

Heat Capacity Measurements of 13 Methyl Esters of *n*-Carboxylic Acids from Methyl Octanoate to Methyl Eicosanoate between 5 K and 350 K

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Molar heat capacities of 13 methyl esters of the linear carboxylic acids from methyl octanoate to methyl eicosanoate were measured from 5 K to 350 K. The derived thermodynamic functions $S_{\text{abs,m}}(T)$ and $H_{\text{m}}(T) - H(0)$ were calculated. A correlation function for the absolute entropy at 298.15 K was found to be $S_{\text{abs}}(n, 298.15 \text{ K}) = \{215.94 + 31.517n\} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, with n being the number of carbon atoms in the parent carboxylic acid minus one. The heat capacity of the liquid phases in the temperature range of 250 K to 350 K can be described by $C_{\text{p}}(n, T) = \{103.16 + 16.273n + 0.04735n(T/K)\} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, with a mean absolute percentage deviation of 0.3%.

Introduction

In this article, we report on the measurement of the molar heat capacity of 13 methyl esters of the normal carboxylic acids with a chain length of 8–20 carbon atoms in the fatty acid group. The measurements were made using adiabatic calorimetry. This work was part of a thesis¹ of one of us (van Bommel) who finished this work in 1986. The data collected were only published in the thesis, and in order to make them more generally available, we present here the data in a concise form. The methyl ester of the carboxylic acids form a homologous series which allowed us to look for relations within the series, like the dependence of the absolute entropy and the heat capacity of the liquid phase, on the chain length. The vapor pressure of these liquid esters was published before.²

The methyl esters form an important group of organic compounds that are used in the production of very different derivatives, often they replace fatty acids in the production.^{3,4}

Experimental Section

The samples used were purchased from MERCK. The compounds were readily available as they are used as gas–liquid chromatography references. Because of the high purity of the samples, no attempt was made to purify them further; the stated purity and the masses used in the calorimeter are given in Table 1. The adiabatic calorimeter used (laboratory design number CALV) was described before.^{5,6} Samples were transferred to the gold-plated sample container and degassed in a vacuum. Before closing the vessel, a helium pressure of about 5 kPa was admitted in order to improve the heat conduction within the vessel. Temperatures were measured using an automated ASL bridge;⁷ the thermometer was calibrated by Oxford Instruments to 0.001 K on the International Practical Temperature Scale of 1968. The performance of the calorimeter

Table 1. Purity of the Compounds as Stated by the Manufacturer and Masses Used in the Calorimetric Experiments

compound	purity/mass %	used mass/g
methyl octanoate	99.8	4.99
methyl nonanoate	99.7	5.56
methyl decanoate	99.8	6.83
methyl undecanoate	99.5	6.03
methyl dodecanoate	99.5	4.50
methyl tridecanoate	99.9	7.67
methyl tetradecanoate	99.5	6.92
methyl pentadecanoate	99.6	6.92
methyl hexadecanoate	99.3	4.61
methyl heptadecanoate	99.0	7.87
methyl octadecanoate	99.0	3.78
methyl nonadecanoate	99.7	7.41
methyl eicosanoate	99.1	3.56

was checked with *n*-heptane and synthetic sapphire;⁸ no deviations from the recommended values larger than 0.2% were found. The methyl esters of the carboxylic acids do show polymorphic behavior and to exclude or minimize effects caused by the thermal history, all samples were treated in the same way. First they were cooled to about 80 K using liquid nitrogen in the cryostat, and then a slow measurement was made with a mean heating rate of about 1.4 K·h⁻¹ to (2 or 3) K below the melting point. At that temperature, the samples were equilibrated for 24 h. In this first heating experiment, some metastability, in the form of a slightly higher heat capacity than in the subsequent measurements and some irregularities, could be detected in methyl tridecanoate, methyl pentadecanoate, and methyl heptadecanoate. After equilibrating the samples close to the melting temperature, these effects have disappeared in the following runs. Subsequently the samples were cooled in a period of 36 h to a temperature of 5 K. Below 80 K, a heater on time was used, which resulted in a temperature rise of 2 K per measurement; the stabilization time used was on the order of 600 s. Above 80 K, a stabilization time of 2000 s and an input time of 1500 s were used. Under these measurement conditions, the melting process generally took 24 h.

