Heat Capacities and Derived Thermodynamic Functions of 1-Dodecanol and 1-Tridecanol between 10 K and 370 K and Heat Capacities of 1-Pentadecanol and 1-Heptadecanol between 300 K and 380 K and Correlations for the Heat Capacity and the Entropy of Liquid *n*-Alcohols

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Molar heat capacities of the linear alcohols 1-dodecanol ($C_{12}H_{26}O$) and 1-tridecanol ($C_{13}H_{28}O$) were measured from 10 K to 380 K. The alcohols 1-pentadecanol ($C_{15}H_{32}O$) and 1-heptadecanol ($C_{17}H_{36}O$) were measured between 300 K and 370 K. Derived thermodynamic functions were given for the first two alcohols, and correlations for the molar heat capacity of the compounds in the liquid state and for the absolute entropy at 360 K were presented. These correlations were fit by using both these data and earlier published data on the linear alcohols with the number of carbon atoms (n) in the chain up to $n = 22$. The molar heat capacities of the liquid 1-alcohols can be described by $C_{p,l}(n,T) = \{-265.2 + 27.41n + 0.02501nT + 0.96196T\}$ J·K^{-1}·mol^{-1}. The correlation for the absolute entropy is $S°(360\text{ K},n) = \{111.80 + 38.607n\}$ J·K^{-1}·mol^{-1}.

Introduction

This is the second article on the heat capacities and derived thermodynamic properties of the normal 1-alcohols. In the first article[1] heat capacity measurements on the compounds 1-octadecanol, 1-nonadecanol, 1-eicosanol, and 1-docosanol were presented. The object of this study is to extend the available data on the 1-alcohols and to look for relations between the thermodynamic properties. While this group of compounds has both commercial and scientific interest, properties such as accurate heat capacities and entropy values have not been measured previously. Most of the work done on these compounds is by Sirota,[2] who made precise DSC measurements. Mosselman et al.[3] published results on the alcohols with a carbon number between 13 and 16. Their work is of a more qualitative nature; results are derived from heating and cooling curves in an adiabatic semi-microcalorimeter. Watanabe[4] presented temperature−time curves in the heating and cooling modes of several *n*-alcohols and also reported X-ray diffraction patterns of pure and mixed alcohols. Meyer and Reid[5] presented cooling curves from the melt of the alcohols with 10 to 18 carbon atoms. For the liquid state there are a few references: Vasil'ev et al.[6] reported the heat capacities of liquid 1-nonanol, 1-undecanol, 1-dodecanol, and 1-pentadecanol, Svensson[7] measured the heat capacities of 1-decanol and 1-dodecanol, and Khasanshin[8] reported analytical expressions for the heat capacities of the normal alcohols with a carbon number of 11 to 18.

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Experimental Section

The compounds were purchased from Fluka Chemica with a stated purity of better than 98%. The compounds were used without further purification; care was taken to avoid contact with the air. The calorimeter vessel was filled in a glovebox under a dry nitrogen atmosphere. 1-Dodecanol and 1-tridecanol were measured in CALV (laboratory design indication).[9,10] Below 30 K, the reproducibility of this calorimeter is about 1%, between 30 K and 100 K, it is 0.05 to 0.1%, and above 100 K, it is 0.03%. The accuracy of the heat capacity measurements was checked with *n*-heptane and with synthetic sapphire. Deviations larger than 0.2% from the recommended values were not found.

1-Pentadecanol and 1-heptadecanol were measured in Cal8, a scaled down version of Cal V. Cal8 is described in detail in a recent article.[11] This calorimeter works with samples of about 0.4 g, and the accuracy is estimated to be 0.5% for heat capacity measurements and 0.2% for latent energy effects such as the enthalpy of fusion. Both calorimeters use a rhodium−iron thermometer calibrated by Oxford Instruments to 0.001 K. The temperature scale used is the ITS-90.[12] Molar masses were calculated using the IUPAC tables of 1991.[13]

The filled vessel was evacuated for half an hour; then a helium pressure of about 1 kPa was admitted before closing, in order to promote the heat exchange within the vessel. Measurements were made in the intermittent mode, using stabilization periods of about 600 s and heat input periods of about 500 s. Between 5 K and 30 K, stabilization and input periods of about 100 to 150 s were used. The temperature increase was generally about 2 to 3 K for each measurement. Each compound was first measured from

