974 *J. Chem. Eng. Data* **2010,** *55,* 974–977

Solid−Liquid Equilibrium of Saturated Fatty Acids + Triacylglycerols

Mariana C. Costa,[†] Laslo A. D. Boros,[‡] Marlus P. Rolemberg,[§] 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, LPT, Department of Chemical Processes (DPQ-FEQ), University of Campinas (UNICAMP), P.O. Box 6066, 13083-970, Campinas, São Paulo, Brazil, and DETQUI, Department of Chemical Technology, Federal University of Maranhão (UFMA), São Luís, Maranhão, Brazil

Phase diagrams of tricaprylin (1,3-di(octanoyloxy)propan-2-yl octanoate) + myristic acid (tetradecanoic acid), commercial triolein + palmitic acid (hexadecanoic acid), and trilinolenin (propane-1,2,3-triyl tris[(9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoate]) + stearic acid (octadecanoic acid) were obtained by differential scanning calorimetry (DSC). The occurrence of an eutectic point very close to the pure triacylglycerol can be assumed in all of the three investigated systems. The liquid phase was modeled using Margules two-suffix, Margules three-suffix, nonrandom two-liquid (NRTL), and universal quasichemical functional group activity coefficient (UNIFAC) Dortmund models. The best modeling results were obtained using the NRTL model. The UNIFAC Dortmund model describes the multicomponent system containing commercial triolein + palmitic acid well.

Introduction

Oils and fats are composed mainly by triacylglycerols that are formed through the esterification of the glycerol molecule by three fatty acids.[1] The use of oils, fats, and fatty acids in the chemical, pharmaceutical, cosmetic, and food industries is steadily increasing, for instance, in the production of coverings, plastics, and cleanliness products.[2]

Because of this widespread industrial use, the knowledge of the solid−liquid equilibrium diagrams of fatty mixtures is very important. Solid−liquid equilibrium data of systems formed by triacylglycerols,[3–6] fatty acids,[5–8] and fatty acids with organic solvents are available in the literature,[9–11] but data of systems formed by fatty acids + triacylglycerols are scarce. In the present work solid−liquid equilibrium data of three fatty mixtures were measured by differential scanning calorimetry (DSC) and modeled using the Margules two-suffix, Margules three-suffix, nonrandom two-liquid (NRTL), and universal quasichemical functional group activity coefficient (UNIFAC) Dortmund equations.

Experimental Section

Reagents. Standards used for calibration of the DSC were indium (0.9999 molar fraction, TA Instruments; CAS Registry No.: 7440-74-6), benzoic acid (min. 0.999 molar fraction, Metler; CAS Registry No.: 65-85-0), and deionized water (Milli-Q, Millipore). The fatty acids and triacylglycerols were obtained from the following suppliers with no further purification: myristic acid (tetradecanoic acid, 0.99 to 1.00 molar fraction; CAS Registry No.: 544-63-8), palmitic acid (hexadecanoic acid, min. 0.99 molar fraction; CAS Registry No.: 57-10-3), and stearic acid (octadecanoic acid, min. 0.99 molar fraction; CAS Registry No.: 57-11-4) from Sigma Aldrich, tricaprylin (1,3-di(octanoyloxy)propan-2-yl octanoate, min. 0.99 molar fraction; CAS Registry No.: 538-23-8) from Sigma, trilinolenin (propane-1,2,3-triyl tris[(9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoate], min. 0.99 molar fraction; CAS Registry No.: 14465-68-0) from Nu Check, and commercial triolein from Merck. The fatty acid composition of commercial triolein was determined by gas chromatography of fatty acid methyl esters according to the American Oil Chemists' Society (AOCS) official method (1-62).[12] Samples were prepared in the form of fatty acid methyl esters according to the Hartman and Lago methodology.[13] Fatty

Table 1. Fatty Acid Composition of Commercial Triolein

fatty acids (i)	symbol	group	molar mass g·mol^{-1}	commercial triolein 100 x_i	100 w_i
myristic	M	C14:0	228.37	2.41	1.97
palmitic	P	C16:0	256.42	4.96	4.56
palmitoleic	Po	C16:1	254.41	5.06	4.62
stearic	S	C18:0	284.48	1.40	1.43
oleic	O	C18:1	282.46	75.28	76.36
linoleic	Li	C18:2	280.45	9.95	10.02
gadoleic	Ga	C20:0	312.53	0.92	1.04

