Solid−Liquid Equilibrium of Binary Fatty Acid Mixtures

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In the present work the phase diagrams of seven fatty acid binary mixtures were obtained by differential scanning calorimetry (DSC). These mixtures were formed by capric acid ($C_{10:0}$) with lauric acid ($C_{12:0}$), myristic acid ($C_{14:0}$), palmitic acid ($C_{16:0}$), or stearic acid ($C_{18:0}$) and by lauric acid ($C_{12:0}$) with myristic acid ($C_{14:0}$), palmitic acid ($C_{16:0}$), or stearic acid ($C_{18:0}$). The spline technique was used to compare the results of this work with prior results available in the literature for some of the investigated systems. The occurrence of the eutectic point in all systems and of the peritectic point in some of the systems was observed. The occurrence of the peritectic point can be associated with the difference in the number of carbon atoms of the fatty acid chains used in the mixture. The approach suggested by Slaughter and Doherty (*Chem. Eng. Sci.* **1995**, *50*, 1679−1694) was used to model the solid phase, and the liquid phase was modeled using the Margules-2-suffix, Margules-3-suffix, UNIFAC Dortmund, and NRTL models. The best modeling results were obtained using the Margules-3-suffix with an average deviation between experimental and calculated values of 0.14 %.

Introduction

Nowadays knowledge about the solid−liquid equilibrium of fatty acids is of great importance for the chemical, pharmaceutical, cosmetic, and food industries. Fatty acids, besides having importance as major components of oils and fats, representing 96 % of their total mass,[1] are substances used, for example, in the production of coverings, plastics, and cleanliness products.[2] Isolating and purifying fatty acids from mixtures can be a difficult task since such substances undergo thermal decomposition easily, precluding the use of distillation techniques in most cases.

These characteristics suggest crystallization as a particularly well-suited process for the fatty acids' purification and separation. The crystallization process can be more easily developed through the knowledge of phase equilibria, for instance using thermodynamic models for predicting equilibrium concentrations at the selected operational conditions. However, in order to better understand the solidification of mixtures and to develop predictive models, it is essential to have precise and reliable experimental data.

A lot of mixtures, including those containing fatty acids, exhibit in their phase diagrams invariant points, such as eutectic and peritectic.[3] The presence of invariant points may have important consequences for choosing the criteria to be used in separation processes.

In this work, we investigated the solid−liquid equilibrium of seven binary mixtures of saturated fatty acids using the DSC technique. The mixtures studied were composed of the following pairs of fatty acids: capric + lauric, capric + myristic, capric + palmitic, capric + stearic, lauric + myristic, lauric + palmitic, and lauric + stearic acids. The liquidus lines for four of these seven mixtures were already reported in the literature: the system capric + lauric acids was investigated by Grondal and Rogers[4] and by Müller and Stage;[5] the mixture lauric + myristic acids was studied by Müller and Stage[5] and also by Heintz;[6] the mixtures lauric + palmitic and lauric + stearic acids were investigated by Heintz.[6] Nevertheless these literature data were measured a long time ago using other experimental techniques, such as the capillary method with visual reading of the melting temperature. Such data were compared with the results of the present work using the spline technique.

Besides the new experimental data for the liquidus line of seven binary fatty acid mixtures, the present work contains a better characterization of the corresponding solidus line, particularly of those transitions related to the occurrence of peritectic and eutectic points, obtained on the basis of the DSC curves. Furthermore, the modeling results show that the Slaughter and Doherty[7] approach can be also applied to systems exhibiting compound formation with an incongruent melting point.

Experimental Section

Reagents. Standards used for calibration of the DSC were indium (99.999 %) certified by TA Instruments; cyclohexane (min 99.99 %) and naphthalene (min 99 %), both from Merck. The fatty acids used to prepare the samples were high purity and were obtained from the following suppliers: capric acid (min 99 %), lauric acid (99 to 100 %), myristic acid (99 to 100 %), palmitic acid (min 99 %) from Sigma Aldrich; and stearic acid (min 97 %) from Merck. Commercial nitrogen (used for preparing binary samples) and high-purity nitrogen (used in the calorimeter) were supplied by Air Liquide.

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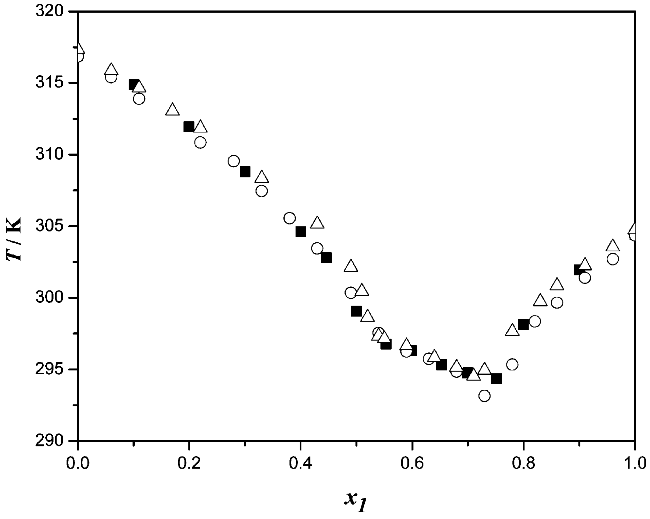

Figure 1. Comparison between the melting temperatures measured in this work and those reported in the literature for the system capric (1) + lauric (2) acids: ■, this work; △, ref 4; ○, ref 5.

