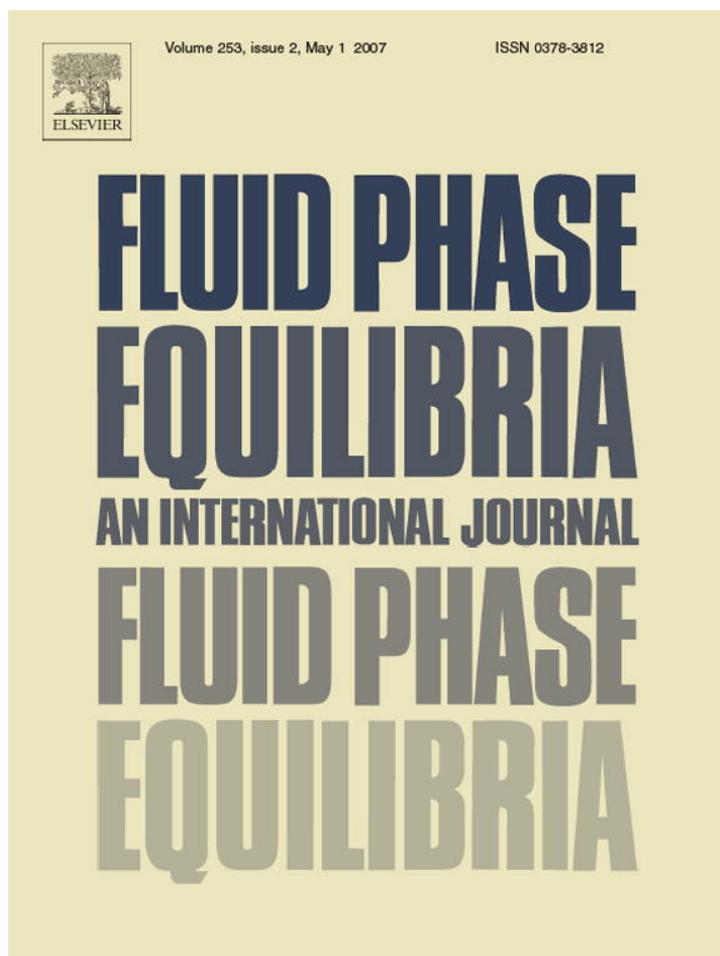


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## High pressure solid–liquid equilibria of fatty acids

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### Abstract

The solid–liquid phase diagrams of two binary mixtures of saturated fatty acids, formed by caprylic acid (C<sub>8:0</sub>) + myristic acid (C<sub>14:0</sub>) and lauric acid (C<sub>12:0</sub>) + myristic acid (C<sub>14:0</sub>), were measured using high pressure microscopy in the range of 0.1–90 MPa. It is shown that unlike for other long chain alkyl compounds such as alkanes the phase diagrams are only slightly affected by the pressure, even in very large pressure ranges such as studied in this work.

The modeling of the measured phase diagrams was attempted using an approach previously developed by the authors for *n*-alkane mixtures. It is here shown that this model can provide an accurate description of the high pressure solid–liquid equilibrium of fatty acid mixtures.

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**Keywords:** Solid–liquid equilibrium; High pressure; Phase diagrams; Caprylic acid; Lauric acid; Myristic acid; Modeling

### 1. Introduction

Fatty acids are the major components of oils and fats [1]. They have critical implications in the understanding of the biological behavior of various lipid systems [2] and lately have been used in the production of coverings, plastics, and cleaning products [3], phase change materials for energy storage [4,5] and biodiesel. The knowledge about the properties of fatty acid mixtures can bring innovations in chemistry, food and pharmaceutical industries due to their influence on the characteristics of consumer products such as cosmetics and confectionary fats. The difficulties due the thermal decomposition in the isolation of fatty acids from their natural mixtures can be overcome through the adequate knowledge of their solid–liquid phase equilibrium.

The high pressure processing technique (HPP) is a non-heat technique used for food processing and food preservation [6].

This technique claims not to change the sensory and nutritious value of food maintaining the original freshness, color, flavor and taste of food [7,8]. It is however possible that the high pressure may cause changes in the crystal structure of the lipids and thus the raw material characteristics [8].