Table 1. Experimental Molar Heat Capacities of 1-Dodecanol

T	C_p	T	C_p	T	C_p	T	C_p	T	C_p
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
4.89	0.50	33.29	39.09	105.66	145.63	203.04	228.14	314.41	460.33
5.30	0.59	33.59	39.70	109.51	149.48	205.94	230.85	315.30	461.65
5.64	0.66	35.53	43.57	113.32	153.04	208.82	233.52	317.24	463.91
6.46	0.92	37.84	47.29	117.13	156.53	211.68	236.20	320.21	467.79
7.31	1.32	40.23	51.76	120.95	160.01	214.51	238.88	323.17	471.66
8.18	1.68	42.65	56.35	124.76	163.33	217.33	241.68	326.12	475.74
8.98	2.19	45.10	60.97	128.50	166.58	220.13	244.41	329.08	479.76
9.56	2.57	47.58	65.63	132.18	169.61	222.91	247.18	332.04	483.75
10.50	3.35	50.09	70.36	135.80	172.64	225.66	250.10	334.99	487.57
11.22	3.92	52.64	74.94	139.37	175.56	228.40	252.97	337.95	491.61
12.40	5.10	55.22	79.43	142.89	178.45	231.12	255.86	340.91	495.50
13.14	5.94	57.83	83.87	146.37	181.11	233.81	258.81	343.86	499.50
14.47	7.50	60.48	88.16	149.80	183.99	236.49	261.87	346.82	503.54
15.22	8.48	63.15	92.38	153.18	186.68	239.15	264.95	349.79	507.22
16.69	10.44	65.84	96.63	156.53	189.52	241.79	268.07	352.75	510.94
17.52	11.65	68.55	100.64	159.83	192.32	244.42	271.21	355.71	514.68
19.12	14.03	71.28	104.62	163.10	194.74	247.02	274.53	358.67	518.23
19.99	15.41	74.03	108.49	166.34	197.23	249.61	277.88	361.63	521.60
21.71	18.20	76.80	112.23	169.55	199.78	251.48	279.87	364.57	525.05
22.62	19.79	79.58	115.93	172.73	202.28	252.69	281.82	367.49	528.36
24.43	22.98	82.38	119.48	175.87	204.86	255.27	284.84	370.41	531.43
25.38	24.82	85.18	122.95	178.99	207.42	259.20	290.64	373.31	534.34
27.17	27.70	88.00	126.31	182.08	209.97	263.11	296.62	376.21	537.10
28.07	29.03	90.83	129.63	185.15	212.58	267.00	303.13	379.09	539.95
29.65	31.86	93.67	132.79	188.19	215.16	270.88	310.85	381.97	542.41
30.40	33.25	96.52	135.91	191.21	217.67	301.51	444.71	384.83	544.86
30.87	34.11	99.37	138.86	194.20	220.28	304.80	448.44	387.69	547.06
31.76	35.98	101.75	141.93	197.17	222.88	308.07	452.29	390.54	549.07
32.40	37.33	103.06	143.05	200.11	225.49	311.32	456.46		

Table 2. Equilibrium Temperatures in the Melt and the Reciprocal of the Melted Fraction of 1-Dodecanol
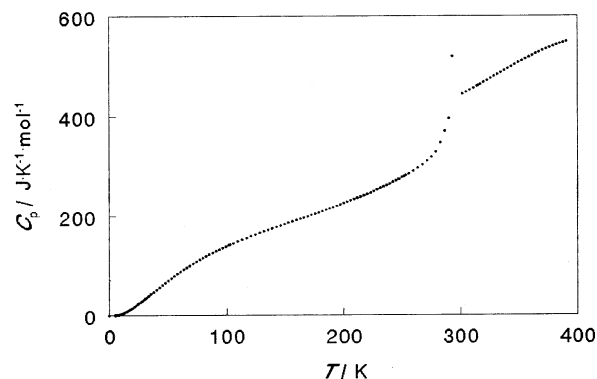
T	F^{-1}	T	F^{-1}
K	-	K	-
295.350	25.335	297.167	1.838
296.413	12.201	297.181	1.658
296.781	7.389	297.192	1.510
296.940	5.206	297.203	1.386
297.026	4.001	297.214	1.282
297.076	3.242	297.218	1.191
297.109	2.724	297.221	1.113
297.133	2.347	297.240	1.044
297.152	2.062	298.555	1.007

Figure 1. Experimental heat capacity data of 1-dodecanol.

Table 3. Melting Experiments of 1-Dodecanol[a]

experiment	triple point K	ΔH_{fus} $J \cdot mol^{-1}$	remarks
1	297.30	40 356	
2	297.29	40 258	used in Table 3
mean value	297.30	40 307 ± 80	

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of fusion: $C_p[\text{solid}] = \{-158.30 + 1.7360T\}$ $J \cdot K^{-1} \cdot mol^{-1}$ and $C_p[\text{liquid}] = \{78.02 + 1.2203T\}$ $J \cdot K^{-1} \cdot mol^{-1}$.

room temperature up to about 360 K. Then a slow, controlled cooling curve was measured by setting the inner adiabatic shield and the wire heater about 10 K below the temperature of the vessel. This resulted in a cooling rate outside the crystallization area of about 4 K·h^{-1}.

After completion of the measurements, all data were combined in one file. The data consist of the mean temperatures, the mean heat capacity over the measurement interval, and the relative enthalpy values. After calculating starting values for the entropy and enthalpy at 10 K, the dataset was interpolated for every degree. The derived properties were calculated by numerical integration. The starting values of $S°$ and $H°(T) - H°(0)$ were calculated assuming that below 10 K the low-temperature limit of the Debye heat capacity function $C_p = \alpha T^3$ holds.

Results and Discussion

1-Dodecanol. From the first melting experiment and the subsequent cooling curve, it was concluded that this compound does not show a solid–solid phase transition. The cooling curve did show an undercooling of the crystallization of 2.6 K. The combined experimental data set is given in Table 1. In the melt, heat capacity values are $>10^5$ $J \cdot K^{-1} \cdot mol^{-1}$; these values are not included in Table 1, instead the equilibrium temperatures in the melt and the reciprocal of the melted fraction are given in Table 2. In Figure 1 the heat capacity curve is shown. The second derivative of the heat capacity curve of the solid becomes positive around 200 K. This temperature is too low to be explained by impurity effects. To calculate the enthalpy of fusion and the fractional melting curve, a linear function was fitted to the heat capacity of the solid between 250 and 270 K. This fit and a linear fit of the heat capacity of the liquid phase were used to construct the baseline of the enthalpy curve. The results of the two melting experiments and the fits for the used baselines are given in Table 3. The second melting experiment was made with stabiliza-
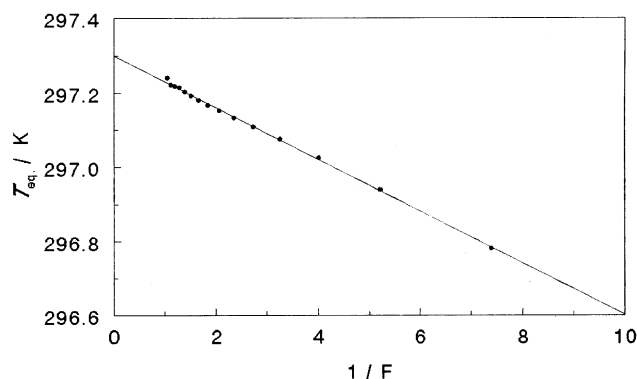
Figure 2. Equilibrium temperature in the melt of 1-dodecanol versus the reciprocal of the melted fraction. The linear behavior of this plot indicates that the impurity does form a eutectic system with the compound.

