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Trends and demands in the solid–liquid equilibrium of lipidic mixtures

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The production of fats and oils has a remarkable impact on economy, in particular, in the developing countries. To deal with the upcoming demands of the oil chemistry industry, studying the solid–liquid equilibrium of fats and oils is highly relevant because it may support the development of new processes and products, as well as improve existing processes and products. However, this task is challenging because lipidic compounds present multiple solid phases leading to behaviors that deserve special attention. The high complexity of these systems requires significant effort in the experimental investigation and theoretical description of their phase behavior. This work addresses perspectives to better understand and overcome some of these concerns.

Introduction

The study of the solid–liquid equilibrium (SLE) of lipidic mixtures is a fundamental tool for the development and optimization of the processing of fatty based products. Fats and oils are suppliers of food, materials, chemicals, as well as energy. In this context, vegetable oils represented more than 150 million tons[1] of materials produced and consumed in 2012. This information reveals the importance that fats and oils should have in research, development and innovation (RD&I) policy agendas, especially in the context of developing countries that account for more than 70% of this amount. Finding alternatives for adding value to a long list of products and byproducts extracted from crops, fruits or seeds, as proposed in the biorefinery concept, is a task that is gaining increasing attention. Fats and oils biorefinery involves all the manufacturing steps concerning the extraction of oil from feedstock and the production of any derived fatty based biochemical.[2,3] It implies that numerous separation and purification processes, such as extraction, refining, crystallization or fractionation, as well as products, such as chocolate, butters, dressings, spreads, cosmetic creams, medicines or biofuels, with specific physicochemical properties should be correctly designed and this can only be achieved by a

reliable evaluation of the phase transition phenomena, involving the compounds presents in fats and oils and their derivatives, and in particular their solid–liquid transitions (Fig. 1).

The melting of lipidic compounds is highly complex when compared with other phase changes. This complexity is especially because of the inherent ability of fatty crystals to self-assemble into stable and metastable structures in their multiple solid phases.[4–7] In addition, in a mixture, fatty components can also present mutual miscibility or even complete immiscibility in the solid phase.[8,9] Consequently, apart from the fact that such phenomena largely affect microstructural changes and, therefore, industrial quality requirements of products, numerous operational and economical reasons emphasize the importance of a critical thermodynamic evaluation of fatty systems for process design and optimization.

This review is aimed at providing an overview of the current understanding of the solid–liquid equilibrium behavior of fatty systems and on the approaches used in the literature for their modeling, taking into account that a deeper knowledge on solid–liquid equilibrium of fatty compounds is still required. The complex nature of fats and oils suggests that the discussion of their phase equilibria is best tackled by starting with the simplest systems. As the complexity of the system increases, the efforts for obtaining a better understanding of the system behavior also increases. Considering that fatty systems comprise a large class of compounds, this review addresses mixtures comprising components directly found in vegetable oils, namely acylglycerols (mono-, di- and triacylglycerols) and fatty acids, as well as those directly produced from these sources, namely fatty alcohols and esters.

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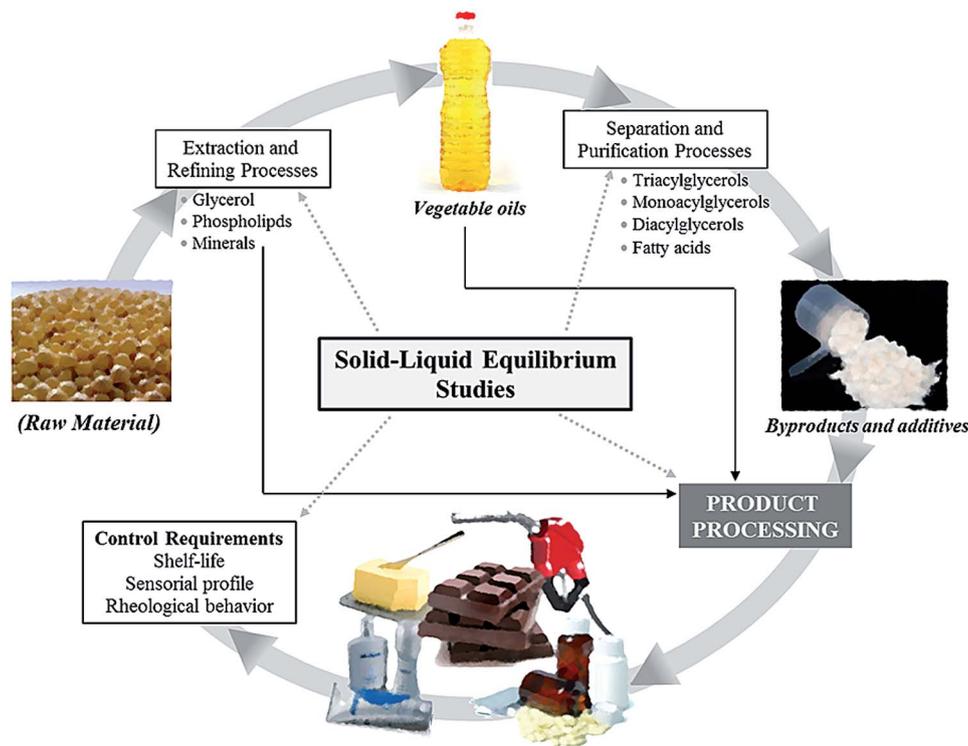
Fig. 1 Action fields of solid−liquid equilibrium studies in the vegetable oil processing industry.

What do fats and oils provide?

Fats and oils are composed of at least 90% triacylglycerols along with a set of minor components[10] but a lot of further information can be added to this very simplified view. First, triacylglycerols are esters composed of a glycerol moiety and three long-chain organic acids. Such fatty acids mostly range from 8 to 20 carbons comprising both saturated and unsaturated compounds. Table 1 shows the most frequently found fatty acids in the triacylglycerols present in vegetable oils. Thus, taking into account that the position of these fatty acids in the glycerol moiety structure of the triacylglycerol can vary, those 90% of triacylglycerols constitute, in fact, a very large variety of molecules. Therefore, assuming that the carbon-chain length and the amount of unsaturation in the molecule have a significant effect on the physicochemical properties of the feedstock, the knowledge of oil composition is crucial.

Considering a predominant fraction composed of triacylglycerols but neglecting the other minority set of compounds is a mistake. Crude oils comprise a group of free fatty acids originating from the hydrolysis of the triacylglycerol molecule, and consequently mono- and diacylglycerol and glycerol molecules are also present. In addition, a fraction of phospholipids (up to 3 wt% for soybean oil), sterols (up to 1.00 wt% for primrose oil), carotenes (up to 0.05 wt% for palm oil), chlorophylls (up to 0.10 wt% for avocado oil), tocopherols and tocotrienols (up to 0.25 wt% for wheat germ oil) are commonly found, as well as several other non-lipidic compounds such as minerals and metal ions.[10,18,20,23–25] Most of them are usually removed or reduced during the refining processes, while a set of

them remain in the refined final product, such as phospholipids (up to 3 mg kg^{-1}), free fatty acids (up to 0.3 wt%) and a small amount of pigments, depending on the source. Consequently, after refining, vegetable oils basically comprise triacylglycerols (higher than 97 wt%) and partial acylglycerols (up to 3 wt%).[10,18,20,26] From an industrial point of view, the presence of such mono- and diacylglycerols highly affects the physico-chemical, sensorial and rheological profile of the final product, despite their low concentrations. Moreover, they may produce undesirable effects for quality requirements, such as changes in crystallization kinetics, stimulating or retarding the nucleation or growth of the crystals, solidification at low temperatures, changing the strain, stress and the yield force during the flow or emulsification of the system, reducing the effectiveness of separation processes, *etc.*[5,10,27,28]

