of data points, $\text{SFC}_{\text{exp},s}$ is the experimental SFC value at point s and $\text{SFC}(\theta)_s$ is the simulated SFC value at point s .

Several minimization methods of varying complexity, convergence intervals and computation speeds exist [10, 43, 45]. In this case, a rather simple parabolic interpolation method is used [44]. This method makes for a fairly transparent approach, where the minimization pathway is easy to monitor and assess. All calculations and simulations are carried out on a standard PC, and the model was programmed in C++.

Parameter Values and Boundaries

In the present work it was of interest to determine all interaction parameters linked to the various oils. Therefore, every possible combination of binary interaction parameters was added to the matrix, θ . The parameter boundaries (minimum = 0, maximum = 8) were defined as suggested by Wesdorp [6]. To ensure that the global minimum was reached during minimization the minimization routine was run using three different matrices, θ_{init} , holding the initial guesses, namely ideal behavior ($\theta_{\text{init}} = 0$), near-immiscible behavior ($\theta_{\text{init}} = 8$) and the correlation suggested by Wesdorp [6] which lay somewhere in between guess 1 and 2.

Parameter Importance and Sensitivity

The developed model is analyzed by evaluating the differential coefficient of every data set for a small change in every adjustable parameter, d [45–47]:

$$S_{s,d} = \frac{\partial \text{SFC}_s}{\partial \theta_d} = \frac{\text{SFC}_s(\theta_d + \Delta\theta_d) - \text{SFC}_s(\theta_d)}{\Delta\theta_d} \quad (14)$$

Then for every parameter the total change over all data sets can be calculated. This would describe the importance of every parameter, δ_d , on the model output:

$$\delta_d = \sqrt{\frac{1}{m} \sum_{i=1}^m S_{s,d}^2} \quad (15)$$

The sensitivity of selected parameters are evaluated by the OAT (one at a time) method [47], where the parameters are repeatedly varied, one at a time, while the rest are kept constant.

Fig. 2 DSC (*left*) and pNMR (*right*) measurements for oil I as a function of time at a holding temperature of 15 °C

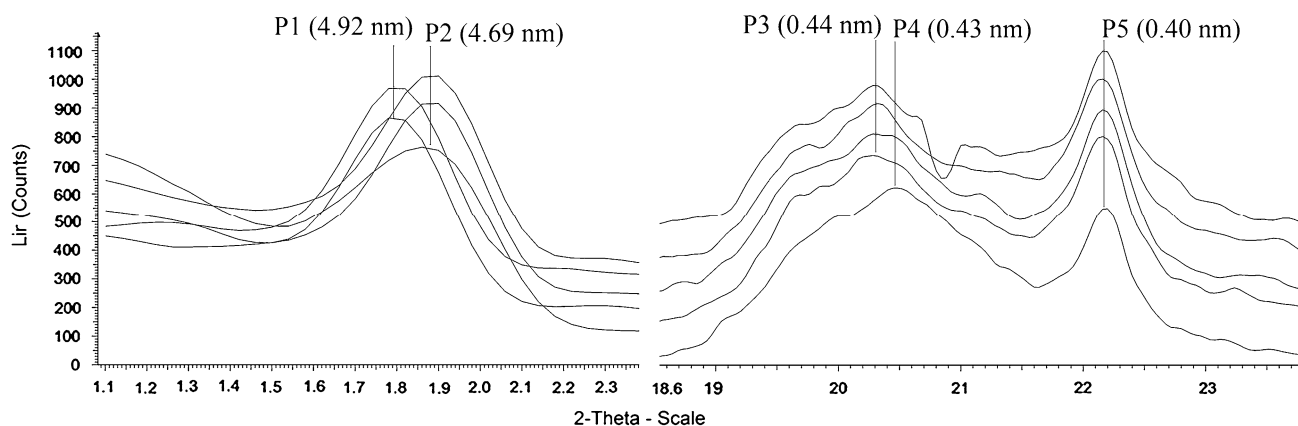
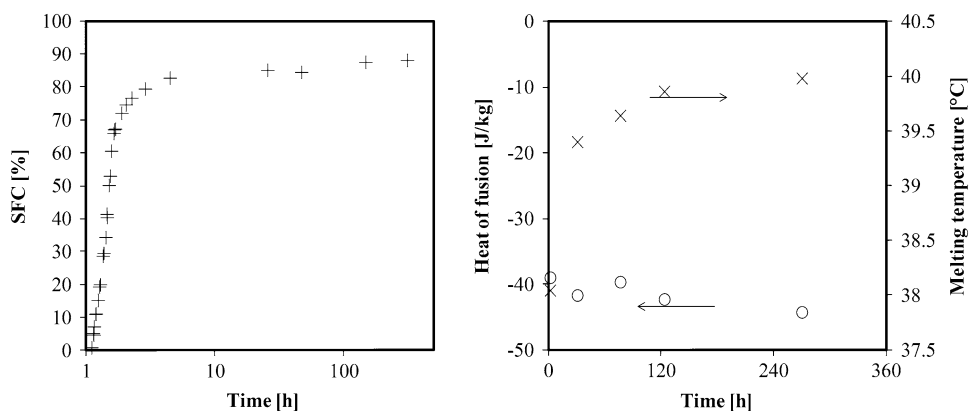


