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Measurements of temperature and melting heat of some pure fatty acids and their binary and ternary mixtures by differential scanning calorimetry

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Abstract

Differential scanning calorimetry (DSC) is used to study the melting process of three pure fatty acids (palmitic, stearic and oleic) and both their binary and ternary mixtures. The results obtained for palmitic ($T = 337$ K, $\Delta H = 208.2$ J g^{-1}) and stearic ($T = 344$ K, $\Delta H = 210.8$ J g^{-1}) acids indicate the existence of a simple process. However, oleic acid presents a reversible solid–solid phase transition ($T = 225$ K, $\Delta H = 3.6$ J g^{-1}) prior to melting ($T = 278$ K, $\Delta H = 75.5$ J g^{-1}). The solidification of this acid is a complex process, since a liquid–liquid transformation ($T = 272$ K, $\Delta H = -10.5$ J g^{-1}) takes place prior to the change of the liquid–solid aggregation state ($T = 260$ K, $\Delta H = -61.0$ J g^{-1}). The presence of the oleic acid in the binary and ternary mixtures produces melting points at different levels of temperature. The eutectic temperature is determined for the palmitic/stearic mixture ($T = 331$ K), its non-ideal behavior being demonstrated. The melting heat in the binary mixtures hardly changes, while in the ternary mixtures a lineal decrease is observed when the oleic composition is increased.
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Keywords: Differential scanning calorimetry; Palmitic; Stearic; Oleic; Melting temperature; Melting heat

1. Introduction

The rubber, textile, food and pharmaceutical industries have been some of the chemical industries that have used fatty acids for diverse applications [1]. In raw and edible soya, sunflower and olive oils, the majority compounds are hexadecanoic (palmitic), octadecanoic (stearic), *cis*-9-octadecenoic (oleic) and 9,12-octadecadienoic acids (linoleic) [2,3]. In the deodorization process, some of the distilled compounds formed are composed of a mixture of fatty acids and the stripping gas used (steam or nitrogen) [3]. These distilled compounds are sent to a fatty acid condenser and then to a barometric condenser. However, the separation of the fatty acids condensed in the barometric condenser is very difficult. For this reason, the substitution of the above equipment by tubes-and-shell exchangers is currently being studied [4]. For design purposes, it is necessary to study the melting point (T_{mp}) and the melting enthalpy (ΔH_{mp}) of both the pure fatty acids, as well as their mixtures.

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Differential scanning calorimetry (DSC) is one of the most widely used techniques for studying the thermal behavior of compounds. This technique has been employed with satisfactory results in the determination of the heat capacities (C_p) of organic compounds and fatty acids [5,6] and the measurement of T_{mp} in vegetables oils and triglycerides [7–9].

This study presents the results of the T_{mp} and ΔH_{mp} measurements in palmitic, stearic and oleic fatty acids, their binary mixtures (palmitic/stearic, palmitic/oleic, and oleic/stearic), and their ternary mixtures (palmitic/stearic/oleic). The presence of oleic acid was increased within the range of compositions so as to reproduce those obtained in raw and deodorized oils. The measurements are compared with published values found by other authors for both pure compounds and binary mixtures.

2. Experimental

Measurements of T_{mp} and ΔH_{mp} were carried out for the palmitic, stearic and oleic fatty acids, and both their binary and ternary mixtures.

The samples were prepared in a Mettler AE240 analytical balance, accurate to ±0.1 mg. The binary mixtures were weighed in three different mass ratios, approximately 1:1, 1:3 and 3:1, where 1:3 means 25% of mass weight from the first and 75% of mass weight from the second. The first selected component corresponded to the compound with the lower molecular mass. The compositions for the ternary mixtures were prepared based on the assumption that the composition of the fatty acids in raw and deodorized oils are practically the same [1]. In this case, the palmitic:-stearic:oleic mass ratios used were 1:1:1, 3:1:1, 3:1:3, 3:1:6, 3:1:12, 3:1:18, 3:1:24 and 3:1:30. The purities of the fatty acids, supplied by Merck, were palmitic acid 99.3%, stearic acid 97%, and oleic acid 99.9% (mass).

A Mettler TA3000 (DSC-30) was used for the thermal analyses, with samples of 5–25 mg, a temperature range from 173 to 373 K (−100 to 100°C), accurate to ±0.2 K, atmospheric pressure and dynamic nitrogen atmosphere. The sample was heated above its fusion temperature and introduced, in the liquid state, into an aluminum pan. The pan was sealed and introduced at room temperature into the DSC. The initial temperature of the experiment (173 K for cooling) was reached quickly (5 min). The heating rate was 10 K min^{-1}. A special pan, included in the standard accessories of the Mettler equipment, was used to perform the temperature and enthalpy calibration. This pan contains an exact, known quantity of indium as well as lead and zinc in separate compartments. The experimental data is obtained from the melting of the three metals at 156.6, 327.4 and 419.5°C, respectively.

