Solid−Liquid Equilibrium of Tristearin with Refined Rice Bran and Palm Oils

Mariana C. Costa,[†] Marlus P. Rolemberg,[‡] Adenilson O. dos Santos,[§] Lisandro P. Cardoso,[||] Maria A. Krähenbühl,[⊥] and Antonio J. A. Meirelles*[,†]

EXTRAE, Department of Food Engineering (DEA-FEA), University of Campinas (UNICAMP), P.O. Box 6121, 13083-862 Campinas, São Paulo, Brazil, DETQUI, Department of Chemical Technology, Federal University of Maranhão (UFMA), São Luís, Maranhão, Brazil, Social Sciences, Health and Technology Center, University of Maranhão - UFMA, 65900-410, Imperatriz, MA, Brazil, LPCM, Institute of Physics Gleb Wataghin (IFGW), University of Campinas (UNICAMP), P.O. Box 6165, 13083-970. Campinas, São Paulo, Brazil, and LPT, Department of Chemical Processes (DPQ-FEQ), University of Campinas (UNICAMP), P.O. Box 6066, 13083-970 Campinas, São Paulo, Brazil

In the present study, phase diagrams of two systems, formed by tristearin (1,3-di(octadecanoyloxy)propan-2yl octadecanoate) with refined rice bran oil or refined palm oil, were obtained by Differential Scanning Calorimetry (DSC) and reported in the literature for the first time. The X-ray diffraction technique was employed to verify the crystallization behavior of the individual components and for the mixture tristearin plus refined palm oil. The UNIFAC model was successfully used to predict the *liquidus* line of these systems, with a root-mean-square deviation between the experimental and calculated melting temperatures below 1.3 %.

Introduction

The world consumption of vegetable oils has been increasing recently due to their application in the chemical, pharmaceutical, cosmetic, and food industries. Besides their wide use in the human diet, vegetable oils are an important raw material in the oleochemical industry and in the production of biodiesel.

Some vegetable oils are rich in nutraceutical components. Palm oil is rich in antioxidant substances such as carotenoids and tocopherols.[1] Similarly, rice bran oil is indicated for human consumption on account of its hypocholesterolemic effect, due to the presence of considerable amounts of vitamin E, γ-orizanol, and tocotrienols.[2]

Due to the widespread industrial applications of vegetable oils, knowledge of their properties and equilibrium behavior is of great importance. Mixtures of triacylglycerols, major constituents of vegetable oils,[3] are often fractionated by crystallization, so that the corresponding solid−liquid equilibrium diagrams are important for design of such a purification process. Knowledge of the equilibrium behavior is also important for checking thermodynamic models, such as the UNIFAC model,[4] as a predictive tool. Furthermore, to better understand the solidification of mixtures and to develop new predictive models, it is essential to have precise and reliable experimental data.

Solid−liquid equilibrium data for several binary systems containing triacylglycerols,[5,6] fatty acids,[7−11] and fatty acids with organic solvents[12−14] were already reported in the literature. On the other hand, equilibrium data for the crystallization of fatty compounds from a complex liquid environment, such as edible oils, are still scarce in the literature. Data on the *liquidus* line obtained for the crystallization of pure palmitic acid from its solution with commercial triolein were recently published.[15] The commercial triolein used in that work contained at least 13 main triacylglycerols, and the measured *liquidus* lines could be well predicted using the UNIFAC Dortmund model. Rice bran and palm oils should be considered liquid systems with a still more complex character than commercial triolein: they contain more than 15 main triacylglycerols with a higher variation in the number of double bonds and carbon atoms in their chains.[2,16] Furthermore, the triacylglycerol composition of these oils is more evenly distributed, increasing the complexity of the liquid phase.

In the present study, the selected edible oils simulate the complexity of the liquid phase present in crystallization processes for fats and oils fractionation. Tristearin was chosen as the triacylglycerol to be crystallized and/or melted during the phase equilibrium measurements because its melting point suggests that it would be the unique component to remain solid after the oil melting. In addition, pure tristearin is also a frequently investigated triacylglycerol, whose melting and polymorphic behavior is well-known.[17−19]

The Differential Scanning Calorimetry (DSC) technique is often used in the measurement of solid−liquid equilibrium of fatty mixtures.[5,6,20−22] In the present work, this technique was complemented with X-ray diffraction to check whether tristearin is the unique component present in both phases along the whole SLE diagram. Moreover, the predictive capacity of the UNIFAC Dortmund model was tested for estimating the *liquidus* lines of both investigated systems.