Figure 3. Molar heat capacity of 1-tridecanol around the solid−solid transition and the melt: (●) the compound as received; (○) measurement after cooling from the melting temperature to 294.7 K (in this cooling process the solid−solid transition did not take place); (▲) measurement after cooling to 260 K; (▽) measurement after cooling to 4 K. The lines drawn are only intended as a guide for the eye.

tion periods of 1500 s. Equilibrium temperatures in the melt were calculated by exponential extrapolation. The stabilization periods used were sufficiently long to give a correspondence of the calculated extrapolated temperature and the temperature at the end of the stabilization period of 0.001 K. The plot of the equilibrium temperature against the reciprocal of the melted fraction (F), as given in Figure 2, is a straight line up to $1/F = 6$. This indicates that the impurity does form a eutectic system with the compound and that the van't Hoff law is applicable. The triple point temperature (at $1/F = 0$) is 297.30 K; the calculated molar purity is 99.62%.

For the numerical calculation of the enthalpy and the entropy increments from 0 K, the relation $C_p = \alpha T^3$ was used. From the data between 4 K and 6 K, α was calculated to be 3.46×10^{-3} J·K^{-4}·mol^{-1}. From 6 K on, the data were interpolated for every degree. The resulting thermodynamic data are given in Table 4. Near the melting point, the heat capacities are extrapolated according to the functions given in Table 3. The result of the second melting experiment is used to calculate the entropy and the enthalpy of the liquid at 297.30 K.

1-Tridecanol. The compound (4.945 g) was loaded as received in the calorimeter. Several measuring series were carried out, followed by a controlled cooling. The first
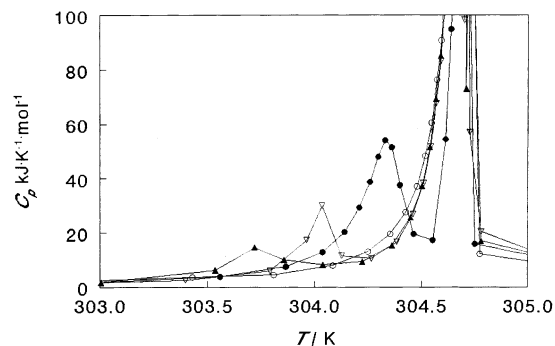
measuring series were used to assess the thermal behavior of the compound and were not tabulated. Some of the results are shown in Figure 3, which shows the dependence of the solid−solid transition on the thermal history. In Table 5 the experimental heat capacity data of the series 5 to 8 are given. These measurements form a continuous set from 5 K to 335 K. The measurements in the transition and fusion region are given separately in Table 6. In this table, enthalpy increments are also given. Three measurements were made for the solid−solid transition and the melt. These two effects could not be separated, as the heat capacity between them does remain anomalously high. From the enthalpy curves of series 1 and 2, we estimate the enthalpy of the solid−solid transition to be 1500 J·mol^{-1}. Series 2 was made on the undercooled high-temperature solid phase. The two enthalpy curves, matched to be equal in the liquid phase, are given in Figure 4. The difference at 300 K is assumed to be the enthalpy of the solid−solid transition. The other melting experiments do give a very different ratio between the solid−solid transition and the melt. However, the first experiment was performed on an annealed sample and is probably closest to thermodynamic equilibrium. In Table 7, the linear fits of the heat capacity of the solid and the liquid phase used

Table 4. Thermodynamic Properties at Selected Temperatures for 1-Dodecanol, Molar Mass = 186.33 g·mol^{-1}

T	$C_{p,m}°$	$S_m°$	$\Delta H_m°$	T	$C_{p,m}°$	$S_m°$	$\Delta H_m°$
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}
10	2.92	1.08	8	220	244.3	260.0	29 837
20	15.42	6.52	94	230	254.7	271.1	32 331
30	32.51	15.97	332	240	265.9	282.2	34 933
40	51.32	27.94	752	250	278.3	293.3	37 653
50	70.18	41.43	1 360	260	291.9	304.5	40 502
60	87.40	55.78	2 150	270	310.4	315.8	43 503
70	102.8	70.43	3 103	280^a	327.8	327.4	46 693
80	116.5	85.06	4 200	290^a	345.1	339.2	50 058
90	128.7	99.49	5 426	297.30^b	357.8	347.9	52 624
100	139.6	113.6	6 769	297.30^c	440.8	483.3	92 882
110	149.9	127.5	8 222	298.15	441.9	484.6	93 257
120	159.2	140.9	9 768	300	444.1	487.3	94 077
130	167.8	154.0	11 403	310	454.8	502.1	98 579
140	176.1	166.7	13 122	320	467.5	516.8	103 203
150	184.2	179.2	14 923	330	481.0	531.4	107 949
160	192.5	191.3	16 805	340	494.3	545.9	112 818
170	200.1	203.2	18 767	350	507.5	560.4	117 808
180	208.3	214.9	20 809	360	519.8	574.8	122 920
190	216.7	226.3	22 933	370	531.0	589.1	128 155
200	225.4	237.7	25 143	380	540.7	603.4	133 511
210	234.6	248.9	27 443				

^{a} Extrapolated. ^{b} Solid. ^{c} Liquid phase.