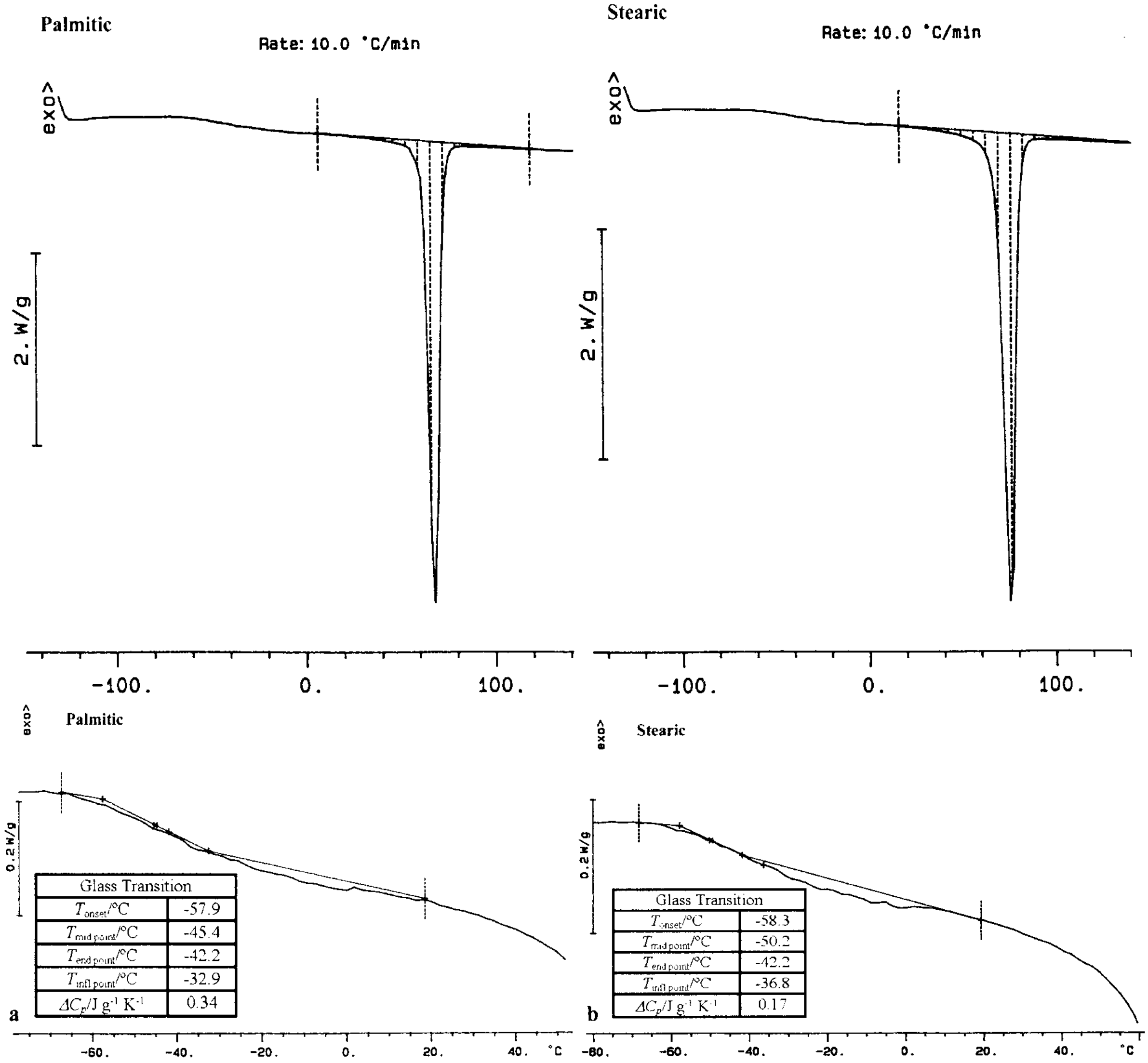
3. Results and discussion

For the measurements, a wide temperature range was chosen to identify the phase transitions. The DSC curve provides the flow heat by mass versus temperature. When the phase change occurs, an abrupt change in the base line is detected, and a peak is obtained. The approach used to measure T_{mp} was the temperature of the peak, though other approaches also usually consider criteria such as the onset temperature or the end of the thermal process [7–9]. The heat of the phase transition, ΔH_{mp}, is obtained by peak integration.

3.1. Pure substances

Until now, no specific thermodynamic models have existed that allow us to estimate with sufficient precision the temperature and heat at the melting point (T_{mp} and ΔH_{mp}) in palmitic, stearic and oleic fatty acids. For this reason, the values employed for comparison in the present study correspond to experimental data [5,10–18].