Experimental Section

Reagents. The standards used for calibration of the DSC were indium (99.99 %) certified by TA Instruments (United States), benzoic acid (min 99.9 %, Mettler), and deionized water (Milli-Q, Millipore). Commercial nitrogen (used for preparing the samples) and high purity nitrogen (used in the calorimeter as a purge gas) were supplied by Air Liquide (Brazil). Tristearin (min 99 %) was supplied by Sigma, and the refined rice bran

---

* Corresponding author. E-mail: tomze@fea.unicamp.br. Tel.: +55 19 3521 4037. Fax: +55 19 3521 4027.

[†] DEA-FEA, UNICAMP.

[‡] Department of Chemical Technology, UFMA.

[§] Social Sciences, Health and Technology Center, UFMA.

[||] IFGW, UNICAMP.

[⊥] DPQ-FEQ, UNICAMP.

10.1021/je100647b

Table 1. Fatty Acid Compositions of Refined Rice Bran and Palm Oils

			PM	refined rice bran oil	palm oil
symbol	fatty acid (i)		$g \cdot mol^{-1}$	$100 \cdot x_i$	$100 \cdot x_i$
L	lauric	C12:0	200.20	-	0.65
M	miristic	C14:0	228.38	1.16	1.10
P	palmitic	C16:0	256.43	19.57	44.69
Po	palmitoleic	C16:1	254.42	0.66	0.08
S	stearic	C18:0	284.49	1.50	4.66
O	oleic	C18:1	282.47	37.66	39.56
Li	linoleic	C18:2	280.45	35.08	8.86
Le	linolenic	C18:3	278.44	2.65	-
A	arachidic	C20:0	312.54	1.57	0.40
Ga	gadoleic	C20:1	310.52	0.15	-

Table 2. Probable Triacylglycerol Composition of Refined Rice Bran and Palm Oils

		PM	rice bran oil	palm oil
group	main triacylglycerol (i)	$g \cdot mol^{-1}$	$100 \cdot x_i$	$100 \cdot x_i$
46:1	LOP	777.28	-	0.85
48:0	PPP	807.35	-	5.91
48:1	MOP	805.33	-	1.55
48:2	OOL/MLiP	803.31	-	0.66
50:0	PPS	835.40	-	1.83
50:1	POP	833.38	4.66	28.75
50:2	PLiP	831.37	4.25	7.06
50:3	PLeP	829.35	0.63	-
52:1	POS	861.44	0.87	5.98
52:2	POO	859.42	11.73	23.42
52:3	POLi	857.41	18.84	9.91
52:4	PLiLi	855.39	8.98	1.12
52:5	PLiLe	853.37	0.80	-
54:1	POA	889.49	-	0.82
54:2	SOO	887.48	1.30	2.49
54:3	OOO	885.46	8.25	5.70
54:4	OOLi	883.44	17.51	3.25
54:5	OLiLi	881.43	15.18	0.70
54:6	LiLiLi	879.43	5.49	-
54:7	LiLiLe	877.38	0.64	-
56:3	OLiA	913.52	0.59	-
56:4	LiLiA	911.50	0.28	-

and palm oils were provided, respectively, by Tio João and Agropalma, both from Brazil.

Rice bran and palm oils were analyzed by gas chromatography of the fatty acid methyl esters according to the official method (1-62) of the AOCS.[23] Samples were prepared in the form of fatty acid methyl esters according to the methodology developed by Hartman and Lago.[24] Details about the chromatographic runs were described elsewhere,[2,16] and the corresponding fatty acid compositions of the edible oils are reported in Table 1. On the basis of these fatty acid compositions, the triacylglycerol compositions of rice bran and palm oils (Table 2) were estimated using the procedure suggested by Antoniosi Filho and co-workers.[2,16,25]

Preparation of Pseudobinary Mixtures. The mixtures, with a total weight of approximately 1 g, were prepared on an analytical balance (Adam AAA/L) with an accuracy of ± 0.2 mg as described in detail elsewhere.[8−10] This experimental procedure allows an appropriate homogenization of the liquid mixture after the complete melting of its components and also avoids oxidation by excessive heating.[10]

Differential Scanning Calorimetry (DSC). The temperature-driven melting processes of the tristearin, refined rice bran oil, refined palm oil, and their mixtures were characterized by DSC using a MDSC 2920, TA Instruments calorimeter. The calorimeter was equipped with a refrigerated cooling system which, in the present study, operated between (230 and 380) K, as explained in previous studies.[8−10] Peak top temperatures were considered as the melting temperatures of the mixtures. The cooling rate of $1.0\ K \cdot min^{-1}$ was chosen to induce the tristearin crystallization in its most stable form. The selected heating rate ($1.0\ K \cdot min^{-1}$) guarantees a quasi-equilibrium state along the experimental run, so that the obtained data are comparable to equilibrium data measured by static methods.[8]

The accuracy of the experimental data was evaluated through five repeated runs performed for the calibration substances, three for pure tristearin and palm oil and two repeated runs for two selected mixtures. Absolute average deviations (AAD) obtained between runs performed with calibration substances was within the range from (0.03 to 0.06) K. In the case of the runs performed with pure tristearin, palm oil, and the selected mixtures, the absolute average deviations (AAD) varied within the range of (0.03 to 0.2) K. On the basis of these replicated runs, the uncertainty of the equilibrium results was estimated as not higher than 0.2 K.

