



The solid–liquid phase diagrams of binary mixtures of even saturated fatty acids differing by six carbon atoms

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ABSTRACT

This study was aimed at using the solid–liquid phase diagrams for three binary mixtures of saturated fatty acids, especially the phase transitions below the liquidus line. These mixtures are compounded by caprylic acid (C_{8:0}) + myristic acid (C_{14:0}), capric acid (C_{10:0}) + palmitic acid (C_{16:0}), lauric acid (C_{12:0}) + stearic acid (C_{18:0}), differing by six carbon atoms between carbon chains. The phase diagrams were obtained by differential scanning calorimetry (DSC). The polarized light microscopy was used to complement the characterization for a full grasp of the phase diagram. Not only do these phase diagrams present peritectic and eutectic reactions, but also metatectic reactions, due to solid–solid phase transitions common, in fatty acids. These findings have contributed to the elucidation of the phase behavior of these important biochemical molecules with implications in various industrial production.

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1. Introduction

Fatty acids are the major components of oils and fats [1] and they have been the focus of intense researches since the early 1900s. The recent accrued interest on these compounds results also from their application for the production of biofuels [2,3] coatings, plastics, cleaning products [4] and phase change materials for energy storage [5,6] among others.

The efficient production and use of fatty acids, including their removal during vegetable oil production, require a good knowledge of their properties and phase behavior, that are necessary for the development of separation process. On the other hand, particularly in the food industry, the phase behavior and crystalline habit of the fatty acid mixtures influence the characteristics of consumer products such as confectionary fats [7].

The study of solid–liquid equilibrium (SLE) of triglycerides and fatty acids was initiated around the 50s and remains a challenging task [8–14] due to the different crystal forms that these substances can present in solid state [15,16]. A number of work has appeared on the thermal properties and behavior of solid fats [17,18,7,19,20], and the phase diagram of fats [21,18,22,19,20] and fatty acids [23–26].

Concerning the phase diagrams of fatty acid binary mixtures differing by six or more carbon atoms, Small [22] proposed, as a general rule, the inexistence of the peritectic point observed for less asymmetric mixtures suggesting that systems differing by six or more carbon atoms would present simple eutectic point. In our previous works [27,28] the solid phase of fatty acids binary systems differing by two or four carbon atoms were studied and showed to be far more complex than previously admitted. In this work we present a similar study for systems that differ by six carbon atoms. The phase transitions were determined by using a differential scanning calorimetry (DSC) and elucidated by polarized light microscopy. A thorough phase diagram will here be proposed for systems that differ by six carbon atoms.

2. Experimental

2.1. Materials

Standards used for the calibration of the DSC were indium (99.99%) certified by TA instruments; cyclohexane (min 99.9%) and naphthalene (min 99%), both from Merck. The fatty acids used to prepare the samples were of high purity and obtained from the following suppliers with no further purification: caprylic acid (min 99%), capric acid (min 99%), lauric acid (99–100%), myristic acid (99–100%), palmitic acid (min 99%): Sigma–Aldrich and stearic acid

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(min 97%); Merck. Commercial nitrogen (used for preparing binary samples) and high purity nitrogen (used in the calorimeter) were supplied by Air Liquide.

2.2. Preparation of fatty acid binary mixtures

The samples used in this work were prepared on an analytical balance (Adam AAA/L) with a ± 0.2 mg accuracy. The weighed compounds were placed in a glass tube, then heated and stirred under a nitrogen atmosphere until 10 K above the higher melting point of the components. The mixtures were then allowed to cool down to room temperature and kept in a freezer at 273 K until analysis.

2.3. Differential scanning calorimetry (DSC)

The solid–liquid equilibrium of pure fatty acids and their mixtures were characterized by DSC, using a MDSC 2920, TA Instruments calorimeter that was equipped with a refrigerated cooling system which, in this work, operated between 258 and 423 K using nitrogen as a purge gas. Samples (2–5 mg) of each mixture were weighed in a microanalytical balance (Perkin Elmer AD6) with a $\pm 0.2 \times 10^{-5}$ mg accuracy and put in sealed aluminum pans. In order to erase previous thermal histories, each sample was submitted to a first heating run at 5.0 K min^{-1} until a temperature 15 K above the highest melting temperature of the components was reached. After 20 min under this temperature, the samples were cooled down to 25° below the lowest melting point of the components at a cooling rate of 1.0 K min^{-1} and allowed to stay at this temperature for 30 min. After this pre-treatment each sample was then analyzed in a heating run, at a heating rate of 1.0 K min^{-1} . Peak top temperatures were measured for pure fatty acids and for the fatty acid mixtures using the analysis program of TA instruments. The standard deviation was obtained through six runs with each calibration substance, the average of standard deviations is approximately 0.1. The deviations of the measurements were estimated to range from 0.03 to 0.06 K for the pure standards and from 0.03 to 0.2 K for the mixtures, the uncertainty of the phase equilibrium data was estimated to be lower than 0.2 K [26].