Table 5. Experimental Molar Heat Capacities of 1-Tridecanol

T	C_p	T	C_p	T	C_p	T	C_p
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
5.43	0.73	76.52	119.31	189.51	230.93	289.35	368.37
6.35	1.02	79.30	123.26	192.27	233.49	291.46	376.60
6.92	1.16	82.09	127.05	195.00	236.07	310.66	490.33
8.19	1.88	84.85	130.74	197.72	238.57	312.48	492.55
8.19	1.83	87.54	134.18	200.42	241.11	314.30	494.79
9.76	2.87	90.16	137.47	203.10	243.70	316.12	496.90
10.00	3.09	92.71	140.59	205.76	246.32	317.93	499.11
11.50	4.42	95.20	143.52	208.41	249.01	318.36	500.33
11.65	4.57	97.63	146.32	211.04	251.60	319.10	501.54
13.42	6.55	100.02	148.83	213.65	254.36	319.75	498.91
13.68	6.87	102.10	152.11	216.25	257.05	320.72	503.57
15.55	9.27	103.32	153.06	218.83	259.88	321.55	504.47
15.88	9.75	105.40	155.26	221.40	262.61	323.23	506.79
17.88	12.68	108.31	158.33	223.95	265.23	323.34	506.92
18.23	13.34	111.20	161.30	226.48	268.00	325.13	509.47
20.35	16.77	114.09	164.14	229.00	270.12	325.74	510.38
20.75	17.36	116.98	166.94	231.50	273.66	326.92	512.04
22.97	21.33	119.88	169.82	234.00	276.54	328.23	513.87
23.40	22.11	122.79	172.58	236.47	279.48	328.70	514.67
25.72	26.65	125.70	175.30	238.93	282.45	330.47	516.98
26.18	27.43	128.61	178.03	241.38	285.45	330.71	517.39
28.64	31.55	131.53	180.59	243.82	288.49	332.24	519.36
29.13	32.62	134.44	183.16	246.23	291.70	333.18	520.69
31.71	37.83	137.36	185.79	248.64	294.92	334.01	520.78
32.22	38.99	140.29	188.32	251.03	298.31	335.63	524.11
32.41	39.60	143.22	190.88	253.40	301.46	335.76	524.37
36.39	47.49	146.15	193.43	255.76	304.48	338.08	527.53
39.65	53.57	149.08	195.91	258.11	308.33	340.52	530.77
42.46	59.29	152.02	198.41	260.44	312.40	342.95	534.08
44.97	64.37	154.95	200.87	262.75	316.76	345.37	537.59
47.40	69.21	157.89	203.87	265.05	321.73	347.78	540.94
49.91	74.17	160.83	206.25	267.33	326.95	350.19	543.91
52.45	79.07	163.77	208.51	269.58	333.12	352.58	546.88
55.02	84.00	166.71	210.96	271.82	334.58	354.97	550.24
57.62	88.82	169.64	213.42	274.06	333.40	357.35	553.06
60.25	93.47	172.55	215.89	276.29	337.23	359.72	556.17
62.91	98.02	175.43	218.51	278.51	341.53	362.08	558.85
65.59	102.47	178.29	220.77	280.71	346.21	364.44	561.58
68.29	106.79	181.13	223.25	282.90	351.04	366.79	564.41
71.02	111.04	183.94	225.88	285.07	356.16	369.13	566.97
73.76	115.26	186.74	228.46	287.22	361.73		

Table 6. Experimental Data Series for 1-Tridecanol around the Melt

T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot mol^{-1}$
293.54	387.13	54 705	304.46	26 734	71 146	304.68	453 154	91 616
295.59	401.86	55 514	304.51	38 260	72 708	304.68	448 798	93 195
297.60	425.87	56 342	304.55	51 668	74 275	304.69	399 633	94 775
299.51	475.65	57 203	304.57	67 687	75 846	304.69	391 378	96 355
301.24	611	58 133	304.59	83 224	77 418	304.70	98 285	97 931
302.58	1 074	59 207	304.61	105 145	78 993	304.71	220 353	99 507
303.40	2 540	60 480	304.62	120 898	80 568	304.73	57 105	101 082
303.79	5 946	61 912	304.64	143 347	82 144	304.78	20 433	102 643
303.96	17 344	63 429	304.65	158 113	83 721	305.45	871	103 971
304.03	29 951	64 983	304.66	192 063	85 298	307.00	486.00	104 968
304.13	11 566	66 529	304.66	239 834	86 877	308.83	488.11	105 860
304.27	10 470	68 057	304.67	269 711	88 456			
304.38	16 652	69 593	304.67	326 029	90 036			

to calculate the baseline and the results of the transition and melt experiments are given. The baseline was calculated by extrapolating both fits to the end melting point. No iterative procedure, as is often done in adiabatic calorimetry to calculate a sigmoid baseline, was applied. The end of the fusion is given as T_{end}. The triple point temperature could not be calculated, as the solid−solid transition distorts the plot of the reciprocal of the melted fraction. The sum of the enthalpies of transition and of fusion is, within the margin of uncertainties, the same for the three experiments. This is remarkable, as it was expected that the enthalpy of the solid would be different.

In Table 8 the calculated thermodynamic properties at selected temperatures are given.