X-ray Diffraction. The X-ray powder diffraction analyses were performed at different temperatures with a Philips diffractometer working in the Bragg−Brentano (θ:2θ) geometry, using Cu−K radiation and a secondary graphite monochromator. The X-ray patterns were collected at a constant temperature, using an Anton PAAR TTK 450 camera with a heating rate of $0.02\ K \cdot s^{-1}$ and 5 min of stabilization time. The measurements were at (250 and 312) K. The patterns were scanned with 0.02° in 2θ steps and acquisition time of 2 s, with scans of (5 to 40)° (2θ scale).

Results and Discussion

Figure 1 shows the thermograms for rice bran oil, palm oil, and tristearin. The thermogram for pure tristearin is in good agreement with previous results found in the literature.[2,16] Tristearin exhibits three different polimorphic forms (α, β', and β), each of them characterized by a particular chain packing and thermal stability.[19]

Despite the thermal treatment described in the Experimental Section, the thermogram exhibits two endothermic peaks, the first one related to the melting of the α-form and the second one to the melting of the β-form. The exothermic peaks in the range from (330 to 335) K are related to the following events: polymorphic transition to the β'-form, melting of this crystalline form, and recrystallization into the β-form.[17−19]

The resting time used in the thermal treatment, 30 min at 295 K, was not sufficient to allow for crystallization into the β-form, the most stable one for pure tristearin, but was efficient to prevent its crystallization in a less stable form in the oil presence, as will be discussed later.

The thermograms for the rice bran and palm oils shown in Figure 1 indicated a large range of melting temperatures, from (240 to 265) K in the case of the rice bran oil and from (250 to 310) K for the palm oil. This behavior is related to the variety of triacylglycerols present in the composition of these oils,[2,16,26−28] and melting temperatures are influenced by the number of carbon atoms in the molecular chain of the different triacylglycerols as well as by the number of unsaturations in these substances. The number of unsaturations is more pronounced in the rice bran oil due to the existence of triacylglycerols with four, five, and six double bonds in its composition.

Figure 2 shows the thermograms for the system tristearin + refined rice bran oil, and Figure 3 shows the phase diagram for this system. The evolution of the peaks with an increase of the tristearin concentration in pure rice bran oil can be observed in these thermograms. For refined rice bran oil, $x_{SSS} = 0.00$, as was discussed above, a large range of melting temperatures is