Fig. 3 Short and wide-angle X-ray measurements vs time for oil I. The lines (from *bottom to top*) represent the isothermal holding time, being 2 h, 1, 4, 7 and 10 days, respectively. The holding temperature

was 15 °C. The diffractograms are printed directly from the X-ray analysis software and the numbers on the axes are therefore very small

Experimental Results and Model Analysis

Experimental Determination of Quasi-Equilibria

Figure 2 shows SFC and DSC measurements for oil I which were used to illustrate the approach to validate quasi-equilibrium states for the oils. From all analyses it was evident that only small changes occurred to the system after 100 h at a given temperature. The X-ray diffractograms in Fig. 3 confirmed that no major polymorphic transitions were occurring after a holding time of approximately 100 h and the values clearly suggested the expected double chain-length packing for oil I [25, 36, 37]. Furthermore, the wide angle diffractograms pointed towards a β' dominated system.

In conclusion the quasi-equilibrium polymorphic state of the crystals seemed to occur rather quickly. Small changes were observed between 2 and 24 h, but after that the system appeared stable with regard to polymorphism. In general, the systems were shown to reach a quasi-equilibrium

in less than 120 h. For this reason, all SFC measurements were performed after 1 week at constant temperature.

Resulting Parameter Fits

Figure 4 depicts the parity plots for experimental vs simulated SFC values using the fitted parameter set. For confidentiality reasons, the actual parameter values obtained are not provided.

There is a very good match between simulations and experimental data over the temperature span with significantly different amounts of solid fat, e.g., oil I contains 93.8 and 44.4 % solid fat at 10 and 25 °C, respectively. This leads to different TAG concentrations in the solid phases at different temperatures. The largest deviation between experimental data and simulations is 3.2 % for both oils I and II. For oil I this deviation occurs for 100 % oil I, while the deviation occurs for oil II diluted with 50 % oil IV. No general trend between deviations and oil composition can be deduced.

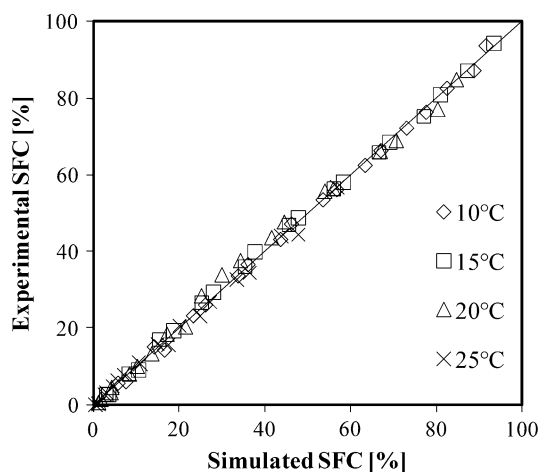


Fig. 4 Parity plots showing the experimental and simulated SFC values for oils I and II at different temperatures and levels of dilution with liquid oil (oil IV). The largest observed experimental standard deviation was 2 %. Error bars have been omitted for simplicity