2.4. Polarized light microscopy

A Leica (DM LM) light microscope was used to acquire the images that at controlled temperatures were obtained by putting the sample on a coverslip in a hot stage FP82H, connected to the central processor unit of DSC Mettler Toledo FP 90. The central processor unit was programmed to heat the sample at a heating rate of 0.1 K min^{-1} until the melting of the sample. Images were acquired with a magnification of fifty times at each 0.5 K.

3. Results and discussion

3.1. DSC

According to the literature [21,22] as a general rule, when fatty acids differ by six or more carbon atoms, a simple eutectic system is formed with narrow partial solid solution regions on the extremes of the phase diagram. According to Timms [18] the most common phase diagram found in fatty systems presents a simple eutectic point with the possible occurrence of a solid solution on the extremes of the phase diagram.

Revisiting the thermograms of the systems caprylic acid + myristic acid, capric acid + palmitic acid, lauric acid + stearic acid, were observed that they were as complex as those that differ by two and four carbon atoms between its chains [27,29,28,30].

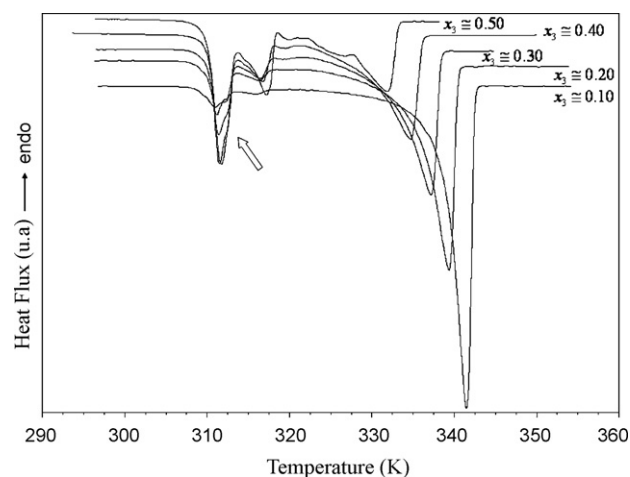


Fig. 1. Thermograms for the system lauric acid (3) + stearic acid (6).

The main difference observed between the thermograms of the systems differing by six carbon atoms and those that differ by only two is the existence of one solid–solid transition below the eutectic temperature, which was also seen on the thermograms that differ by four carbon atoms, but now this transition occurs in the entire concentration range.

In the thermograms of the lauric acid (3) + stearic acid (6) presented in Fig. 1 all transitions occurring before the complete melting of the sample are shown. For all compositions presented in this figure the existence of an overlapped peak at approximately 312 K is noticeable, indicated by a white arrow. These peaks correspond, respectively, to the solid transition and the eutectic transition. With the increase of the lauric acid concentration, other peaks related to other phase transitions are also observed. Fig. 2 presents all the phase transitions observed in this system at the temperature range studied and Table 1 shows the equilibrium data, in molar fraction of the light component, for this system. The shape of the liquidus line (Fig. 2), that seems to present just one inflexion point, would indicate the absence of peritectic reaction, present in the systems that differ by two or four carbon atoms in which the liquidus line have two clear inflexion points corresponding to the peritectic and eutectic points [27,29,28,30]. However, the transitions detected above the eutectic temperature for the system lauric acid + stearic acid and for

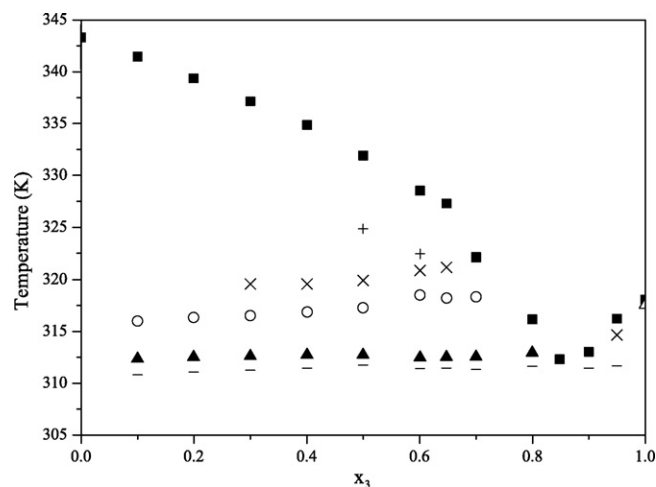


Fig. 2. Observed phase transitions of the system lauric acid (3) + stearic acid (6). (■) fusion temperature; (▲) eutectic temperature; (○) temperature of solid–solid transition; (×), (+), (○) transitions temperatures under liquidus line; (△) transition on the solid phase of the pure component.

