it offers some original concepts which might provide another and simple approach to the problem involving the color evaluation of oils by means of photoelectric photometry. Indubitably, considerable further investigation, particularly of a cooperative nature, remains to be performed before a final and universally acceptable photometric method is evolved.

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Thermal Properties of Fats and Oils

VI. Heat Capacity, Heats of Fusion and Transition, and Entropy of Trilaurin, Trimyristin, Tripalmitin, and Tristearin

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IN previous papers (1) of this series heat capacity data from 180° to 363° K. on cottonseed oil, hydrogenated cottonseed oil, and a cottonseed oil-solvent mixture were reported. The present report presents thermal data between 90° and 373° K. for the simple triglycerides of four commonly occurring fatty acids. The entropy of each compound has been calculated and is reported.

In conformity with the nomenclature recommended by Lutton (2), the three polymorphic forms of the triglycerides are hereinafter referred to as β, β', and α in decreasing order of their melting points. These forms were designated as I, II, and III, respectively, in a previous publication (3) from this laboratory.

Preparation of Samples. The triglycerides were prepared from glycerol and fatty acids according to the method described previously (3). The melting points of the β-form, in Table II, compare favorably with those reported by previous workers (2, 4).

The impurities in trilaurin and tristearin were estimated from measurements of the temperature as a function of the fractions melted. It has been estimated that the purity of the compounds used in this investigation was in each case between 98 and 99 mole per cent. These estimations were made on the assumption of the absence of solid solutions and until means for verifying this assumption are available the thermal values should be considered as minimal values. Since trimyristin and tripalmitin yielded melting point curves as sharp as those of the other two compounds, they were considered to be of the same order of purity.

In each case the material was obtained in the β-form by tempering the solidified sample, contained in the calorimeter, at a temperature slightly (1° to 2°) below the melting point of this form. It was not possible to obtain the relatively fleeting (2) β'-form in the calorimeter which was used in this investigation. Previous work (2, 3) has shown that the α-form of the triglycerides results by rapid or moderately rapidly cooling of the melt. This form was obtained by immersing the calorimeter filled with the melted fat in liquid nitrogen. The thermal examination of the α-forms of trimyristin, tripalmitin, and tristearin was completed without difficulty, since these were sufficiently stable at room temperature for this purpose. However, the heat capacity data on the α-form of trilaurin invariably indicated partial transformation of the sample during the period required for setting up and evacuating the calorimeter, even when the temperature was not allowed to rise above 0° C. Therefore, data for the pure α-form of trilaurin could not be obtained.

Apparatus and Procedure. A detailed description of the apparatus and method was given in the first paper of this series (5). Briefly it is as follows: The samples were sealed in a copper calorimeter which was enclosed in a semi-adiabatic calorimetric system. A measured amount of energy from storage batteries was supplied to the calorimeter. All temperature measurements were made with a single-junction thermocouple. The electrical and temperature measurements were made with a White double potentiometer in conjunction with a high-sensitivity galvanometer. The accuracy of the results is believed to be better than one per cent. Results are reported in terms of the defined calorie, *i.e.*, 1 cal. = 4.1833 int. joules. All weights were corrected to vacuum.

Results and Discussion

Heat Capacity. The results of the heat capacity measurements made on the α- and β-forms of trimyristin, tripalmitin, and tristearin, and the β-form of trilaurin are presented in Table I.

Measurements were not made below 192° K. on the triglycerides in the α-form.

It should be noted that in all of these triglycerides apparent melting is evident at temperatures considerably below the final melting points. This phenomenon is strikingly illustrated by the change in slope of the curve reproduced in Figure 1 in which the heat capacity is plotted as a function of temperature.

The possibility was considered that this change in the rate of increase of the specific heat might result from a change in the crystal structure (polymorphic change), *i.e.*, it might represent a true change in specific heat of the compound. However, the calorimetric data strongly indicates that some melting actually occurs at these low temperatures, and this interpretation is further substantiated by dilatometric measurements previously reported for these triglycerides (6), in which premelting of the samples

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[1] The experimental work reported herein was carried out in part by one of the authors and in part by G. D. Oliver under the direction of A. E. Bailey while the latter were employed with this laboratory.