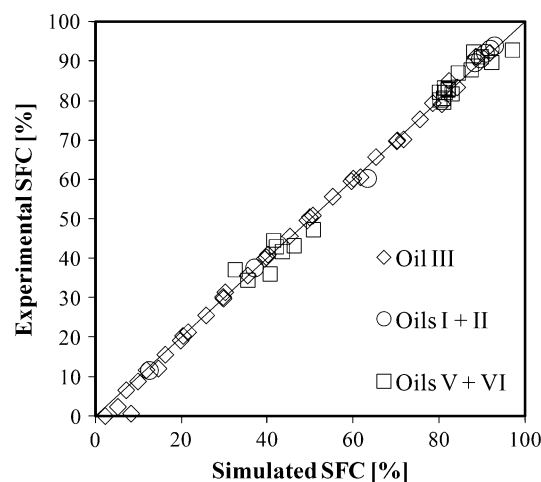


Fig. 5 Parity plot showing experimental and simulated SFC values for oil III, mixtures of oils I and II and mixtures of oils V and VI, diluted with oil IV in different ratios. The largest observed experimental standard deviation was 2 %. Error bars have been omitted for simplicity

Model Validation Against Independent Oils

Validation of the model was carried out using oil III and oils V and VI being rich in symmetric TAG (Table 1), yielding 60 SFC points for validation. Oil III contains two TAG which were not introduced in the fitting routine and hence no interaction parameters for these TAG existed. Therefore, fitting of the interaction parameters, involving these two TAG, was allowed in the validation process. In principle this violated the purpose of the validation. Therefore, oils V and VI were included together with mixtures of oils I and II and mixtures of oils V and VI with and without addition of liquid oil (oil IV). None of these oil blends required additional parameter fitting.

The parity plot in Fig. 5 shows how the SFC of the independent oils are well described by the model. Only at low SFC and 25 °C a large deviation (7.6 %) was observed for oil III (diamonds). Generally, the deviations are slightly larger (up to 4.6 %) for the oils rich in symmetric TAG, especially for Oil V with 60.6 % POP.

Results of the Model and Sensitivity Analysis

For the model and sensitivity analyses Oils I to IV were included, yielding 78 adjustable parameters. Using Eqs. (14–15) the parameters were grouped into 4 subsets containing the 15, 33, 51 and 78 most important parameters. With these subsets at hand, new parameter estimations were carried out, allowing changes in the given subset, while the parameters corresponding to other TAG interactions were assumed to behave ideally ($A_{ik} = 0$).

In Fig. 6 the quality of the fits for the different subsets is depicted. Clearly, ideal ($A_{ik} = 0$) and nearly immiscible

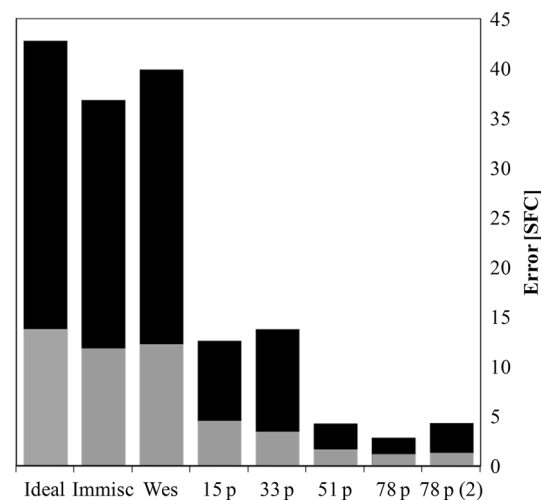


Fig. 6 Graphical representation of the average (grey) and maximal (black) SFC error for all simulated data points. The *x*-axis denotes the approach used to determine the interaction parameters. *p* denotes the number of adjustable parameters included in the minimization routine, chosen by Eq. (10). 78 p (2) represents the case where the system is restricted to a single solid phase

