Measurements and Estimate of Heat Capacity for Some Pure Fatty **Acids and Their Binary and Ternary Mixtures**

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The heat capacities in the liquid phase of the fatty acids hexadecanoic acid, octadecanoic acid, and cis-9-octadecenoic acid were measured, as well as those of their binary and ternary mixtures from temperatures close to solidification to 528 K. The measurements were correlated and contrasted with equations, methods, and values for the pure fatty acids, Ruzicka and Domalski's method providing better results for most of the temperature range studied. For binary and ternary mixtures, molar fraction average and corresponding states methods were used. The convenience of the former with respect to the latter was demonstrated; it is easier to apply and provides suitable results. Furthermore, in the case of the mixtures, only slight variations in heat capacity with composition were experienced. All the measurements were carried out using a DSC differential scanning calorimeter.

Introduction

For a long time, the rubber, textile, food, and pharmaceutical industries have been some of the chemical industries that have used fatty acids for diverse applications (Pattison, 1968). In the raw and edible oils of soya, sunflower, and olive, the majority compounds are hexadecanoic, octadecanoic, cis-9-octadecenoic, and 9,12-octadecadienoic acids (Ruiz et al., 1995; Ghosh et al., 1996). These fatty acids are also present as a majority component in the distillations of the deodorization process (neutral distillation using a stripping gas) in the refining of edible oils. The recovery of these fatty acids could be carried out in the liquid phase using tubes and shell exchangers (Gracianni et al., 1994). For the design of this equipment, it is necessary to study the heat capacity (C_p) of these substances, both pure as well as their mixtures.

The heat capacities of oils such as soya, sunflower, rape seed, and so forth have been published (Kowalski, 1988; Kasprzycka et al., 1991; Clark et al., 1946). At the same time, empirical equations for heat capacity for the hexadecanoic and octadecanoic acids, as well as published determinations for cis-9-octadecenoic acid, in a limited temperature range, have been presented (Formo et al., 1979; Pryde et al., 1979).

Although a great number of methods to estimate this property for pure organic compounds have been published (listed in the bibliography), only a few of these are applicable to liquid mixtures.

This study presents the results of measurements of the heat capacities of the hexadecanoic (palmitic), octadecanoic (stearic), and cis-9-octadecenoic (oleic) fatty acids

and their binary and ternary mixtures in the liquid state. A number of methods that have been proposed for estimating this property are subsequently applied and contrasted with the experimental measurements. The measurements were carried out at 5 K intervals, from temperatures close to solidification for each sample up to 528 K. The binary mixtures (palmitic + stearic), (palmitic + oleic), and (oleic + stearic) and the ternary mixture (palmitic + stearic + oleic) were studied, in which the presence of the oleic acid was increased in order to approach the compositions in raw and deodorized edible oils. Measurements were made with a DSC differential scanning calorimeter.

Estimate of the Heat Capacities of Pure Liquids

In the literature, expressions for organic compounds have been found in which linear behavior is assumed with respect to temperature.

The equation using the method of Rowlinson-Bodi (Reid et al., 1987) has the following principle based on the method of corresponding states:

$$\frac{C_{\rm pl} - C_{\rm p}}{R} = 1.45 + 0.45(1 - T_{\rm r})^{-1} + 0.25\omega[17.11 + 25.2(1 - T_{\rm r})^{1/3}T_{\rm r}^{-1} + 1.742(1 - T_{\rm r})^{-1}]$$
(1)

where $C_{\rm pl}$ is the heat capacity of the liquid, $C_{\rm p}^{\circ}$ is the heat capacity with respect to the ideal gas state $(J \cdot mol^{-1} \cdot K^{-1})$, which is evaluated at the same temperature used to evaluate C_{pl} , ω is the acentric factor, R is the universal constant ($\dot{8}.314~51~J\cdot mol^{-1}\cdot K^{-1}$), and T_r is the reduced temperature.

