Journal of Thermal Analysis, Vol. 34 (1988) 1321–1326

DETERMINATION OF SPECIFIC HEATS OF SOME EDIBLE OILS AND FATS BY DIFFERENTIAL SCANNING CALORIMETRY

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(Received October 14, 1987)

Measurements of specific heat as a function of temperature were carried out with a differential scanning calorimeter on rape-seed, soybean, sunflower and corn oils and on lard.

A knowledge of the specific heats at constant pressure (c_p) of edible oils and fats is of importance in determining the net heat fluxes in all heating and cooling processes involving these products. It is also of considerable value in estimating the rise in temperature for a given set of heat transfer conditions. In the fat industry, c_p values relating to low temperatures are used to distinguish between various polymorphic forms of fats which melt or crystallize to show a particularly complex polymorphism. At elevated or high temperatures, c_p values are often necessary for engineering design purposes in such processes as deep-frying, deodorization and hydrogenation of oils, etc. For the determination of specific heats, classical calorimetric methods are traditionally used, but they are often tedious and time-consuming, and relatively large amounts of samples are necessary for measurements. At high temperatures, their precision can be drastically reduced, due to difficulties with the temperature control of viscous samples and the prolonged duration of determination when oxidative decomposition of fats has to be suppressed.

In recent years, thermoanalytical techniques have been extensively developed for studying the thermal properties [1–9] and oxidative resistance [10–15] of glycerides and edible oils and fats. Among these methods, differential scanning calorimetry seems to be the most valuable.

When an oil or fat is heated in a DSC cell and does not undergo a physical or chemical change, the DSC curve in the resulting thermogram is still usually offset from the theoretical baseline. This is primarily due to the difference in the heat capacities of the test and reference samples. The magnitude of the endothermic

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offset provides us with a means of estimating specific heats at constant pressure. In this paper, the use of DSC in determining the c_p values of some popular edible oils and fats above their melting temperatures is reported.

Experimental

Materials

Commercial rape-seed, soybean, sunflower and corn oils and lard were used. Apart from the corn oil, the materials were products of local factories in Warsaw. The corn oil was an imported product from the USA, and only this oil was artificially inhibited against autoxidation through the addition of TBHQ + citric acid solution in propylene glycol, as stated on the packing box. The fatty acid compositions of samples were determined via a standard GLC procedure [16], with a column packed with 10% PEGA on Chromosorb W and a Pye-Unicam apparatus. The results of GLC analysis are listed in Table 1. In order to protect the samples from uncontrolled autoxidation, they were kept at 280 K under nitrogen in darkness, packed in glass ampoules.

Apparatus and method

A DuPont 1090 B thermal analyser and a DuPont 990 differential scanning calorimeter equipped with a normal pressure cell were used. Calibration of the instrument was carried out with a high-purity indium metal standard. Oils or lard were homogenized at 360 K, and samples weighing several milligrams were placed

Table 1 Fatty acid compositions of fats studied

Fatty acid C_m^{n*}	Rape-seed oil	Soybean oil	Sunflower oil	Corn oil	Lard
	Percentage contents of fatty acids				
C_{14}^0	0.09				1.21
C_{16}^0	4.14	8.36	6.45	8.51	24.00
C_{16}^1	0.30				2.79
C_{18}^0	1.35	3.36	4.84	1.40	12.69
C_{18}^1	51.32	23.62	21.67	25.31	51.24
C_{18}^2	22.95	57.78	66.33	63.32	5.70
C_{18}^3	1.55	1.32	0.68	0.42	0.74
C_{20}^0	8.03	5.55		1.03	1.63
C_{20}^1	3.28				
C_{22}^1	6.98				

* m is number of carbon atoms, and n is number of double bonds

in aluminium pans, positioned in the calorimeter heating chamber and heated at a rate of 20 deg min^{-1}. The reference pan was left empty. The experiments were performed in static air atmosphere or under nitrogen.

Procedure

In the measurements of c_p for the samples studied, two DSC experiments were necessary for each determination. In the first, the instrument was operated under the desired conditions, with no sample in either the sample or reference pans, which were chosen to be as identical as possible and covered with lids, but not closed hermetically. The resulting heat flow curve was recorded. In the second experiment, the sample was placed in one pan, with the reference pan left empty, and both pans were closed with lids by means of a DuPont press. The lids of the pans were punctured with a fine needle, and the experiment was then repeated under the same conditions as for the first run. Because of the change in heat capacity resulting from the presence of the sample, a new offset for the heat flow curve was obtained. The difference between the blank and sample offset thermograms was used to calculate the specific heat at constant pressure. As the experiments were carried out with programmed increases of temperature, the series of c_p values could be calculated directly. All results obtained were the averages of at least triplicate determinations.