Table 2. Probable Composition of Commercial Triolein in Triacylglycerols

triacylglycerol (i)	molar mass g·mol^{-1}	commercial triolein 100 x_i	100 w_i
OLiLi	881.41	2.36	2.38
MOLi	829.33	1.13	1.07
POLi	857.38	2.27	2.22
PoOLi	855.37	2.25	2.19
SOLi	885.44	0.70	0.71
OOLi	883.42	18.01	18.16
PPO	833.35	0.68	0.65
MOO	831.34	4.83	4.59
POO	859.39	8.85	8.68
PoOO	857.38	8.55	8.37
SOO	887.45	2.78	2.82
OOO	885.43	45.79	46.29
OOGa	915.50	1.80	1.88

---

* Corresponding author. Phone: +55-19-3251-4037; e-mail: tomze@fea.unicamp.br.

[†] DEA-FEA, UNICAMP. E-mail: mcdcosta@fea.unicamp.br (M.C.C.).

[‡] DPQ-FEQ, UNICAMP. E-mail: lasloboros@hotmail.com (L.A.D.B.); mak@feq.unicamp.br (M.A.K.).

[§] UFMA. E-mail: marlus@ufma.br (M.P.R.).

10.1021/je900410j

Table 3. Solid−Liquid Equilibrium Data for the Systems: Tricaprilin + Myristic Acid, Commercial Triolein + Palmitic Acid, and Trilinolenin + Stearic Acid

tricaprilin + myristic acid			commercial triolein + palmitic acid			trilinolenin + stearic acid			
x_{tric}	T_{fus}/K	T_{eut}/K	x_{comtriol}	T_{fus}/K	T_{eut}/K	x_{tril}	T_{fus}/K	T_{eut}/K	T_{trans}/K
0.0000	327.07		0.0000	336.47		0.0000	342.25		
0.1019	325.34	282.10	0.0980	333.51	257.62	0.1012	341.31	251.17	271.88
0.1549	324.43	282.14	0.3003	328.58	257.86	0.2992	337.78	251.14	272.42
0.2031	322.82	282.31	0.4998	321.81	258.56	0.5023	334.03	250.94	272.40
0.2459	322.46	282.13	0.6996	312.60	257.38	0.7007	328.37	250.74	272.13
0.2993	321.17	282.03	0.7991	309.13	257.90	0.8002	323.93	250.42	269.47
0.3989	318.98	282.46	0.8497	303.78	257.91	0.8494	319.91	251.15	271.68
0.5241	315.49	282.51	0.8999	301.68	256.99	0.8830	317.57	250.93	268.38
0.6063	312.28	282.35	0.9374	295.62	256.59	0.9102	314.25	250.82	270.96
0.7010	306.72	282.65	0.9677	285.62	258.03	0.9402	311.57	250.60	271.25
0.7997	302.37	282.63	1.0000	258.08		0.9700	305.72	251.32	273.66
0.8500	301.13	282.56				1.0000	251.10		269.56
0.9015	295.64	282.56							
0.9488	289.03	282.53							
1.0000	282.75								

mixtures were prepared by gravimetry and analyzed as described in a previous work.[14] The experimental uncertainty was evaluated on the basis of repeated DCS runs and estimated as not higher than 0.3 K, except for the system containing commercial triolein in which the uncertainty of peak top temperature was not higher than 0.6 K.

Results and Discussion

Table 1 presents the fatty acid composition of commercial triolein. The probable triacylglycerol composition of the commercial triolein was estimated according to the algorithm suggested by Antoniosi Filho et al.[15] (Table 2). Table 3 shows the melting and transition temperatures, with the concentrations given in molar fraction of the light component. Figure 1 shows the thermograms obtained for the system trilinolenin + stearic acid. For pure stearic acid a unique well-defined peak is observed, but in case of pure trilinolenin two well-defined peaks were obtained, the first one, at the lowest temperature, with a much larger transition enthalpy. For the mixtures, three peaks were observed: the one at higher temperature is related to the