The value of C_{p} can be reasonably estimated using the methods of Benson and Rihani and Doraiswamy reported by Luria et al. (1977) and Perry et al. (1992). Both methods are based on group contribution, and both use an equation of the type

$$C_{\rm p}^{\rm o} = a + bT + cT^2 + dT^3$$
 (2)

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Table 1. Thermodynamic Parameters Needed forEstimation of Heat Capacities of Pure Fatty Acids andMixtures of Fatty Acids

parameter	palmitic acid	stearic acid	oleic acid		
ω	0.728	0.798	0.770		
PM	256.42	284.47	282.46		
$V_{\rm c}/{ m cm^3}\cdot{ m mol^{-1}}$	920.82	1056.82	1008.4		
$T_{\rm c}/{ m K}$	799.74	818.85	819.26		

 Table 2. Heat Capacity Measurements for Pure Substances

<i>T</i> /K	palmitic $C_{\rm p}/{ m J}\cdot{ m g}^{-1}\cdot{ m K}^{-1}$	stearic $C_{\rm p}/{ m J}{\cdot}{ m g}^{-1}{\cdot}{ m K}^{-1}$	oleic $C_{\rm p}/{ m J}{\cdot}{ m g}^{-1}{\cdot}{ m K}^{-1}$
318			2.07
323			2.09
328			2.13
333			2.17
338			2.21
343	2.18		2.23
348	2.21	2.22	2.25
353	2.25	2.26	2.29
358	2.33	2.31	2.33
363	2.38	2.36	2.37
368	2.45	2.41	2.41
373	2.49	2.46	2.44
378	2.55	2.52	2.49
383	2.62	2.57	2.54
388	2.70	2.64	2.59
393	2.71	2.69	2.61
398	2.77	2.74	2.67
403	2.83	2.80	2.73
408	2.88	2.88	2.78
413	2.95	2.94	2.84
418	3.04	3.05	2.92
423	3.10		2.95
428	3.17		

where *a*, *b*, *c*, and *d* are the contributions according to the groups and *T* is the absolute temperature.

Another method that allows us to estimate the heat capacities of organic liquids is that of Ruzicka and Domalski (Ruzicka et al., 1993). The equation, based on contribution groups, has the following form:

$$\frac{C}{R} = \sum_{i=1}^{k} n_i \Delta C_i \tag{3}$$

where *C* is the molar heat capacity, *R* is the universal constant of gases, n_i is the number of contribution units of type *i*, *k* is the total number of contribution units in a molecule, and ΔC_i is the dimensionless value of the contribution unit of type *i*. This value has a dependent relationship with respect to temperature, expressed as ΔC_i = $a_i + b_i(T/100) + d_i(T/100)^2$, where *T* is the absolute temperature and a_i , b_i , and d_i are adjustable parameters.

For the fatty acids studied, Formo et al. (1979) and Pryde et al. (1979) report two expressions for heat capacity in the liquid phase. These equations (published by the authors), according to the type of acid and the temperature range, have the following form:

for palmitic acid (between 336 and 365 K)

$$C_{\rm p}/{\rm J}\cdot{\rm kg}^{-1}\cdot{\rm K}^{-1} = 1935 + 7.322 t/^{\circ}{\rm C}$$
 (4)

for stearic acid (between 343 and 353 K)

$$C_{\rm p}/{\bf J}\cdot{\bf kg}^{-1}\cdot{\bf K}^{-1} = 1785 + 7.531 \,t/^{\circ}{\rm C}$$
 (5)

Heat capacity values for stearic and oleic fatty acids are also published (Formo et al., 1979). For stearic acid at the temperatures 423, 473, and 523 K, the respective

Table 3. Heat Capacity^a Measurements for Binary Mixtures

					<i>T</i> /K			
mixture	X_1^b	343	353	363	373	383	393	403
palmitic + stearic	0.52593			2.25	2.28	2.34	2.37	2.42
	0.76896				2.21	2.22	2.32	2.23
	0.26996			2.21	2.23	2.26	2.31	2.29
palmitic + oleic	0.52410		2.14	2.16	2.21	2.24	2.27	2.30
	0.74303		2.16	2.21	2.25	2.26	2.29	2.33
	0.26855	2.01	2.03	2.08	2.10	2.13	2.15	2.18
oleic + stearic	0.50180		2.03	2.04	2.08	2.11	2.14	2.22
	0.72555			2.13	2.16	2.20	2.25	2.28
	0.25133	2.02	2.07	2.08	2.13	2.16	2.20	2.21
					<i>T</i> /K			
mixtures	<i>X</i> 1	413	423	433	443	453	463	473
palmitic + stearic	0.52593	2.47	2.51	2.56	2.61	2.65	2.75	2.88
	0.76896	2.35	2.24	2.34	2.28	2.42	2.49	2.56
	0.26996	2.35	2.43	2.44	2.45	2.51	2.55	2.64
palmitic + oleic	0.52410	2.31	2.34	2.36	2.48	2.55	2.61	2.66
	0.74303	2.35	2.40	2.45	2.57	2.65	2.73	2.79
	0.26855	2.18	2.20	2.26	2.30	2.35	2.42	2.47
oleic + stearic	0.50180	2.23	2.29	2.34	2.36	2.37	2.43	2.47
	0.72555	2.32	2.38	2.44	2.50	2.53	2.59	2.63
	0.25133	2.21	2.24	2.28	2.41	2.46	2.50	2.57
					<i>T</i> /K			
mixtures	<i>X</i> 1				483	493	503	513
palmitic + stearic	0.52593				2.94	2.95	3.02	3.07
•	0.76896				2.62	2.68	2.77	2.83
	0.26996				2.68	2.71	2.77	2.83
palmitic + oleic	0.52410				2.70	2.77	2.81	2.89
-	0.74303				2.82	2.89	3.00	
	0.26855				2.53	2.63	2.71	
oleic + stearic	0.50180				2.53	2.57	2.65	2.69
	0.72555				2.66	2.72	2.78	2.84
	0.25133				2.59	2.65	2.70	2.76