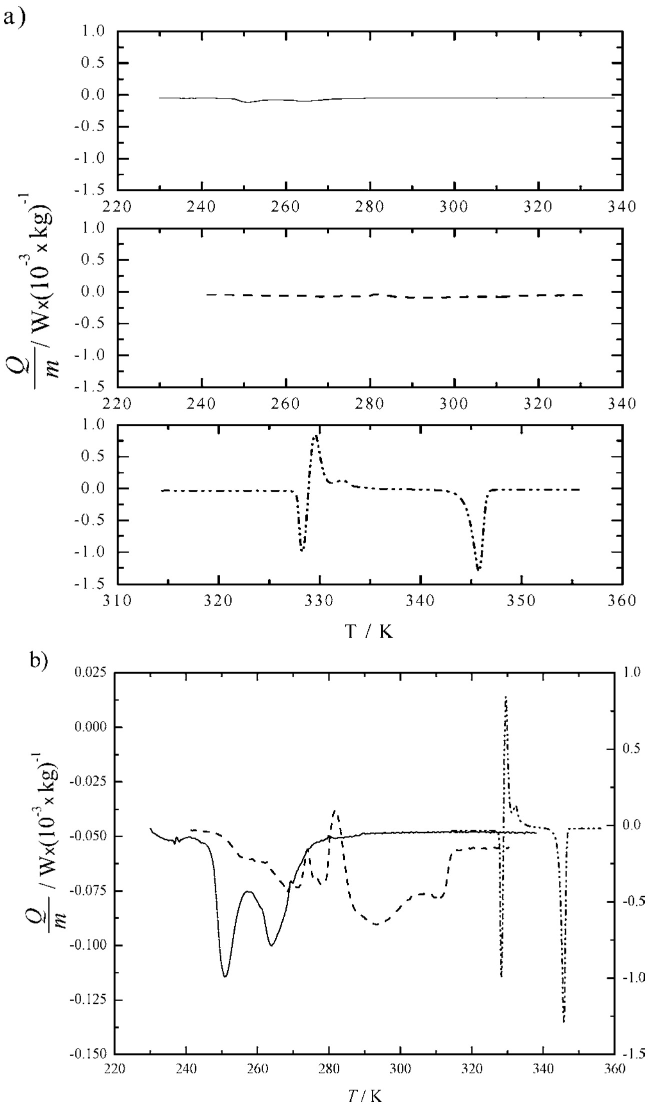

Figure 1. Thermograms of: —, refined rice bran oil; - - -, refined palm oil; • •-• •-, tristearin.

observed. With the increase of the tristearin in the mixture, the appearance of a small peak is perceptible at higher temperatures, around 330 K. This small peak became more intense with the decrease of the refined rice bran oil concentration in the mixture. Although the amount of tristearin increases, for example to $x_{SSS} \cong 0.80$, just three peaks are observed, the first two peaks, at smaller temperature, attributed to the melting of the rice bran oil and the third one, at higher temperature, attributed to the melting of tristearin. Just for pure tristearin, it is possible to see three major peaks: a well-defined peak can be observed at a high temperature plus another two, one endothermic and another exothermic, related to changes in the crystalline forms of tristearin, as discussed above. The disappearance of the peaks related to the polymorphic transitions of the pure tristearin is probably caused by direct crystallization into the β-form during the cooling process, facilitated by the oil presence. This means that the thermal treatment was, in most cases, successful in inducing the tristearin crystallization in its most stable form. This fact makes easier the thermogram interpretation and, consequently, the construction of the corresponding phase diagram.

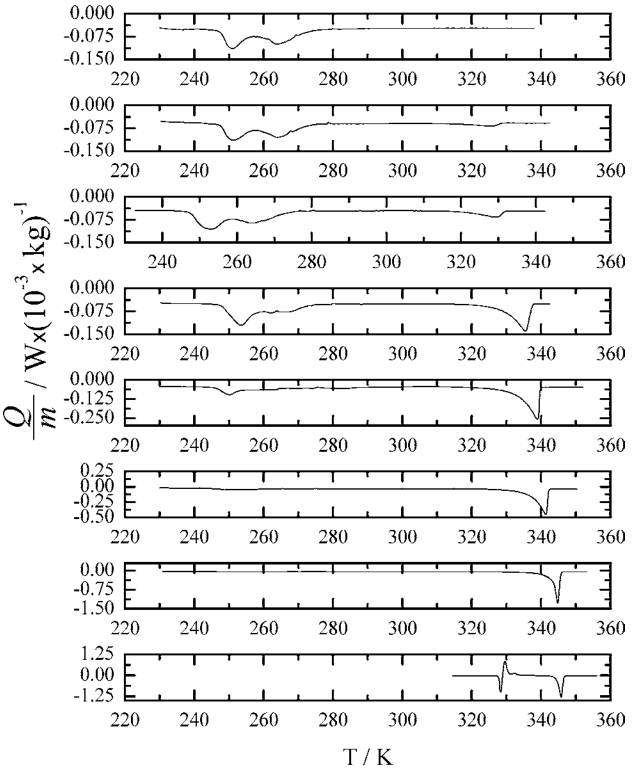

Figure 2. Thermograms of the system refined rice bran oil + tristearin: (a) $x_{SSS} = 0.00$; (b) $x_{SSS} \cong 0.02$; (c) $x_{SSS} \cong 0.05$; (d) $x_{SSS} \cong 0.15$; (e) $x_{SSS} \cong 0.30$; (f) $x_{SSS} \cong 0.50$; (g) $x_{SSS} \cong 0.80$; (h) $x_{SSS} = 1.00$.

