Heats of Fusion for Some Triglycerides by Differential Scanning Calorimetry

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Abstract

Heats of fusion of tristearin, tripalmitin, trimyristin, trilaurin and several standards were determined by the relatively new technique of Differential Scanning Calorimetry. The data obtained on the standards shows good precision and accuracy. The results obtained for the triglycerides are 1–10% lower than values which have been reported elsewhere.

Introduction

Data on the heats of fusion (ΔH_f) of biologically-important triglycerides are scarce and sometimes conflicting. Much of the information obtained before modern advances in chromatography may have been taken from experiments made on materials of questionable purity. At present triglycerides of high purity are obtainable but economics dictate the use of small samples. Differential scanning calorimetry (DSC) appears to be a useful technique for the determination of the energy of phase transitions (10,15). It is the purpose of this paper to determine the precision and accuracy with which ΔH_f for standards can be measured and to extend the measurements to representative triglycerides.

Experimental Procedures

Materials

Indium (99.99%, Fisher Scientific Co.), tin (NBS freezing point standard 42d), benzoic acid (NBS calorimetric standard, a sample supplied by du Pont with their 900 DTA, and James Hinton, 99.99% zone refined), naphthalene (Kodak white label, NBS 38b purified by distillation from ethylene glycol, James Hinton 99.999% zone refined), and urea (Baker Analyzed Reagent), were used to check the apparatus. Two sets of pure triglycerides were used in this study. One set purchased from Applied Science Laboratories, listed as 99+%, and the other set from Hormel Institute was listed as greater than 99% pure. A third sample of tristearin, prepared synthetically at the University of Connecticut, was also used. Samples of lipids were shown to be greater than 99% pure by gas-liquid and thin-layer chromatography.

Method

Samples, contained in covered aluminum pans which were crimped to form flat wafers, were weighed with a Cahn Electrobalance (Model RG) to ±0.005 mg. A sample was placed in the Perkin-Elmer DSC 1-B differential scanning calorimeter and covered with an aluminum dome. A similar though empty assembly served as the reference. Heating rate and sensitivity were 10 C/min, and range 16 respectively. The slope control was adjusted to provide a flat, horizontal baseline. Peak areas were measured with an Infotronics CRS-1 integrator attached to the input of the recorder. The instrument is capable of integrating peaks which go off scale on the 10 mv recorder. Thermal analysis was carried out under nitrogen at a flow of 13.3 ml/min, measured at the bypass outlet.

The instrument was calibrated with indium (ΔH_f = 6.79 cal/g). Ten different samples whose weight varied from 1.708 to 21.45 mg were utilized. The relative mean deviation in peak areas per milligram of sample was 1.01%.

Results

Each value in Table I was obtained using five separately weighed samples. These had the following weight ranges: tin (3.752–12.652 mg), benzoic acid (0.268–12.136 mg), naphthalene (0.416–9.498 mg), urea (0.672–3.480 mg). The organics were weighed before and after thermal analysis to determine if any weight losses had occurred. Benzoic acid lost from 2% to 7.5% of its weight during analyses, the lower weight samples losing the greatest percentage. Naphthalene lost from 2% to 3% of its weight. When volatile-sample containers, provided by Perkin-Elmer, were used no weight losses for benzoic acid nor naphthalene were observed. The best values for the heat of fusion of these compounds were obtained in this manner. Benzoic acid was chosen as a reference material since its ΔH_f had been determined previously and it is available from the institution where the study was made. In the paper describing this work Furukawa summarizes the history of the value of ΔH_f (2). Unfortunately several handbooks report an earlier and incorrect value (3,4).

Urea was used as a reference material since its heat of fusion is greater than that of the triglycerides. No weight losses were observed for urea.

Triglycerides varied in weight from 0.260 to 11.56 mg. Recrystallization of tristearin from acetone, ethanol or benzene did not alter ΔH_f appreciably. Tempering separate samples of tristearin prior to melting at 5, 4, 3, 2 and 1 C below its melting point for 1 hr

TABLE I

Heats of Fusion of Reference Materials and Triglycerides (cal/g 15 C)

Material[a]		Observed	Avg. dev.	Std. dev.	Literature
Tin		14.0	0.06	0.09	14.0 (9); 14.3 (13)
Benzoic Acid	A	35.4	0.6	0.8	35.2 (2); 34.9 (11)
	B	35.0	0.6	0.4	
	C	35.4	0.2	0.4	
	I	35.6	0.1	0.2	
Naphthalene	D	34.6	0.3	0.4	35.4 (14); 35.4 (7); 35.1 (6)
	E	35.5	0.2	0.3	
	I	35.2	0.3	0.3	
Urea		57.0	0.9	1.1	57.8 (8)
Tristearin	F	50.0	0.6	0.8	
	G	50.7	0.2	0.2	54.6 (1); 54.9 (16) 50.0 (5)
	H	49.2	0.6	0.8	
Tripalmitin	F	49.2	0.4	0.5	53.1 (1); 52.8 (16)
	G	48.7	0.8	1.1	
Trimyristin	F	46.2	0.3	0.4	50.3 (1); 49.5 (16)
	G	47.8	1.1	1.5	
Trilaurin	F	45.8	0.7	0.8	46.2 (1)
	G	45.2	1.0	1.3	

[a] Sources: A, du Pont; B, du Pont (in volatile-sample container); C, NBS (in volatile-sample container); D, Eastman Kodak; E, NBS (in volatile-sample container); F, Hormel Institute; G, Applied Science Laboratories; H, University of Connecticut; I, James Hinton (in volatile-sample container).

did not appreciably alter the value of ΔH_f though the apparent melting point was raised about 0.5 C. Similar results were observed for tripalmitin.

Data were rejected if their deviation from the mean exceeded four times the mean deviation computed excluding the value to be tested (12). At the instrumental settings used most of the rejected data were for samples which weighed less than 1 mg and hence had too small an instrument response. Of the 85 distinct samples which weighed more than 1 mg, only the data from two were rejected.

Some doubts have arisen concerning the previously reported enthalpies of fusion for some triglycerides. Lutton has reported a value of 50.0 cal/g for tristearin based upon differential heat of solution measurements (5). This is in good agreement with the data reported here. The earlier value is about 10% greater than this (1) and a recent value, 54.9 cal/g, determined with a commercial DTA apparatus (16). The good agreement between data obtained in this study and that reported in the primary literature for the standards, tin, benzoic acid, naphthalene and urea make it likely that the data reported herein for the triglycerides are accurate as well as precise within the limits dictated by their standard deviation.

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