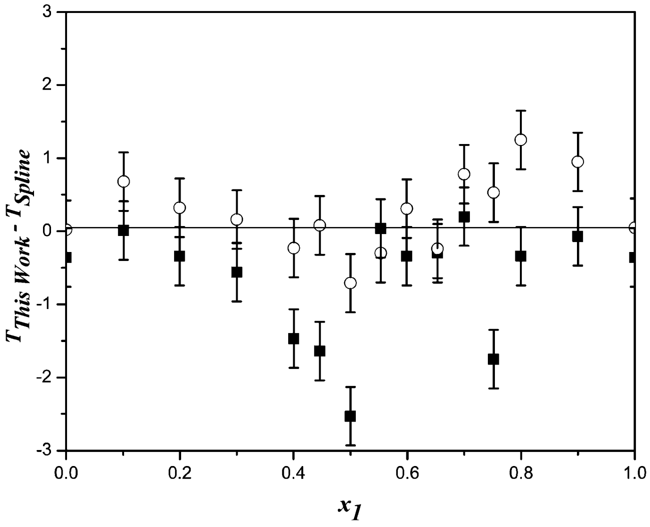

Figure 2. Differences between melting temperatures for capric (1) + lauric (2) acids mixtures reported in the literature[4,5] and the corresponding values measured in the present work: ■, ref 4; ○, ref 5.

Preparation of Fatty Acid Binary Mixtures. The mixtures were prepared on an analytical balance (Adam AAA/L) with a ± 0.2 mg precision. The weighed quantities of the binary mixture components, placed in a glass tube, were heated under stirring in a nitrogen atmosphere. The heating temperature was not higher than 10° above the higher melting point of the components. Subsequently, the solutions were placed in a freezer and kept under refrigeration until later use.

Differential Scanning Calorimetry (DSC). Temperature-driven melting of single fatty acids and of binary fatty acid mixtures were characterized by DSC, using a MDSC 2920, TA Instruments calorimeter. The calorimeter was equipped with a refrigerated cooling system which, in this work, operated between (258 and 423) K. Samples (2 to 5 mg) of each mixture were weighed in a microanalytical balance (Perkin-Elmer AD6) with ± 0.2 × 10^{-5} mg precision and put in sealed aluminum pans. In order to erase previous thermal histories, each sample was submitted to a first heating run at 8.33 × 10^{-2} K·s^{-1} until a temperature 15 K above the highest melting temperature of the components was reached. After 20 min at this temperature, the samples were cooled to 25° below the lowest melting point of the components at a cooling rate of 1.67 × 10^{-2} K·s^{-1} and allowed to stay at this temperature for 30 min. After this pretreatment, each sample was then analyzed in a heating run, at a heating rate of 1.67 × 10^{-2} K·s^{-1}. Onset and peak top temperatures were measured for pure fatty acids, and peak top temperatures were measured for the fatty acid mixtures.

Table 1. Melting Temperatures for Pure Fatty Acids of This Work and Literature

	this work		literature	
fatty acids	T_{onset}/K	T_{peak}/K	T_{fus}/K	T_{fus}/K[7]
capric acid	304.42	305.28	304.95[8]	304.75
lauric acid	316.94	317.71	317.45[9]	317.35
myristic acid	327.48	328.56	327.45[9]	327.55
palmitic acid	335.44	336.47	335.75[9]	336.05
stearic acid	341.91	343.38	342.95[10]	342.75

Table 2. Average Absolute Deviations between the Melting Temperature of the Literature and the Onset and Peak Top Temperatures of This Work[a]

literature	AAD_{onset}	AAD_{peak}
Inoue et al.[8−10]	0.15	0.17
Small[3]	0.14	0.18

[a] $\mathrm{AAD} = \left(\sum_{i=1}^{n} \mathrm{ABS}/n\right) \times 100;\ \mathrm{ABS} = \dfrac{|T_{i,\mathrm{literature}} - T_{i,\mathrm{this\ work}}|}{T_{i,\mathrm{literature}}}$

The accuracy of the experimental data was evaluated on the basis of repeated runs performed for the calibration substances and some of the investigated mixtures. Calibrations of the calorimeter with standards were performed in quintuplicate with absolute average deviations (AAD) ranging from (0.03 to 0.06) K for all the standards. Duplicates of the DSC thermal curves for some selected fatty acid mixtures were used to extract the melting temperatures with AAD ranging from (0.03 to 0.2) K. On the basis of these experimental runs, the uncertainty of the equilibrium data can be estimated as not higher than 0.2 K.

