Surface Tension of Fatty Acids and Triglycerides

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ABSTRACT: Surface tension as a function of temperature was measured for four fatty acids (lauric, myristic, palmitic, and oleic) and two triglycerides (tricaprylin and tripalmitin). These surface tension measurements were performed using a K12 vers. 3.1 (Krüss GmbH) tensiometer at temperatures from 20 (or the melting point of each substance) to 90°C. The constants for a van der Waals-type correlation as well as for a linear equation are presented. Both equations are quite accurate, presenting mean deviations not exceeding 0.570%. Such correlation constants are valuable in the design or evaluation of processing equipment, especially that involving gas–liquid contact such as distillation and stripping columns, deodorizers, reactors, and equipment for physical refining.

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Surface tension is an important physical property of fluids, especially in certain applications in the chemical processing industry. Of particular importance is processing equipment involving gas–liquid contact, such as distillation and stripping columns, deodorizers, reactors, and equipment for physical refining. Better insights into the heat and mass transfer mechanisms involved in such processes, as well as modeling and simulating them, require information about physical properties such as surface tension and viscosity (1–3).

The study of surface tension also represents a fruitful source of indirect information about surface structure in general, especially on adsorption, which is properly a surface phenomenon. Furthermore, the molecules of fats and the derived fatty acids are relatively large and contain well-separated polar and paraffinic regions which behave quite differently in relation to the type of effects they can exert on interaction. The peculiar surface properties of fats are mainly a consequence of this particular aspect of the structure of their molecules (4). Few studies, however, have been published about the surface tension of fats and their components and derivatives (4–6), and what has been published is relatively old.

The aim of this paper is to present extended experimental data concerning the surface tension of specific high-purity fatty acids (lauric $C_{12:0}$, myristic $C_{14:0}$, palmitic $C_{16:0}$, and oleic $C_{18:1}$) and certain triglycerides (tricaprylin and tripalmitin) to ascertain whether the classic values available are reliable and to correlate surface tension and temperature.

EXPERIMENTAL PROCEDURES

Surface tension was measured using a K12 tensiometer (Krüss GmbH). The measuring unit consisted of a force-measuring system, a temperature sensor, a thermostatic jacket with built-in magnetic stirrer, and a platform drive system (to raise and lower the sample automatically and determine its position). The surface tension itself was measured by the plate method of Wilhelmy, using a clean, rectangular platinum plate (flame-dried before each measurement) attached to the force sensor. The sample surface is raised until it comes into contact with the plate edge, with force on the plate rising immediately upon contact with the liquid surface. The instrument then records the surface position to make sure that the bottom edge of the plate is maintained tangent to the surface. Under these conditions, force is directly proportional to surface tension. However, unlike the older ring method, this force requires no correction to provide a true surface tension value in $\text{dynes}\cdot\text{cm}^{-1}$ ($\text{mN}\cdot\text{m}^{-1}$). The equipment was calibrated for double-distilled water. The temperature of the thermostatic jacket was maintained constant to within ±0.05°C by a thermostatic water bath (Cole Parmer Digital Instrument Co., Kenilworth, NJ). All measurements were taken at atmospheric pressure and performed in at least 10 replicates to ensure reproducibility; these results were then averaged, and standard deviation values were found to be within 0.08 $\text{dynes}\cdot\text{cm}^{-1}$.

All chemicals used in the present work were obtained from Sigma (St. Louis, MO). The acids have high purity (99–100%), whereas the triglycerides have purities ranging from 90 (tripalmitin) to 97–98% (tricaprylin). Particularly in the case of triglycerides the compound purities were further certified by chromatographic analysis. This analysis was performed by high-performance liquid chromatography (Perkin-Elmer, Norwalk, CT) with refraction index (Reinhard Melz, Berlin, Germany), using a LiChrosorb RP-18 column (Merck, Darmstadt, Germany) at 25°C with acetone/acetonitrile 62:38 in solution with 5% acetone (Merck) as eluent, and a flow rate of 1 mL/min. The analysis confirmed the purity of tricaprylin as 97.6% and that of tripalmitin as greater than 90.0%. Data were correlated by using version 6.08 of the Statistical Analysis System (SAS, Cary, NC) package.