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Table 2. Thermodynamic Properties of Methyl Octanoate at Selected Temperatures (M = 158.24 gmol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.38	0.13	0.48	120	138.74	131.31	8830	240	301.67	366.89	57286
10	3.03	1.04	7.65	130	146.18	142.71	10255	250	301.39	379.17	60294
20	18.19	7.36	107.6	140	153.44	153.81	11753	260	303.17	391.02	63317
30	33.71	17.65	366	150	160.31	164.63	13322	270	305.83	402.52	66362
40	50.53	29.66	788	160	167.13	175.20	14959	280	308.83	413.69	69435
50	66.36	42.67	1374	170	174.18	185.53	16664	290	312.81	424.59	72543
60	79.75	56.01	2108	180	181.34	195.69	18442	300	316.17	435.25	75688
70	92.33	69.26	2968	190	188.84	205.69	20292	310	320.13	445.67	78870
80	103.39	82.28	3945	200	196.94	215.58	22220	320	323.19	455.9	82086
90	113.40	95.04	5030	210	205.99	225.99	24234	330	327.93	465.92	85342
100	122.25	107.48	6211	220	217.68	235.24	26349	340	332.21	475.77	88643
110	131.10	119.57	7480	230	242.75	245.34	28621	350	336.19	485.46	91985

Table 3. Thermodynamic Properties of Methyl Nonanoate at Selected Temperatures (M = 172.27 gmol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.39	0.13	0.48	120	152.28	140.43	9572	240	330.80	395.87	61702
10	2.96	1.03	7.69	130	160.47	152.94	11136	250	330.84	409.95	65148
20	17.17	7.11	103.6	140	168.48	165.13	12782	260	333.42	422.98	68471
30	34.66	17.30	361	150	175.96	177.01	14504	270	335.90	435.62	71816
40	53.39	29.83	801	160	183.23	188.61	16301	280	338.72	447.87	75188
50	71.31	43.70	1426	170	190.85	199.93	18170	290	342.82	459.82	78595
60	86.46	58.06	2216	180	198.49	211.06	20116	300	346.27	471.49	82040
70	100.55	72.47	3152	190	206.56	222.00	22142	310	350.79	482.91	85526
80	113.08	86.73	4222	200	215.27	232.82	24250	320	354.3	494.10	89051
90	123.98	100.68	5407	210	224.62	243.54	26449	330	359.10	505.08	92618
100	134.32	114.30	6701	220	236.53	254.26	28751	340	363.82	515.87	96232
110	143.79	127.55	8092	230	265.31	265.22	31219	350	368.16	526.47	99892

Table 4. Thermodynamic Properties of Methyl Decanoate at Selected Temperatures (M = 186.29 gmol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.45	0.15	0.56	120	160.63	150.10	10150	240	269.17	292.11	35440
10	3.70	1.12	8.36	130	169.23	163.30	11799	250	300.63	303.61	38258
20	20.01	8.17	119.6	140	177.35	176.14	13532	260	540.13	320.00	41290
30	37.87	19.64	408	150	185.25	188.64	15345	270	361.09	465.32	80090
40	57.28	33.19	884	160	192.99	200.86	17238	280	368.72	478.68	83762
50	75.63	47.99	1550	170	200.77	212.79	19206	290	372.12	491.68	87467
60	91.46	63.18	2386	180	209.01	224.50	21256	300	376.14	504.36	91208
70	105.95	78.38	3374	190	217.44	235.02	23387	310	380.31	516.77	94992
80	119.09	93.41	4501	200	226.26	247.40	25606	320	385.19	528.93	98821
90	131.08	108.15	5754	210	234.91	258.65	27913	330	389.78	540.85	102695
100	141.62	122.53	7120	220	245.06	269.81	30311	340	394.95	552.56	106620
110	151.65	136.52	8588	230	256.05	280.93	32814	350	400.20	564.07	110592

