The Determination of Heat Capacities of Milk Fat by Differential Thermal Analysis

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Abstract

A differential thermal analysis calorimeter was used in determining the heat capacities of milk fat. The heat capacities of milk fat at −43 and 70 C were .423 cal/g/C (average value) and .521 cal/g/C (average value) respectively.

Introduction

A prior publication (1) demonstrated the feasibility of employing differential thermal analysis calorimetry (DTAC) for determining the heats of melting of milk fat. Because of the broad melting range in milk fat, new methods for quantitizing thermogram areas were developed. The methods that were developed for milk fat appeared to be valid for other fats and oils. Important features of DTAC were the rapidity with which the determinations could be made and also the need for only milligram amounts of sample. It was also demonstrated, with numerous pure materials, that good agreement between known and determined heats of fusion could be obtained readily.

A further important application for DTAC is in the area of heat capacity measurements. That its use in fats and oils has scarcely been considered is evidenced by the almost total lack of literature in this area. The determination of this useful thermodynamic property has been described in other publications of which some more recent ones are given (2,3).

The development of suitable methods for obtaining much needed heat capacity data of milk fat, especially in the low temperature regions below 0 C, was the prime objective of the work reported in this paper. It was also felt that methods developed for milk fat would have general applicability for other fats and oils.

Experimental Procedures

Preparation of Milk Fat

Freshly pasteurized cream was converted to butter-oil according to the method presented in a previous publication (1). The clear oil was dried by stirring magnetically with finely powdered CaH_2 for 3 hr. The dried milk fat was stored at −18 C prior to use.

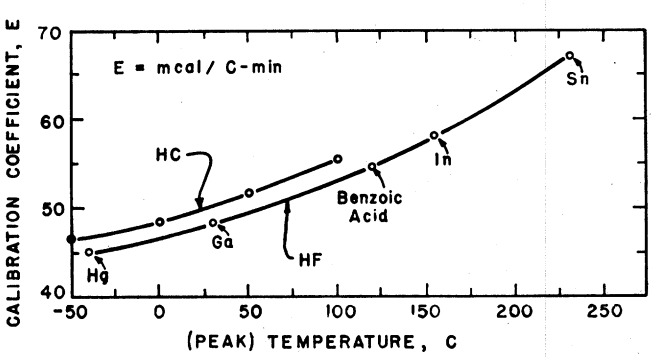

FIG. 1. Calibration curves.

Apparatus

The apparatus employed in the work reported in this paper was the DuPont Calorimeter, a plug-in accessory for the DuPont 900 Differential Thermal Analyzer. A description of the analyzer was given in a previous publication (1).

Calibration

The calibration curve established for heats of fusion, and indicated as HF in Figure 1, was found inadequate for the determination of heat capacities of organic materials. A satisfactory calibration curve, indicated as HC in the same figure, was constructed using high purity palmitic acid, benzoic acid and anthracene. These samples (obtained from James Hinton, Ft. Walton Beach, Fla.) were prepared by zone melting, and their purity was given at 99.9+%. The latter calibration curve was found suitable for all subsequent heat capacity determinations of organic materials.

In determining the heat capacity of a material, it is necessary to measure exactly the temperature lag between sample and reference systems under blank and sample conditions. At some temperature above ambient, and with sample and reference liners in their respective holders, the instrument is put in a temperature hold position to permit the calorimeter to equilibrate. This is necessary to establish the zero differential temperature point, i.e., the temperature at which reference and sample holders are equal. When this equilibrium point is reached, the calorimeter is permitted to heat at some predetermined heating rate until the temperature range of interest has been traversed. After completing this programmed heating sequence, the instrument is again switched to the temperature hold position and the zero differential temperature point is established at this higher temperature. The temperature hold sequence needed to define the zero differential temperature points require about 3 to 5 min holding time. The value of the differential temperature at no-sample

