

HEAT CAPACITIES OF SIX LIQUID ESTERS AS A FUNCTION OF TEMPERATURE

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Heat capacities along the saturation line have been measured in a recently designed calorimeter from the temperature of 293 K up to the temperature given in parentheses behind the esters measured: methyl formate (298 K), ethyl acetate (340 K), butyl acetate (364 K), methyl propionate (342 K), ethyl propionate (348 K), and propyl propionate (367 K).

Even though the first measurements of heat capacities of liquid esters of fatty acids date back to the last century¹⁻³, only very few direct experimental data, except for ethyl acetate, have since appeared. In 1886, R. Schiff² measured 27 esters altogether and drew the conclusion that the specific heat capacity (c , $\text{J g}^{-1} \text{K}^{-1}$) of all esters of fatty acids in the liquid state was the same function of temperature t ($^{\circ}\text{C}$)

$$c = 1.848 + 0.0037t. \quad (1)$$

For 20°C this equation gives the value of $1.922 \text{ J g}^{-1} \text{K}^{-1}$ ($0.459 \text{ cal g}^{-1} \text{K}^{-1}$), which is still cited in a number of thermodynamic tables (Lange's Handbook of Chemistry; Hodgman: Handbook of Chemistry and Physics; International Critical Tables; etc.). In 1979 there appeared a study by Fuchs⁴, who, using a simple isoperibolic calorimeter, measured a greater number of esters at the temperature of 298.15 K . Apart from that, three studies on butyl acetate⁵⁻⁷ and several measurements on ethyl acetate^{1,3,8-13} are known. Ethyl propionate and propyl propionate, as far as we know, have not been remeasured in this century.

EXPERIMENTAL

Calorimeter. All the measurements were performed in a newly designed calorimeter with optimized heat flow between the warmer calorimetric vessel and the colder basic thermostatted wall. Whereas in a strictly adiabatic calorimeter the aim is to prevent any heat exchange between the vessel and the surroundings, in the calorimeter described this heat flow is purposely kept and controlled to be optimum and measurable. In our laboratory this principle has been used

for the vaporization¹⁴ and mixing¹⁵ calorimeters (in the papers^{14,15} are also described used electric circuits). The first attempt to use the mixing calorimeter for measuring heat capacities was made several years ago¹⁶. The new device differs from the foregoing one in the change of temperature during measurement (in practice both the calorimeters^{14,15} work isothermally), in the design of the calorimetric vessel and some improvements of electrical circuits.

The removable calorimetric vessel, cylindrical in shape and with the wall 1 mm thick, is made of silver and is gold-plated on its inner surface. Inside the vessel of 35 ml volume are built-in parts of gold-plated silver sheet. When at work, the vessel is tightly sheathed into a silver housing (wall 1 mm thick), on which a manganin heater to supply the accurately measured energy and a platinum resistance thermometer are coiled. A similar thermometer is coiled on the basic thermostatted wall (called¹⁴ isothermal adiabatic jacket) surrounding the calorimetric vessel, and both are connected into a single bridge which regulates the temperature of the vessel so that it is by 0.01–0.5°C warmer than the wall (the operator can set this temperature difference manually). Both the vessel and the wall are placed concentrically inside the outer thermostat whose temperature is by 0.4–0.8°C lower than that of the basic thermostatted wall. The whole device is placed in a water thermostat maintained at 17°C to prevent the influence of the fluctuation in ambient temperature. The temperature inside the calorimeter is measured by a 100 Ω resistance thermometer (Degussa, Hanau) sheathed tightly into the well inside the calorimetric vessel. The thermometer was calibrated by means of the triple point of water and at each 8°C up to 90°C by means of mercury-in-glass calorimetric standard thermometers. The measurement is carried out by means of QLK compensator and a Tettex 6141 galvanometer. The other electric circuits and the calorimetric control unit are very similar to the vaporization calorimeter described formerly¹⁴. The calorimeter in this arrangement is capable of measuring from the ambient temperature up to about 100°C.