Table 1
Solid–liquid equilibrium data for lauric acid (3) + stearic acid (6) system.

x_3	T_{fus} (K)	T_{perit} (K)	T_{metat} (K)	T_{eut} (K)	T_{trans1} (K)	T_{trans2} (K)	T_{trans3} (K)	$T_{\text{trans,pure}}$ (K)
0.0000	343.98							343.31
0.1003	341.47	316.03			310.82	312.35		
0.1994	339.38	316.35			311.07	312.51		
0.2999	337.16	316.54	319.56		311.25	312.61		
0.4005	334.86	316.86	319.57		311.44	312.72		
0.4999	331.93	317.31	319.93		311.76	312.73	324.84	
0.6007	328.53	318.53	320.87	312.47	311.42		322.44	
0.6477	327.30	318.24	321.19	312.53	311.47			
0.7002	322.13	318.33		312.54	311.33			
0.7999	316.17			312.93	311.62			
0.8485	312.31							
0.8999	313.04				311.44			
0.9499	316.23	314.64			311.69			
1.0000	318.07							317.56

the system caprylic acid + myristic acid and capric acid + palmitic acid are an indication that these systems are more complex than previously reported in the literature [21,22,26] and not coherent with a simple eutectic system. In the following discussion it will be shown that the results obtained by the experimental techniques used in this work are not compatible with the traditional interpretation of these systems.

The enthalpies of the peaks associated with the eutectic point plotted as function of the composition of the mixture (Tamman plot) make possible the identification of the range of concentrations associated with this point [23,25–28]. For a simple eutectic system the Tamman plot would present a maximum at the eutectic point concentration. Tamman plots were drawn for the mixtures studied and the plot for the system of lauric acid (3) + stearic acid (6) is presented in Fig. 3 for the transitions observed at approximately 312 and 317 K. Unlike what would be expected for a simple eutectic system the Tamman plot shows a similar behavior to that displayed by systems that differ by two and four carbon atoms [27,28]. For a simple eutectic, it would be expected that the enthalpies for the transition at 312 K increased linearly up to the eutectic point (for this system at $x_3 \cong 0.85$) and from this point decreased also linearly. What is observed instead, is a break in linearity between $0.50 \leq x_3 \leq 0.60$ indicating that eutectic reaction starts at this concentration range and that the transition observed at 312 K before $x_3 \leq 0.60$ is not related to an eutectic transition. The transition observed at 312 K before $x_3 \leq 0.60$ is probably a solid–solid transition since no liquid was observed by microscopy to be forming

at this temperature. On the other hand, although the enthalpies of the transition at approximately 312 K are larger than those at 317 K, the last one can be attributed to a peritectic reaction, confirming the existence of this transition in systems that differ by six carbon atoms.

The Tamman plot from Fig. 3 also shows that while the biphasic region extends to the pure component with the shorter chain length, a solid solution region is present at the other end of the phase diagram for mixtures richness in the heavier fatty acid. It seems easier for a crystal of a long chain fatty acid to accommodate the presence of a short chain fatty acid on its crystalline structure than the reverse.

Based on the DSC thermograms, the Tamman plots and the phase behavior of the systems investigated previously [27,29,28,30] the phase diagram of the lauric acid + stearic acid system is presented in Fig. 4. This phase diagram shows five solid–liquid domains, four solid–solid domains and four monophasic solid domains. The existence of all of these domains is possible due to the occurrence of the eutectic reaction, peritectic reaction and metatectic reaction. The occurrence of eutectic reaction is clear through the inflexion point in liquidus line, the peritectic reaction is suggested by the phase transitions observed on the thermograms and the results presented in Tamman plot. To confirm the metatectic reaction on this phase diagram some images obtained by light microscopy will be used as described hereafter.

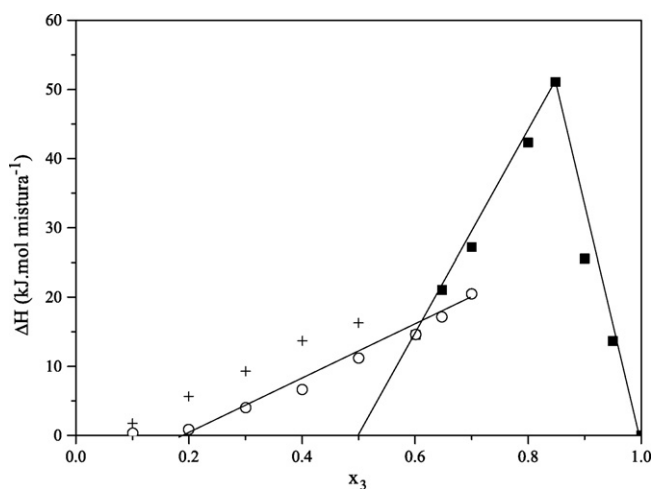


Fig. 3. Tamman plot for lauric acid (3) + stearic acid (6) system. (■) Enthalpy of the eutectic reaction; (○) enthalpy of the peritectic reaction; (+) enthalpy of solid–solid transition; (–) fitting to the experimental results obtained.