Table 5. Thermodynamic Properties of Methyl Undecanoate at Selected Temperatures (M = 200.32 gmol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.42	0.14	0.52	120	173.57	157.96	10835	240	291.77	311.64	38203
10	3.28	1.12	8.36	130	182.89	172.23	12617	250	320.50	324.01	41235
20	18.49	7.63	110.9	140	191.72	186.11	14491	260	576.88	340.00	43904
30	38.09	18.72	391	150	200.53	199.63	16451	270	395.83	494.94	85677
40	59.59	32.61	879	160	209.38	212.87	18503	280	398.95	509.40	89654
50	80.21	48.17	1580	170	217.78	225.81	20638	290	402.95	523.47	93662
60	97.96	64.37	2471	180	226.50	238.50	22859	300	406.99	537.18	97708
70	113.74	80.66	3530	190	235.38	250.00	25169	310	411.22	550.60	101798
80	128.03	96.83	4742	200	244.52	263.29	27568	320	416.08	563.73	105936
90	141.39	112.68	6089	210	253.93	275.45	30060	330	421.78	576.61	110128
100	152.92	128.19	7563	220	264.97	287.51	32654	340	426.55	589.27	114370
110	163.81	143.29	9147	230	276.95	299.55	35363	350	431.52	601.73	118660

Results and Discussion

In Tables 2–14, the molar heat capacity data, the absolute entropy, and the enthalpy difference with reference to 0 K are given at selected temperatures between 5 K and 350 K. These data were calculated from the total measuring sets by extrapolating the heat capacity values below 15 K according to the Debye low-temperature limit

$C_p = \alpha T^3$ and using the value of α to calculate starting values for a numerical calculation of S and $H(T) - H(0)$. The numerical calculation was performed on a data set obtained from the experimental set by using a cubic spline interpolation method.

All compounds showed an increase in the molar heat capacity when nearing the melting point, larger than could be explained by premelting due to impurities. This in-

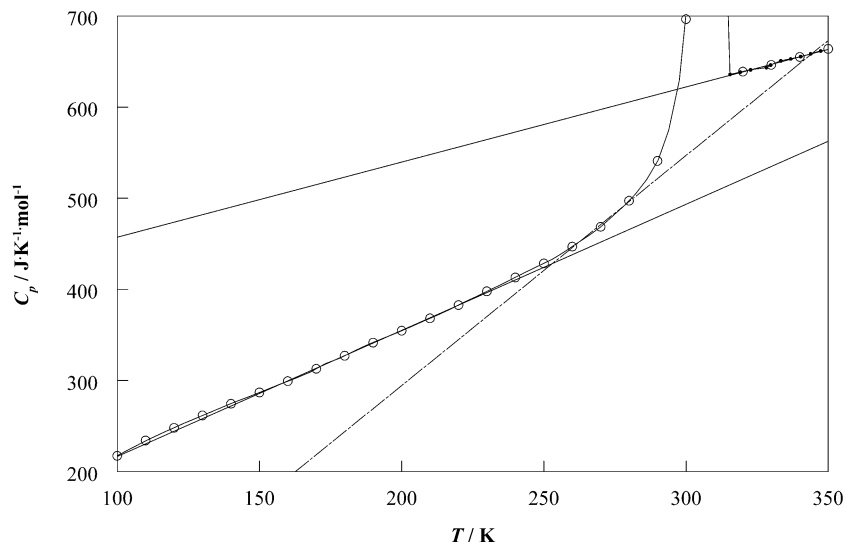


Figure 1. Molar heat capacity of methyl octadecanoate around the melting point showing the anomalous increase of the heat capacity. The solid lines were used as baselines for the calculation of the enthalpy of fusion. See text for the dashed line.