^{*a*} Heat capacity: $C_p/J \cdot g^{-1} \cdot K^{-1}$. ^{*b*} Molar fraction for the component with lower molecular mass of the binary mixtures (first component).

values of heat capacity are 2.45, 2.76, and 3.24 $J \cdot g^{-1} \cdot K^{-1}$. For oleic acid, at the temperatures 283, 323, 373, and 423 K, the respective values are 1.93, 2.05, 2.30, and 2.67 $J \cdot g^{-1} \cdot K^{-1}$.

Estimate of the Heat Capacities of Liquid Mixtures

For binary mixtures, Teja (1983) proposes an equation based on the method of corresponding states, in which the substances that make up the mixture are used as the reference substances. This equation is

$$C_{\rm pm} = x_1 C_{\rm p1} + x_2 C_{\rm p2} \tag{6}$$

where x_1 and x_2 are the molar fractions of the components and C_{p1} and C_{p2} are the values of the heat capacities of the pure compounds, evaluated at the reduced temperature. The mixture temperatures are determined by $T_m = T_r T_{cm}$.

For binary, ternary, and multicomponent mixtures is proposed an equation based on a molar fraction average (Teja, 1983; Prassad et al., 1994), of the type

$$C_{\rm pm} = \sum_{i=1}^{n} x_i C_{\rm pi} \tag{7}$$

where x_i are the molar fractions of the components and C_{pi}

Table 4.	Heat	Capacity	Measurements ^a	of	Ternary	Mixtures	
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						<i>T</i> /K				
mixtures ^b	$\mathbf{x_1}^c$	\mathbf{x}_2^c	\mathbf{x}_3^c	323	333	343	353	363	373	
1:1:1	0.35597	0.32089	0.32314			2.16	2.18	2.23	2.26	
3:1:1	0.62380	0.18742	0.18878				2.15	2.18	2.23	
3:1:3	0.45285	0.13609	0.41107			2.23	2.25	2.27	2.31	
3:1:6	0.32092	0.09642	0.58267		2.15	2.18	2.23	2.28	2.32	
3:1:12	0.20275	0.06091	0.73634		2.18	2.23	2.26	2.28	2.33	
3:1:18	0.14820	0.04453	0.80726	2.00	2.03	2.07	2.10	2.14	2.17	
3:1:24	0.11680	0.03508	0.84812	2.13	2.16	2.18	2.23	2.26	2.28	
3:1:30	0.09634	0.02896	0.87470	2.02	2.04	2.09	2.13	2.16	2.21	
						Τ/	К			
mixture	<i>X</i> 1	<i>X</i> 2	<i>X</i> 3	378	388	398	408	418	428	
1:1:1	0.35597	0.32089	0.32314	2.31	2.34	2.37	2.39	2.41	2.42	
3:1:1	0.62380	0.18742	0.18878	2.27	2.31	2.35	2.39	2.41	2.46	
3:1:3	0.45285	0.13609	0.41107	2.35	2.37	2.41	2.43	2.48	2.52	
3:1:6	0.32092	0.09642	0.58267	2.34	2.39	2.42	2.46	2.52	2.55	
3:1:12	0.20275	0.06091	0.73634	2.36	2.39	2.43	2.49	2.55	2.62	
3:1:18	0.14820	0.04453	0.80726	2.22	2.25	2.28	2.30	2.37	2.44	
3:1:24	0.11680	0.03508	0.84812	2.31	2.33	2.35	2.40	2.45	2.48	
3:1:30	0.09634	0.02896	0.87470	2.26	2.31	2.34	2.34	2.39	2.46	
						T	Ϋ́K			
mixtures	<i>X</i> 1	<i>X</i> ₂	<i>X</i> 3	433	443	453	463	473	483	
1:1:1	0.35597	0.32089	0.32314	2.53	2.62	2.62	2.67	2.72	2.78	
3:1:1	0.62380	0.18742	0.18878	2.55	2.57	2.61	2.65	2.69	2.74	
3:1:3	0.45285	0.13609	0.41107	2.56	2.63	2.68	2.74	2.80	2.88	
3:1:6	0.32092	0.09642	0.58267	2.59	2.65	2.74	2.78	2.84	2.92	
3:1:12	0.20275	0.06091	0.73634	2.68	2.76	2.80	2.91	2.96	0.75	