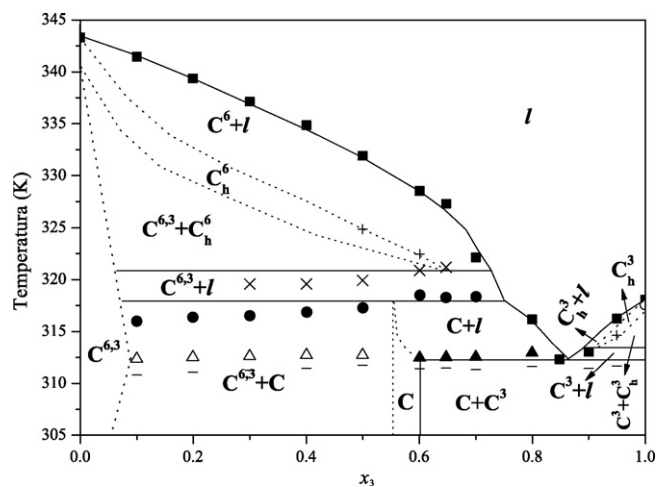


Fig. 4. Phase diagram of the system lauric acid (3) + stearic acid (6). (■) fusion temperature; (●) peritectic temperature; (▲) eutectic temperature; (×) metatectic temperature; (+), (Δ), (–) transitions temperatures on the solid phase; (○) transition on the solid phase of the pure component.

In Fig. 4 the notation used for different domains of the phase diagram has the following meaning: $C^{6,3}$ a solid solution of the component 3 (lauric acid) in the component 6 (stearic acid); C represents the compound formed due to the peritectic reaction, called peritectic compound. The superscripts numbers was used to identify the different fatty acids and the subscript "h" was used to indicate that a new crystal structure is formed due to the metatectic reaction. According to the Tamman plot the systems presented in this study do not present the formation of a solid solution in the extreme of the phase diagram richer in the lower component. So that, in this region, of the phase diagram of the lauric acid + stearic

acid system, the lauric acid is assumed to crystallize in the most stable form also called C form.

3.2. Polarized light microscopy

Temperature scans of samples for a number of mixtures were carried out with polarized light microscopy aiming at identifying the phases present at the phase transitions observed using DSC and confirming the presence of multiple regions in the phase diagram.

Images for the lauric acid (3)+stearic acid (6) system with $x_3 \cong 0.20$, obtained in the temperature range between 308 and