Fig. 1 shows the DSC curves for the palmitic and stearic fusion curves. The melting process is well defined around 340 K (67°C). The T_{mp} and ΔH_{mp} measurements are in good agreement with the majority of the published values (Table 1). A discontinuity in the base line was observed for both of the aforementioned acids between 228 and 223 K (−45 and −50°C), due to a change in the heat capacity of the system. This indicates the existence of a second order transition. This glass transition is characteristic in amorphous materials [19,20]. The method of sample preparation (starting from a liquid obtained by fusion



Glass Transition	
T_{onset}/°C	-57.9
$T_{mid\,point}$/°C	-45.4
$T_{end\,point}$/°C	-42.2
$T_{infl\,point}$/°C	-32.9
ΔC_p/J g^{-1} K^{-1}	0.34

Glass Transition	
T_{onset}/°C	-58.3
$T_{mid\,point}$/°C	-50.2
$T_{end\,point}$/°C	-42.2
$T_{infl\,point}$/°C	-36.8
ΔC_p/J g^{-1} K^{-1}	0.17

Fig. 1. DSC curves and glass transition for palmitic and stearic fatty acids (temperatures reported by DSC in °C).

of the solid commercial fatty acid and subsequent rapid cooling to the initiation temperature of the experiment) means that the analyzed solid is essentially amorphous. The value of the temperature of glass transition can be observed in Fig. 1 for both acids.

The behavior observed for oleic acid is different. The fusion curve presents two peaks (Fig. 2), instead of the single one characteristic of palmitic and stearic acids. The presence of an endothermic process (Peak a) prior to melting is detected here. This process must be related to a solid–solid phase transition (Tr 1). In contrast to both palmitic and stearic acids, the fast solidification of oleic acid originates a solid crystalline which transform at approximately 223 K (−50°C) into a high temperature phase ($\Delta H = 5.0$ J g^{-1}). This solid–solid transition is a reversible process, since in the cooling

Table 1
Melting temperature (T_{mp}) and enthalpy (ΔH_{mp}) for palmitic and stearic fatty acids obtained by DSC and their comparison with other sources (r is the deviation percentage of each published data with respect to our experimental measurement)

	T_{mp} (K)	r (%)	ΔH_{mp} (J g^{-1})	r (%)
Palmitic				
This work	337.5	–	208.20	–
[10]	336.1	0.4	211.85	1.8
[11]	335.0	0.7	163.95	21.3
[12]	336.2	0.4	163.93	21.3
[13]	336.1	0.4	210.14	0.9
[14]	335.7	0.5	209.46	0.6
[15]	–	–	213.83	2.7
[16]	336.1	0.4	212.15	1.9
[17]	–	–	211.85	1.8
Stearic				
This work	343.9		210.80	
[10]	342.8	0.3	219.39	4.1
[11]	342.0	0.6	198.93	5.6
[12]	344.4	0.1	198.91	5.6
[13]	342.8	0.3	240.78	14.2
[14]	343.6	0.1	215.16	2.1
[15]	–	–	222.09	5.4
[16]	342.8	0.3	222.16	5.4
[17]	–	–	240.74	14.2

process an exothermic peak of similar magnitude (Tr 5) is detected in the same temperature zone. The DSC cooling curve of oleic acid presents an important novelty. Between 273 and 253 K (0 and -20°C), two highly defined exothermic peaks appear (Tr 3 and Tr 4). The most intense of these must be associated with the solidification process ($\Delta H = -61.0$ J g^{-1}), while the smaller one detects a molecular re-organization in the liquid state ($\Delta H = -10.5$ J g^{-1}). This explains why the endothermic peak due to the solidification process of the oleic acid is perceptibly wider than that of both the palmitic and stearic fatty acids. For oleic acid, the thermal effect of the melting process overlaps with the re-organization step in the liquid phase.

In the present study, the DSC curves were obtained at a scan rate of 10 K min^{-1}. The previous explanation of Fig. 2 would be incorrect if the data does not represent a situation of equilibrium. In this case, the hysteresis would be a likely explanation for the experimental behavior. Complementary experiments show that the scan rate practically does not modify the DSC curves. Definitively, the experimental data represent thermodynamic states.

Fig. 3 shows the solid–solid and liquid–liquid thermal transitions (Tr) of the oleic acid detected during both heating and cooler processes (being $T_{\mathrm{Solid\,1}} = 173$ K, $T_{\mathrm{Liquid\,1}} = 373$ K). Starting from the results, the values of T_{mp} and ΔH_{mp} corresponding to the solid–liquid transition for the oleic acid, are related with the Tr 2 transition.

Table 2 presents the comparison of the T_{mp} obtained for oleic acid (corresponding with Tr 2) and the T_{mp} data obtained by other sources. The existence of two overlapped processes explains the discrepancies

Table 2
Measurements of T_{mp} and ΔH_{mp} for oleic fatty acid and their comparison with other sources

	T_{mp} (K)	r (%)	ΔH_{mp} (J g^{-1})
This work	278.5	–	75.5
[10]	289.5	4.0	–
[12]	289.5	4.0	–
[13]	286.5	2.9	–
[16]	286.4	2.8	–
[6]	286.9	3.0	–
[18]	281.2	1.0	–