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RESULTS AND DISCUSSION

The measured values of surface tension for the fatty acids and triglycerides are given in Table 1. The values reported in the literature (5–7) are also given for comparison. The results for fatty acids obtained here deviate little from those reported in the literature (approximately, 0.5%, except for $C_{14:0}$, for which the difference is 2.4%). But the discrepancies in the values on triglycerides were substantial.

It should be emphasized that values for saturated fatty acids reported in the original literature were first published by Hunten and Maass in 1929 (8). These values were obtained by measurement from the approximate melting point to 150°C with the capillary-rise method. The acids were purified by crystallization from 95% alcohol until the melting point was constant, but the final purities are not reported. From the data of Hunten and Maass, Singleton (5) calculated the surface tension values for saturated fatty acids at selected temperatures. These calculated values are those reported in the literature (5–7). Unfortunately, Singleton did not report the equation used to interpolate the original data. Fitting a linear equation to the original data for myristic acid of Hunten and Maass led to a decrease in the mean deviation between our data and the new calculated values of 1.87%.

The main source of surface tension data for triglycerides is the work of Benerito *et al.*, published in 1954 (9). Tripalmitin was synthesized in the laboratory of the authors and purified by recrystallization from solvents. Tricaprylin was obtained from a commercial source and redistilled prior to use. The authors controlled the purity of the triglycerides by measuring their saponification values and melting points, but the final purities again were not reported. Surface tension was then determined using a modified version of the capillary-rise method.

Some data for the surface tension of tripalmitin were also reported in the form of a monograph by Othmer *et al.* (10). These data are in better agreement with the values obtained here (approximately, 28.0 dynes·cm^{-1} at 80°C for tripalmitin vs. 28.28 dynes·cm^{-1} obtained in this paper). Dervichian (4) presented some data for surface tension of triglycerides in a graphic form and these data are also in better agreement with the values measured in the present work (approximately, 27.6 dynes·cm^{-1} at 50°C for tricaprylin vs. 28.13 dynes·cm^{-1} measured in this paper; similar results can be obtained for tripalmitin too).

Surface tension–temperature correlations. A van der Waals-type correlation (Eq. 1) was used to correlate the experimental data to temperature (11,12):

$$\sigma = \sigma_0 (1 - T/T_c)^n \qquad [1]$$

where σ is the surface tension (dynes·cm^{-1}), T is the temperature in K, T_c is the critical temperature, and σ_0 and n are parameters used to fit the equation to the experimental data.

The critical temperatures required by Equation 1 can be estimated by Fedors' group contribution method, according to Equation 2 (12,13):

$$T_c = 535 \log [\Sigma \Delta_T] \qquad [2]$$

where Δ_T is the contribution of each group (e.g., -CH_2, -COOH, =CH-, etc.) to the critical temperature of the compound. Δ_T values for many groups were provided by Reid *et al.* (12).

The coefficients for the van der Waals-type correlation and the required critical temperatures are given in Table 2. The mean deviations (r) and the standard deviations (δ), calculated from Equations 3 and 4, respectively, are also included.

$$r = \left[\frac{1}{m} \sum_{j=1}^{N} \frac{|\sigma_{\text{calc}} - \sigma_{\text{exp}}|}{\sigma_{\text{exp}}} \right] \times 100 \qquad [3]$$

TABLE 1
Surface Tension of Fatty Acids and Triglycerides

Temperature	Surface tension (dynes·cm^{-1})					
(°C)	Lauric ($C_{12:0}$)	Myristic ($C_{14:0}$)	Palmitic ($C_{16:0}$)	Oleic ($C_{18:1}$)	Tricaprylin	Tripalmitin
20				32.79	30.04	
30				32.12	29.46	
40				31.90	28.81	
50				31.04	28.13	
60	27.40			30.21	27.18	
70	26.51	27.86	28.20	29.60	26.43	28.85
75	25.97	27.41	27.85			28.68
80	25.64	27.15	27.57	29.29	25.60	28.28
85		26.83	27.36			27.95
90	24.85	26.53	27.04	28.56	25.48	27.72
Data reported in the literature (5–7)						
20				32.5	25.68	
40					24.44	
60	27.3				23.19	
70	26.6	27.4	28.2			
80	25.8	26.6	27.5		21.95	23.85
90	24.8	25.6	26.7			