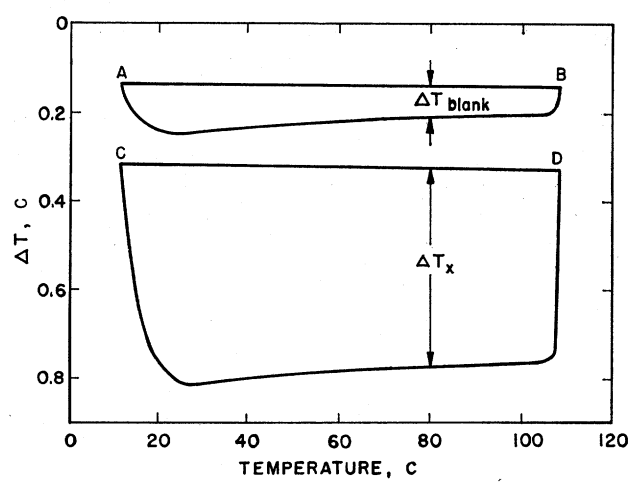

FIG. 2. Typical heat lag curves for heat capacity determinations.

condition, ΔT_{NS}, is the value measured between the line joining the zero differential temperature points and the steady-state curve at some temperature (T). This procedure is repeated in an identical manner for a run containing the weighed sample in the liner previously used for the blank determination and over approximately the same traversed temperature range. The value of the differential temperature at sample conditions, ΔT_S is measured in a similar fashion. Figure 2, taken from an actual determination illustrates typical lag curves obtained under blank and sample conditions. A, B, C and D are defined as zero differential temperature points. The distances corresponding to ΔT_{NS} and ΔT_S are measured to the nearest 1/64 in. and converted appropriately to the absolute differential temperature. The calibration value or specific heat of a sample is calculated by substituting the necessary values in the following formula:

$$(C_p)_T \quad \frac{\text{millicalories}}{\text{mg} - \text{C}} = \frac{(\Delta T_S - \Delta T_{NS})}{\text{Ma}} E_T$$

where $(C_p)_T$ = specific heat at temperature T; ΔT_S = absolute differential temperature for sample and liner, C; ΔT_{NS} = absolute differential temperature for empty liner, C; E_T = calibration coefficient at temperature T, mcal/C − min; M = mass, mg; and a = heating rate, C/min.

The above procedure permits the establishment of a calibration curve that can be used for heat capacity determinations above ambient temperature. In fats and oils, however, the temperature range between ambient and −50 C assumes a great deal of importance in heat capacity measurements. For this reason a new method had to be devised which would allow the establishment of zero differential temperature points at low temperatures and subsequently make possible the calculation of calibration coefficients. This would then permit the calculation of heat capacities at low temperature.

A critical sequence in low temperature work is the accurate definition of the zero differential temperature point which is required to yield a true representation of the heat lag curve. In establishing this curve for subsequent use in constructing the calibration diagram in Figure 1 for heat capacity determinations to at least −50 C, the following operations were performed. As a first step, the calorimeter containing either the empty liner or a sample-filled liner was cooled at about 7–10 C/min down to approximately −90 C. At approximately −90 C, the instrument was put in a temperature hold condition while the addition of liquid nitrogen coolant was continued. This operation which involves a simultaneous heating and cooling process eventually brings reference and sample holders to equal temperatures; a similar temperature hold sequence was described previously for the above-ambient procedure. At the time the instrument was switched to the temperature hold condition, an auxiliary recorder coupled to the calorimeter was activated. The initial auxiliary recorder trace after activation was negative in slope followed by a gradual leveling off. The zero differential temperature point was defined at the position where the auxiliary recorder trace leveled off parallel to the recorder baseline. The prime and sole purpose for employing the auxiliary recorder at this time was to accurately define the zero differential temperature point in the low temperature region. When the zero differential temperature condition was achieved, (after about 3 min) the coolant was removed, the console recorder pen was engaged and the calorimeter was switched to the program heat position. The programmed heating sequence, with either empty liner or sample-filled liner, was permitted to commence until the temperature range of interest was traversed. At some suitable upper temperature, the temperature hold sequence was repeated to establish a second zero differential temperature point, thereby terminating the heat lag curve. The zero differential temperature points illustrated in Figure 2 as B and D, defining the upper temperature range, were always above ambient temperature. This modified procedure, which was shown to be valid in above-ambient determinations, was employed in all low-temperature work for establishing a calibration curve and also for subsequent low-temperature heat capacity determinations. All heat lag curves similar to that shown in Figure 2 were recorded on the fixed bed recorder of the Du Pont instrument. The auxiliary recorder was used only as indicated above or when simultaneous heat capacity (calculated from the Du Pont recorder data) and heat of fusion (calculated from the auxiliary recorder data with appropriate calibration) determinations were performed.