Table 6. Thermodynamic Properties of Methyl Dodecanoate at Selected Temperatures ($M = 214.35 \text{ g mol}^{-1}$)

T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
5	0.50	0.17	0.62	120	181.94	166.91	11406	240	299.95	327.72	40033
10	4.31	1.33	9.95	130	191.82	181.87	13276	250	315.69	340.29	43115
20	19.62	8.52	122	140	201.16	196.43	15241	260	335.52	353.03	46364
30	40.21	20.22	418	150	209.76	210.61	17297	270	392.98	366.39	49905
40	63.08	34.91	934	160	218.85	224.46	19444	280	428.00	535.85	97029
50	85.07	51.39	1677	170	227.97	238.00	21678	290	432.76	551.59	101511
60	103.02	68.57	2622	180	237.26	251.30	24005	300	438.82	566.39	105869
70	119.02	85.73	3738	190	246.66	264.37	26424	310	443.32	580.85	110280
80	134.57	103.76	5014	200	256.21	277.27	28938	320	448.38	595.01	114738
90	148.81	119.42	6430	210	265.84	290.00	31548	330	453.83	608.89	119249
100	160.46	135.69	7975	220	277.21	302.62	34260	340	460.08	622.53	123819
110	171.83	151.52	9638	230	288.57	315.19	37090	350	467.86	635.95	128458

Table 7. Thermodynamic Properties of Methyl Tridecanoate at Selected Temperatures ($M = 228.37 \text{ g mol}^{-1}$)

T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
5	0.53	0.16	0.6	120	195.21	175.72	12105	240	321.07	347.96	42759
10	4.03	1.28	10.58	130	205.64	191.76	14110	250	336.07	361.36	46044
20	19.77	8.36	120	140	215.67	207.37	16217	260	350.98	374.82	49476
30	41.39	20.31	422	150	225.37	222.58	18422	270	371.61	388.43	53083
40	65.69	35.52	957	160	234.95	237.43	20724	280			
50	89.16	52.75	1734	170	244.50	251.96	23121	290	463.91	584.21	108019
60	108.80	70.79	2726	180	254.10	266.21	25614	300	469.05	600.01	112680
70	127.88	88.99	3909	190	264.04	280.21	28205	310	473.89	615.47	117394
80	144.45	107.13	5269	200	274.24	294.01	30896	320	479.30	630.59	122159
90	158.95	124.91	6781	210	284.88	307.65	33691	330	485.18	645.43	126981
100	171.63	142.28	8430	220	296.06	321.16	36595	340	491.82	660.01	131868
110	183.91	159.22	10209	230	307.94	334.58	39614				

crease, leading to a positive second derivative of the heat capacity, started already at about (100 to 50) K below the melting point. In Figure 1, this effect is illustrated for methyl octadecanoate. Similar effects have been reported before, for instance in the *n*-paraffines,⁹ the linear carboxylic acids,^{10,11} and the normal hydrocarbons,¹² where it was explained to be due to an increasing randomization of orientation about the stretched length of the molecule. The enthalpy of fusion of the compounds was calculated by using a linear fit of the solid heat capacity between (150 to 100) K before the melting point as a baseline, together with a fit of the heat capacity of the liquid, using data between (10 to 20) K above the melting point. These fits are shown in Figure 1 for methyl octadecanoate as solid lines. The dashed line, the fit of the heat capacity close to the melting point, is discussed in the comparison of the

enthalpies of fusion with the literature data. The result of these calculations and the end temperatures of the fusion are given in Table 15. These temperatures are not the triple-temple temperatures often reported in adiabatic calorimetry. As the plots of the reciprocal of the melted fraction against the equilibrium temperatures in the melt did not result in straight lines, the fractional melting method based on the van't Hoff relation could not be used. There are two possible explanations for this, one being that the impurity does not form a eutectic system with the main component, the second one being that a possible phase transition is hidden in the melting process. We did not observe any anomaly in the heat capacity curves near the melting point; small exothermic effects however were seen in the stabilization periods at about (2 or 3) K below the end melting point. Aleby¹³ described phase transitions in