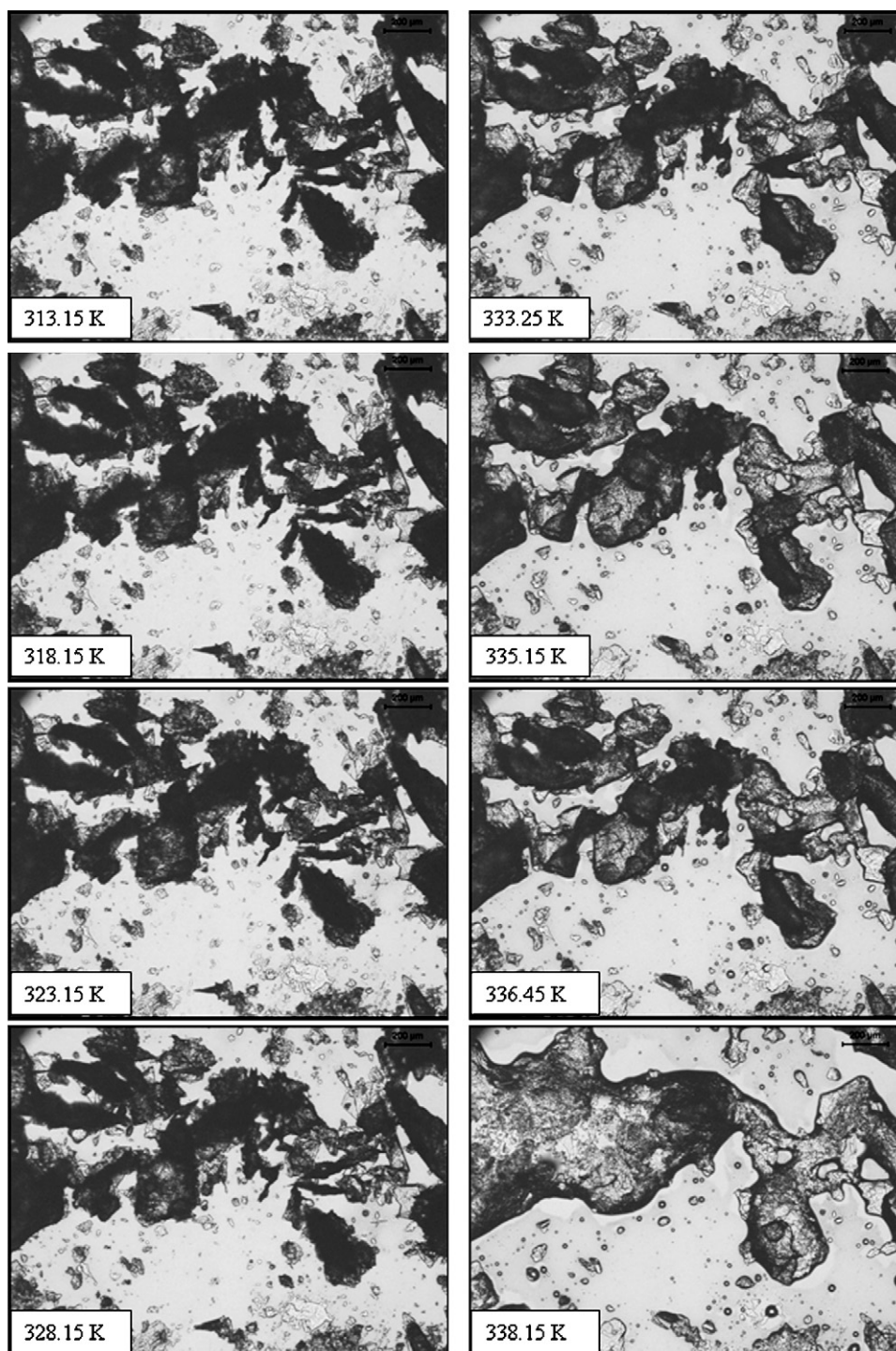


Fig. 5. Light microscopy images of the system lauric acid (3)+stearic acid (6) at $x_3 \cong 0.20$.