Results and Discussion

Table 1 shows the melting temperatures of pure fatty acids available in the literature and the onset and peak top temperatures obtained in the present work. For a reliable comparison, Table 2 gives the AAD values that were calculated between the melting temperatures of the literature and the onset and peak top temperatures of this work. The AAD values are low in both cases, but a slightly better agreement was obtained using the onset temperatures. Except for stearic acid, the difference between peak top and onset temperatures is not larger than 1.1 K. The larger difference observed in the case of stearic acid can probably be attributed to the lower purity of this reagent (min 97 %). Despite this fact, the AAD value for stearic acid is 0.28 % in the case of onset temperature and 0.15 % for the peak top temperature, indicating that even in this case a good agreement with the literature data was obtained.

Tables 3 and 4 show melting temperatures obtained from DSC measurements for the binary mixtures of fatty acids: capric + lauric, capric + myristic, capric + palmitic, capric + stearic, lauric + myristic, lauric + palmitic, and lauric + stearic. In those tables the concentrations are given in molar fraction of the light component. Melting temperatures of binary mixtures of capric + lauric, lauric + myristic, lauric + palmitic, and lauric + stearic acids are already reported in the literature. The system capric + lauric acids was measured by Grondal and Rogers[4] and by Müller and Stage.[5] The systems lauric + myristic acids, lauric + palmitic acids, and lauric + stearic acids were measured by Heintz in 1854, cited in Bailey.[6] In the case

Table 3. Solid−Liquid Equilibrium Data for the Binary Mixtures of Fatty Acids: Capric (1) + Lauric (2), Capric (1) + Myristic (3), Capric (1) + Palmitic (4), and Capric (1) + Stearic (5)

capric (1) + lauric (2) acids		capric (1) + myristic (3) acids		capric (1) + palmitic (4) acids		capric (1) + stearic (5) acids	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	316.94	0.0000	327.48	0.0000	335.44	0.0000	341.91
0.1010	314.86	0.0986	325.01	0.1207	332.87	0.1013	340.66
0.1993	311.94	0.1968	322.49	0.1981	331.23	0.1989	338.62
0.2999	308.80	0.2997	319.72	0.2993	328.87	0.2967	336.62
0.4001	304.61	0.3985	316.49	0.3991	326.06	0.3950	334.28
0.4457	302.80	0.4979	312.27	0.5032	322.75	0.5032	330.81
0.5002	299.06	0.5986	307.94	0.5998	320.07	0.5972	327.79
0.5530	296.77	0.6490	305.12	0.7043	313.38	0.7044	324.43
0.5989	296.31	0.6996	300.26	0.7496	310.15	0.8012	317.93
0.6529	295.33	0.7992	296.78	0.7937	304.68	0.9002	305.78
0.7001	294.75	0.8475	298.20	0.8484	299.28	0.9500	301.72
0.7516	294.35	0.9013	301.10	0.9009	300.20	1.0000	304.42
0.7998	298.15	0.9503	302.31	0.9502	303.08		
0.9000	301.94	1.0000	304.42	1.0000	304.42		
1.0000	304.42						

Table 4. Solid−Liquid Equilibrium Data for the Binary Mixtures of Fatty Acids: Lauric (2) + Myristic (3), Lauric (2) + Palmitic (4), and Lauric (2) + Stearic (5)

lauric (2) + myristic (3) acids		lauric (2) + palmitic (4) acids		lauric (2) + stearic (5) acids	
x_2	T/K	x_2	T/K	x_2	T/K
0.0000	327.48	0.0000	335.44	0.0000	341.91
0.1004	325.72	0.1001	333.95	0.1003	341.47
0.1997	323.24	0.2000	331.76	0.1994	339.38
0.3002	319.37	0.3000	329.19	0.2999	337.16
0.4001	316.37	0.4000	326.06	0.4005	334.86
0.5002	310.96	0.5000	321.88	0.4999	331.93
0.6002	310.42	0.5999	314.39	0.6007	328.53
0.6500	309.68	0.6998	313.89	0.7002	322.13
0.7001	308.85	0.7998	310.44	0.7999	316.17
0.7996	310.61	0.8481	310.64	0.8485	312.31
0.8996	315.03	0.8968	313.50	0.8999	313.04
1.0000	316.94	1.0000	316.94	0.9499	316.23
				1.0000	316.94

Table 5. Comparison between Experimental Data of This Work and Those Reported in the Literature[4,5] for the System Capric (1) + Lauric (2) Acids[a]

comparison	AAD/%
Grondal and Rogers/Muller and Stage	0.31
Grondal and Rogers/this work	0.23
Muller and Stage/this work	0.15

[a] $\text{AAD} = \left(\sum_{i=1}^{n} \text{ABS}/n\right) \times 100;\ \text{ABS} = \dfrac{|T_{i,\text{literature}} - T_{i,\text{this work}}|}{T_{i,\text{literature}}}$

Table 6. Average Absolute Deviations (AAD) between Data Reported by Heintz (cited in Bailey[6]) and Experimental Data Obtained in This Work

system	AAD/%
lauric + myristic acids	0.19
lauric + palmitic acids	0.13
lauric + stearic acids	0.79

Table 7. Characteristics of Phase Diagram of This Work

system	characteristics
capric + lauric acids	peritectic + eutectic points
capric + myristic acids	peritectic + eutectic points
capric + palmitic acids	eutectic point
capric + stearic acids	eutectic point
lauric + myristic acids	peritectic + eutectic points
lauric + palmitic acids	peritectic + eutectic points
lauric + stearic acids	eutectic point

of refs 4 and 5, the melting temperatures were obtained by the capillary method with visual reading of the temperature. The method used by Heintz was not indicated.[6]