The cooling curves are given in Figure 5a. As different cooling rates were used (cool1, 2.848 K·h^{-1}, cool2, 4.605 K·h^{-1}, and cool3, 1.01 K·h^{-1}, all calculated between 310 K and 304 K), the time axes of cool1 and cool2 were scaled in order to represent all three curves in one plot on the same temperature scale. The compound does show polymorphic behavior; it crystallizes in a metastable form, which exists only temporally. The temperature at which this crystallization took place was in the range 303.1 K to 303.2 K, depending on the cooling rate. In Figure 5b an enlarged
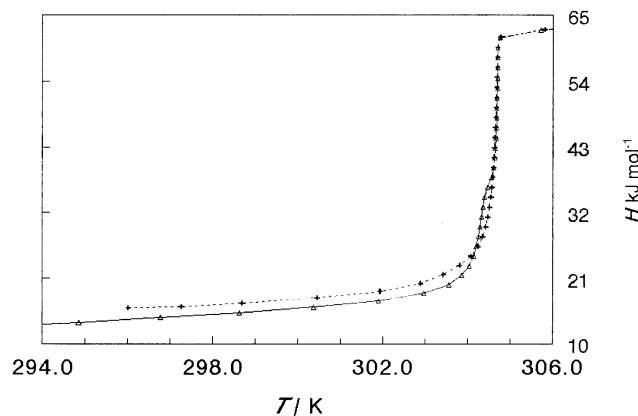
Figure 4. Enthalpy curves of 1-tridecanol around the melt. The solid line gives the enthalpy curve of the compound as received, and the broken line gives the enthalpy curve of the compound after cooling to 294.7 K; in this cooling process, the solid−solid transition did not occur.

Table 7. Melting Experiments of 1-Tridecanol[a]

experiment	T_{end} K	$\Delta H_{trans+fus}$ J·mol^{-1}	remarks
1	304.70	44 748	
2	304.73	44 767	used in Table 8
3	304.75	44 816	
mean value	304.73	44 777 ± 80	

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of the transition and the fusion: C_p[solid, between 275 K and 285 K] = {−281.6 + 2.24226 T} J·K^{-1}·mol^{-1} and C_p[liquid, between 310 K and 320 K] = {86.66 + 1.29985 T} J·K^{-1}·mol^{-1}.

view around the crystallization region is shown. When 15 to 30% of the liquid was crystallized, a sudden transition to the stable crystal form took place. There seems to be no relation between the cooling rate and the amount of metastable crystalline material that could be formed. The solid−solid transition does show an undercooling of 8 to 10 K.

1-Pentadecanol. The compound (0.4102 g) was loaded as received in the calorimeter (Cal8). Two measurement
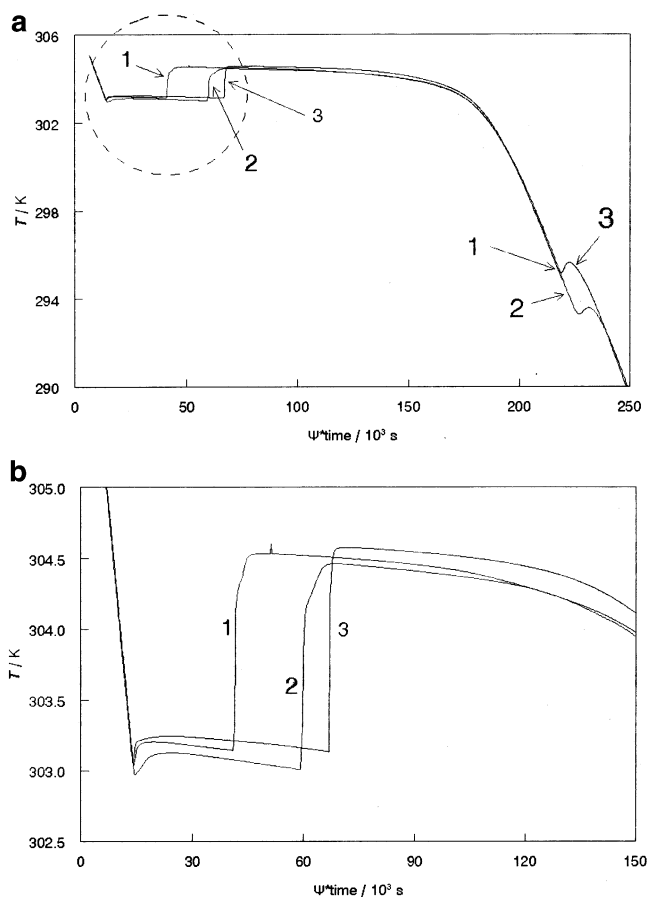

Figure 5. (a) Three controlled cooling curves of 1-tridecanol. The three curves are plotted on one axis by scaling cooling curves 1 and 2 to the time axis of cooling curve 3. Cooling curve 1 was stopped at 294.7 K before the solid−solid transition took place; the encircled part is enlarged in part b. (b) View of a part of the three cooling curves of 1-tridecanol (see Figure 5a); the compound crystallizes in a metastable crystalline form, which transforms spontaneously into the stable high-temperature crystalline form.

series were made. The first series ranged from 297 K to 360 K, with an input time of 600 s and a stabilization time of 1000 s. The actual melting procedure took about 6 h.

Table 8. Thermodynamic Properties at Selected Temperatures for 1-Tridecanol, Molar Mass = 200.365 g·mol^{-1}

T K	$C_{p,m}°$ J·K^{-1}·mol^{-1}	$S_m°$ J·K^{-1}·mol^{-1}	$\Delta H_m°$ J·mol^{-1}	T K	$C_{p,m}°$ J·K^{-1}·mol^{-1}	$S_m°$ J·K^{-1}·mol^{-1}	$\Delta H_m°$ J·mol^{-1}
10	3.08	1.17	8.6	220	261.1	276.9	31 831
20	16.22	6.84	98	230	271.5	288.7	34 494
30	34.40	16.89	352	240	283.8	300.5	37 271
40	54.29	29.37	790	250	296.9	312.4	40 173
50	74.35	43.61	1 432	260	311.6	324.3	43 211
60	93.03	58.85	2 271	270	333.9	336.4	46 431
70	109.5	74.45	3 285	280	344.7	348.7	49 799
80	124.2	90.05	4 455	280	346.2	348.7	49 799
90	137.3	105.4	5 763	290[a]	368.7	361.2	53 374
100	148.8	120.5	7 194	298.15[a]	386.9	371.7	56 453
110	160.1	135.3	8 745	300[a]	391.1	374.1	57 172
120	169.9	149.6	10 395	304.70[b]	401.6	380.3	59 035
130	179.3	163.6	12 141	304.70[c]	482.1	527.2	103 812
140	188.1	177.2	13 978	310	489.2	535.6	106 386
150	196.7	190.5	15 902	320	502.7	551.3	111 346
160	205.6	203.5	17 913	330	516.1	567.0	116 439
170	213.7	216.2	20 009	340	529.5	582.6	121 667
180	222.2	228.6	22 189	350	542.9	598.1	127 029
190	231.4	240.9	24 457	360	556.4	613.6	132 526
200	240.7	253.0	26 817	370	569.8	629.1	138 157
210	250.6	265.0	29 273				

[a] Extrapolated. [b] Solid. [c] Liquid phase.