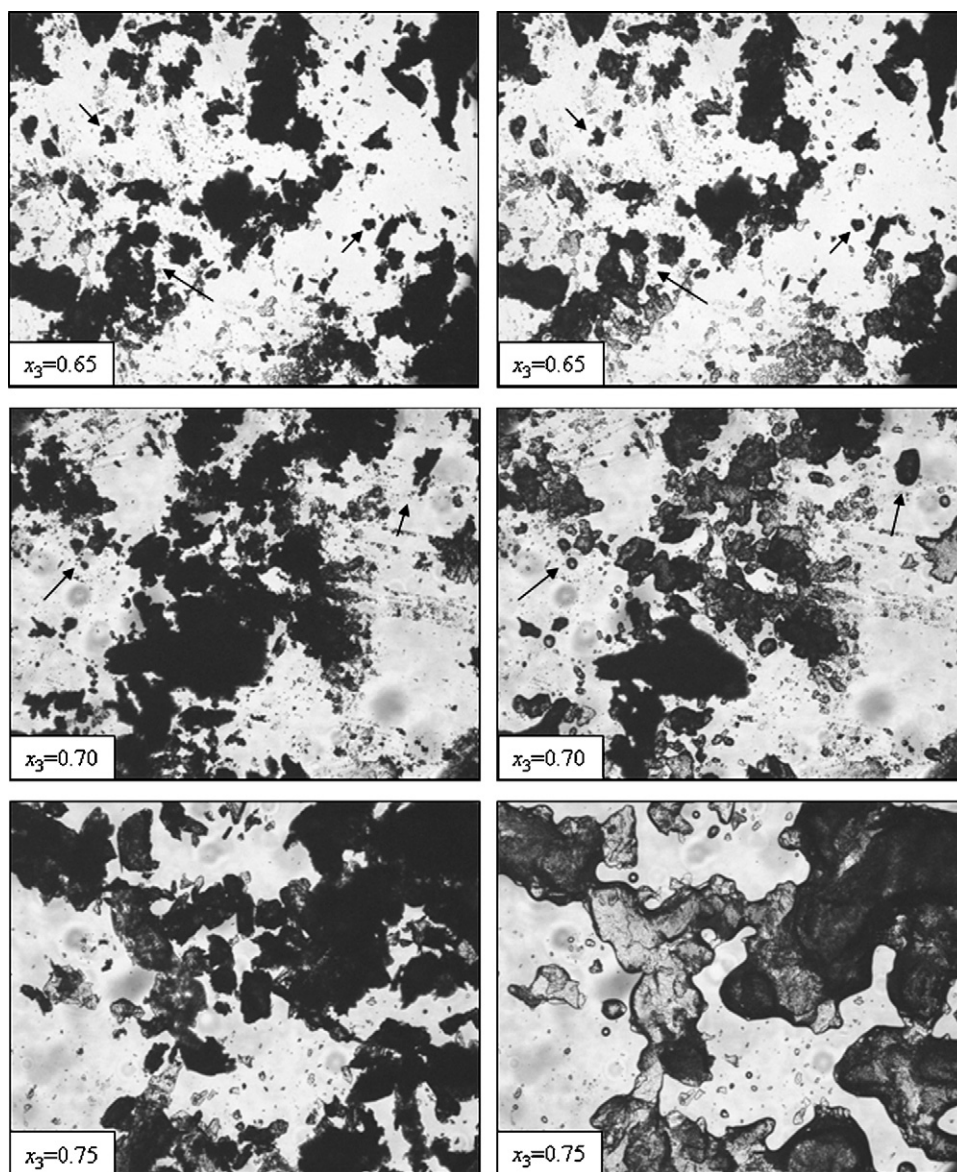


Fig. 6. Light microscopy images of the system lauric acid (3) + stearic acid (6); left column 308.15 K and right column 314.65 K. Magnification of 50 times.

338 K, while heating the sample at 0.1 K min^{-1} , are presented in Fig. 5. At 313.15 K the image shows the sample completely solid, being possible to observe the crystals in thin overlapped layers and presenting an irregular shape. If the conventional interpretation of a simple eutectic for these phase diagrams would hold, in the images at 323.15 and 328.15 K, approximately 28 and 32% of the samples, respectively would be in the liquid state. However, on these images no liquid is observed. With the increase of the temperature to 333.25 K the shape of the crystals changes, becoming round, due to a partial melting of the crystals, but even at this temperature the amount of liquid observed is quite small. With a further increase of the temperature, the portion of liquid in the images increases, indicating that only above 333.25 K a region of two phases, solid–liquid, exists. The absence of liquid below 333.25 K indicates the presence of a peritectic reaction at approximately 317 K and also indicates the presence of metatectic reaction at approximately 320 K, as previously observed for other fatty acid phase diagrams [27,28] as this would explain the absence of a liquid phase up to 333.25 K.

Another series of images (not presented) was obtained for the same system at $x_3 \cong 0.50$. Only at 324.15 K the melting of the sample and the appearance of the solid–liquid equilibrium was observed.

Although the recrystallization of the sample with the increase of the temperature – indicative of the metatectic reaction – is not as extensive as for the systems that differ by two or four carbon atoms [27,28] it is still observed.

If the phase diagram presented in Fig. 4 is correct there should be liquid present at around 315 K for compositions between 0.60 and 0.80 molar fraction of lauric acid. Fig. 6 presents images obtained at two different temperatures, 308.15 and 314.65 K, left and right column, respectively, for three different compositions 0.65, 0.70 and 0.75 molar fraction of lauric acid. At $x_3 \cong 0.65$, with the increase of the temperature, it is possible to observe the melting of a very small portion of the crystal, as indicated by an arrow. With the increase of the concentration it is possible to observe the increase in the liquid portion in the images, indicating that this region is a region of solid–liquid equilibrium formed due to the peritectic reaction.

For the two other systems, capric acid (2) + palmitic acid (5) and caprylic acid (1) + myristic acid (4), it is possible to notice the existence of peritectic reaction at approximately 303 and 288 K, respectively. The occurrence of peritectic reaction for these systems is confirmed by the Tamman plot that presents the same behavior previously observed for the lauric acid (3) + stearic acid (6) system,

Table 2
Solid–liquid equilibrium data for caprylic acid (1) + myristic acid (4) system.

x_1	T_{fus} (K)	T_{perit} (K)	T_{metat} (K)	T_{eut} (K)	T_{trans1} (K)	T_{trans2} (K)	T_{trans3} (K)	$T_{\text{trans,pure}}$ (K)
0.0000	328.88							328.18
0.1000	325.55					284.09		
0.2001	323.27	288.31			282.62	284.46	315.65	
0.2999	320.31	288.01			283.39	284.27		
0.3998	317.62	288.36			283.36	284.59		
0.5000	313.86	288.77			283.49	284.69		
0.6000	307.57	288.64		284.79	282.99			
0.6991	303.61			284.4	283.36			
0.7996	297.88		291.29	284.72	283.33			
0.8999	284.60				283.18			
1.0000	289.63							287.62