Figure 1 shows a comparison between melting temperatures obtained in this work for the system capric (1) + lauric (2) acids with those reported by ref 4 and 5. As can be seen in Figure 1, there is a good agreement between the experimental values obtained in this work and the literature values. Figure 2 shows the differences between the melting temperatures of the binary mixture capric + lauric acids, measured by DSC, and those reported in the literature,[4,5] interpolated for the same molar fractions using a modified spline technique.[11] It can be seen that the temperature differences for most of the molar fractions stay within the range ± 0.5 K, showing that a good agreement between the visual detection of melting temperatures, based on the capillary method, and the temperatures measured by DSC was obtained. A temperature difference of 0.5 K is slightly larger than the uncertainties associated with melting temperatures measured by the capillary method, estimated as ± 0.2 K.[5,12−14]

The AAD between literature data and the data reported in this work for the system capric + lauric acids is presented in Table 5. The AAD values are relatively low, and the value obtained by comparing the data from ref 4 with the data from ref 5 is larger than those calculated when the literature data were compared with the experimental data of this work. Despite the fact that those authors have used similar experimental techniques, the capillary method with visual reading, the difference between their results is larger. Although the AAD values were low, it can be observed that larger deviations between experimental results occur close to the peritectic point in ref 4 data and close to the eutectic point in ref 5 data (Figure 2).

The data for the system lauric + myristic acids were compared with those measured by Heintz, cited in Bailey.[6] The other two systems, lauric + palmitic acids and lauric + stearic

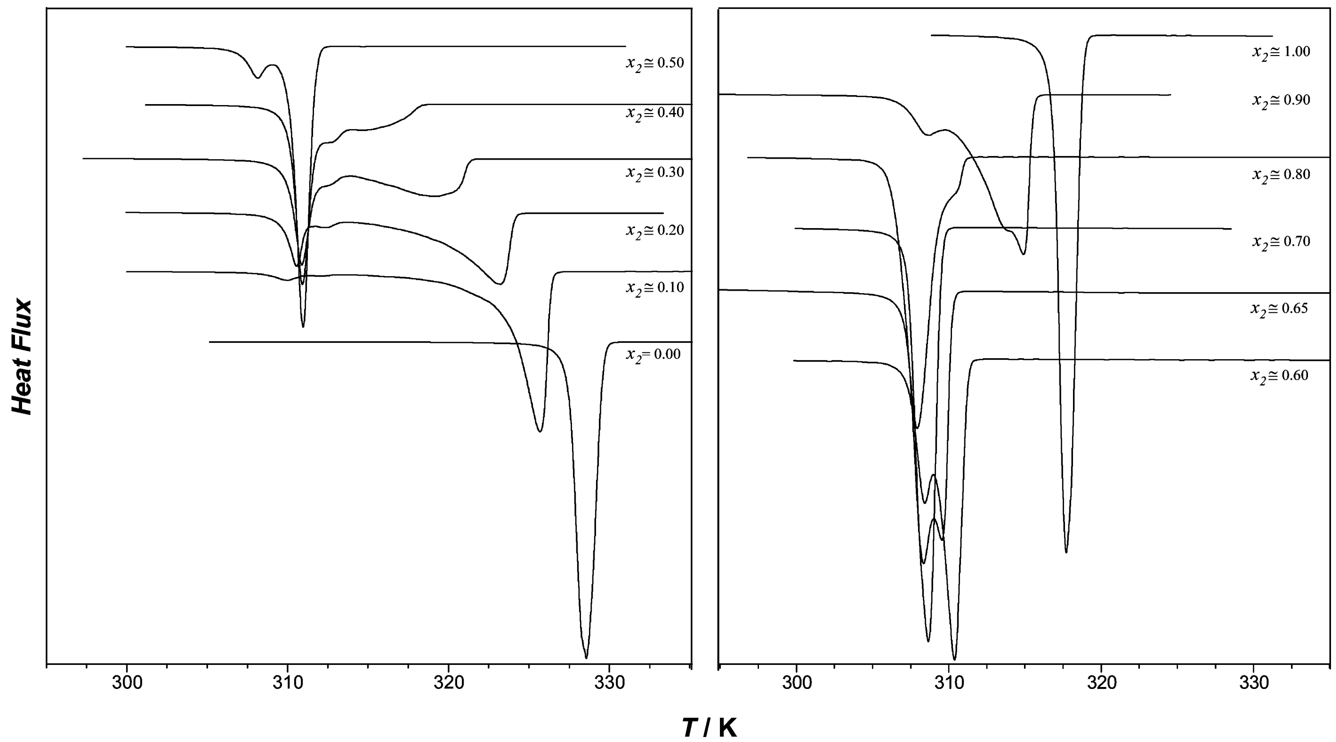

Figure 3. Differential thermal curves for the system lauric (2) + myristic (3) acids.

acids, were also compared. In the case of these systems only six experimental points are available in the literature, a set of data not large enough for a good fitting by the spline technique. In the case of these two last systems, the experimental data of this work were interpolated and compared for the concentrations reported in the literature. The AAD values for these three systems are presented in Table 6. Except for the system lauric + stearic acids, experimental data of the present work were in good agreement with the literature.