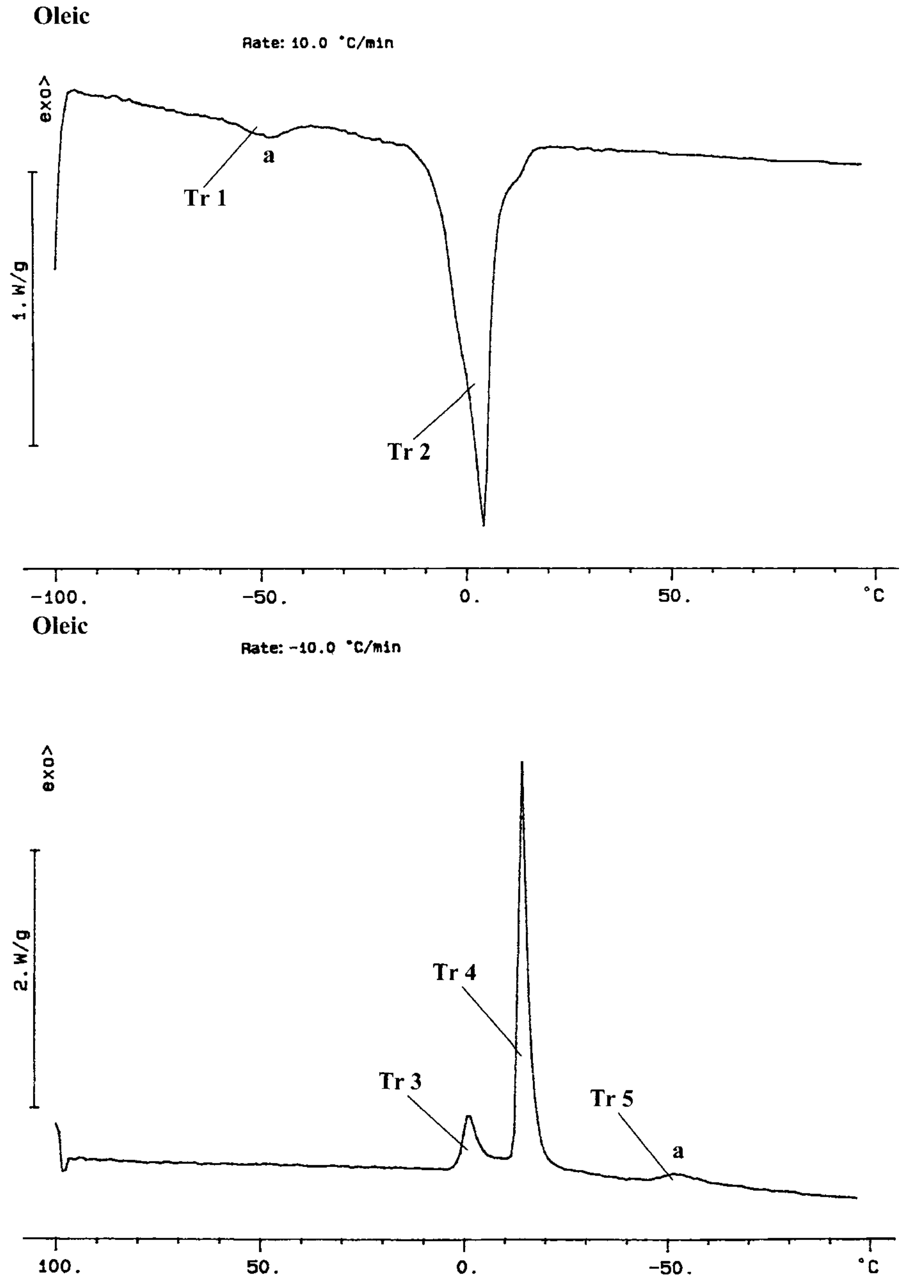


Fig. 2. DSC curves for the heating (melting curve) and cooling (solidification curve) of oleic fatty acid.

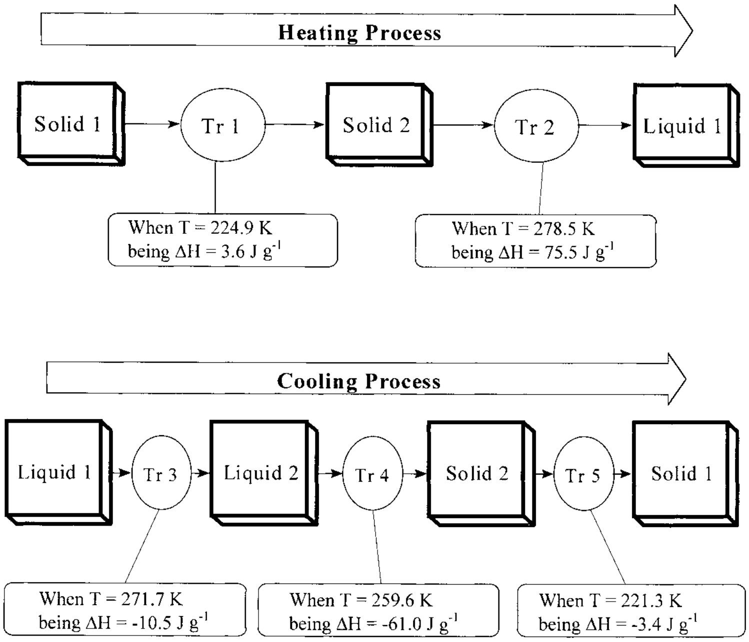


Fig. 3. Thermal cycle of oleic acid from Solid 1 to Liquid 1 (heating process) and from Liquid 1 to Solid 1 (cooling process) with the T and ΔH experimental data for the transitions.

between the temperature data tabulated for oleic acid, as well as the non-existence of ΔH_{mp} values in the bibliography.