Some works with binary mixture of unsaturated fatty acids under high pressure have been presented before [9–11]. In these papers the authors emphasize the effect of pressure on polymorphic phenomena. Studies of the effect of high pressure on saturated fatty acid mixtures are not available in the literature.

Mixtures of saturated fatty acids exhibit in their phase diagrams invariant points, such as eutectic and peritectic points [12]. The presence of invariant points may have important consequences for choosing the criteria to be used in the separation or processing of fatty acid mixtures. This work investigates these behavior under pressure of two binary mixtures of saturated fatty acids that display the two different types of phase diagrams presented by saturated fatty acid mixtures: a pure eutectic phase diagram and a phase diagram presenting simultaneously eutectic and peritectic points. The fatty acid mixtures studied are caprylic acid (C<sub>8:0</sub>) + myristic acid (C<sub>14:0</sub>) and lauric acid

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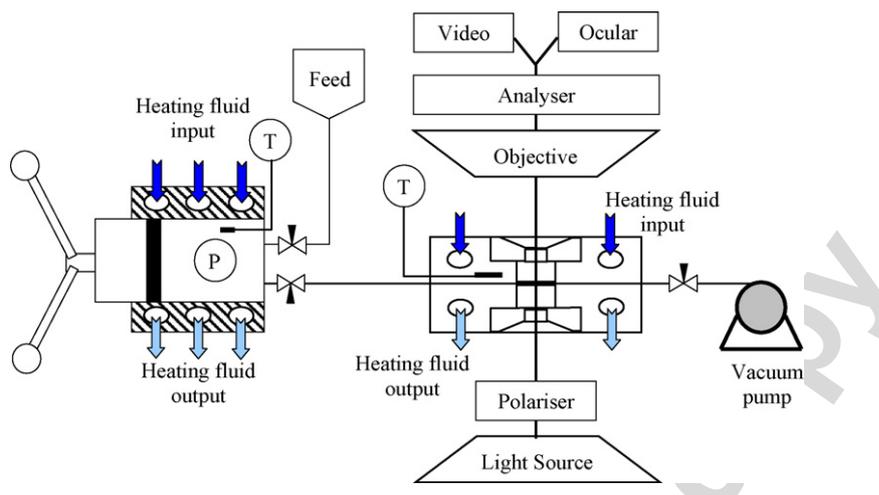


Fig. 1. High pressure microscopy apparatus.

(C<sub>12:0</sub>) + myristic acid (C<sub>14:0</sub>) the liquidus curves of these systems were measured with a high pressure microscope [13,14] from atmospheric pressure up to 90 MPa. Data for these diagrams were previously measured at atmospheric pressure by Heintz (cited in Bailey [15] without mentioning to the method used) and recently [16,17] using a DSC technique. As mentioned before no data under pressure was available for saturated fatty acids.

## 2. Experimental section

Highly pure samples of caprylic acid (minimum 99%) supplied by Fluka and lauric acid and myristic acid (99–100%) supplied by Sigma were used in this work without further purification.

The mixtures were prepared using a high precision balance in order to achieve an accuracy of 0.02% in the molar fraction of the mixtures studied. Weighed quantities (5 g) of the binary mixture components were placed in a glass tube, where they were heated in an oven at a temperature of 350 K until fusion and homogenization of the mixture.

The high pressure solid–liquid equilibrium of the binary fatty acid mixtures was studied in a high pressure microscope developed previously [13,14]. This experimental apparatus is built around an autoclave cell, made up of a stainless steel block and equipped with two sapphire windows through which the studied sample can be observed with the help of a polarizing microscope coupled with a video camera. This technique allows the detection of very small crystals, down to 2 μm in size. A heat-transducing fluid that circulates in flow lines in the metallic thermostat block controls the temperature of the whole cell, which can be maintained between 243 and 373 K. The thermal regulation of this fluid is carried out by a thermostat bath (HUBER) with a temperature stability of 0.01 K. The sample temperature is measured by means of a platinum resistance thermometer (OMEGA) inserted inside a hole made in the cell. The uncertainty of temperature values is estimated at 0.2 K [13,14]. The pressure is transmitted to the sample through a hand pump and measured with a flush diaphragm pressure transmitter (DYNISCO), with a precision

of 0.2%. This probe is regularly checked against a dead weight tester (BUDENBERG). The apparatus is sketched in Fig. 1.