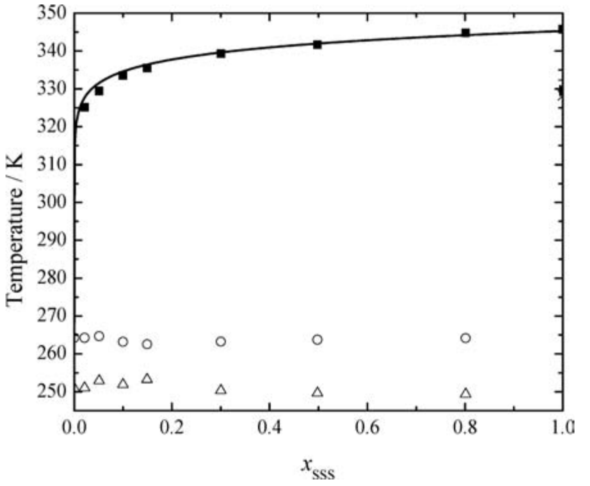

Figure 3. Phase diagram of the rice bran oil + tristearin system. ■, melting temperature of the mixture; ○, temperature of complete oil melting; Δ, transition temperature of the solid phase; ×, solid triangle pointing right, +, −, solid−solid transition of the pure tristearin; —, UNIFAC model.

Some thermograms of the system tristearin + refined palm oil are shown in Figure 4. The addition of palm oil to the pure tristearin also caused disappearance of the peaks related to the polymorphic transitions of pure tristearin, as suggested above.

As shown in the inset in Figure 4, the presence of palm oil resulted in a much more complex thermogram in the whole region close to the complete melting of the oil. This series of peaks was probably related to transitions occurring only in the palm oil, as indicated by the similarities between these peaks and those observed in the thermogram for the pure palm oil. Due to these complexities, it is difficult to associate each peak or region in the thermogram with specific phase transitions. Nevertheless, the complete melting of the mixture, corresponding to the peak at the highest temperature, was very well-defined, and on this basis the *liquidus* line could be precisely determined. The corresponding *liquidus* line is shown in Figure 5.

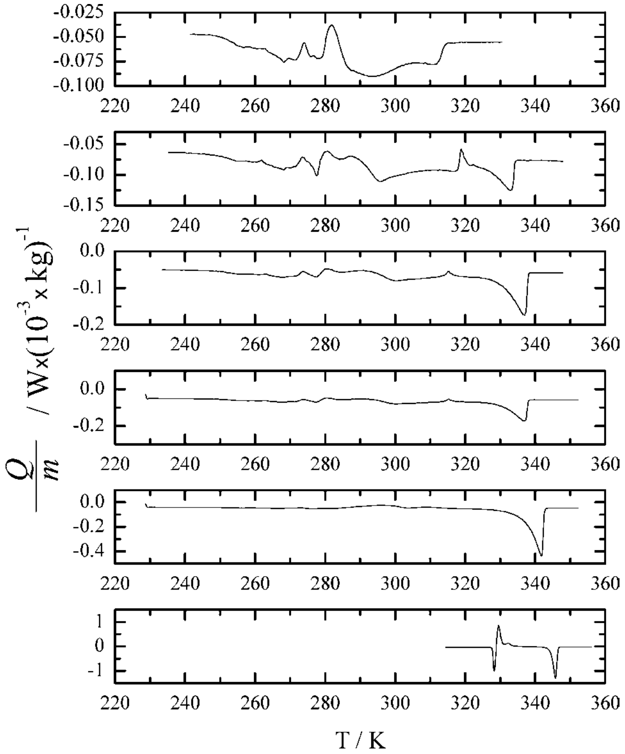

Figure 4. Thermograms of the system refined palm oil + tristearin: (a) $x_{SSS} = 0.00$; (b) $x_{SSS} \cong 0.10$; (c) $x_{SSS} \cong 0.20$; (d) $x_{SSS} \cong 0.30$; (e) $x_{SSS} \cong 0.50$; (f) $x_{SSS} = 1.00$.

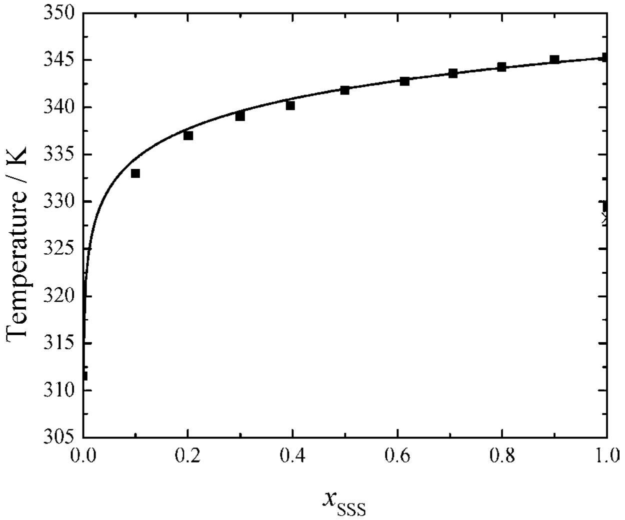

Figure 5. Phase diagram of the palm oil + tristearin system: ■, melting temperature of the mixture; ×, solid triangle pointing right, −, solid−solid transition of the pure tristearin; −, UNIFAC model.