Although compounds are usually removed during refining, they may also be deliberately added to fats and oils or other derived products to play significant roles in the final profile of the product. In fact, some triacylglycerols not present in the original crude oil are sometimes added to the product to obtain the desired effects. In addition, they are also used for the production of other additives in the industry such as fatty alcohols and fatty esters. Fatty alcohols are produced from fatty acids or from triacylglycerols by different routes of esterification and hydrogenation,[29] and are also found in small amounts in vegetable waxes such as those obtained from sugar cane, sunflower or peanuts.[30] Fatty esters are produced by the transesterification of triacylglycerols by alcohols. Both are widely used for the production of other additives, especially surfactants, for food and cosmetic products.[31–33] Furthermore, several

Table 1 Fatty acid mass composition of vegetable oils

Source	<C12	C12:0 lauric	C14:0 myristic	C16:0 palmitic	C16:1 palmitoleic	C18:0 stearic	C18:1 oleic	C18:2 linoleic	C18:3 linolenic	>C18
Rice bran[11]	—	—	0.96	18.17	0.61	1.54	38.50	35.61	2.67	1.92
Palm oil[12]	0.17	1.15	1.24	40.68	0.15	4.72	41.78	8.84	0.18	0.68
Macadamia nut oil[13]	—	—	0.98	9.38	19.28	3.40	59.76	2.03	0.14	5.02
Brazil nut oil[13]	—	—	—	15.86	—	11.34	30.68	42.12	—	—
Cottonseed oil[14]	—	—	0.32	15.53	0.12	3.40	21.23	54.07	4.59	0.72
Jatropha curcas oil[15]	—	—	0.06	13.34	0.89	6.30	41.68	37.00	0.21	0.34
Canola oil[12]	—	—	0.07	4.72	0.25	2.55	62.56	20.13	7.08	9.62
Soybean oil[12]	—	—	0.09	11.18	0.09	4.13	25.62	50.88	4.97	1.49
Coconut oil[16]	13.10	51.00	23.0	6.10	6.10	—	—	—	—	—
Crambe oil[17]	—	—	—	2.07	—	1.03	19.38	8.33	4.53	64.66
Fodder radish oil[17]	—	—	—	5.11	—	2.36	39.47	16.69	12.19	24.18
Macauba oil[17]	—	—	—	21.80	4.08	2.76	58.97	11.64	0.75	—
Cuphea oil[18]	—	76.40	7.80	2.40	—	0.70	5.90	6.90	0.10	—
Olive oil[18]	—	—	—	11.00	0.80	2.20	72.50	7.90	0.60	—
Grapeseed oil[19]	—	0.03	0.11	8.14	0.16	4.05	15.12	71.20	0.57	0.52
Cocoa butter[18]	—	0.10	25.40	0.20	33.20	32.6	2.80	0.10	—	—
Palm kernel oil[18]	54.20	16.40	8.10	—	2.80	11.4	1.60	—	—	—
Buriti fruit oil[20]	—	0.03	0.08	16.78	0.32	1.77	74.06	4.94	1.04	0.83
Tucum oil[21]	3.60	50.60	23.70	5.30	—	2.50	9.30	3.60	0.10	0.10
Sunflower oil[22]	—	0.04	0.10	6.80	0.08	4.16	22.75	63.83	0.82	1.42

studies have evaluated the use of fatty acid ester mixtures as an alternative fuel for the replacement of fossil fuels. The trans-esterification process for biodiesel production is mainly based on the utilization of methanol and ethanol, in convergence, for the large scale production of sugar-cane, especially by several developing countries.[34–36]

The solid–liquid equilibrium of fatty systems

The nature of the solid–liquid equilibrium of fatty mixtures is complex. Comprising multiple solid phases at the same temperature and pressure conditions, literature very frequently fails to correctly describe the phase behavior of these mixtures, which becomes worse as more complex behaviors are observed. What makes the SLE of fatty mixtures so particular is their inherent ability to exhibit polymorphism.[4,7,37,38] It implies that the long-hydrocarbon chains of fatty compounds and consequently their crystal lattices can be configured into numerous micro- and macromolecular arrangements directly related to the thermal treatment to which the mixture is subjected. Tri-acylglycerols, particularly, present three classical and well-known polymorphic forms, α, β′ and β, not accounting for additional sub modifications that appear during thermal processes. The first structure is formed by fast cooling. When subjected to slow heating, such an arrangement melts and recrystallizes into a more stable structure, the β′ form, and sequentially into the β form. Because different crystal lattices are observed in these cases, namely hexagonal, orthorhombic and triclinic, different transition temperatures and enthalpies are also observed. Crystalline structures of fatty acids, alcohols and esters can also pack into different polymorphic forms,

usually at temperatures very close to the most stable form.[9,37,39,40] Considering that polymorphism can be managed by particular thermal treatments, the parameters of the processes to which mixtures are subjected, i.e. time and temperature, can define the profile of the final product.

Evolution

The first studies on the SLE of fatty mixtures published in the literature presented only the melting temperature behavior, also known as the *liquidus* line,[41–44] and most of them only in a restricted concentration range such that phase diagrams could not be completely represented. On the other hand, the interest in the solid–liquid transitions of these systems as well as the capacity of better characterization of their solid phases has increased significantly in the last decades. Table 2 shows the set of binary fatty mixtures that have already been reported in the literature. Efforts to better characterize these systems have been growing but the complexity of their description is also increasing. In this context, four principal phase diagrams could be identified for binary mixtures, as shown in Fig. 2.

The first and simplest phase diagram is the so-called eutectic diagram (Fig. 2A). Some binary mixtures of fatty acids, fatty esters or systems composed of fatty acids and fatty alcohols exhibit this behavior. In simple-eutectic mixtures, during the cooling process, their compounds crystallize independently. The eutectic point establishes the concentration at which the system melts at a single, well defined, and minimum temperature. In a simple eutectic system, there are 4 domains: one homogeneous liquid phase (l); two biphasic solid–liquid domains (regions $C^a + l$ and $C^b + l$); and one biphasic solid–solid domain (region $C^a + C^b$). In such a system when a solid mixture is heated it starts to melt at the same temperature (eutectic

Table 2 Solid–liquid phase diagrams of the binary mixtures of fatty compounds reported in literature[a]