Measuring procedure. After being removed from the housing, the calorimetric vessel was filled with the substance to be measured up to the upper closure, and after being cooled down to –70°C, a part of the substance and air were exhausted from it by a rotary air pump so that a small vapour space might remain in the vessel. The vessel was closed under vacuum, weighed, placed again in the housing, and tempered. Then the temperature of the sample and the thermal loss flow in the preparatory period were determined. In the main period, the temperature of the basic thermostatted wall was increased, and the energy needed to heat the substance to the final temperature was measured. During the measurement, the temperature was increased approximately by 3.5 or 6 K, and the steady state was attained within 16 or 21 minutes, respectively. In the last period, the final temperature and the thermal loss flow were measured. The last period was simultaneously a preparatory period for the next measurement.

The heat capacity of the calorimetric vessel itself and its housing was measured by using heptane as a thermodynamic standard, whose heat capacities as a function of temperature were taken from the study¹⁷. The calculation of the heat capacity along the saturation line C_s was carried out by dividing the amount of energy supplied during the main period (reduced by average thermal loss flow before and after the main period) by the value of the temperature increase and by subtracting the heat capacity of the calorimeter itself. No corrections for the vapour space or evaporation were applied because they proved to be negligible with regard to the accuracy of the measurement. Since the calculated heat capacities are in fact average values taken in the interval of temperature increase, the polynomial dependence of heat capacity on temperature T was used in the form

$$C_s = A_1 + A_2 T + A_3 T^2, \quad (2)$$

and the correction for curvature¹⁸ was made. The calculated C_s were then related to the arithmetic mean of the initial and final temperatures.

Substances used. Methyl formate was prepared by esterification of methyl alcohol and formic acid in the presence of sulphuric acid. The other substances available were commercial products of "p.a." or "pure" grade. All the esters used were purified by anhydrous calcium chloride, shaken with calcined potassium carbonate and dried with molecular sieve A3 for a week. On distilling on a packed column, they were collected into flasks with molecular sieves which had been dried. Their purity was checked by means of a Joel JMS-DX303 mass spectrometer with the following results: methyl formate 96.2 mass %, ethyl acetate 100 mass %, butyl acetate 98.7 mass %, methyl propionate 96.5 mass %, ethyl propionate 100 mass %, propyl propionate 97.9 mass %. The major part of impurities are unreacted alcohols. Heptane, a product of Loba Chemie Wien-Fischamend, "p.a." grade, was also distilled on a column and dried with molecular sieve A3. Its purity was checked by measuring the following physical constants: refractive index n_D^{25} 1.3853 (literature data¹⁹ 1.38511), density at 25°C 0.67960 kg dm⁻³ (literature data¹⁹ 0.67951 kg dm⁻³).

RESULTS AND DISCUSSION

From the ratio of heat capacities of the vacant calorimetric vessel and of its content, which equals approximately 1, it is possible to infer a sufficient sensitivity of the device. Considering that heptane was used to determine the heat capacity of the vessel, any further measurement is subject to the error with which the heptane heat capacity was determined. An analysis of the errors in measurement carried out three years ago²⁰ showed that the maximum error did not exceed 0.5%, which was verified by measuring ethanol and comparing with literature data. This value was affected by uncertainties in determining the thermal loss flows before and after the main period, approximately 0.1%, the errors in electric measurements and in weighing the vessel content amounting to 0.05% each and the error in determining the temperature difference ranging, according to the temperature increase, from 0.06 to 0.1%. Most of the error, however, was caused by the operator himself when manually switching over the levels of heating powers in the main period (which cannot be estimated numerically) and by the up-to-now not yet completely solved calorimetric vessel closure (about 0.1%).

The first shortcoming will be removed by a digital control of heating power of the calorimetric vessel by means of a microcomputer simultaneously performing the data collection for an automatic data processing. As to the calorimetric vessel closure, the Teflon packing hitherto used becomes plastic owing to the temperature and pressure effects, and on increasing temperature, the substance leakage takes place (about 0.05 mass %), which calls for correction (on the assumption of a linear decrease of the substance with temperature and time). Other ways of packing, such as with a metallic ball, steel needle, or lead packing, have not proved to be a good solution either.