The insertion of the sample into the microscope was achieved by maintaining the temperature of the pump and the cell around 333.15 K to avoid the crystallization of the sample. With the sample inside the cell the temperature was decreased 2–3 K below the melting temperature of the sample and kept at this temperature for 5–10 min. The temperature was then slowly increased until the beginning of the fusion and then the temperature was increased in steps of 0.1 K until the disappearance of the last crystal. After complete melting the pressure in the cell was increased resulting in the crystallization of the sample and a new temperature cycle was started.

## 3. Modeling

The modeling of the high pressure phase equilibria of fatty acids was carried using an approach previously proposed by us for alkane mixtures [18–23]. The model is here extended with success to fatty acids as follows.

Equilibrium conditions are obtained from the equality of fugacities of each component in the liquid and solid phase:

$$f_i^L(T, P, x_i^L) = f_i^S(T, P, x_i^S) \quad (1)$$

The liquid phase fugacities can be written as:

$$f_i^L(T, P, x_i^L) = P x_i^L \phi_i^L \quad (2)$$

where the fugacity coefficient  $\phi_i^L$  is calculated using the Soave–Redlich–Kwong equation of state [24], with the LCVM mixing rules [25,26]. The volumetric properties calculated by the cubic EOS are corrected using the volume translation proposed by Peneloux et al. [27].

The solid phase fugacities at a pressure  $P$  are obtained by the equation:

$$\ln f_i^S(P) = \ln f_i^S(P_0) + \frac{1}{RT} \int_{P_0}^P \bar{V}_i^S dP \quad (3)$$

where the fugacity of the component  $i$  in the solid phase at pressure  $P_0$  is calculated from its fugacity in subcooled liquid state

Table 1  
Thermophysical properties for the pure components

	$T_m$ (K)	$\Delta_m H$ (kJ mol <sup>-1</sup> )	$T_c$ (K)	$P_c$ (K)	$\omega$	$\beta$	$\rho_{\text{solid}}^a$ (g cm <sup>3</sup> )	$\rho_{\text{liquid}}^a$ (g cm <sup>3</sup> )
C <sub>8:0</sub>	289.85	21.38	693.00	28.69	0.77063	0.90	1.035	0.90408
C <sub>12:0</sub>	316.98	36.65	743.43	18.68	0.87999	0.88	1.024	0.87162
C <sub>14:0</sub>	327.37	45.10	765.19	16.44	0.93564	0.86	1.020	0.86242
Peritectic	324.1	55.40	n.a.	n.a.	n.a.	0.85	n.a.	n.a.

$T_m$ ,  $\Delta_m H$ ,  $T_c$ ,  $P_c$  from Ref. [28].

<sup>a</sup> Data from DIADEM Public 1.2.

at the same temperature  $T$ :

$$f_i^S(P_0) = x_i^S \gamma_i^S(P_0) f_i^{0,L}(P_0) \exp \left[ -\frac{\Delta_{\text{fus}} H_i}{RT} \left( 1 - \frac{T}{T_{\text{fus},i}} \right) \right] \quad (4)$$

where  $\gamma_i^S$  represents the activity coefficient of the compound  $i$  in the solid phase;  $T_{\text{fus},i}$  and  $\Delta_{\text{fus}} H_i$  are, respectively, the fusion temperature and the enthalpy of fusion of the pure compound  $i$ . The Poynting correction term of Eq. (3) is simplified by the assumption that the partial molar volume of each component is proportional to the subcooled liquid molar volume:

$$\bar{V}_i^S = V_i^{0,S} = \beta V_i^{0,L} \quad (5)$$

where  $\beta$  is assumed to be pressure independent and the same for both compounds in the mixture, so that Eq. (3) can be written as proposed by Pauly and co-workers [14,18–23]:

$$f_i^S(T, P, x_i^S) = x_i^S \gamma_i^S [f_i^{0,L}(T, P_0)]^{1-\beta} [f_i^{0,L}(T, P_0)]^\beta \times \exp \left[ -\frac{\Delta_{\text{fus}} H_i}{RT} \left( 1 - \frac{T}{T_{\text{fus},i}} \right) \right] \quad (6)$$

The thermophysical properties for the pure compounds [28] are reported in Table 1. The thermophysical properties for the peritectic phase are estimates obtained from the few data points available for the peritectic region and have a large uncertainty.