System	Phase diagram	Ref.	System	Phase diagram	Ref.
Fatty acids + fatty acids			**Fatty ester + fatty ester**		
Caprilic acid + capric acid	ESS/P/M	40	Ethyl caprylate + ethyl palmitate	E	56
Caprilic acid + lauric acid	ESS/P/M	9	Ethyl caprylate + ethyl stearate	E	57
Caprilic acid + myristic acid	ESS/P/M	54	Ethyl caprate + ethyl palmitate	E	56
Caprilic acid + oleic acid	ESS	52	Ethyl caprate + ethyl stearate	E	57
Capric acid + lauric acid	ESS/P/M	40 and 58	Ethyl laurate + ethyl palmitate	E	56
Capric acid + myristic acid	ESS/P/M	9 and 58	Ethyl laurate + ethyl stearate	E	57
Capric acid + palmitic acid	ESS/P/M	54 and 58	Ethyl myristate + ethyl palmitate	E	56
Capric acid + stearic acid	E	58	Ethyl myristate + ethyl stearate	E	57
Capric acid + oleic acid	ESS	52 and 61	Ethyl palmitate + ethyl stearate	E	57, 59 and 60
Lauric acid + myristic acid	ESS/P/M	40 and 58	Ethyl palmitate + ethyl oleate	E	56
Lauric acid + palmitic acid	ESS/P/M	9 and 58	Ethyl palmitate + ethyl linoleate	E	56
Lauric acid + stearic acid	ESS/P/M	54 and 58	Ethyl stearate + ethyl oleate	E	57
Lauric acid + oleic acid	E	62	Ethyl stearate + ethyl linoleate	E	57
Myristic acid + palmitic acid	ESS/P/M	40	Methyl laurate + methyl palmitate	E	63
Myristic acid + stearic acid	ESS/P/M	9	Methyl myristate + methyl palmitate	ESS/P/M	39, 63 and 64
Myristic acid + oleic acid	E	62	Methyl myristate + methyl stearate	ESS/P/M	39
Palmitic acid + stearic acid	ESS/P/M	40	Methyl palmitate + methyl stearate	ESS/P/M	39, 59 and 63
Palmitic acid + oleic acid	E	65	Methyl palmitate + methyl oleate	E	63
Palmitic acid + linoleic acid	E	65	Mehtyl palmitate + methyl linoleate	E	63
Oleic acid + stearic acid	E	61 and 66	Methyl stearate + methyl oleate	E	63
Oleic acid + linoleic acid	E	61	Methyl stearate + methyl linoleate	E	63
			Methyl oleate + methyl linoleate	E	63
Fatty alcohols + fatty alcohols			**Triacylglycerol + triacylglycerol**		
1-Octanol + 1-decanol*	ESS/P/M	67	Trilaurin + tripalmitin	ESS	4
1-Decanol + 1-dodecanol	ESS/P/M	67	Trilaurin + tristearin	ESS	4
1-Dodecanol + 1-tetradecanol	nd	68	Trimyristin + tripalmitin	ESS	4
1-Dodecanol + 1-hexadecanol	ESS/P/M	67	Tripalmitin + tristearin	ESS	50
1-Dodecanol + 1-octadecanol	ESS	49	Tripalmitin + triolein	ESS	4, 50 and 65
1-Tetradecanol + 1-hexadecanol	nd	68	Tripalmitin + trilinolein	ESS	65
1-Tetradecanol + 1-octadecanol	ESS/P/M	67	Tristearin + triolein	E	4
1-Hexadecanol + 1-octadecanol	SS	60 and 69			
Fatty acid + fatty alcohol			**Triacylglycerol + fatty acid**		
Capric acid + 1-dodecanol	ESS/P	71	Tricaprylin + myristic acid	E	70
Lauric acid + 1-dodecanol	P	71	Tripalmitin + oleic acid	ESS	61 and 65
Lauric acid + 1-tetradecanol	ESS	8	Tripalmitic + linoleic acid	ESS	65
Myristic acid + 1-dodecanol	P	71	Tristearin + palmitic acid	ESS	50
Myristic acid + 1-tetradecanol	P	71	Tristearin + linoleic acid	ESS	50
Myristic acid + 1-hexadecanol	E	8	Triolein + palmitic acid	E	65 and 70
Palmitic acid + 1-dodecanol	P	71	Trilinolein + palmitic acid	E	65
Palmitic acid + 1-tetradecanol	E	71 and 72	Trilinolenin + stearic acid	E	70
Palmitic acid + 1-hexadecanol	P	71			
Palmitic acid + 1-octadecanol	ESS	8	**Triacylglycerol + fatty alcohol**		
Stearic acid + 1-dodecanol	E	71	Trilaurin + 1-hexadecanol	ESS	73
Stearic acid + 1-tetradecanol	E	71	Trilaurin + 1-octadecanol	E	73
Stearic acid + 1-hexadecanol	P	71	Trimyristin + 1-hexadecanol	ESS	73
Stearic acid + 1-octadecanol	P	71 and 74	Trimyristin + 1-octadecanol	ESS	73
			Tripalmitin + 1-hexadecanol	ESS	73
			Tripalmitin + 1-octadecanol	ESS	73
			Triolein + 1-hexadecanol	E	51
			Triolein + 1-octadecanol	E	51

[a] E = simple eutectic, P = peritectic, M = metatectic, ESS = eutectic with partial miscibility in the solid phase, SS = continuous solid solution, nd = not defined.

temperature) and the composition of the liquid phase changes along one of the branches of the *liquidus* line, according to the initial concentration of the solid mixture.

The second case (Fig. 2B) shows the phase diagram of a mixture with a solid solution in the extremes of the phase diagram. Depending on the concentration of the mixture, the molecules of a compound are incorporated into the lattice of another crystal[45] during crystallization. It implies that within this concentration range, generally close to one of the pure components, the compounds do not crystallize independently.
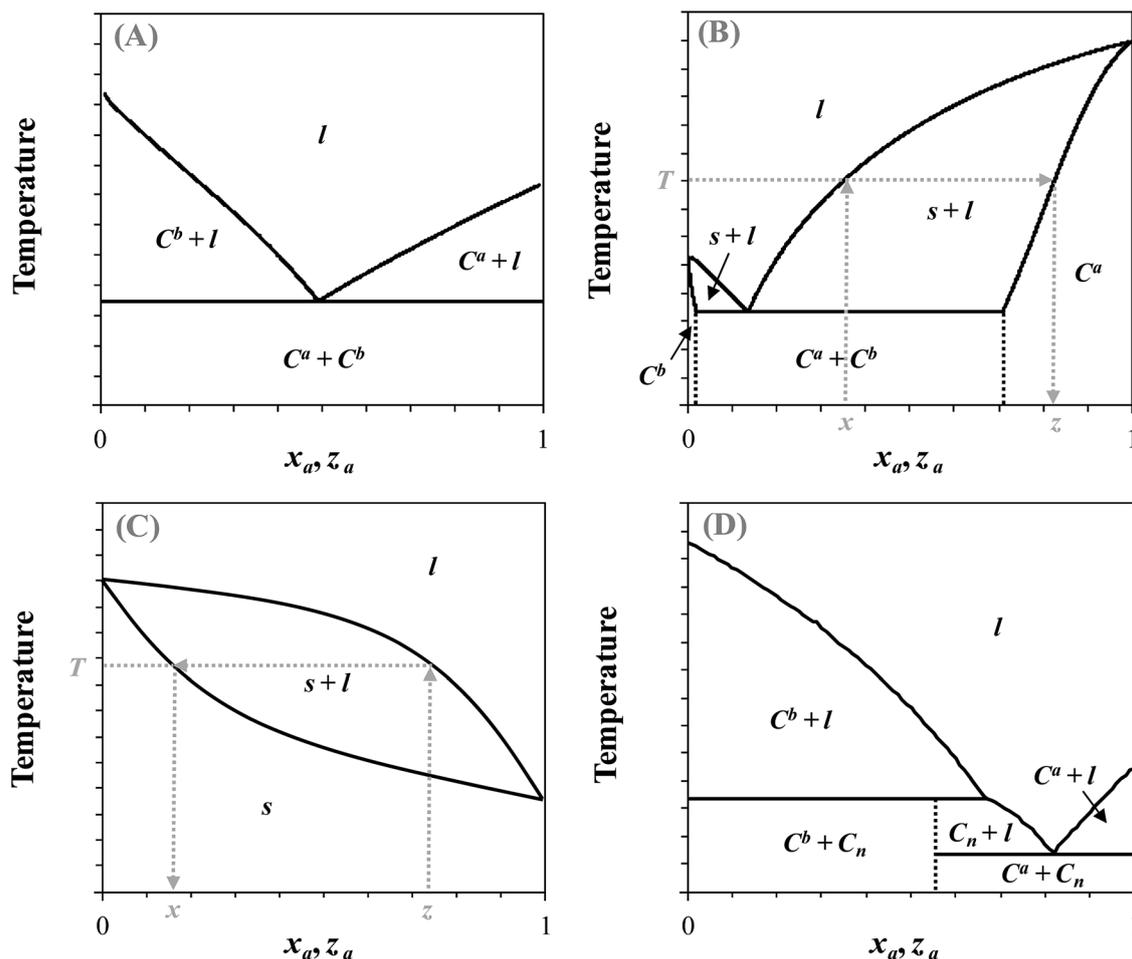
Fig. 2 Most common phase diagrams of binary fatty mixtures with the following nomenclature: mole fraction of component a in the liquid (x_a) and solid (z_a) phases, respectively, liquid phase (l), solid phase pure or rich in component a (C^a) or b (C^b), solid phase comprising both compounds (s), solid phase with a new structure formed by peritectic transition (C_n).