($A_{ik} = 8$) behavior led to large errors. The interaction-parameter correlation suggested by Wesdorp also resulted in large errors. The average error (grey bars) could be reduced substantially by fitting the 15 most important parameters while the maximal deviation (black bars) was still unacceptably large. By increasing the number of adjustable parameters to 51, the individual data point deviations were lowered substantially with a maximum value of 4.3 %. Only small improvements were acquired when

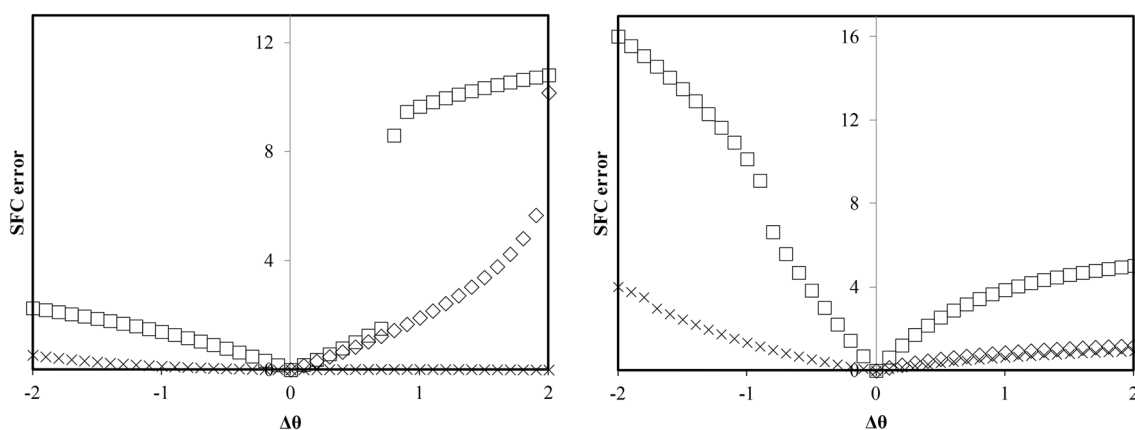


Fig. 7 Sensitivity analysis of three chosen parameters, varied (if possible) ± 2 from their estimated value, for oil I (left) and oil II (right). The y-axis represents the SFC deviation. Squares (POP-PPO), dia-

monds (PStO-PLiP) and crosses (PPO-PStO) represent the three interaction parameters in order of decreasing importance

going from 51 to 78 adjustable parameters. Curiously, by restraining the system to one solid phase it was possible to obtain a fit only slightly worse than the multi-phase simulations.

For the sensitivity analysis three parameters were chosen for the sake of simplicity. The following interactions were investigated: PPO-PStO, PStO-PLiP and POP-PPO, listed in order of increasing importance. The result of the OAT analysis (Fig. 7) showed pronounced discontinuities in the average deviation as a function of change in the parameter value. Moreover, increasing the change of the parameter in question generally increased the SFC error. No clear trend was observed with respect to the direction of the delta change, although the figure suggests a slight tendency towards larger deviations as the parameters were moved toward ideal interactions (negative delta values). Finally, the dependency of a specific parameter varied significantly for oil I and II, manifested in the very different trends observed in the two plots.