Results and discussion

Examples of scans in blank/sample pairs of experiments are shown in Figs 1 and 2. The specific heats of the sample at any temperatures were calculated by using the following expression:

$$c_p[\mathrm{J\,K^{-1}\,g^{-1}}] = \frac{60E\Delta h_s}{\mathrm{HR}}\frac{\Delta Y_i}{m} \qquad (1)$$

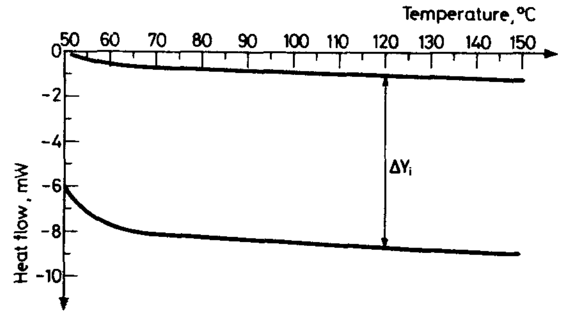

Fig. 1 Blank [top line] and sample [bottom line] DSC scans for rapeseed oil. Heating rate 20 deg/min, size 12.5 mg

where E is the cell calibration coefficient determined in the calibration procedure with the high-purity indium metal standard, Δh_s is the Y-axis range setting, HR is the heating rate, m is the mass of sample, and ΔY_i is the measured difference in the positions of the blank/sample thermograms at the desired temperature T_i, as shown in Fig. 1. As the masses of the empty sample and reference pans used were almost identical, no corrections were applied to Eq. (1).

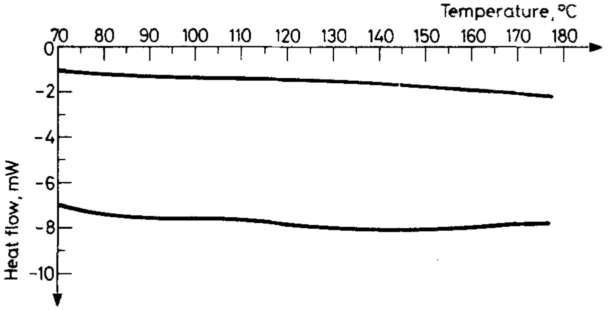

Fig. 2 DSC blank/sample scans performed under nitrogen for sunflower oil. Heating rate 20 deg/min, size 10.0 mg, in nitrogen 6 dm^3/h

Table 2 Experimental specific heats (c_p) and these calculated from Eq. (2) for the materials studied

Temp., K	Specific heat (c_p) J K^{-1} g^{-1}									
	Rape-seed oil		Soybean oil		Sunflower oil*		Corn oil		Lard	
	exper.	calcul.	exper.	calcul.	exper.	calcul.	exper.	calcul.	exper.	calcul.
343	1.953	1.9524	1.892	1.9084			2.033	2.0376	1.891	1.8911
348	1.957	1.9587	1.936	1.9235	1.992	2.0002	2.055	2.0500	1.895	1.8955
353	1.965	1.9651	1.946	1.9378	2.018	2.0119	2.064	2.0614	1.899	1.9000
358	1.978	1.9717	1.957	1.9512	2.025	2.0230	2.071	2.0717	1.907	1.9046
363	1.981	1.9785	1.964	1.9638	2.038	2.0337	2.080	2.0809	1.910	1.9094
368	1.984	1.9854	1.972	1.9756	2.047	2.0438	2.087	2.0891	1.914	1.9146
373	1.986	1.9925	1.984	1.9865	2.054	2.0535	2.097	2.0963	1.921	1.9202
378	1.991	1.9997	1.992	1.9965	2.057	2.0626	2.103	2.1025	1.925	1.9262
383	2.004	2.0071	2.000	2.0058	2.067	2.0712	2.106	2.1076	1.933	1.9328
388	2.017	2.0147	2.016	2.0142	2.077	2.0793	2.112	2.1116	1.936	1.9400
393	2.030	2.0224	2.024	2.0217	2.086	2.0869	2.115	2.1147	1.948	1.9480
398	2.035	2.0303	2.031	2.0285	2.099	2.0939	2.117	2.1166	1.960	1.9567
403	2.043	2.0383	2.035	2.0343	2.092$^+$		2.074$^+$		1.967	1.9664
408	2.046	2.0464	2.039	2.0394	2.041$^+$		2.055$^+$		1.979	1.9770
413	2.048	2.0548					2.049$^+$		1.986	1.9886

* Experiments performed in nitrogen atmosphere.