The systems studied in this work exhibit two types of phase diagrams. The first one presents peritectic and eutectic points and the second one presents only the eutectic point. Table 7 summarizes the observed behavior for each system. Figure 3a,b shows the differential thermal curves for the system lauric + myristic acids, which exhibits peritectic and eutectic points.

On the differential thermal curves presented in Figure 3, we can observe the evolution of the peaks with the increase of the lauric acid concentration. For pure myristic acid ($x_2 = 0.00$), a unique well-defined peak is observed. When lauric acid is added to the mixture, the curve shows three peaks ($x_2 \cong 0.20$): the first and the second, related to the fusion of the peritectic compound and to a transition in the solid phase, respectively, are relatively small; the third, related to the melting of the mixture, is larger. With the increase of lauric acid concentration ($x_2 \cong 0.40$), the first peak becomes larger and the third peak, related to the mixture's fusion, gets close to the first two ones. At $x_2 \cong 0.50$, it is possible to define only two peaks, the first is now referring to the eutectic point and the second one to the melting temperature. These two peaks appear if lauric acid concentrations is lower than 0.70. At $x_2 \cong 0.70$, a rather sharp single peak was observed, suggesting that this composition corresponds approximately to the eutectic point. At $x_2 \cong 0.90$, the curve again presents more than a unique peak, the first one related to the eutectic transition and the last one to the melting of the mixture. At $x_2 = 1.00$, just one well-defined peak of lauric acid melting can be seen.

Although for pure fatty acids the onset temperatures gave better results of the melting temperature in comparison with values available in the literature (Tables 1 and 2), in the case of mixtures, especially for determining the liquidus line, the peak maximum temperature should be used.[15] Inoue and coworkers used the peak top temperatures for constructing the solid-phase diagrams of several binary mixtures of oleic acid with saturated fatty acids.[8−10] The same procedure is used in the present work for the peaks related to the mixtures' transitions.

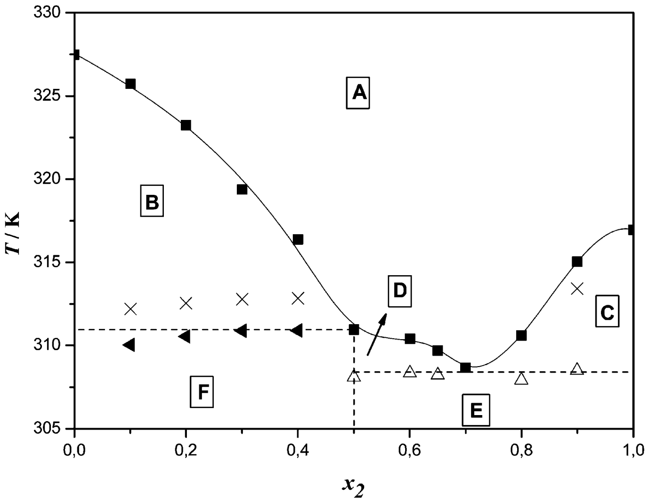

Figure 4. Phase diagram of lauric (2) + myristic (3) acids: ■, fusion temperature; △, eutectic temperature; ▲, peritectic temperature; ×, transitions in solid phase; —. liquidus line; - - -, solidus line.

The phase diagram corresponding to the DSC curves shown in Figure 3 is given in Figure 4. It indicates that in addition to a eutectic temperature at approximately 308.2 K, lauric + myristic acids also display a peritectic temperature around 310.7 K. According to the literature, the peritectic point corresponds to the formation of a compound due to physical interactions or chemical reaction.[7,16] In the case of incongruent peritectics, its melting results in a liquid and a solid with a different composition from the solid compound that generates them.[16]

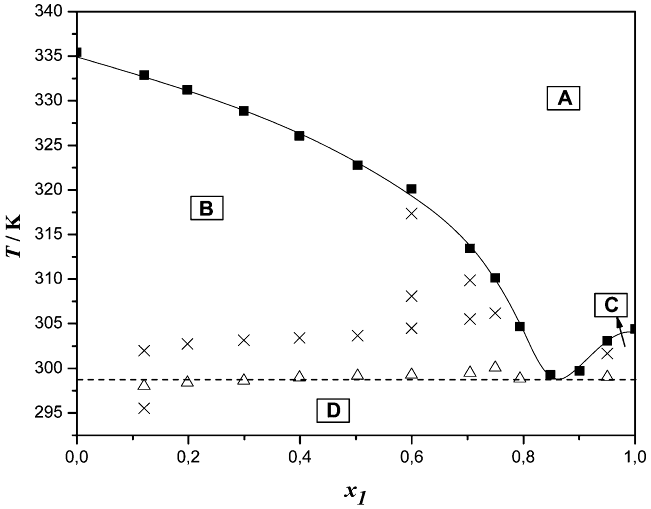

Figure 5. Phase diagram of capric (1) + palmitic (4) acids: ■, fusion temperature; △, eutectic temperature; ×, transitions in solid phase; —, liquidus line; - - -, solidus line.