Extending the Interaction Parameter Matrix

It was of interest to investigate whether the model could be extended to deal with mixtures including other TAG, keeping the estimated interaction-parameter values constant. Oils containing lauric-acid moieties were of particular interest as these systems show incompatibility in the solid phase when mixed with non-lauric oils [2, 48]. For this purpose an interesterified palm-kernel oil was mixed with oil I in different ratios (from 70 to 10 % lauric oil) and the SFC measured after isothermal storage at two different temperatures (20 and 25 °C) for a week. The interaction parameters for the introduced TAG, containing lauric acid, were then fitted while the rest were kept at their values estimated earlier. A drop in SFC was already present when adding 10 %

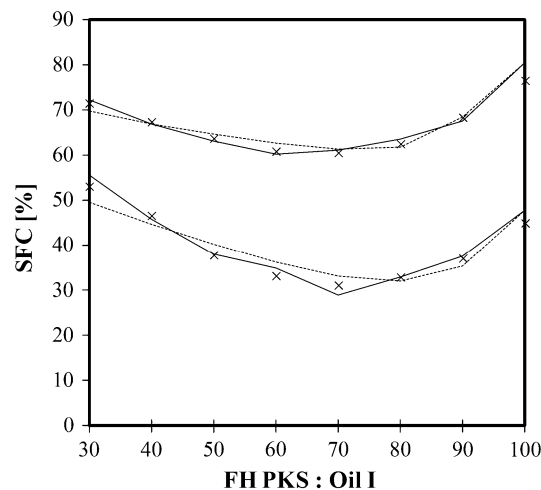


Fig. 8 SFC curves of mixtures of oil I with an interesterified lauric-rich oil. Upper and lower curves are measured at 20 and 25 °C, respectively. Crosses represent experimental data. The solid line represents simulations where any number of phases are allowed. The dashed line represents simulations where the number of solid phases is restricted to one

lauric-rich oil (see Fig. 8). The SFC was described well by fitting solely the interaction parameters linked to the lauric-rich oil. Again, it was possible to arrive at good fits by restraining the system to one solid phase.

Discussion

The new approach presented for estimating interaction parameters from quasi-equilibrium SFC measurements works well for a large range of compositions at different temperatures. SFC measurements have been utilized to obtain interaction parameters for complex oils, yielding

an easy, quick and reliable way to predict SFC values for a wide span of oil compositions.

Oil Composition and Polymorphism

Interaction parameters obtained as suggested in this work are not guaranteed to resemble the values obtained for pure binary systems. It could be argued that effects originating from the lumping procedure and content of minor components are embedded in the estimated parameters. Yet, the type and concentration of impurities and minor components vary from oil to oil and ultimately the estimated parameters seem to be linked closely to the actual TAG interactions. Furthermore, the interaction parameters estimated for the complex oils in question all lie within the suggested value boundaries of 0–8.

The importance of allowing for non-ideal behavior in the β' phase is clearly manifested in Fig. 6 where the model performance is increased dramatically by introducing non-ideal interactions. On the other hand, assuming nearly immiscible behavior for all TAG also leads to very large errors in the simulated SFC values. Ideal (average and maximal errors in SFC: 14 and 43) and nearly immiscible (average and maximal errors in SFC: 12 and 37) behavior lead to large over and underpredictions of the SFC, respectively. The correlation suggested by Wesdorp (average and maximal errors in SFC: 12 and 40) performs slightly better than ideal conditions but underestimates the non-ideality of mixing for the systems studied. Conclusively, individual interaction-parameter values for different TAG–TAG interactions are clearly needed. According to our model these values should be larger than suggested in the literature, giving rise to a larger degree of non-ideality in the β' phase.

Molecular compound formation was not introduced in the model and good fits were obtained without taking this phenomenon into consideration.

Solid–Liquid Equilibrium Calculations

It can be argued that other activity-coefficient model could be used to arrive at the SFC results presented in this work. Nonetheless, compared to the Margules 2-suffix, most existing activity-coefficient models are more complex and require more parameters to describe the activity coefficients. For example, by choosing the Margules 3-suffix model, it would be possible to account for asymmetric interactions which are unquestionably a reality for some binary mixtures of TAG. Utilizing this model would require fitting of twice as many parameters, rendering the SLE model more flexible with no promise of a more predictive model or estimated parameters of a more universal character. Although asymmetric interactions are occurring for pure binary TAG mixtures it seems the overall trends

and interaction patterns for complex oils can be described adequately assuming symmetric interactions. Hence, in this work no incentive to implement more complex activity coefficient models have been encountered, and the Margules 2-suffix model is recommended to describe non-ideal behavior when dealing with industrial-grade vegetable oils.