Table 9. Experimental Data Series for 1-Pentadecanol

T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$
K	J·K^{-1}·mol^{-1}	J·mol^{-1}	K	J·K^{-1}·mol^{-1}	J·mol^{-1}	K	J·K^{-1}·mol^{-1}	J·mol^{-1}	K	J·K^{-1}·mol^{-1}	J·mol^{-1}
					Series 1						
297.94	422.5	0	315.33	33346	21 818	320.07	574.1	64 147	340.85	601.3	76 339
299.88	428.9	822	315.45	31972	25 494	321.80	577.5	65 137	342.60	604.4	77 393
301.65	435.5	1 585	315.59	20626	29 118	323.52	577.3	66 130	344.35	607.2	78 456
303.55	445.9	2 425	315.91	6721	32 455	325.24	579.7	67 126	346.11	609.9	79 526
305.44	457.0	3 275	316.31	9211	35 639	326.97	581.3	68 127	347.87	611.7	80 602
307.29	473.1	4 139	316.56	25403	39 086	328.69	583.8	69 132	349.64	614.4	81 685
309.12	502.9	5 031	316.67	51679	42 769	330.42	586.5	70 143	351.41	616.4	82 776
310.89	570.7	5 975	316.73	84104	46 530	332.15	589.1	71 160	353.19	618.9	83 870
312.55	811	7 109	316.77	121219	50 324	333.88	592.0	72 184	354.97	620.8	84 972
313.88	1882	8 774	316.80	161524	54 139	335.62	594.2	73 214	356.75	624.0	86 083
314.67	6303	11 331	316.82	111374	57 952	337.36	596.1	74 249	358.54	625.5	87 203
315.03	15380	14 603	317.16	4370	61 255	339.10	599.2	75 290	360.34	629.2	88 328
315.21	26089	18 162	318.35	575.1	63 153						
					Series 2						
299.89	444.5	0	315.75	8 677	31 086	327.69	583.1	67 589	353.64	618.3	83 183
301.82	443.3	844	316.15	6 866	34 188	329.37	584.6	68 570	355.44	622.7	84 298
303.56	453.4	1 629	316.46	19 647	37 442	331.05	586.2	69 558	357.24	624.3	85 427
305.44	468.4	2 491	316.60	39 591	40 985	332.75	589.8	70 551	359.06	626.9	86 564
307.28	491.2	3 372	316.67	66 347	44 628	334.44	592.1	71 555	360.90	630.2	87 715
309.07	525.9	4 285	316.72	95 322	48 314	336.15	594.2	72 567	362.74	631.2	88 879
310.80	614	5 267	316.75	126 942	52 019	337.86	596.9	73 586	364.60	635.5	90 054
312.39	882	6 438	316.78	130 363	55 732	339.58	599.0	74 616	366.47	637.2	91 246
313.69	1 792	8 081	316.84	41 728	59 399	341.31	602.6	75 652	368.36	639.4	92 448
314.53	4 785	10 467	317.69	663	61 749	343.05	603.6	76 699	370.26	641.4	93 668
314.96	11 826	13 527	319.34	571.9	62 765	344.79	607.0	77 754	372.18	643.6	94 900
315.18	23 063	16 944	321.01	576.7	63 728	346.54	610.9	78 820	374.11	644.9	96 144
315.31	34 808	20 506	322.68	578.2	64 689	348.30	613.1	79 897	376.06	647.9	97 405
315.40	40 149	24 118	324.34	580.0	65 646	350.07	615.0	80 983	378.03	650.7	98 684
315.51	29 926	27 715	326.01	580.7	66 615	351.85	616.8	82 080	380.02	651.3	99 982

The experimental results are given in Table 9. In this table, the temperatures in the midpoints of the heat inputs, the molar heat capacities, and the relative enthalpy at the aforementioned temperatures are given. A controlled cooling curve gave two thermal arrests. The first arrest, when liquid transformed into the rotator phase, shows hardly any undercooling. The second arrest, when the rotator phase changes to the crystalline phase, does show an undercooling of 4.3 K. The second heat capacity measurement series was made with a stabilization time of 2000 s; it ranged from 299 K to 380 K. Both measurement series do not indicate a metastable form; the drift of the calorimeter in the stabilization periods is within the normal range. The heat capacities of the two series are comparable within the reproducibility limit of the calorimeter (0.03%). This remark should be considered in connection with the results of 1-heptadecanol (in the next section) and 1-nonadecanol;[1] both these compounds crystallize from the liquid in a
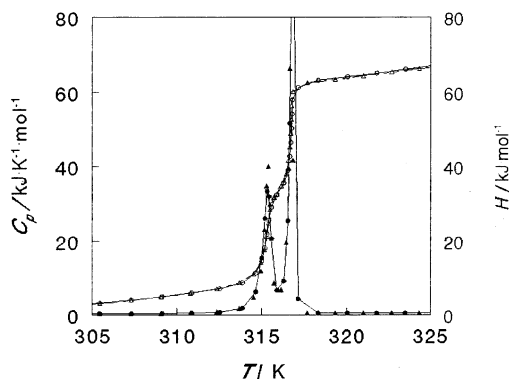

Figure 6. Experimental heat capacity curve and enthalpy curve for 1-pentadecanol in the transition and fusion region: (●) heat capacity measurement on the compound as received; (▲) heat capacity curve of the once melted sample; (○) and (△) give the corresponding enthalpy curves.