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TABLE I

Heat Capacity in Calories per Gram of Substance

T., °K.	Cp	T., °K.	Cp	T., °K.	Cp
		Trilaurin, β-form			
90.5	0.154	152.4	0.221	211.2	0.275
95.1	0.161	162.6	0.229	219.7	0.284
104.6	0.172	172.5	0.238	228.8	0.296
114.2	0.183	182.3	0.247	236.6	0.305
124.1	0.192	192.0	0.255	243.9	0.315^a
133.1	0.200	197.8	0.262	256.8	0.334^a
142.6	0.210	204.6	0.269		
		Trilaurin, liquid			
330.9	0.507	346.8	0.515	362.6	0.524
339.1	0.510	355.0	0.519	370.2	0.530
		Trimyristin, β-form			
89.1	0.152	149.3	0.218	214.7	0.278
93.9	0.158	158.6	0.225	224.2	0.287
109.0	0.176	168.2	0.234	233.5	0.298
113.7	0.182	177.9	0.242	243.1	0.310
122.7	0.192	187.6	0.252	252.4	0.322^a
132.7	0.201	196.7	0.260	261.9	0.335^a
138.3	0.205	201.4	0.264		
		Trimyristin, α-form			
192.1	0.282	214.6	0.313	241.1	0.357^a
198.7	0.291	222.5	0.323	246.9	0.368^a
205.7	0.300	233.7	0.342^a		
		Trimyristin, liquid			
331.5	0.514	345.3	0.520	358.4	0.530
338.4	0.518	352.4	0.524	365.0	0.534
		Tripalmitin, β-form			
87.3	0.148	158.7	0.225	229.6	0.294
96.7	0.160	169.3	0.235	238.5	0.304
105.7	0.172	181.2	0.246	248.1	0.317
115.9	0.183	192.1	0.257	257.4	0.327
126.1	0.194	202.5	0.265	266.6	0.341^a
136.9	0.204	211.4	0.274	272.9	0.360^a
148.8	0.216	220.4	0.285	281.2	0.361^a
		Tripalmitin, α-form			
194.6	0.281	216.9	0.315	240.3	0.353
200.9	0.291	223.5	0.326	245.5	0.364^a
209.0	0.302	230.5	0.336	251.9	0.378^a
		Tripalmitin, liquid			
338.8	0.519	352.6	0.528	366.9	0.538
345.9	0.525	359.9	0.533	369.1	0.539
		Tristearin, β-form			
95.8	0.160	156.7	0.224	213.5	0.277
101.9	0.166	166.6	0.230	223.0	0.288
107.6	0.174	176.6	0.240	233.0	0.299
116.7	0.183	186.2	0.252	242.8	0.310
127.5	0.196	196.0	0.259	252.4	0.321
137.3	0.205	198.2	0.261	262.3	0.336^a
148.2	0.214	203.7	0.266	272.1	0.360^a
		Tristearin, α-form			
192.1	0.273	218.6	0.316	246.5	0.367^a
197.6	0.283	227.2	0.330	256.7	0.388^a
207.7	0.298	236.6	0.346	266.5	0.405^a
		Tristearin, liquid			
346.5	0.528	356.8	0.533	367.1	0.540
352.1	0.530	361.9	0.536	371.6	0.542

[a] These values include a portion of the heat of fusion.

occurred at substantially the same temperatures as indicated by the thermal change in the present case and as an abrupt change in volume in the former case.

Heats of Fusion. The numerical values for the heats of fusion, obtained from duplicate measurements, and for the melting points, determined from plots of time *vs.* temperature of the fusion measurements, are recorded in Table II for the β-form. In both the α- and β-forms of each compound a considerable amount of premelting occurred. The values for the heats of fusion for tripalmitin and tristearin in the β-form (53.1 and 54.5 cal./g., respectively) are lower than those reported by Rao and Jatkar (7) (62.3 and 61.6 cal./g., respectively). However, the values obtained by these workers were not corrected for sensible heat absorbed during premelting of the samples.

When rapidly heated in a capillary tube, the α-forms melt directly with the formation of a clear isotropic liquid. Melting points of the α-form, as determined by the rapid-heating technique of Clarkson and Malkin (4), are recorded in Table III.