3:1:18	0.14820	0.04453	0.80726	2.48	2.51	2.58	2.65	2.68	2.75	
3:1:24	0.11680	0.03508	0.84812	2.53	2.60	2.67	2.69	2.11	2.84	
3:1:30	0.09634	0.02896	0.8/4/0	2.51	2.53	2.56	2.59	2.65	2.66	
							<i>T</i> /K			
mixtures	<i>X</i> 1	<i>X</i> 2	<i>X</i> 3		488	498	508	518	528	
1:1:1	0.35597	0.32089	0.32314		2.86	2.93	3.02	3.13		
3:1:1	0.62380	0.18742	0.18878		2.78					
3:1:3	0.45285	0.13609	0.41107		2.95	3.02	3.12	3.23		
3:1:6	0.32092	0.09642	0.58267		2.98	3.08	3.12			
3:1:12	0.20275	0.06091	0.73634		9.90	9.90	9.01	2.00	2.00	
3:1:18 9:1:94	0.14820	0.04453	0.80/20		2.80	2.80	2.91	3.00	3.08	
3:1:24	0.11080	0.03508	0.84812		2.91	2.99	3.00	3.13	2.06	
511.50	0.09034	0.02890	0.8/4/0		6.16	2.01	2.00	2.09	2.90	

^{*a*} Heat capacity: $C_p/J \cdot g^{-1} \cdot K^{-1}$. ^{*b*} Mixtures: Mass ratios used in the ternary mixtures. ^{*c*} x_1 , x_2 , x_3 : Molar fraction for the palmitic, stearic, and oleic fatty acids, in ternary mixtures.

are the values of the heat capacities of the pure compounds, evaluated at the mixture temperature.

On the basis of the application of the method of corresponding states, an equation is presented for estimating the densities, viscosities, and thermal conductivities of liquid mixtures (Teja, 1980; Teja et al., 1981). The present study proposes the same method for estimating the heat capacities of ternary mixtures, by the following equation:

$$(C_{\rm pm}\xi_{\rm m}) = (C_{\rm p}\xi)^{\rm r_1} + \frac{\omega_{\rm m} - \omega^{\rm r_1}}{\omega^{\rm r_2} - \omega^{\rm r_1}} [(C_{\rm p}\xi)^{\rm r_2} - (C_{\rm p}\xi)^{\rm r_1}] \quad (8)$$

where C_p are the heat capacities of the mixture (m) or of the reference substances r_1 and r_2 , ω are the acentric factors of the mixture or of the reference substances, and ξ is a parameter defined as $\xi = V_c^{2/3}/(T_c \cdot PM)^{1/2}$, for the mixture or for the reference substances, V_c , T_c , and PMbeing the critical molar volume, the critical temperature, and the molecular weight, for the mixture or for the reference substances, respectively.

The variables related to the composition of the mixture are defined by the terms $V_{\rm cm}$, $T_{\rm cm}$, $PM_{\rm m}$, and $\omega_{\rm m}$. The rules suggested by several authors for these parameters of the mixture are

$$V_{\rm cm} = \sum_{i} \sum_{j} x_i x_j V_{\rm cij} \tag{9}$$

$$V_{c_{ij}} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8}$$
(10)

$$T_{\rm cm} = \frac{\sum_{i} \sum_{j} x_i x_j T_{\rm c_{ij}} V_{\rm c_{ij}}}{V_{\rm cm}}$$
(11)

$$T_{c_{ij}}V_{c_{ij}} = \varphi_{ij}(T_{ci}T_{cj}V_{ci}V_{cj})^{1/2}$$
(12)

$$PM_{\rm m} = \sum_{i} x_i PM_i \tag{13}$$

$$\omega_{\rm m} = \sum_{i} x_i \omega_i \tag{14}$$

In eq 12, the parameter φ_{ij} is an interaction parameter, which is close to unity, and that parameter is determined from experimental measurements.