3.2. Mixtures

As occurs with the pure fatty acids, it is difficult to find methods to estimate T_{mp} and ΔH_{mp} in mixtures of fatty acids. With respect to T_{mp} performance, it is observed that the temperature value in a mixture of two fatty acids is always lower in the fatty acid with the lower fusion temperature [21]. Likewise, Markley [22] presents the behavior of temperature versus composition in binary mixtures of fatty acids, where the presence of minimum points or an eutectic point are observed; it being demonstrated that the behavior of fatty acids mixtures is non-ideal.

Figs. 4 and 5 present the melting curves containing the endothermic peaks obtained in the binary and ternary mixtures. For the palmitic/stearic mixtures, due to the similar T_{mp} values of these fatty acids, a well-defined single peak of phase transition is observed. In contrast to this, the presence of oleic acid in the palmitic/oleic and oleic/stearic mixtures makes the solidification process more complex. Employing the term "Peak 1" to denote the peak located around the solidification point of the oleic acid and "Peak 2" to denote the peak located around the solidification point of the other acid, we can see two moments of the release of heat for these mixtures. These release heats are different in magnitude and are functions of the composition of the molar fractions. When the concentration of oleic acid in the mixture is increased, the appearance of an endothermic peak at around 223 K (−50°C) is also observed (as with the pure oleic acid), attributable to the solid-state phase transition (Peak a).

Tables 3 and 4 show the T_{mp} and ΔH_{mp} data obtained from the DSC measurements. The results are in good agreement with those published by Markley [22], highlighting the existence of a eutectic point for a slightly higher composition than that of the

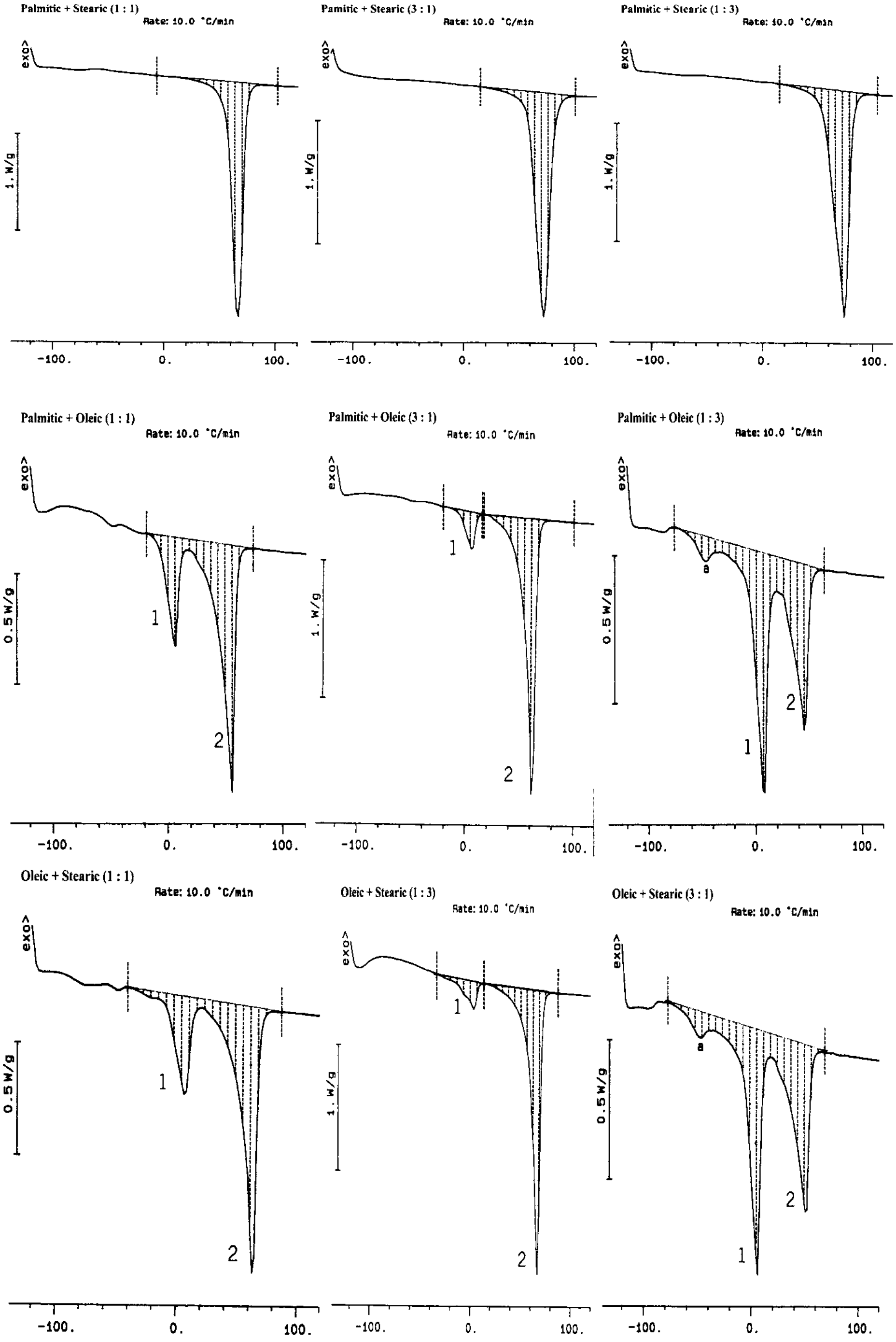


Fig. 4. DSC curves in binary mixtures of fatty acids.