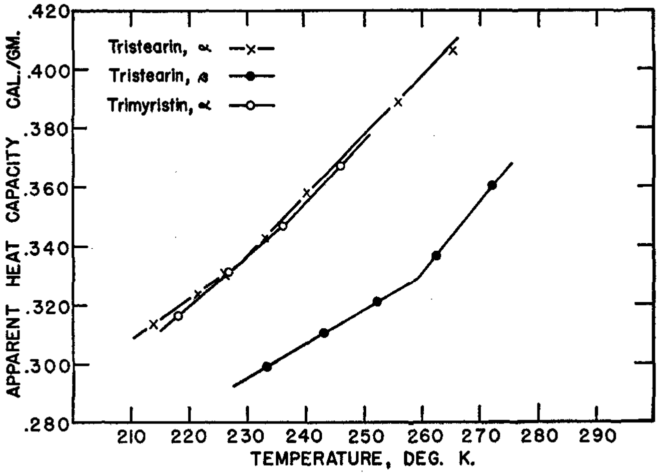

FIG. 1. Apparent heat capacity-temperature curves of tristearin and trimyristin showing premelting.

TABLE II

Fusion Data on the β-Forms of Synthetic Triglycerides

Substance	Melting point		Heat of fusion (cal. per gm.)		
	°K.	°C.	I	II	Mean
Trilaurin	319.5	46.3	46.2	46.2	46.2
Trimyristin	330.2	57.0	50.4	50.2	50.3
Tripalmitin	338.9	65.7	53.0	53.2	53.1
Tristearin	345.7	72.5	54.4	54.6	54.5

TABLE III

Heats of Fusion and Transition of the α-Forms of Synthetic Triglycerides

Substance	Melting point		Heat of fusion Cal./gm.	Heat of transition α- to β-form Cal./gm.
	°K.	°C.		
Trimyristin	305.5	32.3	34.6	—12.6
Tripalmitin	317.9	44.7	37.4	—13.3
Tristearin	327.2	54.0	38.9	—13.7

When heated relatively slowly in the calorimeter, during the course of the thermal investigation, melting of the α-forms did not occur; on the contrary there was a rapid transformation to the β-form, beginning at a temperature approaching the melting point of the α-form. This transformation was accompanied by an evolution of heat which immediately raised the sample to a temperature near the melting point of the β-form. Thereafter, fusion of the β-form proceeded normally. The typical behavior of the α-form during a fusion experiment is illustrated in Fig. 2. The portion of the curve from *A* to *B* indicates the rapid irreversible transformation of the unstable form. Heat input to the system during the fusion was maintained at a constant rate. Inasmuch as transformation takes place at the beginning of the fusion, it was not possible to determine heats of fusion of the α-forms directly. However, estimates of the heats of fusion of the α-forms were made by calculating in each case the difference in heat content of the solid α-form and the liquid phase at the previously determined melting point of the α-form. The average values calculated in this manner are recorded in Table III. To explain these calculations, the derivation of the heat of fusion for the α-form of tristearin will be used as an example: The temperature (T), voltage (V), and current (I)

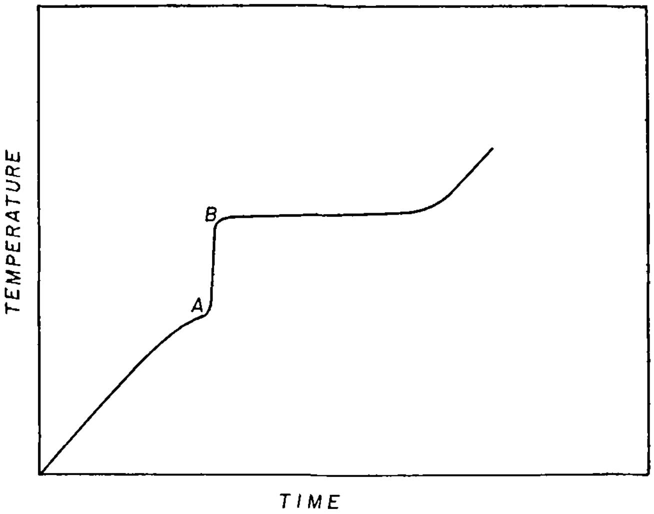

FIG. 2. Typical heat of fusion curve for the alpha form.