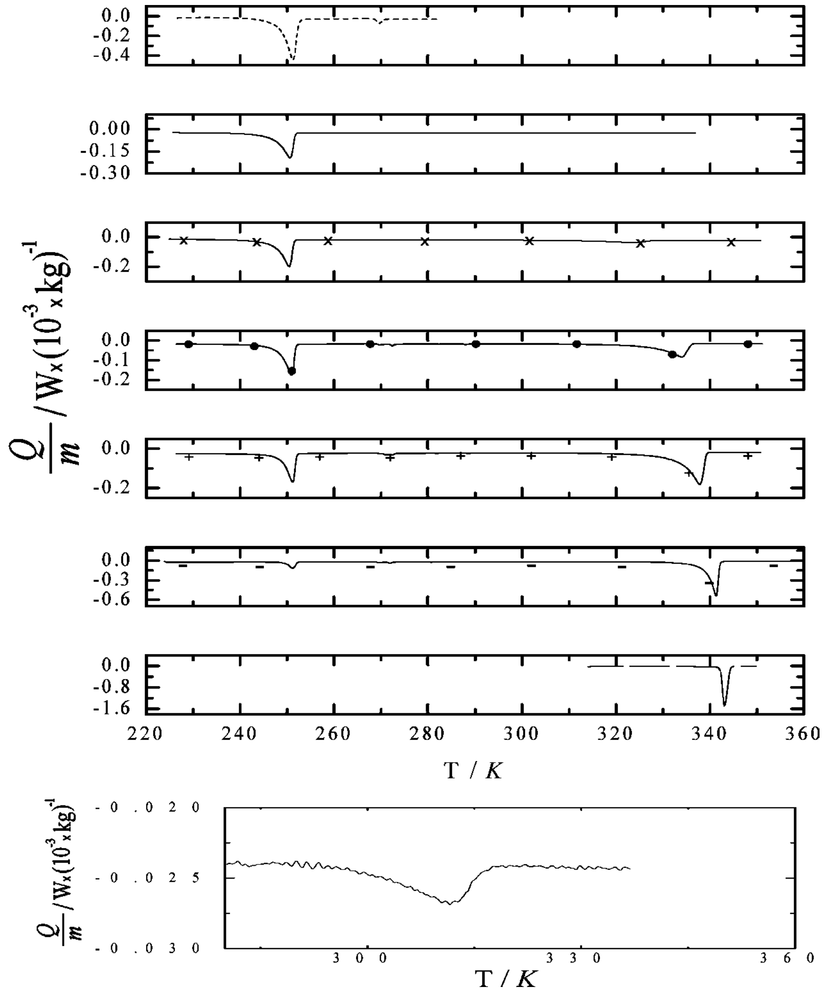

Figure 1. (a) Thermograms of the system trilinolenin + stearic acid: - - -, $x_{\mathrm{tril}} = 1.00$; —, $x_{\mathrm{tril}} \cong 0.94$; —×, $x_{\mathrm{tril}} \cong 0.80$; —•, $x_{\mathrm{tril}} \cong 0.50$; —+, $x_{\mathrm{tril}} \cong 0.30$; ——, $x_{\mathrm{tril}} \cong 0.10$; — — —, $x_{\mathrm{tril}} = 0.00$. (b) Inset in the thermogram of the composition $x_{\mathrm{tril}} \cong 0.94$ for the temperature range between (280 and 340) K.