It can be observed in both phase diagrams that the oils melted completely at a temperature of approximately 264 K in the case of rice bran oil and at 311 K for the palm oil, and, in turn, almost all the tristearin remained in the solid state, generating a region of solid−liquid equilibrium within the temperature range located between the melting temperatures of the oils and the *liquidus* line.

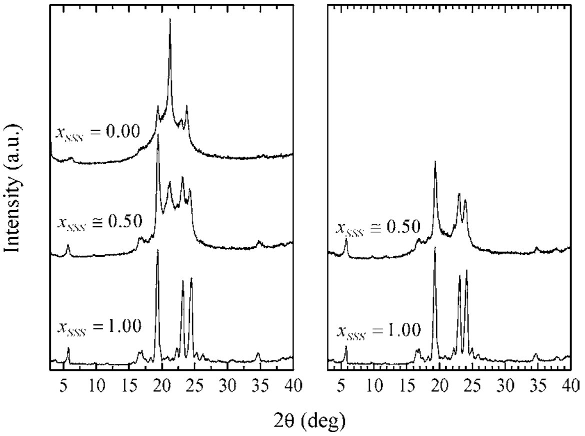

Figure 6. Diffraction patterns of the system tristearin + refined palm oil at two temperatures: (a) 250 K and (b) 312 K.

Table 3. Melting and Transition Temperatures of the Systems Tristearin with Rice Bran Oil and Palm Oil

	tristearin + refined rice bran oil				tristearin + refined palm oil	
	T_{fus}	$T_{complete\ oil\ melting}$	T_{trans}	$T_{trans\ of\ pure\ tristearn}$		T_{fus}
x_{SSS}	K	K	K	K	x_{SSS}	K
0.0000	264.03	264.24	250.91		0.0000	311.56
0.0213	325.14	264.25	251.04		0.0995	333.00
0.0509	329.45	264.67	252.91		0.2010	336.97
0.0999	333.50	263.17	251.94		0.3000	339.03
0.1493	335.50	262.53	253.25		0.3952	340.17
0.3003	339.30	263.23	250.34		0.4997	341.80
0.4981	341.66	263.75	249.62		0.6141	342.78
0.8015	344.79	264.18	249.37		0.7058	343.58
1.0000	345.27			332.33 328.27 329.51	0.7995	344.28
					0.9004	345.06
					1.0000	345.27

To obtain a better characterization of the phase transitions below the *liquidus* line, diffraction patterns were measured for individual components and for the mixture tristearin + refined palm oil, at $x_{SSS} \cong 0.50$. The diffraction patterns are presented in Figure 6. Figure 6a shows the diffraction pattern obtained at 250 K, a temperature in which, according to the phase diagram, all components, including pure tristearin and palm oil, are in a solid state. Figure 6b was obtained at 312 K. At this temperature, most of the tristearin presented in the mixture is in a solid state, while palm oil is completely molten.

As can be seen in Figure 6a, the most important region of diffraction is comprised within the range $15° \leq 2\theta \leq 27°$. Pure tristearin presents three intense diffraction peaks at $2\theta \cong 19°$, $2\theta \cong 23°$, and $2\theta \cong 24°$, respectively. Palm oil exhibits just one intense diffraction peak at $2\theta \cong 21°$. In the diffraction pattern for the mixture, it is clear that both refined palm oil and pure tristearin coexist in the solid phase, but they were independently crystallized because the four diffraction peaks previously mentioned can be observed for the composition $x_{SSS} \cong 0.50$, although with a lower intensity.

At 312 K, it is possible to observe almost the same diffraction patterns for pure tristearin. The unique difference is a small shift to the left side of the peaks at $2\theta \cong 23°$ and $2\theta \cong 24°$ when the temperature was increased from (250 to 312) K. This shift can be attributed to the expansion of the unit cell parameters. Comparing the diffraction patterns obtained for pure tristearin and for the mixture at 312 K, it is clear that tristearin is in a solid state, and the broadening that can be noted in the base of the peaks should be attributed to the presence of liquid palm oil.