Table 8. Thermodynamic Properties of Methyl Tetradecanoate at Selected Temperatures (M = 242.40 g·mol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.55	0.18	0.68	120	203.55	185.01	12685	240	334.49	364.62	44650
10	4.56	1.46	10.93	130	214.52	201.74	14776	250	349.48	378.57	48067
20	21.34	9.38	134.7	140	224.93	218.02	16973	260	368.64	392.64	51655
30	43.99	22.18	458	150	235.23	233.89	19274	270	388.14	406.90	55435
40	69.20	38.26	1023	160	244.79	249.38	21675	280	429.30	421.61	59480
50	93.62	56.37	1839	170	254.91	264.52	24173	290			
60	113.90	75.32	2882	180	265.19	279.39	26774	300	500.03	624.53	118932
70	133.41	94.38	4121	190	275.63	294.00	29478	310	504.66	641.00	123954
80	150.35	113.34	5542	200	286.07	308.41	32287	320	510.00	657.11	129028
90	165.54	131.92	7122	210	296.67	322.62	35201	330	515.86	672.89	134156
100	179.38	150.09	8848	220	308.85	336.69	38225	340	522.03	688.38	139345
110	192.06	167.80	10707	230	321.05	350.68	41373	350	528.04	703.60	144580

Table 9. Thermodynamic Properties of Methyl Pentadecanoate at Selected Temperatures (M = 256.43 g·mol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.50	0.17	0.63	120	216.45	192.35	13347	240	355.90	383.45	47360
10	4.15	1.34	10.05	130	228.03	210.13	15570	250	371.28	398.28	50994
20	21.13	8.62	125	140	239.15	227.44	17906	260	387.35	413.16	54788
30	43.92	21.10	441	150	249.97	244.31	20352	270	403.92	428.06	58735
40	71.36	37.46	1016	160	260.57	260.78	22904	280	432.13	443.24	62911
50	97.58	56.30	1865	170	272.29	276.90	25564	290	740.09	458.95	67386
60	120.37	76.10	2954	180	282.10	292.71	28330	300	524.33	655.54	125101
70	141.42	96.26	4265	190	293.10	308.26	31206	310	534.12	672.98	130483
80	159.35	116.32	5769	200	304.43	323.58	34193	320	539.26	690.02	135850
90	175.80	136.02	7444	210	316.28	338.72	37297	330	544.80	706.70	141270
100	190.15	155.28	9273	220	328.72	353.71	40521	340	551.15	723.05	146750
110	203.86	174.06	11244	230	341.80	368.61	43873				

Table 10. Thermodynamic Properties of Methyl Hexadecanoate at Selected Temperatures (M = 270.45 g·mol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.66	0.22	0.83	120	226.50	205.81	14123	240	372.37	405.82	49721
10	5.56	1.76	13.20	130	238.62	224.42	16449	250	388.24	421.33	53522
20	23.70	10.48	149	140	250.27	242.54	18894	260	405.39	436.89	57490
30	47.98	24.47	503	150	261.54	260.19	21453	270	423.81	452.54	61636
40	75.87	42.05	1120	160	272.73	277.43	24125	280	448.60	468.38	65993
50	104.12	62.04	2021	170	284.03	294.30	26908	290	482.70	484.81	70668
60	129.69	83.35	3194	180	295.27	310.85	29804	300	740.48	505.58	76774
70	151.19	105.13	4610	190	306.80	327.12	32814	310	570.55	708.87	138668
80	167.13	126.24	6193	200	318.65	343.16	35941	320	576.47	727.67	144404
90	184.19	146.91	7949	210	330.97	359.00	39189	330	583.02	746.08	150201
100	198.32	167.01	9858	220	343.93	374.70	42564	340	590.14	764.13	156066
110	213.49	186.66	11921	230	357.74	390.29	46072	350	597.66	781.86	162005

Table 11. Thermodynamic Properties of Methyl Heptadecanoate at Selected Temperatures (M = 284.48 g·mol⁻¹)