To estimate the heat capacity of the mixture at a certain temperature using eq 8, the values of the heat capacities



Figure 1. Heat capacity measurements of the pure fatty acids and their comparison with other sources: (A) palmitic acid; (B) stearic acid; (C) oleic acid. (\blacklozenge) Measurements; (\blacktriangle) eq 1; (\blacklozenge) eq 3; (\blacksquare) eq 4 and 5; ($^{-*-}$) values report with other sources; and (-) correlations obtained with eqs 16–18.

of the reference substances need to be known. These values are determined at the reference temperatures, $T(T_c^{r_1}/T_{cm})$ for reference substance 1 and $T(T_c^{r_2}/T_{cm})$ for reference substance 2. According to Teja's studies, the selection of the reference substances is to be carried out preferably from among the components of the mixture, although they may also be arbitrary.

Experimental Procedure

Measurements of the heat capacity were carried out for the fatty acids palmitic, stearic, and oleic, for the binary mixtures (palmitic + stearic), (palmitic + oleic), and (oleic + stearic), and for the ternary mixture (palmitic + stearic + oleic). The mixtures were prepared in a METTLER (AE 240) (Switzerland) 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. For example, 1:1 means 50% of mass weight from the first and 50% of mass weight from the second, and 1:3 means 25% of mass



Figure 2. Heat capacity measurements of binary mixtures for fatty acids: (A) mix oleic + stearic; (B) mix palmitic + oleic; (C) mix palmitic + stearic. (\blacklozenge) Measurements 1:1; (\blacktriangle) measurements 1:3; (\blacksquare) measurements 3:1; (-) eq 6 for 1:1; (- -) eq 6 for 1:3; ($^{-*-}$) eq 6 for 3:1.

weight from the first and 75% of mass weight from the second.

The first selected component corresponded to the component with the lower molecular mass. Under the supposition that the compositions of the fatty acids in raw and deodorized oils are practically the same (Ruiz, 1995), we have supposed values of the compositions for the ternary mixtures. In this case, the 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 99.3% (palmitic acid), 97% (stearic acid), and 99.9% (oleic acid) (by mass). For the heat capacity measurements, a differential calorimeter model METTLER TA4000 (DSC-30) was employed, with a temperature range from 103 to 873 K and an accuracy of ± 0.2 K. The heating rate used was 10 K·min⁻¹. The experimental heat capacities are within $\pm 1\%$ precision. The standard crucible employed was α -alumina, and a nitrogen current was used for the extraction of vapors in the furnace core.



Figure 3. Heat capacity measurements of ternary mixtures for fatty acids: (A) mix 1:1:1; (B) mix 3:1:6; (C) mix 3:1:24. (\blacklozenge) Measurements; (\blacksquare) eq 7; (-) eq 8.

The heat capacity measurements below or above the defined temperature range were not taken into account, due to the appearance of the phenomenon of solidification or the starting of evaporation.

Results and Discussion

Table 1 presents the thermodynamic parameters needed to estimate the heat capacities in pure fatty acids and mixtures (Reid et al., 1987; Cedeño et al., 1999).

Tables 2–4 present the results of the measurements corresponding to the pure substances and binary and ternary mixtures.

Starting from the measurements, the coefficients of a polynomial adjustment of an equation of the type $C_p = A + BT$ are obtained for the pure substances, and the parameters that appear in the equations proposed to estimate the mixtures are adjusted. The values that are obtained starting from the estimate equations were compared with the measurements, using the mean deviation r, by means of the expression

$$r = 100 \left[\frac{\sum (|C_{p_{est}} - C_{p_{mea}}| / C_{p_{mea}})}{n} \right]$$
(15)

where *n* is the number of experimental points, $C_{\rm pest}$ is the heat capacity estimated, and $C_{\rm pmea}$ is the heat capacity measurement.