Table 3 gives the melting temperatures obtained from the DSC measurements of both systems. In this table, the compositions are given in molar fraction of tristearin, and the temperatures presented were obtained determining the peak top temperature of each mixture, as indicated in previous studies.[8,11]

In the present study, the objective was to investigate the solid−liquid behavior of these oils in mixtures with a pure

Table 4. Root-Mean-Square Deviation (rmsd) between the Experimental and Calculated Data[a]

system	rmsd/K
rice bran oil + tristearin	1.22
palm oil + tristearin	0.58

[a] rmsd $= [\sum_{i=1}^{n}(T_{i,\mathrm{exp}} - T_{i,\mathrm{calc}})^2/n]^{1/2}$, where T is the temperature and n is the number of experimental points.

triacylglycerol and to verify the applicability of the UNIFAC model[4] for predicting the *liquidus* line of systems with much more complex liquid phases than in previously tested systems.[15] To use the UNIFAC model, the triacylglycerol compositions of rice bran and palm oils were required, and this information was obtained in Rodrigues et al.[2] and Gonçalvez et al.[16] It should be noted that exactly the same samples used in those works were employed in the present one.

Figures 3 and 5 indicated that the UNIFAC model was able to correctly predict the experimental data for both systems. The root-mean-square deviation (rmsd) was used to evaluate the quality of the prediction made by the model, and the results obtained for both systems are presented in Table 4. Although the rmsd for the system palm oil + tristearin showed a better value, the rmsd for the system rice bran oil + tristearin was also good, and both corroborated the fact that the UNIFAC model succeeded in predicting the phase equilibrium of such complex systems.

Conclusion

Differential scanning calorimetry was a successful technique for measuring the SLE data of complex fatty systems. X-ray diffraction patterns allowed concluding that the oils and tristearin, in each system, crystallize individually and confirm that tristearin is the unique component in the mixture that remains in both phases along the whole SLE diagram. The UNIFAC model was used to predict the *liquidus* line of these systems and was shown to be adequate, presenting low deviations in comparison to the experimental data.

Literature Cited

(1) Ng, M. H.; Choo, Y. M.; Ma, A. N.; Cheng, H. C.; Hashim, M. A. Separation of vitamin E (tocopherol, tocotrienol, and tocomonoenol) in palm oil. *Lipids* **2004**, *39* (10), 1031–1035.

(2) Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. Equilibrium data for the system rice bran oil plus fatty acids plus ethanol plus water at 298.2 K. *J. Chem. Eng. Data* **2003**, *48* (2), 367–373.

(3) Naudet, M. *Oils & Fats Manual: A Comprehensive Treatise, Properties, Production, Applications*; Lavoisier: Paris, 1996.

(4) Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor-Liquid-Equilibria by Unifac Group Contribution 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30* (10), 2352–2355.

(5) Boodhoo, M. V.; Bouzidi, L.; Narine, S. S. The binary phase behavior of 1,3-dicaproyl-2-stearoyl-sn-glycerol and 1,2-dicaproyl-3-stearoyl-sn-glycerol. *Chem. Phys. Lipids* **2009**, *157* (1), 21–39.

(6) Boodhoo, M. V.; Kutek, T.; Filip, V.; Narine, S. S. The binary phase behavior of 1,3-dimyristoyl-2-stearoyl-sn-glycerol and 1,2-dimyristoyl-3-stearoyl-sn-glycerol. *Chem. Phys. Lipids* **2008**, *154* (1), 7–18.

(7) Costa, M. C.; Krähenbühl, M. A.; Meirelles, A. J. A.; Daridon, J. L.; Pauly, J.; Coutinho, J. A. P. High pressure solid-liquid equilibria of fatty acids. *Fluid Phase Equilib.* **2007**, *253* (2), 118–123.

(8) Costa, M. C.; Rolemberg, M. P.; Boros, L. A. D.; Krähenbühl, M. A.; Oliveira, M. G.; Meirelles, A. J. A. Solid-liquid equilibrium of binary fatty acids mixtures. *J. Chem. Eng. Data* **2007**, *52*, 30–36.

(9) Costa, M. C.; Rolemberg, M. P.; Meirelles, A. J. A.; Coutinho, J. A. P.; Krahenbuhl, M. A. The solid-liquid phase diagrams of binary mixtures of even saturated fatty acids differing by six carbon atoms. *Thermochim. Acta* **2009**, *496* (1−2), 30–37.

(10) Costa, M. C.; Sardo, M.; Rolemberg, M. P.; Coutinho, J. A. P.; Meirelles, A. J. A.; Ribeiro-Claro, P.; Krähenbühl, M. A. The solid-liquid phase diagrams of binary mixtures of consecutive, even saturated fatty acids. *Chem. Phys. Lipids* **2009**, *160*, 85–97.

(11) Costa, M. C.; Sardo, M.; Rolemberg, M. P.; Coutinho, J. A. P.; Meirelles, A. J. A.; Ribeiro-Claro, P.; Krähenbühl, M. A. The solid-liquid phase diagrams of binary mixtures of consecutive, even saturated fatty acids: differing by four carbon atoms. *Chem. Phys. Lipids* **2009**, *157*, 40–50.