TABLE 2
Van der Waals-Type Correlations for Fatty Acid and Triglyceride Surface Tension[a]

Compound	T_c (K)	σ_0 (dynes·cm^{-1})	n	m	r (%)	δ (dynes·cm^{-1})	Temperature range (°C)
Lauric	756.21	59.245150	1.330643	5	0.164	0.070	60–90
Myristic	779.07	50.122923	1.014961	5	0.114	0.054	70–90
Palmitic	799.89	46.869695	0.908847	5	0.104	0.041	70–90
Oleic	819.82	50.695485	0.981724	8	0.395	0.171	20–90
Tricaprylin	937.84	54.009525	1.556993	8	0.568	0.199	20–90
Tripalmitin	1020.29	51.512477	1.410259	5	0.150	0.064	70–90

[a] T_c, critical temperature: σ_0 and n, parameters used to fit Equation 1 to the experimental data; r, mean deviation; δ, standard deviation; m, number of experimental points.

TABLE 3
Linear Correlations for Fatty Acid and Triglyceride Surface Tension[a]

Compound	a	b	m	r (%)	δ (dynes·cm^{-1})	Temperature range (°C)
Lauric	32.464000	−0.085200	5	0.172	0.074	60–90
Myristic	32.340000	−0.064800	5	0.114	0.053	70–90
Palmitic	32.100000	−0.056200	5	0.102	0.041	70–90
Oleic	34.060119	−0.061298	8	0.396	0.171	20–90
Tricaprylin	31.524643	−0.070607	8	0.569	0.202	20–90
Tripalmitin	33.080000	−0.059800	5	0.151	0.064	70–90

[a] a and b, linear coefficients. For abbreviations see Table 2.

$$\delta = \left[\frac{1}{m-p} \sum_{j=1}^{N} \left(\sigma_{\text{cal}} - \sigma_{\text{exp}} \right)^2 \right]^{1/2} \qquad [4]$$

where σ_{exp} and σ_{calc} are the experimental and calculated values for the surface tension, respectively, m is the number of experimental points, and p is the number of adjusted parameters.

For all data, the r-value is less than 0.400%, except for tricaprylin, which shows a mean deviation of 0.568%. The highest standard deviation is 0.199 dynes·cm^{-1}. Figure 1 shows the experimental and predicted surface tensions for pure fatty acids and the triglycerides.

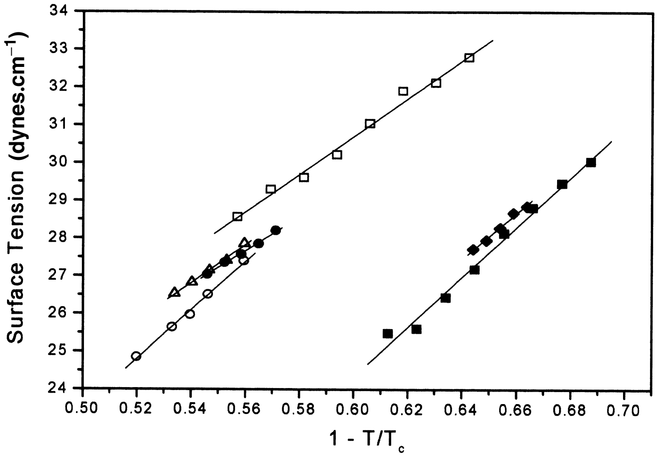

FIG. 1. Temperature and surface tension of fatty acids and triglycerides. The lines are correlation derivatives (from Eq. 1) and the points are measured data. (○), lauric acid; (△), myristic acid; (●), palmitic acid; (□) oleic acid; (■), tricaprylin; (◆), tripalmitin.

At reduced temperatures (ratios of 0.4–0.7), the surface tension dependence on temperature can be well represented by a linear equation, as reported by Reid *et al.* (12), and Equation 5 was thus used in the correlation of the experimental data:

$$\sigma = a + bt \qquad [5]$$

where t is the temperature in degrees Celsius.

The linear coefficients are reported in Table 3, which also includes the mean deviations and the standard deviations between the experimental and calculated values.

In this work, measured and calculated data reveal consistent behavior and show that at least for fatty acids, even with the improved methods available today, the classic values remain accurate.

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