<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>	<i>T</i>	<i>C_{p,m}</i>	ΔS_m	<i>H(T) - H(0)</i>
K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	K	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹
5	0.56	0.20	0.73	120	238.40	212.23	14684	240	399.49	424.55	52514
10	4.36	1.56	11.70	130	252.69	231.88	17140	250	418.37	441.22	56600
20	23.27	10.05	145	140	265.74	251.06	19730	260	438.62	458.02	60882
30	48.82	24.13	500	150	275.72	269.67	22428	270	456.93	474.93	65363
40	77.97	42.13	1133	160	284.57	287.87	25250	280	480.24	491.94	70042
50	106.88	62.67	2059	170	302.09	305.64	28181	290	517.76	509.36	75007
60	131.71	84.44	3257	180	313.76	323.23	31259	300	980.45	528.34	80605
70	154.68	106.58	4696	190	326.38	340.53	34461	310	599.17	746.03	147001
80	175.53	128.63	6350	200	340.04	357.50	37769	320	605.44	764.27	152746
90	192.90	150.31	8193	210	355.66	374.47	41248	330	609.25	782.96	158820
100	208.51	171.45	10201	220	367.89	391.26	44859	340	615.40	802.10	165221
110	224.09	192.08	12367	230	382.88	407.90	48603	350	622.81	820.06	171411

the methyl esters which he observed using a temperature-programmable X-ray powder diffraction camera. If the observed exothermic effect were the onset of a transition to a more stable crystal form, this transition is extremely slow, and in that case, the data reported in this publication were measured on a metastable phase. In practice however, this will be the phase most likely to occur.

The melting points clearly show an even-odd effect; in Figure 2, the melting points of the even and odd compounds are plotted.

Comparison with the Literature. Literature data for the heat capacity and derived properties of the methyl esters on which we report here are scarce. For methyl octanoate, two sources are available^{17,18} for the heat

Table 12. Thermodynamic Properties of Methyl Octadecanoate at Selected Temperatures ($M = 298.50 \text{ g}\cdot\text{mol}^{-1}$)

T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
5	0.82	0.28	0.93	120	248.17	224.83	15377	240	413.11	445.45	54763
10	5.96	2.20	16.49	130	261.72	244.83	17927	250	428.51	462.63	58971
20	26.20	12.05	168	140	274.54	264.69	20608	260	446.92	479.77	63342
30	52.72	27.52	599	150	286.99	284.06	23416	270	468.64	497.03	67917
40	82.60	46.74	1234	160	299.33	302.97	26348	280	497.34	514.58	72743
50	112.11	68.38	2210	170	312.93	321.50	29403	290	541.05	532.70	77908
60	137.80	91.14	3462	180	327.18	339.81	32609	300	696.62	552.91	83874
70	162.71	114.27	4966	190	341.65	357.91	35965	310			
80	182.89	137.22	6686	200	354.70	375.77	39438	320	639.00	792.61	159212
90	201.46	159.90	8614	210	368.18	393.93	43052	330	646.44	812.38	165638
100	217.35	181.95	10709	220	382.77	410.86	46806	340	655.14	831.80	172153
110	234.15	203.49	12970	230	397.82	428.20	50708	350	664.03	850.92	178743

Table 13. Thermodynamic Properties of Methyl Nonadecanoate at Selected Temperatures ($M = 312.53 \text{ g}\cdot\text{mol}^{-1}$)

T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
5	0.69	0.23	0.89	120	259.07	233.96	16074	240	432.32	464.04	57053
10	5.10	1.85	13.90	130	273.22	255.26	18734	250	450.65	482.07	61470
20	26.27	11.96	171	140	286.84	276.01	21536	260	469.65	500.10	66067
30	55.13	27.91	574	150	300.17	296.25	24471	270	491.94	518.24	70874
40	87.37	48.15	1285	160	313.53	316.04	27539	280	518.01	536.60	75924
50	117.80	70.82	2308	170	327.31	335.43	30737	290	549.43	555.29	81252
60	143.77	94.67	3619	180	339.52	354.46	34068	300	586.63	574.53	86928
70	168.98	118.77	5186	190	353.20	373.18	37531	310			
80	190.79	142.79	6988	200	367.35	391.66	41133	320	691.61	829.73	166761
90	210.18	166.39	8993	210	380.94	409.91	44875	330	677.17	850.79	173605
100	228.66	189.53	11190	220	397.52	428.02	48768	340	684.76	871.12	180415
110	244.31	212.06	13557	230	413.93	446.04	52825	350	693.78	891.09	187307