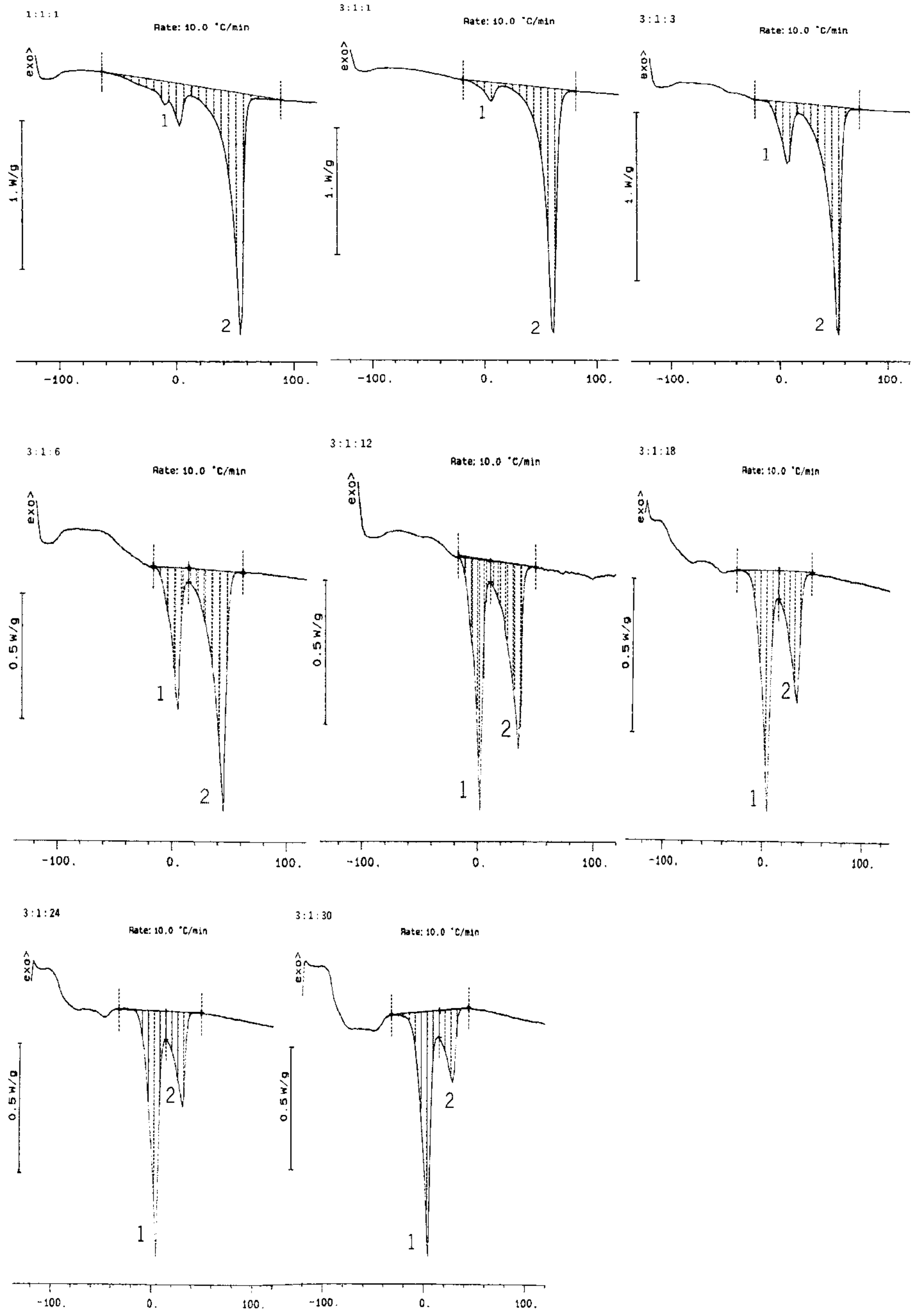


Fig. 5. DSC curves in ternary mixtures of fatty acids.

Table 3
Measurements of T_{mp} and ΔH_{mp} for the binary mixtures of fatty acids

x_1	Peak 1		Peak 2		Total ΔH_{mp} (J g^{-1})
	T_{mp} (K)	ΔH_{mp} (J g^{-1})	T_{mp} (K)	ΔH_{mp} (J g^{-1})	
Palmitic + stearic					
0.26996	340.7	185.3			
0.52593	333.8	184.0			
0.76896	332.4	176.9			
Palmitic + oleic					
0.26855	279.3	73.5	316.5	53.8	127.3
0.52410	278.3	33.4	326.7	96.2	129.6
0.74303	277.2	16.6	332.3	137.1	153.7
Oleic + stearic					
0.25133	275.6	18.2	338.1	141.7	159.9
0.50180	278.2	40.8	333.6	105.5	146.3
0.72555	277.9	73.1	322.3	63.0	136.1

binary mixture (3:1) palmitic/stearic, and coinciding with the composition pointed out by Markley. The eutectics points for $x_{oleic} \approx 1.0$ were found for the palmitic/oleic and oleic/stearic binary mixtures, being 0.95 and 0.98, respectively [22]. For none of the three binary mixtures is the T_{mp} value lower than the lowest fusion temperature of mixed fatty acids, as published in [21].