The measured values of molar heat capacities on the saturation line C_s (in limits of accuracy identical with isobaric heat capacities C_p) for all 6 esters measured are given in Table I. For ethyl acetate and butyl acetate, the values determined are in addition plotted in the graphs (Figs 1 and 2) to compare them with the literature values

TABLE I

Measured values of molar heat capacities C_s ($\text{J K}^{-1} \text{mol}^{-1}$) as a function of temperature T (K). M is molecular mass (g mol^{-1})

T	C_s	T	C_s	T	C_s
Methyl formate ^a $M = 60.05$					
293.26	115.12	295.15	116.94	298.75	120.57
Ethyl acetate ^b $M = 88.11$					
293.79	169.69	312.07	174.12	330.54	178.24
298.32	170.59	316.67	175.12	335.14	179.17
302.91	171.00	321.31	175.90	340.33	181.96
307.49	172.95	325.93	177.09		
Butyl acetate ^c $M = 116.16$					
293.76	227.30	321.37	234.41	344.36	240.42
298.35	228.11	325.97	235.79	348.96	243.50
302.94	229.00	330.58	236.74	353.57	244.92
307.53	230.00	335.19	238.68	358.72	246.02
312.16	231.30	339.81	239.47	363.83	248.15
316.76	233.26				
Methyl propionate ^d $M = 88.11$					
295.72	174.02	312.92	176.89	330.16	178.24
301.45	174.60	318.67	177.17	335.92	178.79
307.19	175.56	324.41	177.80	341.69	179.25
Ethyl propionate $M = 102.13$					
293.87	199.04	316.67	202.08	335.07	205.57
298.33	199.58	321.28	202.91	339.67	207.78
302.91	200.10	325.88	203.91	344.28	209.17
307.50	200.78	330.48	204.08	348.89	210.61
312.08	201.32				
Propyl propionate $M = 116.16$					
293.78	228.01	321.29	236.77	348.94	242.59
298.38	229.00	325.90	237.53	353.57	244.08
302.95	231.53	331.09	238.40	358.18	246.20
307.46	232.75	335.75	239.22	362.80	247.39
312.09	233.21	339.77	239.90	367.29	249.14
316.70	234.45	344.34	241.95		

^a 119.7 ± 0.5 at 298.15 K by Fuchs⁴; 129.6 at 293.15 K by Berthelot³; 121.35 ± 1.76 at 288.15 K by Mehl²². ^b 167.7 ± 0.7 and 167.4 ± 0.1 at 298.15 K by Fuchs⁴; 169.22 at 293.6 K by Parks⁸; 170.94 at 288.15 K by Schmidt¹³; 169.5 at 298.15 K and 173.9 at 313.15 K by Roux¹¹; 168.8 at 303.61 K and 170.7 at 319.13 K by Zhdanov¹⁰; selected value 170.6 at 298.15 K by Wilhoit²¹. ^c 228.4 ± 0.4 at 298.15 K by Fuchs⁴; 242.1 at 292.51 K by Kolosovskii⁵. ^d 174.5 ± 0.4 and 173.6 ± 0.5 at 298.15 K by Fuchs⁴.

given in notes under Table I. The constants A_1 , A_2 , and A_3 of Eq. (2) were computed by the least-squares method from our values. An exception was methyl formate for which, owing to its low boiling point, only three values were measured and these

TABLE II

Constants of Eq. (2) of the dependence of molar heat capacity C_s ($\text{J K}^{-1} \text{mol}^{-1}$) on temperature T (K) valid in temperature range ($T_1 - T_2$) (K)

Substance	($T_1 - T_2$)	A_1	A_2	$A_3 \cdot 10^3$	$\bar{\delta}^a$	σ^b
Methyl formate	293–299	–176.63	0.99478	–	0.024	0.045
Ethyl acetate	293–340	205.93	–0.44660	1.1000	0.31	0.45
Butyl acetate	293–364	246.89	–0.36624	1.0165	0.33	0.43
Methyl propionate	295–342	12.316	0.91943	–1.2615	0.13	0.21
Ethyl propionate	293–349	429.35	–1.6134	2.8267	0.25	0.37
Propyl propionate	293–367	174.34	0.11484	0.2373	0.47	0.61

^a Mean deviation $\bar{\delta} = (\sum |d_i|)/N$. ^b Standard deviation $\sigma = [(\sum d_i^2)/(N - 3)]^{1/2}$, where d_i is the difference between the measured and calculated value of C_s for individual points and N is the total number of the points measured.