Table 14. Thermodynamic Properties of Methyl Eicosanoate at Selected Temperatures ($M = 326.56 \text{ g}\cdot\text{mol}^{-1}$)

T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$	T	$C_{p,m}$	ΔS_m	$H(T) - H(0)$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
5	0.75	0.25	0.94	120	271.01	244.38	16774	240	443.77	483.60	59344
10	5.46	2.00	15	130	285.48	266.65	19558	250	461.58	502.07	63871
20	28.85	13.00	186	140	299.45	288.33	22483	260	480.50	520.55	68582
30	56.97	29.60	605	150	313.11	309.46	25547	270	501.55	539.06	73486
40	89.89	50.46	1338	160	326.52	330.09	28745	280	525.09	557.71	78617
50	122.31	74.05	2402	170	339.86	350.29	32077	290	551.06	576.59	83997
60	149.98	98.89	3768	180	353.31	370.09	35543	300	585.33	595.84	89676
70	176.80	124.12	5408	190	366.99	389.56	39144	310	667.58	616.03	95838
80	199.80	149.20	7289	200	381.11	408.74	42884	320			
90	220.14	173.90	9388	210	395.71	427.69	46767	330	714.47	890.20	183976
100	235.76	198.05	11682	220	411.05	446.45	50801	340	722.28	911.64	191159
110	255.12	221.50	14144	230	427.04	465.07	54991	350	732.20	932.71	198432

capacity at 298.15 K. These values correspond to our value at that temperature to within 0.3%. For methyl tetradecanoate, one value for the heat capacity at 298.15 K was found;¹⁸ the correspondence of our value is within 0.25%. For the enthalpy of fusion and or the melting points, three data sources were found.^{14–16} The values are given in Table 15. While there is generally a good correspondence in the melting points, the enthalpy of fusion data of the literature are all lower than our values. We think that this can be partly explained by an aforementioned anomalous pre-melting effect in the compounds. The measurements in the literature were started at a much higher temperature; in ref 15, the starting temperature was 291 K for methyl octadecanoate. This implies that the authors used a baseline for the enthalpy calculation, constructed from the fit of the heat capacity data as given in Figure 1 by the dashed line. When we calculated the enthalpy of fusion using the fit given by the dashed line in Figure 1, the calculated enthalpy was 64 200 $\text{J}\cdot\text{mol}^{-1}$, 2 150 $\text{J}\cdot\text{mol}^{-1}$ lower than our value, and very close to the value of ref 15. So a large part of the differences is due to the way the enthalpy of fusion is defined. A second reason for the differences might be

the annealing of the sample close to the melting point we applied. Without this annealing, we would have measured lower values for those compounds that showed metastability in the freshly crystallized samples. The annealing process was not mentioned in the refs 14 and 15, and this could explain, together with the choice of the baseline, the large differences for some of the compounds.

Liquid Heat Capacity and a Correlation for the Absolute Entropy at 298.15 K. The data for the liquid heat capacity of these 13 esters do not show an even–odd effect. This effect is restricted to the solid phase as it is caused by differences in molecular packing. The heat capacity of the liquids can be described as a function of temperature and n , where n is the number of carbon atoms in the molecule in the parent carboxylic acid minus one. This implies that the shortest ester, methyl formate, is taken as the start of the series with n being zero. The correlation function found, optimized by using the Solver option of the Excel program was

$$C_p(n, T) = \{103.16 + 16.273n + 0.04735n(T/K)\} \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