In the case of lipidic systems, solid solutions are particularly interesting because they can be intentionally developed such that physicochemical properties could be adjusted to specific requirements.[46–48] Several fatty binary mixtures present solid solution formation at some concentrations, especially those composed of triacylglycerols or fatty alcohols.[4,8,49,50] The phase diagrams of such mixtures comprise 6 domains, as shown in Fig. 2B. The domains are explicitly circumscribed by two boundaries: the *liquidus* line, in which the last crystal of the mixture melts, and the *solidus* line, which indicates the limits of the melt of the first crystal. The eutectic point in this case establishes a triphasic equilibrium in which the liquid phase is in equilibrium with two solid solutions with distinct compositions. The evaluation of the eutectic point and the solubility region of the solid phase is usually carried out using the Tammann plot (Fig. 3).[50–53] This diagram relates the enthalpy of the eutectic reaction as a function of the concentration of the mixture in which the enthalpy increases up to the eutectic point and then begins to decrease. The concentration at which a solid solution is formed is obtained when the enthalpy of such a reaction $\Delta H_{\text{eut}} = 0$.
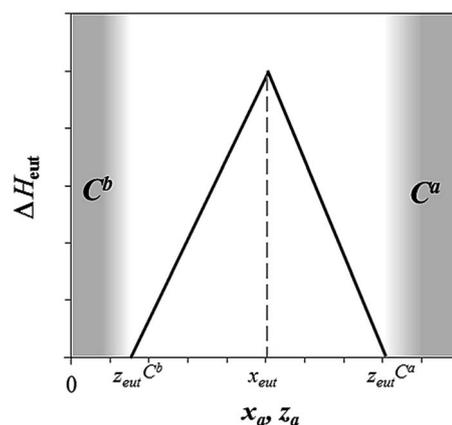

Fig. 3 Tammann plot of the eutectic reaction: enthalpy of the eutectic reaction as a function of the concentration of the mixture (full line); mole fraction of the component a at the eutectic point in the liquid phase x_{eut} (dashed line), and in the solid phases (z_{eut}) rich in component a (C^a) or b (C^b); represented in gray, solid solution regions rich in component a or b.

An uncommon behavior occurs when the components of the liquid phase crystallize as a solid solution throughout the entire concentration range. It implies that only 3 domains are observed (Fig. 2C): the liquid region, the solid domain and the region in which both the liquid and solid phases co-exist. Several mixtures of triacylglycerols with similar molecular sizes, such as PPS (glycerol 1,2-palmitate,3-stearate) + PPP (tri-palmitin) or SOS (glycerol 1,3-stearate,2-oleate) + POS (glycerol 1-palmitate,2-oleate,3-stearate)[4] are able to form solid solutions. In this case, the systems are continuous solid solutions.

Frequently, during the crystallization of lipidic compounds, associative phenomena can occur during the building of the crystal lattice. Such associative behavior may lead to the appearance of a new crystalline structure that acts as a new compound. This is the so-called peritectic reaction. This reaction is defined as an isothermal and reversible process between a liquid and a solid phase resulting in new solid phases during the cooling of the system.[45] It is possible to understand such phenomena by taking into account the inherent polymorphic ability of fatty compounds. Some studies suggested interpretation of such phenomena as a chemical reaction such that the original components form a product according to a specified stoichiometry. If the new compound crystallizes independently of the mixture's compounds, the phase diagram behavior is the one that is presented in Fig. 2D. This implies that there are two biphasic solid regions, each with two immiscible crystalline structures, the new compound C_n and one of the pure components of the original mixture C^b or C^a. Furthermore, there are 3 solid–liquid domains involving one of the pure components in the crystalline form and the liquid phase or the new compound and the liquid phase. Note that the new compound exists only in the solid phase, and disappears during the melting of the system melting. Literature reports the appearance of peritectic profiles in binary mixtures of fatty acids and some systems composed of methyl esters.[9,39,40,54]

Despite the classification of several fatty mixtures into the typical four phase diagrams shown in Fig. 2, the understanding of phase behavior of fatty systems is still far from complete. It is not uncommon for the solid phase to present further transitions that are still unclarified.[55] Metatectic transitions have also been identified in these systems. In this case, the mixture can recrystallize during the melting process, *i.e.* on heating above the *solidus* line.[40] It implies that the crystalline profile of the solid phase clearly changes along with a corresponding set of other particular properties. Recent studies[9,40,54] describe fatty systems with up to 15 different domains (Fig. 4). In these mixtures all the previously discussed phenomena are present in a single phase diagram, depending on concentration and temperature; eutectic, peritectic and metatectic transitions as well as the partial miscibility of the solid phases.

In fact, a large set of fatty binary mixtures are not evaluated yet: mixtures of triacylglycerols; systems composed of triacylglycerols and fatty acids, alcohols or esters; systems comprising methylic and ethylic fatty esters; mixtures of fatty esters and fatty acids or alcohols; and numerous mono- and diacylglycerol mixtures. In addition, studies concerning the effect of *cis–trans* isomerism on the melting point of lipidic
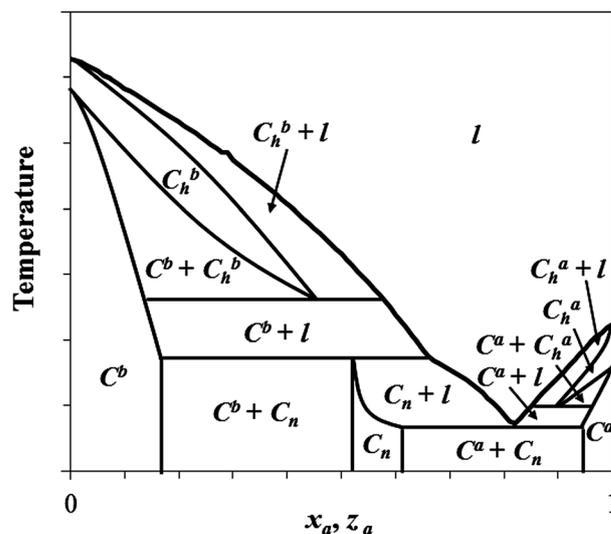

Fig. 4 Sketch of the SLE phase diagram observed in the mixtures of fatty acids (as presented by Costa, *et al.*[9]) for some fatty acid + fatty acid binary systems. C^a and C^b are solid solutions rich in one of the components of the mixture a or b; C_n is the solid phase formed by the peritectic reaction; C_ha and C_hb are the solid phases formed after the metatectic reaction; l is the liquid phase.

mixtures are still scarce. It is known that the melting point of *trans*-isomers are higher than *cis*-isomers.[75] Note that *trans*-fatty compounds can be formed during industrial processes and are related to coronary heart diseases.[76] Moreover, beyond these binary fatty systems, several studies, aiming at the design of products and processes, have evaluated the SLE of the binary systems of these fatty compounds with other organic solvents such as cyclohexane and ethanol,[77] alkanes,[78] aromatic compounds[79] and drugs.[80] In addition, the SLE of several lipid-derivative based mixtures composed of surfactants,[81] phospholipids,[53] glycolipids,[82] lipidic-based ionic liquids[83] or aqueous mixtures of partial acylglycerols[84] have also been reported, aiming at the formulation of food or personal care products, supporting media,[85] or drug delivery systems.[86] These mixtures display a set of liquid crystalline states or mesophases. Such mesophases are called the "fourth state of matter" because their physicochemical properties are similar to those of the liquid state but the orientation of the molecules confers particular properties of a solid state.[87] The presence of these mesophases highly increases the complexity of the system equilibrium.