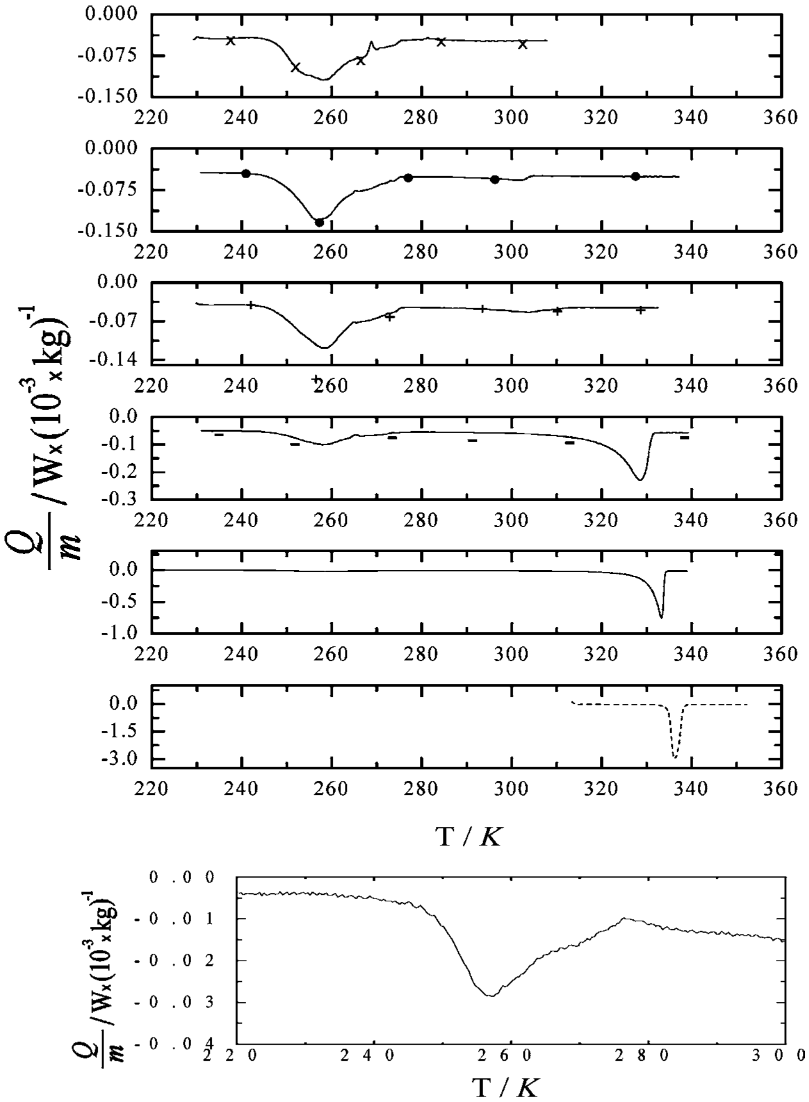

Figure 2. Thermograms of the system commercial triolein + palmitic acid: —×, $x_{\text{comtriol}} = 1.00$; —•, $x_{\text{comtriol}} \cong 0.90$; —+, $x_{\text{comtriol}} \cong 0.84$; —–, $x_{\text{comtriol}} \cong 0.30$; —, $x_{\text{comtriol}} \cong 0.10$; - - -, $x_{\text{comtriol}} = 0.00$. (b) Inset in the thermogram of the composition $x_{\text{comtroil}} \cong 0.10$ for the temperature range between (220 and 300) K.

complete melting of the mixture, and that at lower temperature corresponds to the eutectic transition. The additional transition occurs between the liquidus line and the eutectic temperature, and it is probably related to a transition in pure trilinolenin. Such transitions are common in fatty systems, but their exact characterization requires the use of other experimental techniques, such as Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction.[6–8,16] In Figure 1a the peak of stearic acid is almost imperceptible for $x_{\text{tril}} \geq 0.94$, but an inset on the thermogram is sufficient to show the existence of a third peak that represents, as mentioned above, the melting temperature of the mixture (Figure 1b). The thermograms of the system commercial triolein + palmitic acid are shown in Figure 2. Two peaks were obtained. The first one, at higher temperature, is well-defined and corresponds either to the melting of pure palmitic acid ($x_{\text{comtriol}} = 0.00$) or to the complete melting of the mixture. The second one, at smaller temperature, is broad and spread along a larger range of temperature. It corresponds either to the melting of commercial triolein or to the eutectic transition. The shape of this broader peak can be attributed to the presence of other triacylglycerols in the commercial triolein (Table 2). It should be noted that the peak shape did not change significantly with the decrease of the commercial triolein composition in the mixture, as can be seen in Figure 2b in the temperature range of (240 to 280) K. Furthermore, the peak top temperature also did not change significantly along the

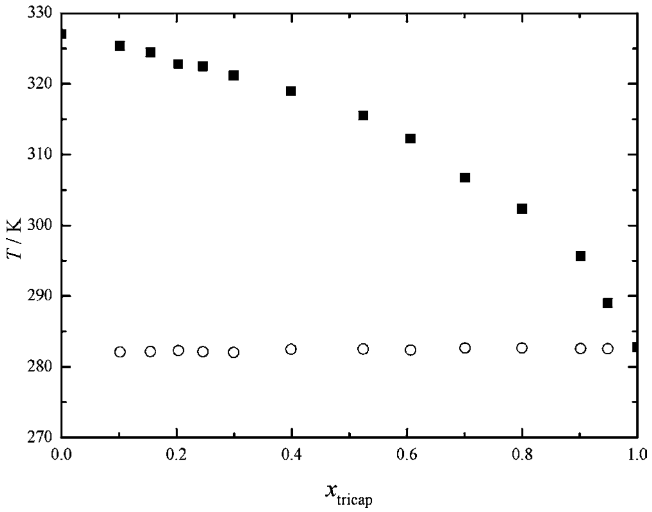

Figure 3. Phase diagram of tricaprylin + myristic acid. ■, melting temperature; ○, eutectic temperature.