$^+$ Data not included in correlation.

Table 3 Coefficients of Eq. (2) for the samples studied

Coefficient	Rape-seed oil	Soybean oil	Sunflower oil	Corn oil	Lard
a_0	1.8928	-1.1356	-0.6634	-1.2917	-2.8049
a_1	$-0.8973\cdot10^{-3}$	$0.1464\cdot10^{-1}$	$0.9492\cdot10^{-2}$	$0.1683\cdot10^{-1}$	$0.3924\cdot10^{-1}$
a_2	$0.3122\cdot10^{-5}$	$-0.1681\cdot10^{-4}$	$-0.1021\cdot10^{-4}$	$-0.2078\cdot10^{-4}$	$-0.1116\cdot10^{-3}$
a_3					$0.1083\cdot10^{-6}$
Stand. dev.	0.0049	0.0069	0.0047	0.0074	0.0017

The values of c_p obtained from the experiments are listed in Table 2; they were correlated with the well-known form of the equation

$$c_p = \sum_{i=0}^{k} a_i T^i \tag{2}$$

where a_i are adjustable coefficients and T is absolute temperature. The coefficients a_i were calculated by means of the least squares method and are listed in Table 3. The number (k) of coefficients was optimized until the best fit was obtained.

During the experiments, it became clear that sunflower oil is too unstable to be measured in a reasonable range of temperatures in air atmosphere. At temperatures above 380 K, sunflower oil undergoes autoxidation, and the exothermal effect of this reaction moves the recorded DSC curve upward. Accordingly, the experiments for this oil were repeated in nitrogen atmosphere. Under nitrogen, the exothermal effect was shifted towards higher temperatures, but not completely suppressed. This shows that, for highly unsaturated oils, there are also exothermal events other than oxidation in heated samples. The results obtained showed that, in the temperature ranges studied, the specific heats of the samples do not vary substantially; the values of 2.00 J K^{-1} g^{-1} for rape-seed and soybean oils, 2.05 J K^{-1} g^{-1} for sunflower oil, 2.10 J K^{-1} g^{-1} for corn oil and 1.93 J K^{-1} g^{-1} for lard can be recommended for engineering design purposes.

Because of the specific character of the samples studied, a direct comparison of the results with literature data was not possible. However, published [4, 17] values of c_p for related substances show that the results reported here fit the data reported in the literature.

References

1 N. V. Lovegren and M. S. Gray, J. Amer. Oil Chem. Soc., 55 (1978) 310.

2 N. V. Lovegren and M. S. Gray, J. Amer. Oil Chem. Soc., 55 (1978) 601.

3 K. Kawamura, J. Amer. Oil Chem. Soc., 57 (1980) 48.

4 M. Ollivon and R. Perron, Thermochim. Acta, 53 (1982) 183.

5 S. M. Dyszel, Thermochim. Acta, 57 (1982) 209.

6 M. Ollivon and R. Perron, Proc. 16th ISF Congress, Budapest, 1983, pp. 107–116.

7 J. W. Hampson and H. L. Rothbart, J. Amer. Oil Chem. Soc., 60 (1983) 1102.

8 J. W. Hagemann and J. A. Rothfus, J. Amer. Oil Chem. Soc., 60 (1983) 1123.

9 J. Schlichter, S. Sarig and N. Garti, Thermochim. Acta, 85 (1985) 517.

10 C. K. Cross, J. Amer. Oil Chem. Soc., 47 (1970) 229.

11 J. Śliwiok and T. Kowalska, Thermochim. Acta, 3 (1972) 247.

12 R. L. Hassel, J. Amer. Oil Chem. Soc., 53 (1976) 179.

13 M. Yamazaki, A. Nagao and K. Komamiya, J. Amer. Oil Chem. Soc., 57 (1980) 59.

14 M. Wesołowski, Seifen, Öle, Fette, Wachse, 82/7 (1986) 231.

15 B. Kowalski, Acta Aliment. Polonica, (1988) in print.

16 O. R. Schupp, Gas Chromatography (Polish translation), PWN, Warszawa 1972.

17 A. E. Bailey, Melting and Solidification of Fats, Interscience, London 1950.

Zusammenfassung — Es wurden Messungen der spezifischen Wärme als Funktion der Temperatur von Raps-, Soia-, Sommerblumen- und Mais-ölen und von Schmalz mit Hilfe von einem Dynamische-Differenz-Kalorimeter durchgeführt.

Резюме — С помощью дифференциального сканирующего калориметра были измерены удельные теплоемкости рапсового, соевого, подсолнечного и кукурузного масел, а также свиного сала.