In summary, all these studies reveal the diversity of the solid–liquid equilibrium behavior of lipidic mixtures and that several experimental studies are still required for a detailed characterization and understanding of these systems.

Brief overview on the techniques for measuring SLE data

The temperatures and enthalpies of the transitions of both solid–liquid and solid–solid phenomena, including those due to polymorphic transitions, can be obtained by differential

scanning calorimetry (DSC). Such a technique is classically used for the description of solid–liquid phase diagrams of fatty systems. However, due to the polymorphism of the solid phase, multiple crystalline structures can be present in a mixture. Thus, some studies[58] propose that samples should be subjected to a thermal treatment before measuring the melting properties. First, with the complete melting of the mixture, the previously organized crystalline structures, that literature terms thermal history, are deleted. Considering that the polymorphic forms are highly dependent on temperature and the heating/cooling rates, specific procedures are required to assess the temperature and enthalpies of such different crystal structures. This can be achieved by melting the sample above the highest melting point of the components, cooling at low rates, followed by an isothermal treatment at a very low temperature and a slow heating run up to the melting of the component or a mixture of compounds. In fact, DSC is not a classical static method for the determination of equilibrium data. However, slow rates allow the assessment of a quasi-equilibrium state in which crystal structures can be rearranged such that the temperatures and enthalpies of the transitions can be measured. Moreover, this technique can also detect endo- and exothermic events, which means that it detects not only melting transitions but also the recrystallization phenomena of solid phase such as polymorphic or metatectic transitions.

In addition to DSC, a set of other analytical techniques, such as X-ray diffraction, microscopy and nuclear magnetic resonance (NMR), are frequently used to characterize the phase behavior of the system in more detail, and are often used in literature for the evaluation of fatty mixtures.[5,9,28,47,88] Single-crystal and powder X-ray diffraction techniques allow the assessment of information on the crystal structure of the pure compounds and their mixtures. From a molecular point of view, through the knowledge of the molecular structure of the compounds, enthalpic and entropic molecular interactions can be inferred and the ideal/non-ideal thermodynamic behavior of the mixture can be explained. Controlled-temperature microscopy allows the visual observation of the beginning and the end of the melting, crystallization and recrystallization phenomena, and the determination of the growth and disappearance of the crystals. NMR is the most applied experimental technique for describing the solid fat content (SFC) curve of fatty mixtures in the fats and oils industry. The manipulation of the solid fraction of the mixtures is of utmost importance because it provides parameters for monitoring industrial processes and product formulation. Information obtained by these techniques can clarify the transitions observed by DSC such as polymorphic transitions, formation of solid solutions, solid phase immiscibility, peritectic and metatectic reactions.

But, in fact, what is literature looking for?

Although several transitions or even complete behaviors have been clarified in the literature, the solid–liquid phase diagrams of various fatty mixtures are still unknown or were published with limited information concerning various aspects of their real behavior. The systematic evaluation of the SLE behavior of fatty systems could enable new applications or increase the understanding of unclear industrial or biochemical phenomena involving such substances. In fact, the study of phase equilibrium creates an *additive design concept*. It implies that if one aims to change the nutritional, sensorial or physicochemical profile of a fatty product by the introduction or removal of components and increasing or decreasing the melting point, the evaluation of the phase change profile is essential. In this context, a SLE phase diagram is a powerful tool.

The solid–liquid equilibrium of fatty systems has been evaluated to obtain an assessment of the description of numerous processes or development of products.[5–7,27,48] Some examples are: (a) optimization of fractionation in which the material is separated into fractions depending on the melting point by a set of crystallization procedures;[89] (b) optimization of interesterification processes in which fatty acid moieties are added or removed from the triacylglycerols to obtain lower or higher melting point materials. This process is a classical alternative for the replacement of hydrogenation which promotes the formation of saturated or *trans*-unsaturated fatty compounds related as the precursors of cardiovascular diseases.[10] (c) Developing structured lipids for the improvement of the nutritional or physicochemical characteristics of the product. This process involves chemical or enzymatic pathways and is aimed at the modification of fatty acid profile of triacylglycerols.[38] (d) Controlling crystallization in lubricants or oils for frying, in which solid particles or even compounds that can promote crystallization are undesirable, or in butters, creams and analogous products, in which the crystalline structure is responsible for the desired texture.[5,6,27,48]

Other special cases take into account the production of new materials for applications in the food, pharmaceutical, materials or energy industries. The mixtures of fatty acids and fatty alcohols, for example, had been evaluated for the formulation of organogels[90,91] and phase change materials.[92–94] Moreover, mixtures of fatty esters have long been used as biofuels, where the crystallization of saturated esters is a major challenge limiting their operation at low temperatures.[35,36,39,95,96]

Organogels are structured materials formed by the self-assembling of components through noncovalent interactions. They can become an alternative for structuring fat-based systems, making it possible to replace traditional industrial processes such as hydrogenation, fractionation and interesterification. Fatty acids and alcohols are compounds[31,32] that can replace saturated fats by acting as gelator agents and promoting the formation of organogels. Thus, the rheological properties of these products can be controlled by the formation of structured networks with different packing arrangements and particular shear strain and stress profiles.[97]

Phase change materials are materials for energy storage. Concerning a phase-change heat storage system, energy could be stored and released by reversible solid–solid or solid–liquid phase changes. Fatty acids, alcohols and esters have relatively low melting point, low vapor pressure, low toxicity and high latent heats, which is suitable for thermal storage processes.[92,98]

Such materials play an important role as an environmentally friendly way of accumulating and saving energy, replacing traditional storage fluids such as those used in refrigeration systems and contributing to the reduction of the emission of greenhouse-gases.

Biodiesel is a mixture of the mono-alkyl esters obtained as derivatives of fats and oils and thus, it is a renewable energy source. Consequently, it is environmentally attractive, promoting the reduction of the emission of pollutant gases for the replacement of fossil fuels. Because of this, nowadays, biodiesel is mandatorily added to petrodiesel in several countries. However, the biofuel industry is still looking for alternatives to overtake several technical problems associated with biodiesel production, storage and use. The solidification at low temperatures is one of them. The presence of fatty esters with high melting temperature, such as methyl stearate and methyl palmitate, is a factor that makes the use of this biofuel difficult at low temperatures. Moreover, other minor components such as monoacylglycerols of saturated fatty acids can also be present and can precipitate in storage tanks at low temperatures, leading to the clogging of tubes and filters of the vehicles. In all these cases a deeper knowledge of the solid–liquid equilibrium of fatty mixtures can help optimize industrial processes and improve the formulation of products with desirable properties.