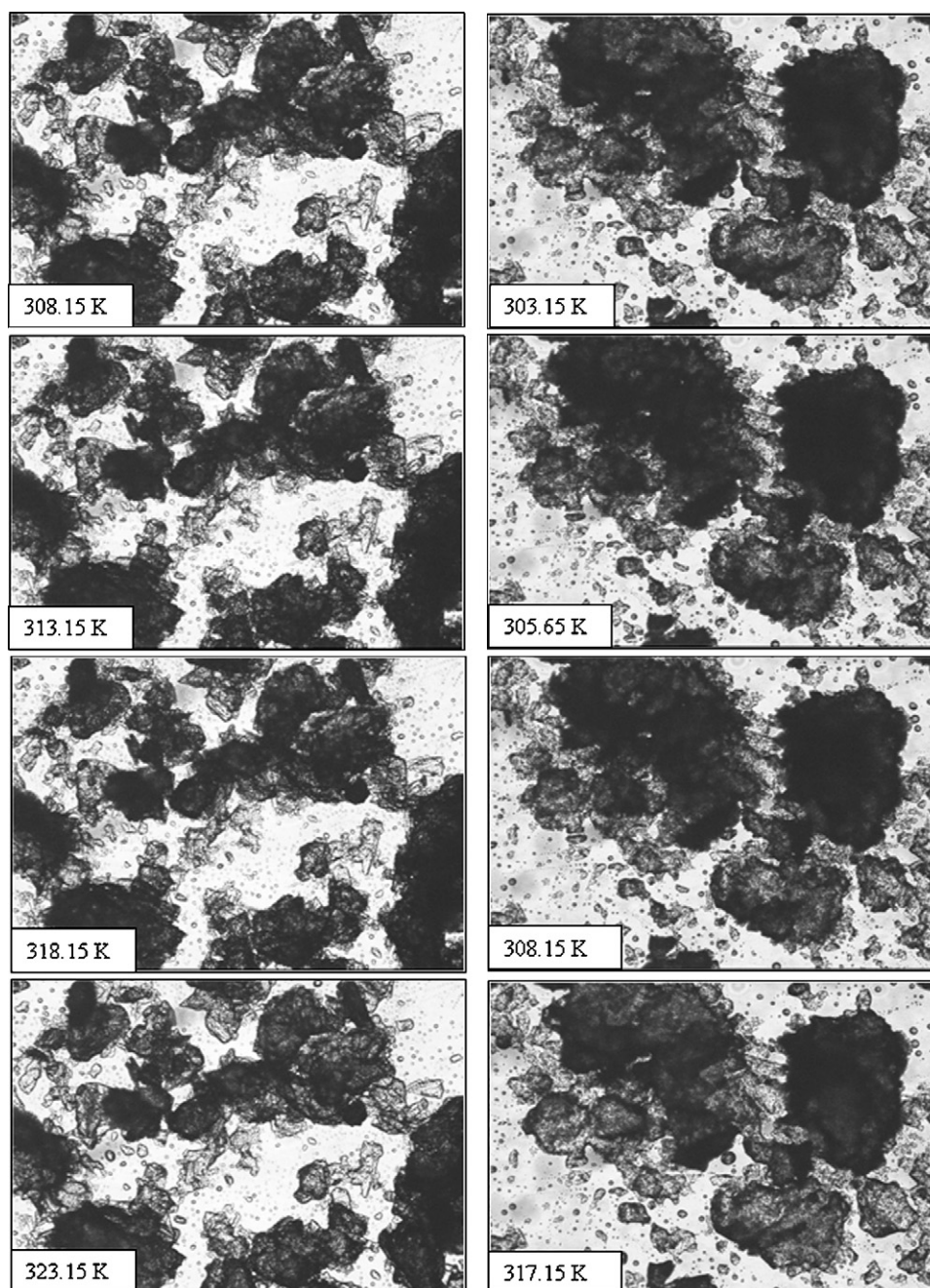


Fig. 7. Light microscopy images of the system capric acid (2) + palmitic acid (5); left column $x_2 \cong 0.20$ and right column $x_2 \cong 0.40$. Magnification of 50 times.

Table 3
Solid–liquid equilibrium data for capric acid (2) + palmitic acid (5) system.

x_2	T_{fas} (K)	T_{perit} (K)	T_{metat} (K)	T_{eut} (K)	T_{trans1} (K)	T_{trans2} (K)	T_{trans3} (K)	T_{trans4} (K)	$T_{\text{trans,pure}}$ (K)
0.0000	337.22								335.95
0.1207	334.41	301.73	306.15		295.60			297.99	
0.1981	331.28	302.61			295.78	332.96	321.15	298.30	
0.2993	328.95	303.11			295.72			298.63	
0.3991	326.1	303.47	306.15				313.15	298.98	
0.5032	322.74	303.63						299.20	
0.5998	319.51	304.29	305.51	298.94					
0.7043	313.43			299.54		315.95			
0.7496	305.79			299.86	296.86	309.79			
0.7937	304.69			298.81					
0.8484	299.37					300.52			
0.9009	298.41								
0.9502	302.9			299.33					
1.0000	305.46					301.69			304.54