In constructing the calibration curve HC in Figure 1, a minimum of five determinations on each calibrating standard was made and an average E value was used. A check on the reproducibility of E at 20 C with benzoic acid as the calibrating standard gave a value of 49.0 with an average deviation of ±0.5. Sample materials used for calibration, as well as other materials used in this study, were weighed to the nearest ±.01 mg with a Cahn Electrobalance, Model 1500. The calibrating standards employed were: palmitic acid for −50, 0 and 20 C; benzoic acid for 20 C; and anthracene for 50 and 100 C. A ΔT sensitivity of 0.2 C/in. was used. Within experimental error, the E calibration values obtained at heating rates of 5 and 10 C/min were the same. In the calibration curves shown in Figure 1, the E values for specific heats are plotted versus temperature, whereas, in heats of fusion they are plotted versus peak temperature. After the calibration curve was established, an examination of the reproducibility of heat capacity measurements at 20 C was performed on seven samples of benzoic acid ranging in weight from about 8 to 14 mg. An average deviation of ±.007 cal/g/C was obtained.

Sample Preparation and Materials

Though sample tempering had a decided effect on the heats of melting values of milk fat (1), this treatment has no detectable influence on the heat capacities at the temperatures reported in this study. No special pretreatment or precise programmed cooling was necessary to bring the milk fat samples to a low temperature appropriate for performing the heat capacity determinations.

All materials, except tristearin, were used as received in determining their heat capacities. The tristearin, tripalmitin and lauric acid used to check the accuracy of the calorimeter was obtained from the Hormel Institute, University of Minnesota, Austin, Minnesota. Their purity was given as greater than 99% as determined by TLC. The dextrose was certified reagent grade material obtained from the Fisher Scientific Company. Tristearin, as received, contained minute amounts of the α form which would

have interfered in the determination of its heat capacity. The final selection of the β form over the other forms for heat capacity measurements was dictated by the ease and certainty with which this crystalline form could be obtained. It was found that α and β' forms could be eliminated by heating the sample in the calorimeter to 55 C and holding at this temperature for 15 min. The sample was then cooled to an appropriate low temperature in preparation for a heat capacity measurement. Heat capacities for tristearin and other materials were made to evaluate the calorimeter and are given in Table I.

In determining the heat capacities of the organic materials and the milk fat, three specially prepared seamless aluminum liners 4 mm in diameter and 3 mm high were used. The sample liners weighing approximately 12 mg were used in all forthcoming determinations. A fourth liner used in the reference holder was about 1 mg less in weight than the sample liners. The sample liners were carefully marked and once their temperature lag profiles were determined under no-sample conditions, the ΔT_{NS} values thus obtained were used in all subsequent determinations. In preparing solid samples for heat capacity measurements, it was found best to pulverize or flatten the sample to achieve a more intimate contact with the sample holder. Large irregular sample crystals tended to produce undulations in the heat lag curve which were eliminated when the sample particle size was reduced. A most imperative requirement for highest accuracy at low temperature work is a calorimeter cell that is virtually air tight. Even slightest traces of condensed moisture in the cell will vitiate all well executed preliminaries aimed at highest quantitative performance.

Results and Discussion

The determination of heat capacities of milk fat and other organic materials at low temperatures presented no problems once the difficulty of defining the zero differential temperature point was resolved. Frequently, it was necessary in fats and oils to pass through the melting range to arrive at the upper temperature zero differential temperature point. During this transition it was necessary to reduce temporarily at ΔT sensitivity on the console recorder to avoid pen hang-up on the recorder baseline. This operation was performed without disturbing the original pen position. The auxiliary recorder could, however, be employed at this point to obtain a heat of fusion profile simultaneously with the heat capacity determination. After the melting transition was passed the original ΔT sensitivity was re-established for the remainder of the determination.