Demands on modeling

The growing number of new experimental data has not been followed by proportional efforts to better model these complex phase diagrams. The greater the interest in new systems or applications, the higher the demand to improve reliable modeling approaches. The modeling of the melting profile of lipidic systems is best tackled by depicting melting temperature T as a function of the composition of the mixture or, in other words, by depicting the phase diagram. This problem is solved by evaluating the well-known thermodynamic equilibrium condition. Thermodynamic equilibrium is established when at the same temperature and pressure, the chemical potential of a compound in every phase is the same, in the present case, a liquid and a solid phase. Theoretically, eqn (1) relates the mole fraction of component i in the liquid phase x_i and the melting temperature T_{fus} and enthalpy $\Delta_{fus}H$ of the pure compound, such that the melting temperature of the mixture T can be calculated.[99]

$$\ln x_i = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_{fus}} - \frac{1}{T}\right) \quad (1)$$

where R is the gas constant. However, this equation is far from being adequate to accurately depict the real state of the system. SLE can be fully considered, and thus better described, by eqn (2).[99,100]

$$\ln \frac{x_i \gamma_i^L}{z_i \gamma_i^S} = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_{fus}} - \frac{1}{T}\right) + \sum_{tr=1}^{n}\left[\frac{\Delta_{tr}H}{R}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right)\right]$$
$$+ \frac{\Delta_{fus}C_p}{R}\left(\frac{T_{fus}}{T} - \ln\frac{T_{fus}}{T} - 1\right) \quad (2)$$

where z_i is the mole fraction of component i in the solid phase, γ_i^L and γ_i^S are the activity coefficients of component i in the liquid and solid phases, respectively, T_{tr} and $\Delta_{tr}H$ are thermal transition temperatures and enthalpies of the n solid–solid transitions (polymorphic forms) of the component i, respectively, and $\Delta_{fus}C_p$ is the difference between the heat capacity of the pure component i of the liquid and solid phases. If both the equations are compared, it is observed that eqn (1) was built under three main considerations. First, the equation does not consider the non-ideality of the phases, i.e, the activity coefficients of component i in both phases liquid γ_i^L and, if it is the case, solid γ_i^S. Moreover, it assumes that the solid phase is composed of immiscible pure components such that $z_i \gamma_i^S = 1.0$. In addition, it neglects the presence of polymorphic transitions and thus the effects of thermal transition temperatures T_{tr} and enthalpies $\Delta_{tr}H$ that are present in the heating profile of mixture components.

Through eqn (2), the non-ideality of both phases is completely considered. In addition, it presents two terms: the first term takes into account the effects of the polymorphic forms of the mixture components on the melting profile and the second term is related to the specific heat capacity $\Delta_{fus}C_p$ that is usually neglected because of the clear lack of reliable experimental data and because the magnitude of this property supposedly does not affect the solid–liquid equilibrium calculation. Moreover, eqn (2) reveals that the modeling of fatty mixtures' phase diagrams is based on a fundamental problem: the miscibility of solid phase or the presence of solid solutions, such that $z_i \gamma_i^S \neq 1.0$. This is related to the calculation of the *solidus* line. The *solidus* line depicts the behavior of melting temperature T as a function of the solid phase composition z_i.

Despite the fact that solid solutions are more common than usually admitted, most authors have adopted modeling approaches based on solid phase immiscibility. In the studies that take into account a more comprehensive approach and consider the formation of such solid solutions[4,38,96] two main focuses can be identified. From an academic viewpoint, the solid–liquid equilibrium theory is formulated for a complete description of the solid–liquid phase diagram of a system of interest, this implies for calculating the *liquidus* and *solidus* lines. From an industrial viewpoint, the knowledge of the solid content behavior of a vegetable oil or a mixture of tri-acylglycerols has a particular interest in the formulation of products. This behavior is best assessed by the construction of a diagram that represents the solidified fraction of the system as a function of temperature. The aim is the manipulation of the melting point of the mixture by the right choice of its composition. For instance, it is known that many sensorial aspects, such as crispness, spreadability, aroma and oiliness, are largely affected by the solid–liquid ratio in lipidic products, such as cocoa and peanut butters, but also in case of cosmetic creams.[5,6] Analogously, the melting behavior of a biodiesel mixture is largely dependent on the original fat or oil composition as well as the alcohol used in the transesterification reaction.[35] Thus, blends with high concentrations of long carbon saturated fatty esters are more susceptible to high solid content at low temperatures, worsening their flow properties.[36,63] Another

example for the construction of solid fat content diagrams is the development of the so-called structured lipids. By changing the fatty acid composition of triacylglycerols, it is possible to improve specific properties.[38] High amounts of saturated or *trans*-unsaturated fatty acids can, for instance, have negative effects concerning the nutritional claim of the product and, additionally, can increase its melting point. Thus, by the adequate right choice of fatty acids the desired solid content profile of a mixture can be designed avoiding the presence of *trans*-unsaturated fatty acids for instance.

To assess the SLE described by eqn (2), reported studies mainly apply two well-known algorithms: the minimization of Gibbs energy and the isoenthalpic *flash* calculation.[4] The first is based on the stability criteria in which a mixture at equilibrium conditions presents the minimum Gibbs energy. The second one, in analogy with the vapor–liquid equilibrium, considers the feeding of a mixture in an isothermic and isobaric vessel, and the equilibrium condition is then calculated through the analysis of mass balance and fundamental SLE equations. Both the approaches are robust for obtaining the equilibrium state of the mixture but sensitive to initial concentration estimates.

For the description of the non-ideality of the system, these optimization procedures calculate the activity coefficients of the liquid and solid phases. The activity coefficients of the components in liquid phase γ_i^L are usually calculated using equations for excess Gibbs energy[99] such as Margules or UNIQUAC equations[101] or the group-contribution UNIFAC model.[102,103] Eqn (3) shows the 2-suffix Margules equation, commonly used in the SLE modeling of binary systems, comprising one adjustable parameter A_{12}, related to the interaction between the compounds of the binary.

$$RT \ln(\gamma_1^L) = A_{12} x_2^2 \qquad (3)$$

where x is the composition of the component in the liquid phase, T is the melting temperature of the mixture and R is the ideal gas constant. Despite the slight non-linearity of this model, which is favorable for optimization, its disadvantage is the calculation of symmetric non-ideal behaviors. It implies that the compounds should present positive or negative deviations but not both depending on the concentration. The UNIFAC equation is a predictive method commonly used for liquid–liquid and vapor–liquid equilibrium and can also be applied for the calculation of γ_i^L in the case of SLE studies.[103] This model is based on the group-contribution concept such that the activity coefficient of the component is calculated by a sum of terms related to enthalpic and entropic interactions. It is well-applied for the description of liquid phase in the SLE of fatty systems, presenting slight deviations from ideality. However, the model can fail in the prediction of strong non-ideal behaviors such as those observed when the compounds are very different in size.

Till now, two approaches were used for the calculation of activity coefficients of the components in the solid phase of fatty systems: the two-suffix Margules equation[4] for the description of the solid phase of mixtures of triacylglycerols and a predictive version of the UNIQUAC model[96,104] for the description of mixtures of fatty esters. Applying the Margules equation, eqn (3) is used for

evaluating the composition of the compound in the solid phase z_i. In the predictive version of the UNIQUAC model, the binary interaction parameters are calculated by using the physicochemical properties of the pure compound, as described by the authors.

Apart from the discussions on the effectiveness of these approaches, taking into account the description of the lipidic systems listed in Table 2 that present different kind of behaviors as well as numerous mixtures that were not evaluated yet, the SLE modeling of fatty systems is a field yet to be explored.

Remarks

In this large and open context, several demands are clearly evident. The first and most obvious is the enlargement of the number of reliable experimental data for binary, ternary and even more complex mixtures of fatty systems. In addition, experimental data of pure compound, melting temperatures and enthalpies as well as solid–solid transition properties and specific heat capacities of the phases are highly demanded because all these parameters are required for modeling. The second demand is the improvement of the description of non-ideality of the solid phase by reliable equations or predictive models as a tool for the designing of mixtures with specific behaviors. The third is the evaluation of the modeling of systems comprising the peritectic reaction whose efforts are too incipient in the literature. The fourth is deepening the understanding of the solid phase with experimental and modeling tools to describe its behavior according to the well-known thermodynamic theories. The better the description of the SLE behavior of fatty systems the easier is the development or optimization of fat-based products and processes. New alternatives can be thus found to overcome industrial problems, opening pathways for new academic studies.