were all plotted as a function of time as in the case of the fusion determinations of the β-form. The temperature-time (fusion) curve of Figure 3 was then divided into time intervals, not necessarily of equal lengths, and the temperature at the beginning and end of each interval determined. The temperature at the end of interval 4 was taken as point A, and that at the start of interval 5 as point B. For each interval the average V, I, T, and change of temperature were calculated. The product of average V, average I, time interval, and constant factor at the average temperature of the interval, gave numerical values for the calories supplied for each interval. This energy was then corrected for the amount supplied to the calorimeter, leadwire loss, and for the non-adiabatic system. The results gave for each interval the heat supplied solely to the sample. Dividing these values by the weight of sample, the cal./gm. for each interval were determined. The amount of heat at the end of each interval was cumulative, *i.e.*, the heat content at point C was 0, at D it was that corresponding to the calculated value for interval 1, at E that of intervals 1 and 2, and so on to point F, the end of the determination. Thus, the total heat content for the entire operation, with respect to zero heat content at point C, was known. From specific heat determinations of the α-form, extrapolated to the previously determined melting point A, of this form, the accumulated heat supplied to point A was found to be 36.867 cal./gm. Likewise, specific heat determinations for liquid tristearin, extrapolated to point B, gave the specific heat of each time interval from F to B, which when subtracted cumulatively from the total heat supplied, gave the value of 75.727 cal./gm. as the specific heat of the liquid at point B. The difference between the heat content of the liquid and the solid, at the melting point, 38.9 cal./gm., of the α-form was the calculated value for the heat of fusion of the α-form of tristearin. The same procedure was followed for calculating the heat of fusion of the α-forms of the other triglycerides.

Heat of Transition. The average heat of transition values are given in Table III. These values represent the differences between the heat contents of the α- and β-forms at the melting points of the α-forms. The calculated heat of transition of tristearin (13.7 cal./gm.) is lower than the value (15.4 cal./gm.) reported by Rao and Jatkar (7). The latter value, however, was determined from heat of solution data at a temperature (*ca.* 27° C.) which is considerably below the melting point of the α-form.

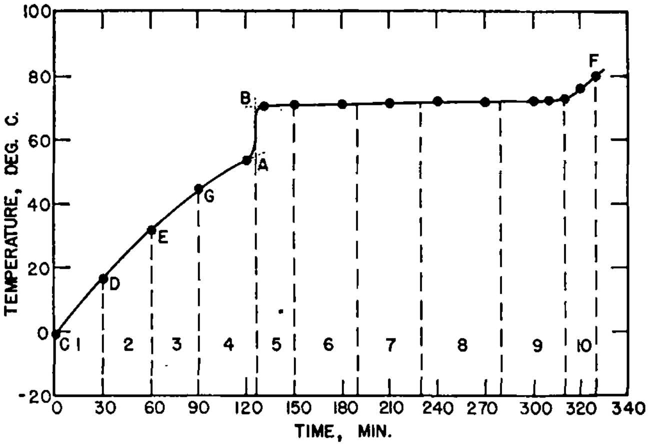

FIG. 3. Time-temperature curve of tristearin showing α- to β-transformation and fusion.

Entropy. The data for the heat capacity were used to calculate the entropy of the β-form of each triglyceride throughout the temperature range to 298.16° K. The extrapolation method of Kelly, Parks, and Huffman (8) for estimating the increase in entropy for the crystals from 0° to 90° K. and the revised data for the standard substances therein (9) were employed in making these calculations (Column 3 in Table IV). The entropy increment from 90° to 298.16° K. was determined by the method of graphical integration, directly from experimental data. The results are summarized in Table IV.

TABLE IV

Molal Entropies of the β-Forms of Synthetic Triglycerides

Substance	Mol. wt.	Entropy, cal./deg.		
		0° to 90°K.	Above 90°	S298.16
Trilaurin	638.97	81.0	184.1	265.1
Trimyristin	723.12	91.1	206.7	297.8
Tripalmitin	807.27	99.2	232.4	331.6
Tristearin	891.43	110.6	256.2	366.8

Summary

Heat capacities of the α- and β-forms of trimyristin, tripalmitin, and tristearin, and the β-form of trilaurin were measured. The heats of fusion of the β-forms of these four compounds were determined.

The heats of fusion of the α-forms of trimyristin, tripalmitin, and tristearin were calculated from heat content data. Calculations were also made of the heats of transition, α- to β-form.

The molal entropy at 298.16° K. was calculated for the β-form of each compound.

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