Fig. 6 presents the behavior of ΔH_{mp} versus composition for the three binary mixtures. In the palmitic/stearic mixture, a decrease is observed with respect to the pure fatty acids (approximately 20–30 J g^{-1}). In both the palmitic/oleic and oleic/stearic mixtures, intermediate values are observed among the ΔH_{mp} values of the pure compounds mixed.

Fig. 7 presents the behavior of T_{mp} and ΔH_{mp} obtained for the ternary mixtures (between the 3:1:1 and 3:1:30 compositions). The experimental data shows two trends for T_{mp}, one practically unalterable around 278 K (Peak 1 of Table 4) and another that decreases lineally as the concentration of oleic acid increases (Peak 2 of Table 4). The former behavior corresponds to the pure oleic measurement (278.5 K), demonstrating that this acid solidifies practically in an independent way in the mixture, while the latter demonstrates a gradual solidification, presumably due to the contribution of the other two acids. Macroscopic observations of the solidification process of these samples highlight similar values between the T_{mp} of Peak 2 and the fusion temperatures observed.

Table 4
Measurements of T_{mp} and ΔH_{mp} for the ternary mixtures of fatty acids

Mixture	x_1	x_2	x_3	Peak 1		Peak 2		Total	
				T_{mp} (K)	ΔH_{mp} (J g^{-1})	T_{mp} (K)	ΔH_{mp} (J g^{-1})	T_{mp} (K)	ΔH_{mp} (J g^{-1})
1:1:1	0.3560	0.3209	0.3231	548.6	33.4	598.5	128.9	325.4	166.2
3:1:1	0.6238	0.1874	0.1888	551.9	9.0	603.1	143.9	330.0	159.2
3:1:3	0.4528	0.1361	0.4111	551.7	30.1	597.8	111.1	324.7	135.5
3:1:6	0.3209	0.0964	0.5827	550.2	33.1	590.2	73.8	317.1	107.2
3:1:12	0.2027	0.0609	0.7363	549.1	42.9	582.1	48.2	276.0	92.3
3:1:18	0.1482	0.0445	0.8073	549.8	49.6	579.6	34.0	276.7	84.1
3:1:24	0.1168	0.0351	0.8481	550.0	56.9	576.2	27.3	276.9	83.0
3:1:30	0.0963	0.0290	0.8747	550.3	60.6	574.6	20.6	277.2	82.1