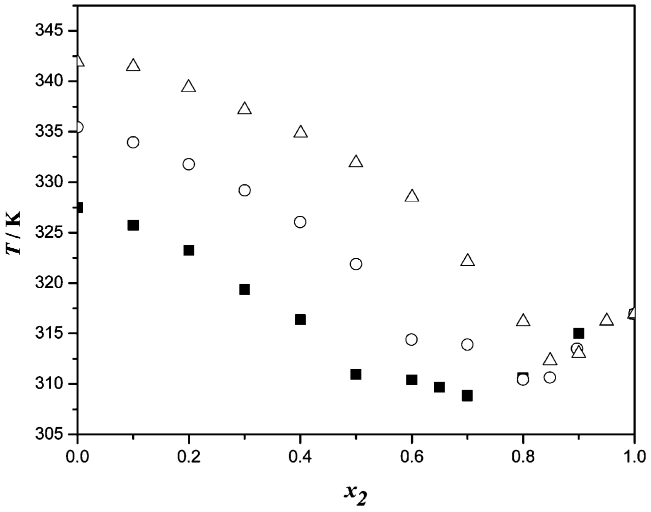

Figure 6. Overlapping of phase diagrams: ■, lauric (2) + myristic (3) acids; ○, lauric (2) + palmitic (4) acids; △, lauric (2) + stearic (5) acids.

So the phase diagram of this mixture can be divided into six regions: region A, above the liquidus line is comprised of a liquid phase; in region B, solid myristic acid coexists with the liquid mixture; in region C solid lauric acid coexists with the liquid mixture; in regions D, E, and F, the solid mixture of lauric and myristic acids (or the so-called compound) coexist with the liquid phase, pure solid lauric acid, and pure solid myristic acid, respectively.

Small[3] reported that mixtures differing by two and four carbon atoms in the fatty acids chains exhibit the formation of an equimolar compound with incongruent melting point, or, in other words, they form a peritectic compound with a 1:1 proportion. Although a similar behavior can be observed in some binary solutions differing by six carbon atoms, Small[3] suggested, as a general rule, that mixtures differing by six or more carbons in the fatty acids chains would normally form simple eutectic systems. In the experimental data of the present work, compound formation was observed by the corresponding endothermic peaks in the DSC curves as well as by a very clear inflection in the liquidus curve, but this occurred only in the case of mixtures with fatty acids differing by two or four carbon atoms.

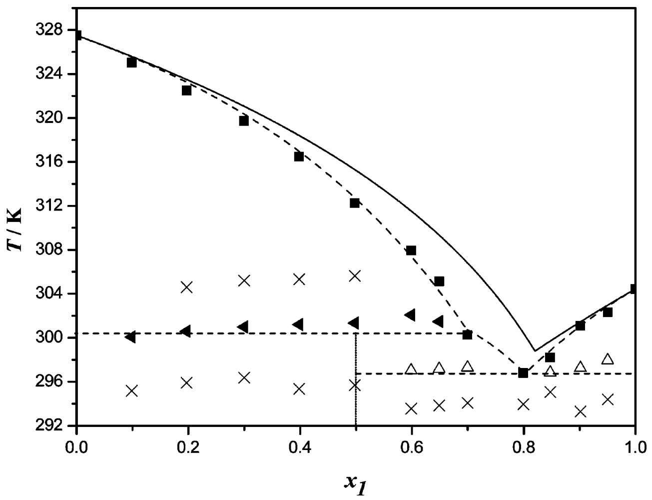

Figure 7. Adjustment to the system capric (1) + myristic (3) acids: ■, fusion temperature; left-facing solid triangle, temperature of peritectic point; △, temperature of eutectic point; ×, temperature of transitions on solid phase; - - - Margules-3-suffix model; —, UNIFAC Dortmund model.

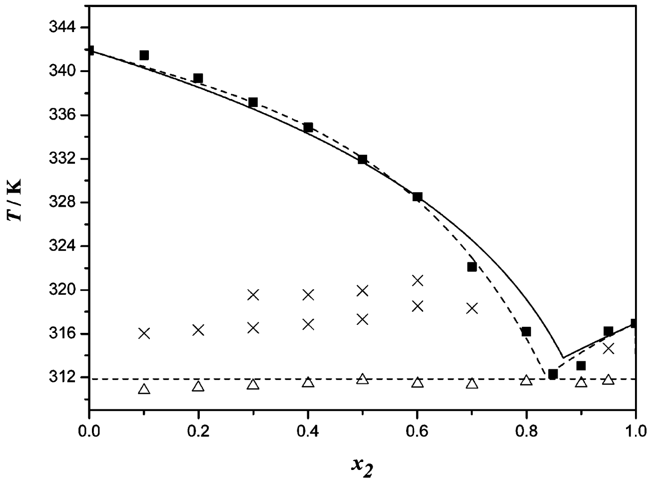

Figure 8. Adjustment to the system lauric (2) + stearic (5) acids: ■, fusion temperature; △, temperature of eutectic point; ×, temperature of transitions on solid phase; - - -, Margules-3-suffix model; —, UNIFAC Dortmund model.