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Notes and references

1 F.A.O., OECD-FAO Agricultural Outlook 2013, http://www.fao.org, accessed 09/01/2013, 2013.
2 S. Octave and D. Thomas, *Biochimie*, 2009, **91**, 659.
3 J. H. Clark, V. Budarin, F. E. I. Deswarte, J. J. E. Hardy, F. M. Kerton, A. J. Hunt, R. Luque, D. J. Macquarrie, K. Milkowski, A. Rodriguez, O. Samuel, S. J. Tavener, R. J. White and A. J. Wilson, *Green Chem.*, 2006, **8**, 853.
4 L. H. Wesdorp, PhD thesis, Delft University of Technology, 1990.
5 C. Himawan, V. M. Starov and A. G. F. Stapley, *Adv. Colloid Interface Sci.*, 2006, **122**, 3.
6 K. W. Won, *Fluid Phase Equilib.*, 1993, **82**, 261.
7 R. E. Timms, *Prog. Lipid Res.*, 1984, **23**, 1.

8 G. J. Maximo, N. D. D. Carareto, M. C. Costa, A. O. dos Santos, L. P. Cardoso, M. A. Krähenbühl and A. J. A. Meirelles, *Fluid Phase Equilib.*, 2014, **366**, 88.

9 M. C. Costa, M. Sardo, M. P. Rolemberg, P. Ribeiro-Claro, A. J. A. Meirelles, J. A. P. Coutinho and M. A. Krähenbühl, *Chem. Phys. Lipids*, 2009, **157**, 40.

10 F. Shahidi, *Bailey's Industrial Oil and Fat Products*, Wiley Interscience, 2005.

11 C. E. C. Rodrigues, R. Antoniassi and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2003, **48**, 367.

12 M. Lanza, G. Sanaiotti, E. A. C. Batista, R. J. Poppi and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2009, **54**, 1850.

13 C. E. C. Rodrigues, F. A. Silva, A. Marsaioli and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2005, **50**, 517.

14 C. E. C. Rodrigues, É. C. D. Reipert, A. F. de Souza, P. A. P. Filho and A. J. A. Meirelles, *Fluid Phase Equilib.*, 2005, **238**, 193.

15 C. A. S. da Silva, G. Sanaiotti, M. Lanza, A. J. A. Meirelles and E. A. C. Batista, *J. Chem. Eng. Data*, 2010, **55**, 2416.

16 J. Bezard, M. Bugaut and G. Clement, *J. Am. Oil Chem. Soc.*, 1971, **48**, 134.

17 R. C. Basso, F. H. Miyake, A. J. A. Meirelles and E. A. C. Batista, *Fuel*, **117**, 590.

18 J. A. Kent, *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology*, Springer Science + Business Media, New York, 2007.

19 I. Dalmolin, M. A. Mazutti, E. A. C. Batista, M. A. A. Meireles and J. V. Oliveira, *J. Chem. Thermodyn.*, 2010, **42**, 797.

20 S. Silva, K. Sampaio, T. Taham, S. Rocco, R. Ceriani and A. A. Meirelles, *J. Am. Oil Chem. Soc.*, 2009, **86**, 611.

21 J. R. O. Lima, R. B. da Silva, E. Miranda de Moura and C. V. Rodarte de Moura, *Fuel*, 2008, **87**, 1718.

22 M. S. Cuevas, C. E. C. Rodrigues and A. J. A. Meirelles, *J. Food Eng.*, 2009, **95**, 291.

23 S. M. Silva, K. A. Sampaio, R. Ceriani, R. Verhé, C. Stevens, W. De Greyt and A. J. A. Meirelles, *J. Food Eng.*, 2013, **118**, 341.

24 R. Ceriani and A. A. Meirelles, *J. Am. Oil Chem. Soc.*, 2004, **81**, 305.

25 K. M. Phillips, D. M. Ruggio, J. I. Toivo, M. A. Swank and A. H. Simpkins, *J. Food Compos. Anal.*, 2002, **15**, 123.

26 P. T. Gee, *Eur. J. Lipid Sci. Technol.*, 2007, **109**, 373.

27 K. Smith, K. Bhaggan, G. Talbot and K. Malssen, *J. Am. Oil Chem. Soc.*, 2011, **88**, 1085.

28 A. G. Marangoni, N. Acevedo, F. Maleky, E. Co, F. Peyronel, G. Mazzanti, B. Quinn and D. Pink, *Soft Matter*, 2012, **8**, 1275.

29 U. Kreutzer, *J. Am. Oil Chem. Soc.*, 1984, **61**, 343.

30 M. H. Gordon, in *Oils and fat authentication*, ed. M. Jee, Oxford, 2002, p. 143.

31 R. W. Johnson and E. Fritz, *Fatty Acids in Industry: Processes, Properties, Derivatives, Applications*, Marcel Dekker, Nova York, 1989.

32 H. Maag, *J. Am. Oil Chem. Soc.*, 1984, **61**, 259.

33 R. D. Farris, *J. Am. Oil Chem. Soc.*, 1979, **56**, 770A.

34 M. B. Dantas, M. Conceição, V. J. Fernandes Jr, N. Santos, R. Rosenhaim, A. B. Marques, I. G. Santos and A. G. Souza, *J. Therm. Anal. Calorim.*, 2007, **87**, 835.

35 G. Knothe, *Fuel Process. Technol.*, 2005, **86**, 1059.

36 G. Knothe, *Energy Fuels*, 2008, **22**, 1358.

37 L. Ventolà, M. Ramírez, T. Calvet, X. Solans, M. A. Cuevas-Diarte, P. Negrier, D. Mondieig, J. C. van Miltenburg and H. A. J. Oonk, *Chem. Mater.*, 2002, **14**, 508.

38 M. Santos, G. C. Roux and V. Gerbaud, *J. Am. Oil Chem. Soc.*, 2011, **88**, 223.

39 M. C. Costa, L. A. D. Boros, J. A. P. Coutinho, M. A. Krähenbühl and A. J. A. Meirelles, *Energy Fuels*, 2011, **25**, 3244.

40 M. C. Costa, M. Sardo, M. P. Rolemberg, J. A. P. Coutinho, A. J. A. Meirelles, P. Ribeiro-Claro and M. A. Krähenbühl, *Chem. Phys. Lipids*, 2009, **160**, 85.

41 E. Müller and H. Stage, *Experimentelle vermessung von dampf-flüssigkeits-phasengleichwichten*, Springer, Berlin, 1961.

42 B. J. Grondal and D. A. Rogers, *Oil Soap*, 1944, **21**, 303.

43 F. Francis, F. J. E. Collins and S. H. Piper, *Proc. R. Soc. London, Ser. A*, 1937, **158**, 691.

44 A. E. Bailey, *Melting and solidification of fats*, Interscience publishers, New York, 1950.

45 IUPAC, *Compendium of Chemical Terminology*, Blackwell Scientific Publications, Oxford, 1997.

46 E. Deffense, *J. Am. Oil Chem. Soc.*, 1993, **70**, 1193.

47 A. G. Marangoni and S. S. Narine, *Food Res. Int.*, 2002, **35**, 957.

48 S. S. Narine and A. G. Marangoni, *Food Res. Int.*, 1999, **32**, 227.

49 N. D. D. Carareto, M. C. Costa, M. P. Rolemberg, M. A. Krähenbühl and A. J. A. Meirelles, *Fluid Phase Equilib.*, 2011, **303**, 191.

50 M. C. Costa, L. A. D. Boros, J. A. Souza, M. P. Rolemberg, M. A. Krähenbühl and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2011, **56**, 3277.