Table 4. Adjustment Parameters Obtained for Margules Three-Suffix, Margules Two-Suffix, and NRTL Models

	Margules three-suffix		NRTL ($\alpha_{12} = 0.30$)		Margules two-suffix
	A_{12}	A_{21}	Δg_{12}	Δg_{21}	A_{12}
systems	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
tricaprilyn + myristic acid	597.78	1930.39	54149.80	−2171.57	1480.08
trilinolenin + stearic acid	1076.48	2079.66	4127.06	−1562.43	1618.73

Table 5. Deviations Obtained for Margules Three-Suffix, Margules Two-Suffix, NRTL, and UNIFAC Dortmund Models

	rmsd[a]		
model	tricaprilyn + myristic acid	trilinolenin + stearic acid	commercial triolein + palmitic acid
Margules three-suffix	1.03	1.02	
NRTL ($\alpha_{12} = 0.30$)	0.84	0.95	
Margules two-suffix	1.42	1.07	
UNIFAC Dortmund	2.22	5.20	1.48

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

sequence of thermograms. In fact, this temperature varied around (257.58 ± 0.57) K at the same time as the mixture composition was changed. In a way similar to transitions observed in simple binary mixtures, we assumed for this complex system that the top temperature of this broad peak corresponds to the eutectic temperature.

The temperatures presented in Table 3 were obtained by determining the peak top temperature of each observed transition.[14,17] The phase diagram of the tricaprylin + myristic acid system is given in Figure 3. The thermograms for this system showed well-defined peaks similar to those obtained for the mixtures containing trilinolenin and stearic acid. All three phase diagrams exhibit an eutectic point at a concentration very close to the pure triacylglycerol. Only in the case of the trilinolenin + stearic acid system an additional transition was observed. The binary systems were modeled by Margules two-suffix, Margules three-suffix, and NRTL models and also predicted using the UNIFAC Dortmund model, according to our previous work.[14] Table 4 shows the obtained parameters. The multicomponent system formed by palmitic acid + commercial triolein was predicted using the UNIFAC Dortmund model.[18] In this last case the liquid-phase activity coefficients were calculated taking into account the presence of palmitic acid and all triacylglycerols shown in Table 2 (commercial triolein). The root-mean-square deviation (rmsd) was used to evaluate the quality of the model fitting. Table 5 shows the rmsd values. The best results were obtained using the NRTL model. In the case of the UNIFAC Dortmund model the deviations are larger, but this model is predictive, so no further adjustment was done to represent the nonideality of the liquid phase.

Conclusion

DSC has been an excellent technique for measuring solid−liquid equilibrium data. All three systems exhibit an eutectic point very close to the pure triacylglycerol. The NRTL model allowed the best modeling of the equilibrium data. The UNIFAC Dortmund model has predicted appropriately the liquidus line of the complex system commercial triolein + palmitic acid.

Literature Cited

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

(2) Huibers, D. T. A.; Fritz, E. *Fatty Acids in Industry*; Marcel Dekker: New York, 1989.

(3) 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*, 21–39.

(4) 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*, 7–18.

(5) Bailey, A. E. *Melting and solidification of fats*; Interscience Publishers: New York, 1950.

(6) Garti, N.; Sato, K. *Crystallization and polymorphism of fats and fatty acids*; Marcel Dekker: New York, 1989.

(7) 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.

(8) 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.

(9) 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.

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

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

(12) AOCS. *Official methods and recommended practices of the American Oil Chemists' Society*; 3rd ed.; AOCS: Champaign, IL, 1988; Vol. 1−2.

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

(14) 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.

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

(16) Gbabode, G.; Negrier, P.; Mondieig, D.; Moreno, E.; Calvet, T.; Cuevas-Diarte, M. A. Fatty acids polymorphism and solid-state miscibility in pentadecanoic acid-hexadecanoic acid binary system. *J. Alloys Compd.* **2009**, *469*, 539–551.

(17) 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*, 143–152.

(18) Gmehling, J.; Lohmann, J.; Jakob, A.; Li, J. D.; Joh, R. A modified UNIFAC (Dortmund) model. 3. Revision and extension. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876–4882.

Received for review May 8, 2009. Accepted January 11, 2010. The authors are grateful to CNPq (306250/2007-1), FAPESP (08/09502-0 and 08/56258-8), and FAEPEX/UNICAMP for the financial support.

JE900410J