The activity coefficients  $\gamma_i^S$  of the rotator phase were described by means of the new Predictive UNIQUAC model recently proposed by us [29,30]. The UNIQUAC model can be written as:

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left( \frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \times \ln \left[ \sum_{j=1}^n \theta_j \exp \left( -\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (7)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (8)$$

The predictive local composition concept [31–35] allows the estimation of the interaction energies,  $\lambda_{ij}$ , used by this model without fitting to experimental data. The pair interaction energies between two identical molecules are estimated from the enthalpy of sublimation of an orthorhombic crystal of the pure

component:

$$\lambda_{ii} = -\frac{2}{Z} (\Delta_{\text{sub}} H_i - RT) \quad (9)$$

where  $Z$  is the coordination number. A value of the coordination number of 10 will be used for UNIQUAC [36,37]. The enthalpies of sublimation,  $\Delta_{\text{sub}} H = \Delta_{\text{vap}} H + \Delta_{\text{fus}} H$ , are calculated at the melting temperature of the pure component.

The pair interaction energy between two non-identical molecules is given by:

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} (1 - \alpha_{ij}) \quad (10)$$

where  $j$  is the compound with the shorter alkyl chain of the pair  $ij$ . The interaction parameter  $\alpha_{ij}$  may be of importance for the description of the solid solution formation but has little impact on the liquidus line. For the caprylic acid + myristic acid system a zero value was used while for the lauric acid + myristic acid system a value of 0.03 was used.

The high pressure solid–liquid equilibrium model is thus a predictive model that uses in the calculation of the phase behavior only pure component properties with the possibility of fine-tuning to actual experimental data. Using a flash calculation it is possible, using the proposed thermodynamic model, to draw the solid–liquid phase diagrams for the mixtures studied.

#### 4. Results and discussion

The melting temperatures for pure fatty acids are in good agreement with melting temperatures reported in literature [12,38,39] showing that the compounds used in this study were of high purity.

The solid–liquid equilibrium data measured is presented in Table 2 for the system lauric acid (C<sub>12:0</sub>) + myristic acid (C<sub>14:0</sub>) and in Table 3 for the system caprylic acid (C<sub>8:0</sub>) + myristic acid (C<sub>14:0</sub>).

A comparison between the data for the system of lauric acid (C<sub>12:0</sub>) + myristic acid (C<sub>14:0</sub>) measured at atmospheric pressure in this work and data previously reported in the literature [17] is presented as deviations in Fig. 2. A good agreement between the different sets of data is found with average absolute deviation (AAD) of  $\pm 0.4$  K obtained around the peritectic point. A similar comparison for the system caprylic acid (C<sub>8:0</sub>) + myristic acid (C<sub>14:0</sub>) is presented in Fig. 3. A good agreement is also obtained here with an AAD of 0.2 K.

Small [12] reported that mixtures differing by two and four carbon atoms in the fatty acids chains exhibit the formation of

Table 2  
Solid–liquid equilibrium data for the system lauric acid (C<sub>12:0</sub>) + myristic acid (C<sub>14:0</sub>)

$x_{(C_{12:0})}$	T (K)						
	0.1 MPa	20 MPa	40 MPa	60 MPa	70 MPa	80 MPa	90 MPa
0.0000	327.50	332.30	337.25	342.31	344.68	346.55	348.93
0.1009	325.58	330.23	334.76	339.97	342.25	344.89	347.03
0.1966	324.08	328.32	333.07	337.35	339.97	342.53	345.35
0.3026	321.01	325.66	330.31	334.74	336.75	339.22	341.22
0.3915	317.19	321.12	326.29	330.37	332.65	334.89	337.27
0.5002	311.95	316.50	320.92	325.15	327.07	330.00	332.45
0.6025	310.19	314.37	318.49	322.42	324.37	326.41	329.53
0.6469	308.49	312.85	317.18	321.40	323.28	325.04	326.75
0.6996	308.45	313.35	317.55	322.32	324.32	326.29	328.45
0.7498	309.98	315.10	318.85	323.95	325.48	327.78	329.95
0.7990	312.05	316.85	321.35	326.15	328.45	330.35	332.05
0.9000	315.15	319.45	323.95	328.15	330.15	332.05	334.35
1.0000	316.18	320.60	325.17	329.76	331.86	334.10	336.10