51 G. J. Maximo, M. C. Costa and A. J. A. Meirelles, *Braz. J. Chem. Eng.*, 2013, **30**, 33.

52 T. Inoue, Y. Hisatsugu, M. Suzuki, Z. Wang and L. Zheng, *Chem. Phys. Lipids*, 2004, **132**, 225.

53 G. G. Chernik, *Adv. Colloid Interface Sci.*, 1995, **61**, 65.

54 M. C. Costa, M. P. Rolemberg, A. J. A. Meirelles, J. A. P. Coutinho and M. A. Krähenbühl, *Thermochim. Acta*, 2009, **496**, 30.

55 M. C. Costa, M. P. Rolemberg, L. A. D. Boros, M. A. Krähenbühl, M. G. Oliveira and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2007, **52**, 30.

56 M. C. Costa, L. A. D. Boros, M. L. S. Batista, J. A. P. Coutinho, M. A. Krähenbühl and A. J. A. Meirelles, *Fuel*, 2012, **91**, 177.

57 L. Boros, M. L. S. Batista, R. V. Vaz, B. R. Figueiredo, V. F. S. Fernandes, M. C. Costa, M. A. Krähenbühl, A. J. A. Meirelles and J. A. P. Coutinho, *Energy Fuels*, 2009, **23**, 4625.

58 M. C. Costa, M. P. Rolemberg, L. A. D. Boros, M. A. Krähenbühl, M. G. de Oliveira and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2007, **52**, 30.

59 E. S. Lutton and F. R. Hugenberg, *J. Chem. Eng. Data*, 1962, **7**, 208.

60 J. C. Smith, *J. Chem. Soc.*, 1931, 802, DOI: 10.1039/jr9310000802.

61 M. P. Rolemberg, PhD thesis, Universidade Estadual de Campinas, 2002.

62 T. Inoue, Y. Hisatsugu, R. Ishikawa and M. Suzuki, *Chem. Phys. Lipids*, 2004, **127**, 161.

63 H. Imahara, E. Minami and S. Saka, *Fuel*, 2006, **85**, 1666.

64 C. A. Lockemann and E. U. Schluender, *J. Chem. Eng. Data*, 1993, **38**, 432.

65 K. Nishimura, K. Maeda, H. Kuramochi, K. Nakagawa, Y. Asakuma, K. Fukui, M. Osako and S.-i. Sakai, *J. Chem. Eng. Data*, 2011, **56**, 1613.

66 T. Inoue, Y. Hisatsugu, R. Yamamoto and M. Suzuki, *Chem. Phys. Lipids*, 2004, **127**, 143.

67 N. D. D. Carareto, A. O. dos Santos, M. P. Rolemberg, L. P. Cardoso, M. C. Costa and A. J. A. Meirelles, *Thermochim. Acta*, 2014, **289**, 137.

68 N. D. D. Carareto, Master thesis, Universidade Estadual de Campinas, 2010.

69 D. G. Kolp and E. S. Lutton, *J. Chem. Eng. Data*, 1962, **7**, 207.

70 M. C. Costa, L. A. D. Boros, M. P. Rolemberg, M. A. Krähenbühl and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2010, **55**, 974.

71 M. C. Costa, *Estudo do equilíbrio sólido-líquido de misturas de alcoóis graxos com ácidos graxos*, Post-Doctoral Report, University of Campinas, 2011.

72 J. Zeng, Z. Cao, D. Yang, F. Xu, L. Sun, L. Zhang and X. Zhang, *J. Therm. Anal. Calorim.*, 2009, **95**, 501.

73 G. J. Maximo, PhD thesis, University of Campinas, 2014.

74 F. G. Gandolfo, A. Bot and E. Flöter, *Thermochim. Acta*, 2003, **404**, 9.

75 S. Ueno, T. Suetake, J. Yano, M. Suzuki and K. Sato, *Chem. Phys. Lipids*, 1994, **72**, 27.

76 A. Aro, M. Jauhiainen, R. Partanen, I. Salminen and M. Mutanen, *Am. J. Clin. Nutr.*, 1997, **65**, 1419.

77 U. Domańska, *J. Solution Chem.*, 1989, **18**, 173.

78 M. Benziane, K. Khimeche, A. Dahmani, S. Nezar and D. Trache, *J. Therm. Anal. Calorim.*, 2013, **112**, 229.

79 U. Domańska, P. Morawski and M. Piekarska, *J. Chem. Eng. Data*, 2009, **54**, 1271.

80 S. Benessam, K. Khimeche, F. Djellouli, M. Benziane and A. Dahmani, *J. Therm. Anal. Calorim.*, 2013, **112**, 317.

81 G. G. Chernik, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 381.

82 R. Koynova and M. Caffrey, *Chem. Phys. Lipids*, 2002, **115**, 107.

83 G. J. Maximo, R. J. B. N. Santos, J. A. Lopes da Silva, M. C. Costa, A. J. A. Meirelles and J. A. P. Coutinho, *ACS Sustainable Chem. Eng.*, 2014, **4**, 672.

84 H. Qiu and M. Caffrey, *Biomaterials*, 2000, **21**, 223.

85 R. L. de Souza, E. L. P. de Faria, R. T. Figueiredo, L. S. Freitas, M. Iglesias, S. Mattedi, G. M. Zanin, O. A. A. dos Santos, J. A. P. Coutinho, A. S. Lima and C. M. F. Soares, *Enzyme Microb. Technol.*, 2013, **52**, 141.

86 A. Yaghmur and O. Glatter, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 333.

87 I. Dierking, *Textures of liquid crystals*, Wiley-VCH, Weinheim, 2003.

88 M. C. Costa, M. P. Rolemberg, A. O. dos Santos, L. P. Cardoso, M. A. Krähenbühl and A. J. A. Meirelles, *J. Chem. Eng. Data*, 2010, **55**, 5078.

89 R. E. Timms, *Eur. J. Lipid Sci. Technol.*, 2005, **107**, 48.

90 H. M. Schaink, K. F. van Malssen, S. Morgado-Alves, D. Kalnin and E. van der Linden, *Food Res. Int.*, 2007, **40**, 1185.

91 F. G. Gandolfo, A. Bot and E. Floter, *J. Am. Oil Chem. Soc.*, 2004, **81**, 1.

92 G. J. Suppes, M. J. Goff and S. Lopes, *Chem. Eng. Sci.*, 2003, **58**, 1751.

93 L. Shilei, Z. Neng and G. H. Feng, *Energ. Buildings*, 2006, **38**, 708.

94 J. J. Zhang, J. L. Zhang, S. M. He, K. Z. Wu and X. D. Liu, *Thermochim. Acta*, 2001, **369**, 157.

95 J. V. Gerpen, *Fuel Process. Technol.*, 2005, **86**, 1097.

96 J. A. P. Coutinho, M. Gonçalves, M. J. Pratas, M. L. S. Batista, V. F. S. Fernandes, J. Pauly and J. L. Daridon, *Energy Fuels*, 2010, **24**, 2667.

97 J. Daniel and R. Rajasekharan, *J. Am. Oil Chem. Soc.*, 2003, **80**, 417.

98 D. Feldman, M. M. Shapiro, D. Banu and C. J. Fuks, *Sol. Energy Mater.*, 1989, **18**, 201.

99 R. C. Reid, J. M. Prausnitz and B. E. Pouling, *The properties of gases and liquids*, McGraw-Hill, New York, 1987.

100 J. Gmehling, B. Kolbe, M. Kleiber and J. Rarey, *Chemical Thermodynamics for Process Simulation*, Wiley-VHC, Weinheim, 2012.

101 D. S. Abrams and J. M. Prausnitz, *AIChE J.*, 1975, **21**, 116.

102 A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, 1975, **21**, 1086.

103 J. G. Gmehling, T. F. Anderson and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.*, 1978, **17**, 269.

104 J. A. P. Coutinho, *Ind. Eng. Chem. Res.*, 1998, **37**, 4870.