TABLE I

Results of Heat Capacity Determinations

Sample	Sample size mg	Heating rate C/min	Cal. 15°/g/C Determined, C_p		Cal. 15°/g/C Known, C_p
Anthracene[d]	11.53	10	50C	.302	.308[b]
			100C	.351	.350
Anthracene	12.49	5	50C	.314	
			100C	.342	
Anthracene	12.00	5	50C	.318	
			100C	.357	
Benzoic Acid[d]	14.01	5	20C	.292	.287[b]
Benzoic Acid	7.83	10	20C	.281	
Dextrose	10.10	5	0C	.269	.277[b]
(anhydrous)			20C	.274	.275
Dextrose	5.11	10	0C	.272	
(anhydrous)			20C	.287	
Benzoic Acid	7.26	10	0C	.269	.265[c]
Benzoic Acid	12.66	5		.259	
Benzoic Acid	13.98	5		.263	
Tristearin (β form)	7.68	10	−60C	.285	.277[a]
(form)			−30C	.318	.310
Palmitic Acid[d]	3.36	10	−50C	.304	.306[b]
Palmitic Acid	4.74	10	0C	.387	.382
Tripalmitin	9.90	5	96C	.524	.539[a]
Lauric Acid	14.15	5	−30C	.437	.430[b]

[a] Referenec 5.
[b] Reference 6.
[c] Reference 7.
[d] Recheck on additional samples after establishing the calibration curve.

TABLE II

Heat Capacities of Milk Fat

Sample size mg	Heating rate C/min	Cal. 15°/g/C determined, C_p	
9.88	5	−43 C	.420
10.00	5	−43 C	.422
13.05	5	−43 C	.429
5.81	10	−43 C	.219
8.25	10	−43 C	.425
8.49	5	70 C	.521
9.08	5	70 C	.507
9.97	5	70 C	.524
10.00	5	70 C	.522
10.15	5	70 C	.521
7.97	10	70 C	.522
8.25	10	70 C	.520
8.49	10	70 C	.528

In order to minimize errors in measuring the ΔT value from the heat lag curve, it was found necessary to use a sample size somewhat larger than that used in heats of fusion or melting determinations. Also, as indicated previously, it appeared necessary to establish a new calibration curve for heat capacity measurements to obtain highest accuracy. It also appeared necessary to employ organic compounds as calibrating standards for use with organic type materials. Preliminary use of high purity metals in establishing a heat capacity calibration curve appeared to yield values that coincided very closely to those established for heats of fusion determinations. When these latter values, obtained from metals, were used with organic materials, consistently large errors resulted. That a discrepancy in calibration for organic and inorganic materials existed was suggested by David (2).

In determining the heat capacities of milk fat, two temperatures were arbitrarily selected which would represent the fat in either solid or liquid form. The −43 C temperature, representing the solid form, was just slightly below the onset of melting. A tabulation of the heat capacities of milk fat at −43 and 70 C is given in Table II. A prior work on the heat capacity of milk fat gave a value of .524 cal/g/C at 74 C (5).

The application of DTA calorimetry to heat capacity measurements, though demonstrated here only with milk fat, should be useful with other fats and oils. A decided advantage of this method, where extremely high accuracy is not desired, is the small sample requirement and the ease and rapidity of the determination.

REFERENCES

1. Yoncoskie, R. A., JAOCS *44*, 446 (1967).
2. David, D. J., Anal. Chem. *36*, 2162 (1964).
3. Wendlandt, W. W., "Delta Therm," Application Note No. 58, Technical Equipment Corporation, Denver, Colorado.
4. Mikhaylov, I., Mol. Prom. *10*(1), 25 (1949).
5. Mattil, K. F., F. A. Norris, A. J. Stirton and D. Swern, "Bailey's Industrial Oil and Fat Products," D. Swern editor. Interscience, New York, 1964.
6. Hodgman, C. D., "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, 1960.
7. Furukawa, G. T., R. E. McCloskey and G. J. King, J. Res. Nat. Bur. Std. *47*, 256 (1951).