Table 3  
Solid–liquid equilibrium data for the system caprylic acid (C<sub>8:0</sub>) + myristic acid (C<sub>14:0</sub>)

$x_{(C_{8:0})}$	T (K)					
	0.1 MPa	20 MPa	40 MPa	60 MPa	80 MPa	90 MPa
0.0000	327.50	332.30	337.25	342.31	346.55	348.93
0.2022	324.18	329.07	334.15	338.91	343.37	345.40
0.4010	318.25	322.31	326.55	330.79	335.35	337.15
0.6025	310.25	314.95	319.45	323.60	328.05	329.95
0.7982	299.25	303.64	308.20	312.45	317.00	318.89
0.8502	293.15	297.25	301.45	305.75	310.25	312.25
0.8997	285.53	289.53	294.15	298.50	302.65	304.15
0.9500	287.35	291.75	295.95	300.55	304.85	306.55
1.0000	289.86	294.52	299.35	303.85	308.09	309.98

an equimolar compound with incongruent melting point, or, in other words, they form a 1:1 peritectic compound. Although a similar behavior can be observed in some binary solutions differing by six carbon atoms, Small [12] suggested, as a general

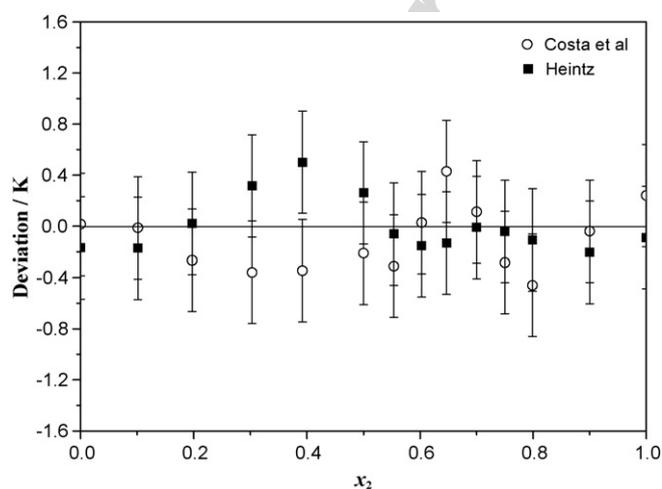


Fig. 2. Deviations between liquidus temperatures for lauric acid (2) + myristic acid (3) mixtures reported in the literature [17] and the corresponding values measured in the present work.

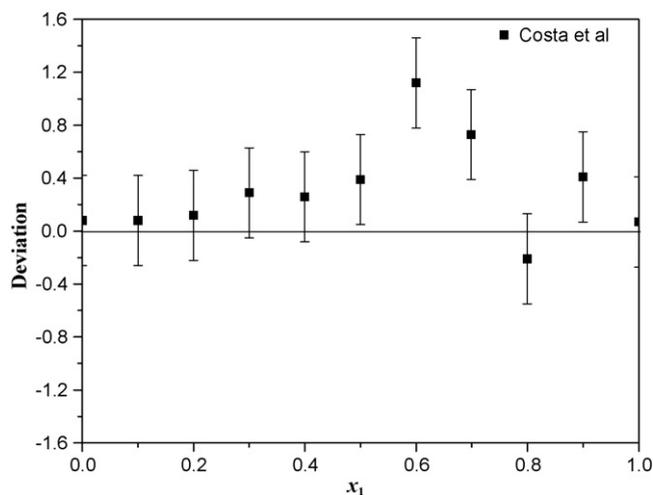


Fig. 3. Deviations between liquidus temperatures for caprylic acid (1) + myristic acid (3) mixtures reported in the literature [16] and the corresponding values measured in the present work.

rule, that mixtures differing by six or more carbons in the fatty acid chains would normally form simple eutectic systems. The experimental data measured in the present work shows compound formation by a clear inflection in the liquidus curve for the case of the lauric acid + myristic acid mixture with fatty acid chains differing by two carbon atoms. This is observed over the entire pressure range studied, as shown in Fig. 4. For the system caprylic acid + myristic acid just an eutectic point was observed as shown in Fig. 5.