In Figure 1 are represented the measurements of heat capacity for the fatty acids and also the results of applying eqs 1, 3, 4, and 5, together with the values published by Formo et al. (1979) and Swern (1979). Lineal behavior is observed in all the cases. Ruzicka's method (eq 3) was applied to the palmitic and stearic acids. It can be seen how the measurements have similar values to those obtained by applying the method. Rowlinson-Bodi's method (eq 1) was also applied, and it is observed that the estimated values agree with experimental measurements in the temperature range 360-430 K for palmitic and stearic and 270-428 K for oleic acids. For temperatures higher than 430 K, the values of heat capacity estimated by this method differ from the values of the measurements. The values obtained when applying eqs 4 and 5 differ from the measurements obtained for palmitic acid and stearic acid. In relation to the published values for the stearic and oleic acids, there is an agreement with the measurements in the low-temperature range, a difference being observed in the case of oleic acid for temperatures >400 K. The mean deviations r in all the cases were as follows: palmitic acid ($r_{\text{Ruzicka}} \simeq 4.27\%$, $r_{\text{Rowlinson-Bodi}} \simeq$ 5.68%, and $r_{\text{ec.}(4)} \simeq 17.47\%^*$), stearic acid ($r_{\text{Ruzicka}} \simeq 5.48\%$, $r_{\text{Rowlinson-Bodi}} \simeq 4.30\%$, $r_{\text{ec.}(5)} \simeq 12.18\%^*$, and $r_{\text{values published}} \simeq$ 1.63%), and oleic acid ($r_{\text{Rowlinson-Bodi}} \simeq 3.14\%$ and r_{values} published $\simeq 2.48\%$). [The values of the mean deviations that appear with an asterisk have been obtained by applying and extrapolating the correlation obtained (eqs 16-18).] The correlations obtained from the measurements for each fatty acid, in the measured temperature range, were as follows:

palmitic acid (between 343 and 428 K)

$$C_{\rm p}/{\rm J}\cdot{\rm g}^{-1}\cdot{\rm K}^{-1} = 0.0591 + 0.0059\,T/{\rm K}$$
 (16)

stearic acid (between 348 and 418 K)

$$C_{\rm p}/{\rm J}\cdot{\rm g}^{-1}\cdot{\rm K}^{-1} = 0.1001 + 0.0057 \, T/{\rm K}$$
 (17)

oleic acid (between 318 and 423 K)

$$C_{\rm p}/{\rm J}\cdot{\rm g}^{-1}\cdot{\rm K}^{-1} = 0.6198 + 0.00459\,T/{\rm K}$$
 (18)

All correlation coefficients were >0.99.

For each binary mixture, and with the correlation obtained, eq 6 was used from $T_r = 0.45$ to 0.63. To obtain the temperature of the binary mixture, we need to determine the $T_{\rm cm}$ value; this is why eqs 9–14 were applied. The interaction parameter φ_{ij} was obtained using the method of least squares from measures of heat capacity to several temperatures and compositions. In Figure 2, measurements for the three binary mixtures are represented with the mass ratios 1:1, 1:3, and 3:1. For all the mixtures, "small" differences are observed in the heat capacity, depending on the mass ratios. The coefficients obtained by adjusting the measurements for eq 6 were the following: $\varphi_{\text{palmitic-stearic}} \simeq 1.1487$, $\varphi_{\text{palmitic-oleic}} \simeq 1.1071$, and $\varphi_{\text{oleic-stearic}}$ \simeq 1.2585. The mean deviations for these mixtures were $r_{\text{palmitic-stearic}} \simeq 3.84\%$, $r_{\text{palmitic-oleic}} \simeq 3.26\%$, and $r_{\text{oleic-stearic}}$ $\simeq 0.95\%$.

Figure 3 presents the measurements and results of the application of eqs 7 and 8 for the ternary mixtures 1:1:1, 3:1:6, and 3:1:24. The coefficients of eq 8 obtained by adjustment for all the mixtures were $\varphi_{\text{palmitic-stearic}} \simeq 1.4286$, $\varphi_{\text{palmitic-oleic}} \simeq 1.0231$, and $\varphi_{\text{oleic-stearic}} \simeq 0.8334$. The values of the heat capacity obtained by applying eqs 7 and 8 tend to coincide as the presence of oleic acid increases, being practically the same as those for the mixture 3:1:24. The mean deviations for eqs 7 and 8 were $r_{(7)} \simeq 3.14\%$ and $r_{(8)} \simeq 2.47\%$, respectively. Once again, a small variation is observed in the values of the heat capacity with respect to composition for the analyzed samples. In this case, it is noteworthy that the results of heat capacity estimation using eq 7 are as good as those obtained using eq 8, with the advantage of the easy application of the former.

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