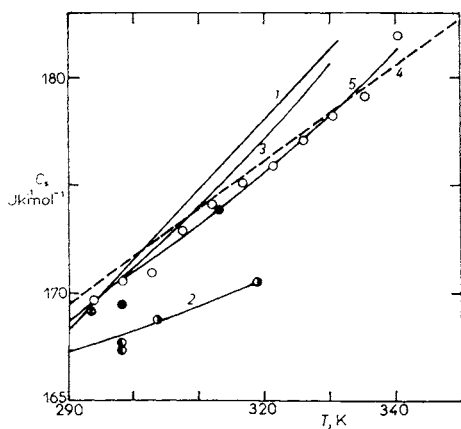


FIG. 1

Dependence of heat capacity C_s ($\text{J K}^{-1} \cdot \text{mol}^{-1}$) on temperature T (K) for ethyl acetate. Curves: 1 Schiff², 2 Zhdanov¹⁰, 3 Wilhoit²¹, 4 Karabanov¹², 5 our measurements. Points: \bullet Fuchs⁴, \odot Parks⁸, \bullet Zhdanov¹⁰, \bullet Roux¹¹, \circ our measurements

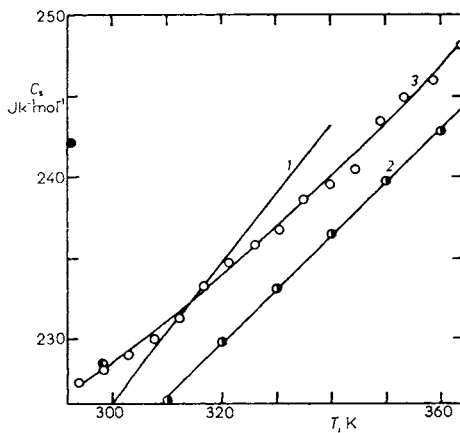


FIG. 2

Dependence of heat capacity C_s ($\text{J K}^{-1} \cdot \text{mol}^{-1}$) on temperature T (K) for butyl acetate. Curves: 1 Schiff², 2 Vasilev⁶, 3 our measurements. Points: \bullet Fuchs⁴, \bullet Balakina⁷, \bullet Kolosovskii⁵, \circ our measurements

were treated in terms of a two-constant linear dependence. The values of constants for the esters measured are given in Table II.

The dependence of heat capacity on temperature for ethyl acetate is depicted in Fig. 1, where are plotted the measured values (points) and the correlated functions (lines). Straight line 1 represents Eq. (1) proposed by Schiff², which is in good agreement with curve 3 calculated by Wilhoit and coworkers²¹, who in their compilation stemmed from data^{1,4,8,11}, for the temperatures above 303 K only very old data by Favre and Silberman¹ (from 1846) having been available obtained as mean values in a wide temperature range by means of a drop calorimeter. Our data 5 are in relatively good agreement with straight line 4 calculated by Karabanov and Chastukhina¹² from the data presented in different Soviet "spravochnik's" (not specified further). Of course, the linear dependence of C_p on T may not be valid in the whole temperature range of applicability of their equation (0–77°C). Rather different are the data and curve 2 obtained from only 3 values by Zhdanov¹⁰. Two measurements by Kurnakov and Voskresenskaya⁹ were not considered at all. These authors do not report precisely the temperature, and the reproducibility of their data is 12%.

Fig. 2 represents the same dependence for butyl acetate. Straight line 1 depicting the Schiff² equation (1) has another slope than our data 3, but in the vicinity of 310 K, which corresponds to the mean temperature of his measurement, the agreement is very good. The same holds for the only value by Fuchs⁴. The data reported in papers by Vasilev and coworkers^{6,7} show a systematic deviation about $4 \text{ J K}^{-1} \cdot \text{mol}^{-1}$ (about 1.7%) from our data. Particular values by 10 K are given in the study⁷ whereas in the paper⁶ there are constants for an equation valid within the range of 6.85–97°C. As it is obvious from Fig. 2, the same correlated data are referred to, for which the authors give the accuracy of 0.3–1%. The only mean value by Kolosovskii and Udovenko⁵ is plainly wrong.

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