Within the entire pressure range it is possible to observe that the liquidus line of the lauric acid + myristic acid system is divided in three regions with different slopes: the first region begins at  $x_2 = 0.0$  and finishes at the peritectic point ( $x_2 \approx 0.5$ ), the second region is comprised between the peritectic and eutectic point ( $x_2 \approx 0.65$ ) and the last one begins at the eutectic point and ends at  $x_2 = 1.0$ . For the caprylic acid + myristic acid system the liquidus lines have two different slopes and the inflection point is the eutectic point ( $x_1 \approx 0.90$ ). These regions result from the formation of different crystalline structures with different enthalpies of melting. This is clearly observed from the  $dP/dT$  slopes that can be related to the enthalpies and temperatures

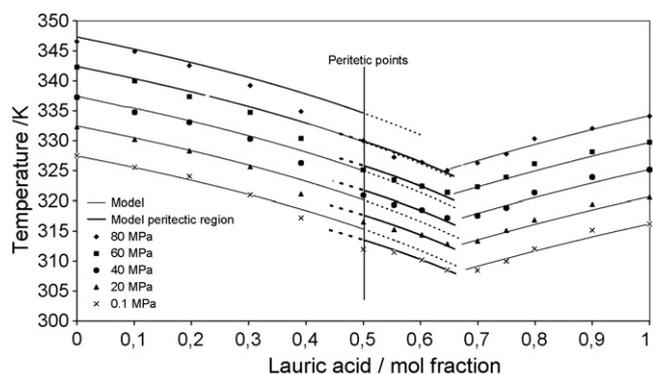


Fig. 4. Liquidus curves of the lauric acid (2) + myristic acid (3) system under pressure.

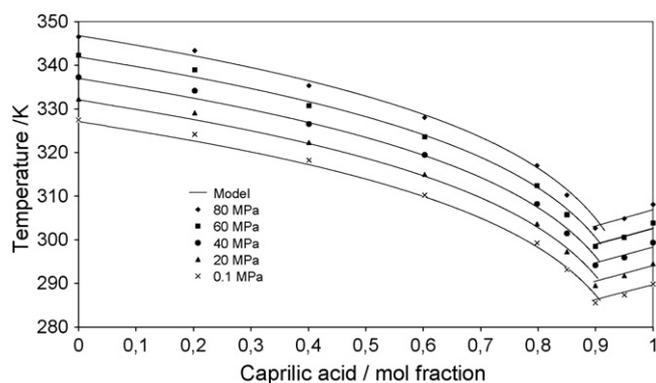


Fig. 5. Liquidus curves of the caprylic acid (1) + myristic acid (3) system under pressure.

of fusion and the molar volumes of the crystal through the Clausius–Clapeyron equation, see in Fig. 6a and b. The regions represented by horizontal straight lines correspond to different slopes and thus to different crystalline structures.

The coefficient  $\beta$  in Eq. (6) is also related to the melting enthalpies and the pressure dependence of the melting temperature through the Clausius–Clapeyron equation. As the average slope calculated with the following equation:

$$\frac{\Delta T}{\Delta P} = \frac{T(P_{\max}) - T(P_0)}{P_{\max} - P_0} \quad (11)$$

For caprylic acid the solid phase is different from that for lauric and myristic acid, and these are different from those of the peritectic phase as shown in Fig. 6a and b. The value of the coefficient  $\beta$  will be different for each phase. The  $\beta$  values used were fitted to the pure compound pressure dependence of the melting temperatures. The model results shown in Figs. 4 and 5 were obtained using the  $\beta$  values presented in Table 1. Although these  $\beta$  values do not have exactly the values predicted by Eq. (5) they are very close to these and follow the trend of the theoretical values that would be obtained from their definition.