Table 8. Absolute Average Deviations of Systems Adjustment[a]

	AAD/%			
kind of system	Margules-2-suffix	Margules-3-suffix	NRTL	UNIFAC Dortmund
peritectic + eutectic points	0.15	0.12	0.15	0.44
eutectic point	0.23	0.16	0.20	0.41
average global deviations	0.19	0.14	0.17	0.42

[a] $\mathrm{AAD} = \left(\sum_{i=1}^{n} \mathrm{ABS}/n\right) \times 100; \ \mathrm{ABS} = \dfrac{|T_{i,\mathrm{exp}} - T_{i,\mathrm{calc}}|}{T_{i,\mathrm{exp}}}$

Another aspect of the DSC curves shown in Figure 3 and in the phase diagram of Figure 4 is the occurrence of other transitions below the liquidus line, beyond the eutectic and peritectic ones. In almost all systems studied at least one further transition on the solid phase was observed. In fatty acid systems the occurrence of polymorphic transitions in the solid phase[8,17,18] as well as the formation of dimers in solid and liquid phases[19−21] are common events. The literature also reports the possibility of partial solid solutions of fatty acids on either edge of the phase diagrams,[3,6] especially in the case of systems exhibiting simple eutectic points.[20]

In order to better characterize solid transitions, the DSC measurements should be complemented with investigations

Table 9. Adjustment Parameters Obtained for Margules-3-Suffix and UNIFAC Dortmund Models

	Margules-3-suffix				UNIFAC Dortmund	
	A_{ij}	A_{ji}	ΔG_{ij}^{o}	AAD	ΔG_{ij}^{o}	AAD
system	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	%	J·mol^{-1}	%
capric (1) + lauric (2) acids	−1309.36	−1563.96	−1234.09	0.12	−392.19	0.32
capric (1) + myristic (3) acids	−1541.61	−2518.51	−848.14	0.14	225.00	0.66
capric (1) + palmitic (4) acids	−977.57	−1991.01		0.18		0.62
capric (1) + stearic (5) acids	73.45	−1035.68		0.17		0.27
lauric (2) + myristic (3) acids	−2307.29	−3017.82	−1889.33	0.08	−340.63	0.30
lauric (2) + palmitic (4) acids	−1776.71	−5013.88	−2109.64	0.13	5200.00	0.47
lauric (2) + stearic (5) acids	354.4	−1965.36		0.13		0.34

using other techniques, such as Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction. Using these three techniques, Inoue et al.[8] confirmed the occurrence of solid solutions in the systems capric + oleic acids and caprylic + oleic acids and the presence of a compound in the first system. They also obtained DSC curves with multiple peaks at mixture concentrations outside the range of solid solution formation. These curves with multiple peaks are similar to some of the curves presented in Figure 3. A procedure similar to that suggested by Inoue et al.[8] for interpreting such DSC curves is also used in the present work: in the case of multiple peaks, the top temperatures of the two largest peaks are taken as the most important phase transitions, related either to eutectic or peritectic points or to the melting of the mixture (liquidus line). In most cases the two largest peaks corresponded to the lowest and highest transition temperatures observed in the DSC curves.

The phase diagram of Figure 4 was obtained on the basis of the above-mentioned criteria, and similar ones can also be represented for the other three systems that exhibit a peritectic point (Table 7). Furthermore, it should be observed that in a recent work Iwahashi et al.[20] reported a very similar solid−liquid equilibrium behavior for the system capric + lauric acids.

In the second type of phase diagrams investigated in the present work, only a eutectic point was observed. In the diagram shown in Figure 5 capric + palmitic acids form an eutectic mixture at a concentration of approximately 0.85 and a temperature of approximately 299.3 K. Although other transitions were also detected in the solid phase, an inflection similar to that shown in Figure 4 was not observed in the present case. The phase diagram of Figure 5 can be subdivided in the following regions: region A, above the liquidus line, is comprised of a liquid phase; in region B solid palmitic acid coexists with the liquid mixture; in region C solid capric acid coexists with the liquid mixture; and region D comprises the mixture of solid capric and palmitic acids.

Figure 6 shows a comparison of the liquidus lines for three binary mixtures containing lauric acid. As can be seen in this figure, the inflection in the liquidus line corresponding to the peritectic point does not occur for the mixture differing by six carbon atoms. In this case only a eutectic point exists.