Table 10. Melting Experiments of 1-Pentadecanol[a]

experiment	$T_{transition}$	T_{fus}	ΔH_{total}
	K	K	J·mol^{-1}
1	315.4	316.9	53 686
2	315.4	316.9	53 551
mean value	315.4	316.9	53 618 ± 100

[a] The following linear fits of the heat capacity were used to calculate the enthalpies of transition and of fusion together: C_p[solid] = {$-622.93 + 3.5084T$} and C_p[liquid] = {$267.19 + 0.96076T$} J·K^{-1}·mol^{-1}. The total enthalpy of transition and of fusion can be divided into 21.4 kJ·mol^{-1} for the solid−solid transition and 32.1 kJ·mol^{-1} for the fusion.
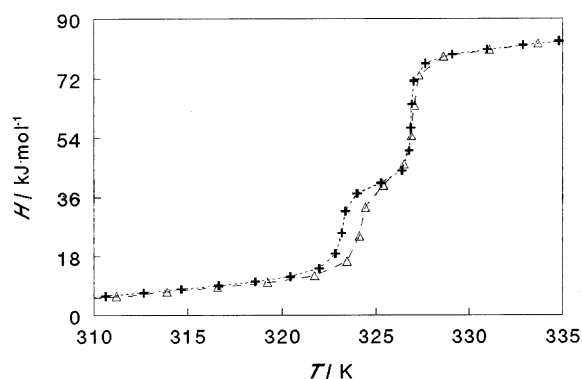
metastable form. In Figure 6, the heat capacity curves and the enthalpy curves around the transition and the melt are given. The sum of the enthalpies of transition and of fusion was calculated and is given in Table 10. The solid−solid phase transition is not separated from the melting process. From the enthalpy curve and the cooling curve it was estimated that the enthalpy of transition is about two-thirds of the enthalpy of fusion. So the total enthalpy of transition and of fusion as given in Table 10 can be divided into 21.4 kJ·mol^{-1} for the solid−solid transition and 32.2 kJ·mol^{-1} for the fusion process.

1-Heptadecanol. The calorimeter was loaded with 0.4473 g. Four measurement series were made; the experimental data are given in Table 11. In this table the relative enthalpies are shifted in such a way that they coincide in the liquid state. In Figure 7, the enthalpy curves of the first two measurements are given. The two linear fits of the enthalpies of the solid phase do show that the enthalpy of the recently melted product is higher than the enthalpy of the product as received, which was annealed by storing at room temperature. The observed difference at 310 K is 1000 J·mol^{-1} (Table 12).

Liquid State. In a previous article on the *n*-alcohols,[1] we presented a fit of the heat capacities of the liquid state

Table 11. Experimental Data Series for 1-Heptadecanol

T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$	T	C_p	$H - H_{start}$
K	J·K⁻¹·mol⁻¹	J·mol⁻¹	K	J·K⁻¹·mol⁻¹	J·mol⁻¹	K	J·K⁻¹·mol⁻¹	J·mol⁻¹	K	J·K⁻¹·mol⁻¹	J·mol⁻¹
Series 1											
298.53	455.2	0	313.92	512.1	7 394	324.43	22 527	33 058	328.63	1 037	78 545
300.65	461.7	961	316.60	533.8	8 800	325.42	3 031	39 748	331.09	653.8	80 589
302.93	469.2	2 033	319.24	603.5	10 284	326.51	12 819	46 077	333.67	663.6	82 278
305.71	477.0	3 337	321.72	999	12 250	326.91	53 290	54 626	336.26	660.2	84 010
308.47	487.9	4 675	323.45	5 682	16 575	327.08	55 372	63 878	338.87	665.9	85 732
311.21	499.1	6 026	324.12	38 484	24 245	327.31	28 942	72 921			
Series 2											
302.49	468.8	2 549	320.44	925	12 225	326.87	125 903	57 123	336.71	659.9	84 305
304.60	478.1	3 538	321.97	2 543	14 664	326.93	128 809	64 196	338.65	664.9	85 584
306.52	485.7	4 461	322.84	12 329	19 159	327.03	42 322	71 107	340.58	669.1	86 875
308.59	491.4	5 471	323.17	32 152	25 333	327.64	3 724	76 443	342.52	671.9	88 177
310.63	501.9	6 488	323.38	31 994	31 920	329.09	797.3	79 138	344.47	671.1	89 484
312.66	514.3	7 515	323.98	4 067	37 249	330.95	672.9	80 497	346.42	676.1	90 793
314.67	532.5	8 565	325.28	1 396	40 398	332.87	653.1	81 773	348.37	678.6	92 118
316.65	558.0	9 648	326.40	8 219	44 127	334.79	659.9	83 032	350.33	683.4	93 453
318.60	633.0	10 807	326.78	53 314	50 166						
Series 3											
297.57	460.6	390	318.32	620.5	10 881	326.71	19 947	45 442	334.12	658.3	82 543
299.55	465.8	1 304	320.03	800	12 095	326.86	59 824	49 877	335.90	661.7	83 719
301.36	473.6	2 158	321.48	1 731	13 815	326.92	98 501	54 482	337.69	664.5	84 905
303.32	480.0	3 089	322.34	7 510	16 731	326.96	117 207	59 129	339.48	667.0	86 098
305.25	486.2	4 023	322.71	17 477	20 673	327.00	127 591	63 787	341.28	670.2	87 300
307.18	494.5	4 965	322.91	28 816	24 966	327.05	80 841	68 427	343.08	672.8	88 511
309.08	499.9	5 914	323.05	32 660	29 367	327.15	30 063	72 957	344.89	676.4	89 731
310.97	508.9	6 868	323.22	21 227	33 719	327.63	3 741	76 709	346.71	676.9	90 958
312.84	521.7	7 831	323.72	3 746	37 381	328.87	834	78 928	348.52	680.0	92 191
314.70	535.8	8 810	324.89	1 050	39 700	330.57	665.7	80 197	350.35	683.4	93 434
316.53	564.2	9 816	326.13	2 948	41 896	332.34	657.7	81 372			
Series 4											
305.09	465.0	4 248	323.31	35 648	28 475	327.52	4 072	76 563	348.35	678.9	92 114
307.04	482.6	5 161	323.44	32 529	32 912	328.73	838	78 825	350.17	682.7	93 353
308.80	491.5	6 019	323.74	8 105	37 004	330.43	692.7	80 111	352.00	686.2	94 604
310.70	499.0	6 961	324.73	1 083	39 698	332.18	663.3	81 305	353.83	688.2	95 865
312.59	508.5	7 911	326.00	2 551	41 826	333.96	658.9	82 482	355.67	688.7	97 134
314.45	525.0	8 873	326.64	15 785	45 232	335.74	661.2	83 659	357.52	691.1	98 407
316.30	550.2	9 865	326.81	56 656	49 612	337.53	663.4	84 841	359.37	697.4	99 691
318.10	629.7	10 928	326.88	111 275	54 221	339.32	666.9	86 032	361.23	699.7	100 989
319.82	763.0	12 132	326.91	150 525	58 882	341.12	670.0	87 234	363.10	701.9	102 299
321.35	1 373	13 700	326.94	147 430	63 553	342.92	671.7	88 441	364.98	704.8	103 622
322.41	4 161	16 218	326.98	96 062	68 202	344.72	675.1	89 657	366.87	706.4	104 956
322.94	14 002	19 844	327.07	34 774	72 753	346.53	677.8	90 882	368.77	708.1	106 300
323.17	26 099	24 073									