The modeling was carried using the approach described above. The UNIQUAC model predicts an eutectic system for the caprylic acid + myristic acid mixture with no solubility in

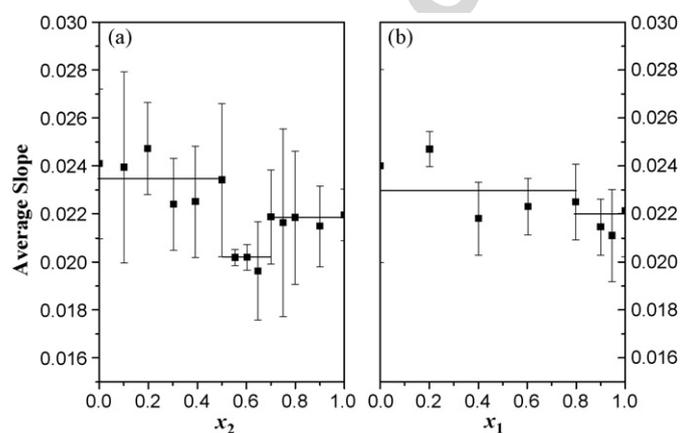


Fig. 6.  $dP/dT$  of the liquidus lines: (a) lauric acid (2) + myristic acid (3); (b) caprylic acid (1) + myristic acid (3).

the solid phase in agreement with the suggestion of Small [12] and the phase diagram established previously by DSC [16]. A good description of the phase diagrams is obtained within the entire pressure range as shown in Fig. 5.

The phase diagram for the lauric acid + myristic acid mixture is far more complex. A model such as UNIQUAC is obviously unable to predict the appearance of intermediate compounds such as those that create a peritectic point. But besides this limitation the model also predicts the formation of partial solid solution in the extremes of the phase diagram. The data measured in this work is not enough to confirm this, although evidence for this solid solution formation has been collected using RAMAN spectroscopy and DSC analysis and will be subject of a future article. The model seems to be able to provide an excellent description of the liquidus line measured in this work over the entire pressure range for both regions outside the peritectic as shown in Fig. 4. A good prediction of the eutectic point is also achieved as well as of its pressure dependence.

The modeling of the peritectic phase has been achieved by fitting the melting temperature and enthalpies for the data on this region at atmospheric pressure. Giving the limited amount of data available the uncertainty on these values is fairly large but an excellent description of the peritectic region and its pressure dependence was nevertheless achieved. Curiously, unlike what was observed for the *n*-alkanes systems studied in a previous work [14], the peritectic region appears at temperatures below those predicted by the model for the other liquidus regions. This means that the intermediate compound forming is thermodynamically less stable than the pure compounds and should thus constitute a metastable phase. This unexpected feature seems however to be common in the phase behavior of fats and is known as a monotropy [2,40]. In a monotropic polymorphism the phase which is thermodynamically less stable may form more easily and remain stable due to steric hindrance. This is what it is observed in the lauric acid + myristic acid system between molar fractions  $x_2 \approx 0.5$  and  $x_2 \approx 0.65$  and explains the location of the liquidus line at temperatures below those expected for the crystallization of the pure compounds. Curiously unlike what was observed for the *n*-alkanes [14] no other metastable phases were observed in this system.

## 5. Conclusions

Liquidus lines of two systems formed by lauric acid ( $C_{12:0}$ ) + myristic acid ( $C_{14:0}$ ) and caprylic acid ( $C_{8:0}$ ) + myristic acid ( $C_{14:0}$ ) were determined for the first time at high pressure using a high pressure microscope described in the first part of this work.

In both systems it was observed a translation of the liquidus line with the increase of the pressure. This translation in the liquidus line results from a change of the melting point in both, pure compounds and mixtures, but this change is reversible thus not affecting the properties of foods with high percentage of saturated fatty acids in their composition.

A model, previously applied to alkanes, was used in this work to describe the phase behaviour of these systems at high pressure. The results obtained show that this approach can be extended

with success to other compounds than alkanes. The model can predict the differences between pure eutectic systems and those where the formation of partial solid solutions may take place and provides a description of the phase behaviour over large pressure ranges. It can also describe the peritectic region forming in many of these systems and allows also a good description of its behaviour with pressure.

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