(12) Domanska, U.; Domanski, K.; Klofutar, C.; Paljk, S. Excess-Enthalpies of Nonan-1-Ol and Undecan-1-Ol with Octane at High Dilutions and at 298.15-K. *Thermochim. Acta* **1990**, *164*, 227–236.

(13) Hofman, T.; Domanska, U. Solubilities of normal alkanoic acids by the UNIFAC group contribution method. *J. Solution Chem.* **1988**, *17* (3), 237–248.

(14) Domanska, U.; Rolinska, J. *Solid-liquid equilibrium data collection organic compounds monocarboxilic acids*; PWN-Polish Scientific Publishers: Warszawa, 1988.

(15) Costa, M. C.; Boros, L. A. D.; Rolemberg, M. P.; Krahenbuhl, M. A.; Meirelles, A. J. A. Solid-Liquid Equilibrium of Saturated Fatty Acids plus Triacylglycerols. *J. Chem. Eng. Data* **2010**, *55* (2), 974–977.

(16) Goncalves, C. B.; Meirelles, A. J. A. Liquid-liquid equilibrium data for the system palm oil plus fatty acids plus ethanol plus water at 318.2 K. *Fluid Phase Equilib.* **2004**, *221* (1−2), 139–150.

(17) Elisabettini, P.; Desmedt, A.; Durant, F. Polymorphism of stabilized and nonstabilized tristearin, pure and in the presence of food emulsifiers. *J. Am. Oil Chem. Soc.* **1996**, *73* (2), 187–192.

(18) OH, J. H.; McCurdy, A. R.; Swanson, B. G. Characterization and thermal stability of polymorphic forms of synthesized tristearin. *J. Food Sci.* **2002**, *67* (8), 2911–2917.

(19) Singh, S. K.; Jalali, A. F.; Alden, M. Modulated temperature differential scanning calorimetry for examination of tristearin polymorphism: I. Effect of operational parameters. *J. Am. Oil Chem. Soc.* **1999**, *76* (4), 499–505.

(20) Inoue, T.; Hisatsugu, Y.; Ishikawa, R.; Suzuki, M. Solid-liquid phase behavior of binary fatty acid mixtures 2. Mixtures of oleic acid with lauric acid, myristic acid, and palmitic acid. *Chem. Phys. Lipids* **2004**, *127* (2), 161–173.

(21) Inoue, T.; Hisatsugu, Y.; Suzuki, M.; Wang, Z.; Zheng, L. Solid-liquid phase behavior of binary mixtures 3. Mixtures of oleic acid with capric acid (decanoic acid) and caprylic acid (octanoic acid). *Chem. Phys. Lipids* **2004**, *132*, 225–234.

(22) Inoue, T.; Hisatsugu, Y.; Yamamoto, R.; Suzuki, M. Solid-liquid phase behavior of binary fatty acid mixtures 1. Oleic acid stearic acid and oleic acid behenic acid mixtures. *Chem. Phys. Lipids* **2004**, *127* (2), 143–152.

(23) A.O.C.S. *Official methods and recommended practices of the American Oil Chemists' Society*, 3rd ed.; A.O.C.S.: Champaign, 1988; Vols. 1−2.

(24) Hartman, L.; Lago, R. C. A. Rapid Preparation of Fatty Acid Methyl Esters from Lipids. *Lab. Pract.* **1973**, *22*, 475–476.

(25) Antoniosi Filho, N. R.; Mendes, O. L.; Lanças, F. M. Computer Prediction of Triacylglycerol Composition of Vegetable Oils by HRGC. *Chromatography* **1995**, *40*, 557–562.

(26) Tan, C. P.; Man, Y. B. C. Comparative differential scanning calorimetric analysis of vegetable oils: I. Effects of heating rate variation. *Phytochem. Anal.* **2002**, *13* (3), 129–141.

(27) Braipson-Danthine, S.; Gibon, V. Comparative analysis of triacylglycerol composition, melting properties and polymorphic behavior of palm oil and fractions. *Eur. J. Lipid Sci. Technol.* **2007**, *109* (4), 359–372.

(28) Vereecken, J.; Foubert, I.; Smith, K. W.; Dewettinck, K. Effect of SatSatSat and SatOSat on crystallization of model fat blends. *Eur. J. Lipid Sci. Technol.* **2009**, *111* (3), 243–258.

Received for review June 11, 2010. Accepted August 26, 2010. The authors are grateful to CNPq (306250/2007-1, 480992/2009-6), FAPESP (08/09502-0, 08/56258-8), CAPES, and FAEPEX/UNICAMP for their financial support and assistantship.

JE100647B