Figure 7. Enthalpy curves of 1-heptadecanol around the transition and melt: (△) series 1 on the compound as received; (+) series 2 after cooling from the melting temperature.

of 1-octadecanol, 1-nonadecanol, 1-eicosanol, and 1-docosanol. The fit used was given by

$$C_{p,meas}/\text{J·K}^{-1}\text{·mol}^{-1} =$$
$$(-450.41 + 36.4968n + 1.47317T) \quad (1)$$

where n is the number of carbon atoms in the molecules and T the temperature in Kelvin. Then we combined these

Table 12. Melting Experiments of 1-Heptadecanol[a]

	$T_{transition}$	T_{fus}	ΔH_{total}
experiment	K	K	J·mol⁻¹
1	324.1	327.3	63 043
2	323.2	327.3	63 081
mean value		327.3	63 062 ± 100

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of transition and fusion together: C_p[solid] = {−713.81 + 3.9224T} and C_p[liquid] = {181.33 + 1.44359T} J·K⁻¹·mol⁻¹. The division of the total enthalpy between the enthalpy of transition and the enthalpy of fusion is about 23.7 kJ·mol⁻¹ for the transition and 39.4 kJ·mol⁻¹ for the fusion.

data with the results in this article. All data for the liquid state were used and combined in a file consisting of temperature−number of carbon atoms−heat capacity triplets. A total of 339 data points (N) were used. Using the same fit-coefficients as in eq 1, a mean percentage deviation,

$$M\% = \frac{\sum_{i=1}^{i=N} \dfrac{\text{abs}(C_{p,meas} - C_{p,fit})}{C_{p,meas}} 100}{N} \quad (2)$$

Table 13. Measured and Correlated Absolute Entropies at 360 K[a]

compound	n^b	$S_{abs}(360\ K)$ meas $J \cdot K^{-1} \cdot mol^{-1}$	$S_{abs}(360\ K)$ correl $J \cdot K^{-1} \cdot mol^{-1}$	dev %
1-dodecanol	12	574.8	575.1	0.05
1-tridecanol	13	613.6	613.7	0.01
1-octadecanol	18	806.8	806.8	0.00
1-nonadecanol	19	845.8	845.4	0.05
1-eicosanol	20	885.1	884.1	0.12
1-docosanol	22	960.2	961.3	0.12

[a] The correlation is $S_{abs}(360\ K) = (111.52 + 38.627n)\ J \cdot K^{-1} \cdot mol^{-1}$. [b] Number of carbon atoms.

of 0.4% was found. This result could be improved significantly by adding one parameter. Fitting the data to the form

$$C_{p,meas}/J \cdot K^{-1} \cdot mol^{-1} = (a_0 + a_1 n + a_2 nT + a_3 T) \quad (3)$$

resulted in

$$C_{p,meas}/J \cdot K^{-1} \cdot mol^{-1} =$$
$$(-265.2 + 27.41n + 0.0250nT + 0.96196T) \quad (4)$$

The mean percentage deviation ($M\%$) of this fit was 0.13%, which is on the order of the experimental error, considering that two different calorimeters were used.

Correlation of the Entropy at 360 K. In Table 13 the experimental absolute entropy values at 360 K are given for the *n*-alcohols with the carbon numbers 12, 13, 18, 19, 20, and 22. A linear fit as a function of the number of carbon atoms in the molecules resulted in the correlation

$$S(360\ K) = (111.80 + 38.607n)\ J \cdot K^{-1} \cdot mol^{-1}$$

The standard deviation of this equation is 0.8 $J \cdot K^{-1} \cdot mol^{-1}$, and the maximum deviation is 0.12% for $n = 22$. The deviations from the linear fit are within the expected experimental uncertainty.

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