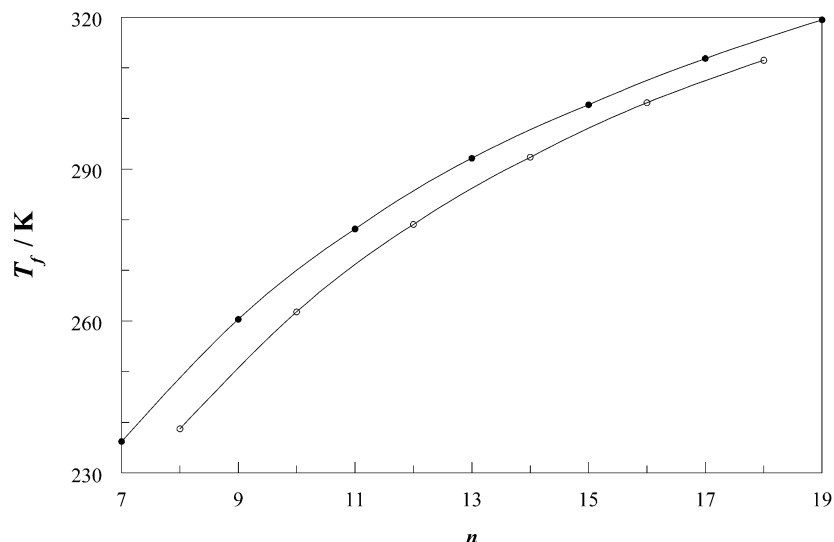


Figure 2. Even and odd effect in the melting points (T_f) of the methyl esters. n is the number of carbon atoms in the parent carboxylic acid minus one.

Table 15. Melting Temperatures and Enthalpies of Fusion of the Methyl Esters

compound	$T_{\text{fusion}}/\text{K}$	$\Delta_{\text{fus}}H/\text{J}\cdot\text{mol}^{-1}$	ref
methyl octanoate	236.20 ± 0.02	25636 ± 500	this work
	236.4 ± 0.1	25100 ± 1000	14
methyl nonanoate	238.72 ± 0.02	27342 ± 500	this work
	238.8 ± 0.1	27600 ± 1100	14
methyl decanoate	260.33 ± 0.02	35917 ± 500	this work
	260.4 ± 0.1	34300 ± 1300	14
methyl undecanoate	261.80 ± 0.02	36204 ± 500	this work
	261.8 ± 0.1	35900 ± 1400	14
methyl dodecanoate	278.18 ± 0.02	43147 ± 500	this work
	278.2 ± 0.1	43100 ± 1700	14
methyl tridecanoate	279.07 ± 0.02	45566 ± 500	this work
	278.9 ± 0.1	43300 ± 1700	14
methyl tetradecanoate	292.14 ± 0.02	52008 ± 500	this work
	292.2 ± 0.1	50000 ± 2000	14
	291.5 ± 0.3	44500	15
methyl pentadecanoate	292.35 ± 0.02	54283 ± 500	this work
	292.2 ± 0.1	48000 ± 1900	14
methyl hexadecanoate	302.71 ± 0.02	60039 ± 500	this work
	303.70 ± 0.05	55400	16
	302.2 ± 0.2		15
methyl heptadecanoate	303.09 ± 0.02	63895 ± 500	this work
	302.8 ± 0.5		14
methyl octadecanoate	311.84 ± 0.02	66354 ± 500	this work
	312.15 ± 0.05	64400	16
	310.9 ± 0.3		15
methyl nonadecanoate	311.49 ± 0.02	70925 ± 500	this work
	311.6 ± 0.1	62200	14
	311.8 ± 0.3		15
methyl eicosanoate	319.48 ± 0.02	78794 ± 500	this work
	320 ± 0.1	73700	14
	319.75 ± 0.05		16
	318.5 ± 0.2		15

This function was derived with 85 data points in the temperature range between 250 K and 350 K, the values of n were 7–19, the absolute mean percentage deviation was 0.3%, and the maximum deviation was 1%. As with all correlation functions, one should be careful if the function is used to calculate heat capacity data outside the mentioned temperature range or is used to extrapolate to esters with other chain lengths. We used this correlation function within these limits to calculate the absolute entropy of the compounds at 298.15 K, taking the experimental values at 340 K as starting points. At that temperature the compounds ranging between methylhexadecanoate and methyleicosanoate are in the solid phase, the correlation for the entropy at 298.15 K was made for stable

and undercooled liquids at that temperature. The correlation function found was

$$S_{\text{abs}}(298.15 \text{ K}) = \{215.94 + 31.517n\} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The value of n is the same as that used in the correlation function for the heat capacity of the liquid phase. The standard deviation of this fit was $3.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; this corresponds to about 0.5%.

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