Modeling Approach

The solid−liquid equilibrium of fatty acid mixtures can be described by eq 1:[22]

$$\ln\left(\frac{x_i^{s}\,\gamma_i^{s}}{x_i^{l}\,\gamma_i^{l}}\right) = \frac{\Delta H_{i,\mathrm{fus}}}{RT_{i,\mathrm{trp}}}\left(\frac{T_{i,\mathrm{trp}}}{T}-1\right) - \frac{\Delta C_{pi}}{R}\left(\frac{T_{i,\mathrm{trp}}}{T}-1\right) + \frac{\Delta C_{pi}}{R}\ln\frac{T_{i,\mathrm{trp}}}{T} \qquad (1)$$

where x_i is the mole fraction of component i; γ_i^{s} and γ_i^{l} are the activity coefficients in solid and liquid phases, respectively; $\Delta H_{i,\mathrm{fus}}$ is the fusion enthalpy of component i; ΔC_{pi} is the difference between the heat capacity of the liquid and solid phases; $T_{i,\mathrm{trp}}$ is the triple-point temperature; T is the equilibrium temperature; and R is the universal gas constant. Considering that the triple-point temperature is close to the fusion temperature, the triple-point temperature can be changed by the fusion temperature. Considering also that the difference between the heat capacities of liquid and solid phases is small and that the contribution of enthalpy is higher than the heat capacity contribution, eq 1 can be written as

$$\ln\left(\frac{x_i^{s}\,\gamma_i^{s}}{x_i^{l}\,\gamma_i^{l}}\right) = \frac{\Delta H_{i,\mathrm{fus}}}{RT_{i,\mathrm{fus}}}\left(\frac{T_{i,\mathrm{fus}}}{T}-1\right) \qquad (2)$$

For correlating, the systems that present only the eutectic point the solid phase in eq 2 were considered as a pure component ($x_i^{s}\,\gamma_i^{s} = 1$).[23−26] For systems that present a peritectic point, the solid phase in eq 2 was modeled according to the approach suggested by Slaughter and Doherty,[7] who originally tested their procedure for correlating mixtures with compound formation and congruent melting point. These authors suggest that the peritectic compound can be described as a product of a chemical reaction or by a physical association between the pure components in a fixed stoichiometric proportion, generating a new "component" in the system (aA + bB ⇔ cC).

The equilibrium constant of the chemical reaction (K) that forms the peritectic compound is given by

$$K = \prod_{i=1}^{d} (x_i^{s}\,\gamma_i^{s})^{\upsilon_i} \qquad (3)$$

where υ_i is the stoichiometric coefficient for component i and d is the number of components in the solid phase. In the case of the present work, υ_i is always equal to 1 for the mixtures with the peritectic point corresponding to an equimolar compound.[3,6] The equilibrium constant (K) is related to the variation in the Gibbs energy of reaction (ΔG^{o}):

$$K = \exp\left(-\frac{\Delta G_{ij}^{o}}{RT}\right) \qquad (4)$$

Considering that the solid phases are not miscible and supposing that $x_i^{s}\,\gamma_i^{s} \equiv 1$, the reaction constant (K) would be equal to 1. This inconsistency can be prevented with a simple model for the activity coefficient of the solid phase:[1]

$$\gamma_i^{s} = \frac{1}{x_i^{s} + \epsilon} \qquad (5)$$

where ϵ is a small positive number (lower than 10^{-4}). As the peritectic compound dissociates during the mixture fusion, it does not exist in the liquid phase, and the equilibrium equation (eq 2) should be formulated only for the original components of the mixture.

In order to calculate the activity coefficients in the liquid phase the following models were used: Margules-3-suffix model,[22] NRTL model,[22] UNIFAC Dortmund model,[27,28] and Margules-2-suffix.[22] The interaction parameters were obtained by adjusting the models to the experimental equilibrium data, using the Simplex Downhill method.[29] The algorithm used fits simultaneously the ΔG^{o} value of the peritectic reaction and the interaction parameters of the selected models. The objective function is presented in eq 6, in which N is the number of experimental measurements and σ_{T_i} represents the temperature uncertainty:

$$S = \frac{1}{2}\sum_{i=1}^{N}\left(\frac{T_i^{\mathrm{exp}} - T_i^{\mathrm{calc}}}{\sigma_{T_i}}\right)^2 \qquad (6)$$

Table 8 shows the AAD values for each activity coefficient model adopted for the liquid phase. The best results were obtained using the Margules-3-suffix model for the systems only with a eutectic point as well as for the systems exhibiting also a peritectic transition. The NRTL and Margules-2-suffix models present good adjustments too. In the case of UNIFAC Dortmund model, the deviations are slightly larger because this model is predictive and no further adjustment is done to represent the nonideality of the liquid phase. As shown in the present work, the approach suggested by Slaughter and Doherty[7] also gives good results for systems with incongruent peritectic transitions.

The adjustment parameters for the Margules-3-suffix model are shown in Table 9. This table also gives the ΔG^{o} values obtained when the UNIFAC Dortmund model is used for predicting the liquid phase activity coefficients. Figures 7 and 8 show the modeling results for the systems capric (1) + myristic (3) and lauric (2) + stearic (5) acids, respectively.

Conclusion

Phase diagrams were determined in the present work using the DSC technique, which has proved to be an efficient and reliable method for studying fatty acid mixtures. All phase diagrams presented eutectic points, and some of them also presented peritectic points. The occurrence of peritectic points can be related to the difference between the numbers of carbon atoms of the fatty acid chains that form the mixture. Peritectic points were only observed when this difference was lower than six carbon atoms.

The Slaughter and Doherty approach allowed a good fit of the phase diagrams with peritectic points. The Margules-3-suffix model allowed the best modeling of the equilibrium data, and the UNIFAC Dortmund model has shown to be adequate for systems exhibiting only eutectic points.

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