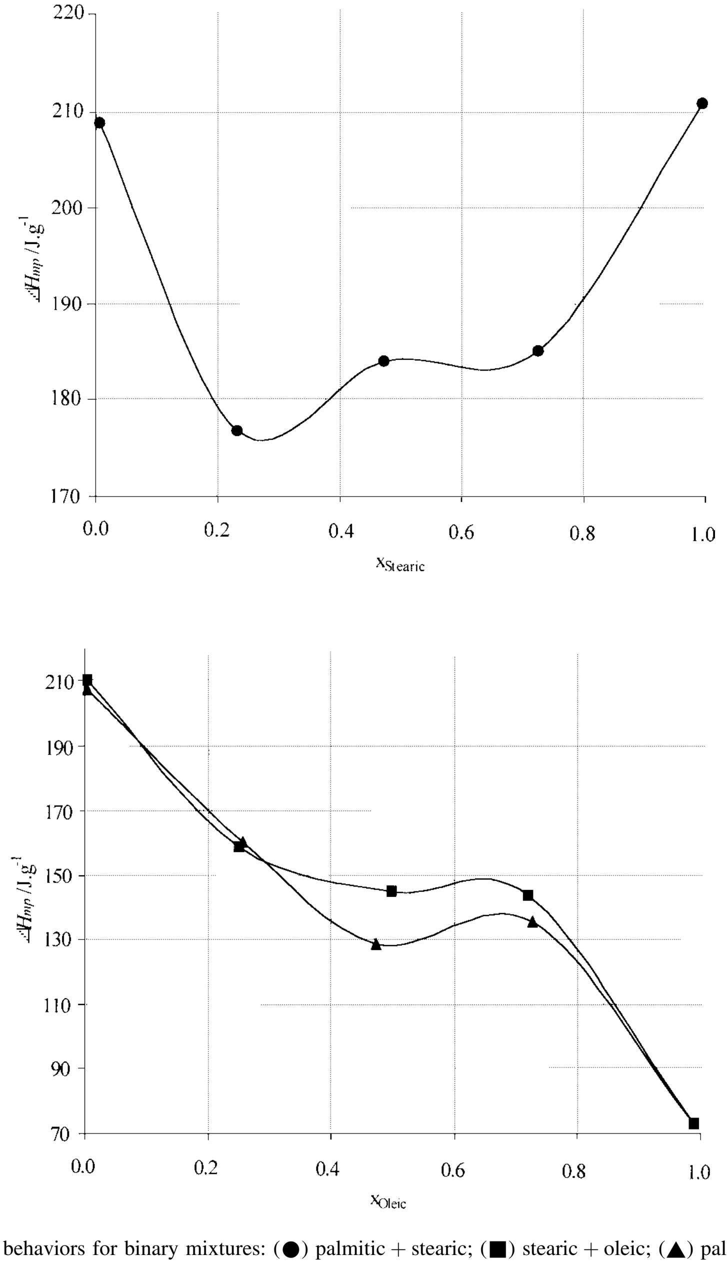


Fig. 6. ΔH_{mp} behaviors for binary mixtures: (●) palmitic + stearic; (■) stearic + oleic; (▲) palmitic + oleic.

A lineal increase in the transition heat corresponding to ΔH_{mp} of Peak 1 is observed when the concentration of oleic acid increased in the mixture. Simultaneously, a lineal decrease in the peak associated with the other two fatty acids (ΔH_{mp} of Peak 2) is detected. The trend of the total heat of transition phase (the sum of the two peaks, ΔH_{mp} of Total) coincides with ΔH_{mp} of Peak 2, indicating that the palmitic and stearic fatty acids exert a strong influence on the enthalpy behavior of the mixture.

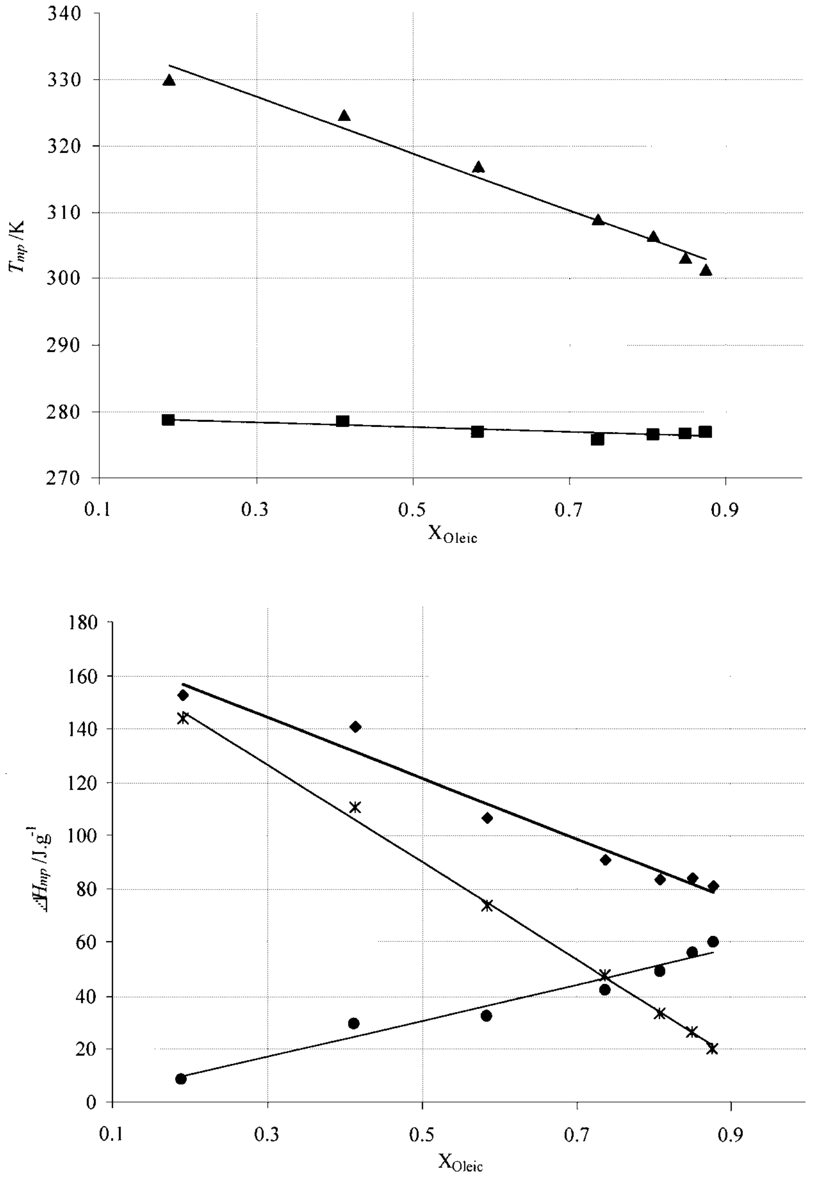


Fig. 7. T_{mp} and ΔH_{mp} behaviors for ternary mixtures: (■) T_{mp} Peak 1; (▲) T_{mp} Peak 2; (●) ΔH_{mp} Peak 1; (✱) ΔH_{mp} Peak 2; (◆) ΔH_{mp} Total.

Acknowledgements

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