and microscopy. For these systems, however, it was not possible to observe in thermograms the phase transition above the temperature of the peritectic reaction related to the metatectic reaction, as observed for the lauric acid (3) + stearic acid (6) system. Nevertheless, images obtained by microscopy for capric acid (2) + palmitic acid (6) at $x_2 \cong 0.20$ and $x_2 \cong 0.40$ presented in Fig. 7 clearly indicate the presence of metatectic reaction due the absence of liquid in the region between the peritectic temperature and 323.15 K for $x_2 \cong 0.20$ and 313.15 K for $x_2 \cong 0.40$. According to the lever rule, if no metatectic reaction was present and this was a solid–liquid region, for $x_2 \cong 0.20$ at 308.15 and 318.15 K there should be approximately 25 and 33% of the sample in the liquid state, respectively. However, only at 323.15 K some liquid starts to form as it can be observed by the round shape of the crystals border's. In the smaller range of temperature studied for $x_2 \cong 0.40$ the same is observed. For this composition, at 303.15 and 308.15 K, approximately half of the samples would be in the liquid state if no metatectic exists. However, only at 317.15 K it is possible to observe the formation of liquid on the sample. These observations are coherent with the presence of a metatectic reaction for these systems, coherently with what is observed for other binary mixtures of fatty acids, and a similar behavior was also observed for the caprylic acid (1) + myristic acid (3) system. The phase diagrams of these systems are presented in Figs. 8 and 9 respectively. These phase diagrams were obtained based on the phase transitions observed by DSC, microscopy observations, on the phase diagrams of the binary mixtures of fatty acids

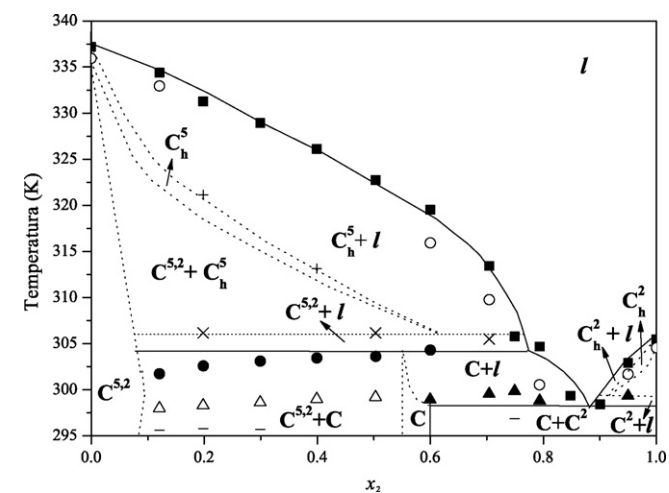


Fig. 8. Phase diagram of the system capric acid (2) + palmitic acid (5). (■) fusion temperature; (●) peritectic temperature; (▲) eutectic temperature; (x) metatectic temperature observed by light microscopy; (+), (Δ), (-) transition temperature on the solid phase; (○) transition on the solid phase of the pure component.

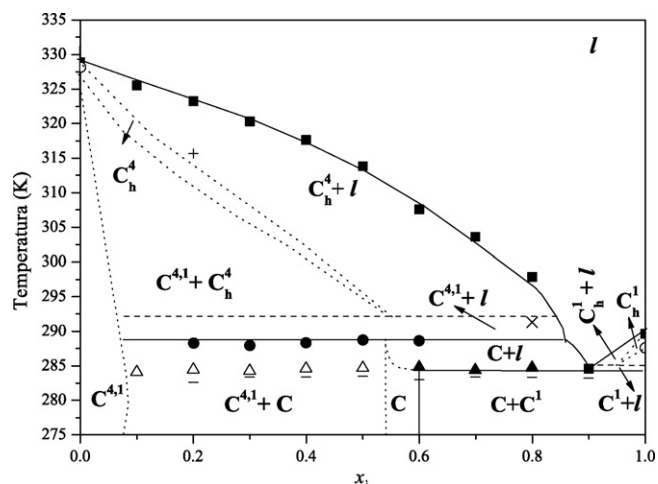


Fig. 9. Phase diagram of the system caprylic acid (1) + myristic acid (6). (■) fusion temperature; (●) peritectic temperature; (▲) eutectic temperature; (x) metatectic temperature observed by light microscopy; (+), (Δ), (-) transition temperature on the solid phase; (○) transition on the solid phase of the pure component.

previously described [27,28] and obtained for the system lauric acid + stearic acid discussed above. The equilibrium data of these systems are reported, in molar fraction of the light component, in Tables 2 and 3.

4. Conclusions

The phase diagrams for binary systems of fatty acids with differences of six carbons on the alkyl chain have been reported in this study. It is shown that these phase diagrams are far more complex than previously stated. The general rule proposed by Small stating that these systems had no peritectic point, does not hold. It was possible to confirm the existence of peritectic reaction and metatectic reaction for saturated fatty systems that differ by six carbon atoms between the carbon chains. Furthermore, the formation of a complete miscibility region between the fatty acids in the extreme of the higher fatty acid of the phase diagram was also observed through Tamman plot. The complexity of the phase diagrams for these systems has had important impacts on the design of separation and purification process for fatty acids and also on the development of products based on these compounds.

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