The need for a multi-phase SLE model, allowing more solid phases to co-exist, does not seem that essential for the oils in question and for static SFC simulations good results can be obtained by simplifying the equations to deal with 1 solid phase only.

Parameter Importance

The sensitivity analysis suggests that the calculated SFC is rather sensitive with regard to interaction-parameter values. Also, the analysis accentuated the discontinuity of the model making it evident that small changes in parameter values can have a profound effect on the SFC and hence the deviation between experimental and calculated results. This is a consequence of small changes of the interaction parameters sometimes leading to changes in phase behavior so that additional phases occur or phases disappear.

The model appears to contain excess adjustable parameters, giving rise to an overly complex model. The numbers in Fig. 6 provide a convenient overview of the average and maximal SFC errors obtained using different parameter sets. Looking only at average errors it would be tempting to suggest that the 15 most important parameters would describe SFC adequately. However, for 15 and 33 adjustable parameters the largest deviations are 12.6 and 13.7 %, respectively, which the authors consider unacceptable. Increasing the number of adjustable parameters to 51 or 78 greatly reduces the largest errors to 4.3 and 2.9 %. Although the average error is only reduced with a few percent when increasing the number of adjustable parameters, the error fluctuations are reduced substantially, giving rise to a more reliable model.

Based on the discussion above, the number of adjustable parameters could be reduced from 78 to 51 without reducing the quality of the fits substantially. However, if kinetic considerations are to be included, the picture might very well change. Phenomena such as induction time, seeding capability and rate of crystallization may be influenced by specific components and interactions. Therefore, better parameter estimates could probably be obtained by pairing the static SFC measurement with dynamic SFC measurements, describing the overall course of crystallization. On the other hand, such a fitting procedure is much more demanding with respect to the number of required simulations and seems overly ambitious considering the computer power at hand.

In any case, the developed model and estimated parameters should provide a solid foundation for further refinement and inclusion of kinetic phenomena.

Conclusion

An approach to determine interaction parameters for TAG mixtures based on SFC has been developed and validated. The method allows for simple, quick and reliable estimations of interaction parameters, and can be used to predict SFC of industrial-grade oils with a large compositional span comprising oils rich in asymmetric as well as symmetric TAG.

To estimate the needed interaction parameters a mathematical model, describing SFC of various oils as a function of chemical composition and isothermal crystallization temperature, has been developed. The model is based on the Margules 2-suffix activity-coefficient model and minimization of the Gibb's free energy to determine the composition of the different phases present at equilibrium. This activity-coefficient model required interaction parameters for every binary pair of TAG present. These parameters were estimated from experimental SFC data obtained at quasi-equilibrium conditions for two industrial-grade oils with complex chemical compositions mixed with a liquid oil in different ratios. The obtained interaction parameters described the experimental data very well and were subsequently validated against three other oils being rich in asymmetric and symmetric TAG, respectively.

The final model was extended to deal with oils rich in lauric acid. This oil was highly incompatible with the other oils in the solid phase and led to pronounced drops in SFC when mixed. The model predicted this effect well, rendering it flexible with respect to inclusion of other oils comprising different TAG.

The number of interaction parameters included seemed too high and good fits could have been obtained using fewer parameters. The model appeared to be rather sensitive with regard to adjustable parameter values.

In conclusion, the approach presented appears to be a powerful way to obtain interaction parameters without the need for pure binary-oil mixtures. The predictive nature of the model renders it a good starting point whether one needs to extend the model to deal with kinetics or requires an industrial tool for optimizing screening trials and evaluating new oil blends. By using this model, screening of hundreds of oil blends can be carried out in a matter of minutes instead of hours, days or even weeks. It thus provides developers and specialists with a qualified first-hand guess of the outcome when specific oils are mixed at various temperatures.

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