Heat Capacities and Derived Thermodynamic Functions of 1-Hexanol, 1-Heptanol, 1-Octanol, and 1-Decanol between 5 K and 390 K

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Molar heat capacities of the linear alcohols 1-hexanol ($C_6H_{14}O$), 1-heptanol ($C_7H_{16}O$), 1-octanol ($C_8H_{18}O$), and 1-decanol ($C_{10}H_{22}O$) were measured from 5 K to 390 K. The derived thermodynamic functions $S_{abs,m}(T)$ and $H_m(T) - H_m(0)$ were calculated. Including earlier published data, a correlation for the heat capacity of the liquid 1-alcohols with the carbon number n in the chain ranging between 6 and 22 was fitted. The molar heat capacities of the liquid alcohols can be described by $C_{p,l}(n,T)/J{\cdot}K^{-1}{\cdot}mol^{-1} = -3163.5 + 21.0156n + 0.04223nT + 9.89055T + 322705.7/T - 0.0093225T^2$, with the mean absolute percentage deviation being 0.22%. The correlation for the absolute entropy is $S°(360\ K,n) = (111.86 + 38.613n)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$.

Introduction

This work is concerned with heat capacity measurements on lower 1-alcohols from about 5 K up to room temperature and higher (to 390 K). 1-Hexanol was measured from 5 K to 400 K, 1-heptanol was measured from 5 K to 370 K, 1-octanol was measured from 5 K up to 380 K, and 1-decanol was measured from 5 K to 390 K. In earlier publications heat capacity data and derived thermodynamic properties of the normal 1-alcohols with carbon numbers 12, 13, 15, 17, 18, 19, 20, and 22 were presented.[1,2] We are especially interested in the heat capacity of the liquid 1-alcohols, and in order to get a consistent set of data, the measurements were extended to the alcohols presented in this article with the number of carbon atoms in the chain of 6, 7, 8, and 10. A survey of the literature sources on saturated liquid heat capacities of 1-alcohols is given in the monograph by Zábranský et al.[3] We compare our results to those data measured by adiabatic calorimetry or microcalorimetry, and we have included in the figures the data from the NIST databank[4] given at 298.15 K, which were measured by different methods, but mostly by DSC. Another object of this study is to extend the available absolute entropy data of the 1-alcohols and to find the correlation of these values with the number of carbon atoms in the chain.

Experimental Section

1-Heptanol was bought from Aldrich, and 1-hexanol, 1-octanol, and 1-decanol were bought from Merck. All the compounds were purified by fractional distillation at a reduced pressure of approximately 70 Pa in a 110 cm long packed column with a heated outer housing. After distillation the compounds were stored over molecular sieves (Merck) with a pore diameter of 0.4 nm, for a minimum of 4 days.

Table 1. Purity of the Compounds As Given by the Supplier and Measured by Gas Chromatography, Fischer Titration, and Adiabatic Calorimetry

compd	stated purity mol %	meas purity without water mol %	water content mass%	tot purity mol %	calorim value mol %
1-hexanol	98	99.98	0.03	99.81	99.80
1-heptanol	98	99.93	0.02	99.80	99.78
1-octanol	>99	99.97	0.02	99.83	99.82
1-decanol	>99	99.88	0.007	99.82	99.78

The purity of the compounds was determined using a Hewlett-Packard 6890 series gas chromatograph, using a flame ionization detector. The water content was determined by a Fischer titration. The final purity (excluding water content) and water content are given in Table 1.

Care was taken to avoid contact with the air. The calorimeter vessel was filled in a glovebox under a dry nitrogen atmosphere. 1-Hexanol and 1-octanol were measured in CALV (laboratory design indication).[5,6] 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%. 1-Heptanol and 1-decanol were measured in CALVII (laboratory design indication). This calorimeter is identical to CALV, but uses a platinum 100 Ω thermometer instead of a Rh/Fe resistance thermometer. Oxford Instruments calibrated the thermometers to an accuracy of 0.001 K using the ITS-90[7] temperature scale. The accuracy of the heat capacity measurements was checked for both calorimeters by measuring n-heptane and synthetic sapphire. No deviations from the recommended values larger than 0.2% were found. Measurements were made in the intermittent mode, using stabilization periods of about 600 s and heat input periods of about 500 s. Below 30 K shorter time periods were used. In the melting region longer stabilization periods, up to 1200 s, were used. For each compound a slow controlled cooling curve with a

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Table 2. Experimental Molar Heat Capacities[a] of 1-Hexanol

T	C_p	T	C_p	T	C_p	T	C_p
4.73	0.23	63.39	55.26	223.11	241.18	308.95	250.94
4.73	0.26	66.08	57.66	224.91	519	310.79	252.61
5.03	0.22	68.79	60.06	225.81	1592	312.63	254.44
5.25	0.28	71.52	62.40	226.17	3906	314.46	256.30
6.01	0.41	74.27	64.69	226.34	7148	316.29	258.11
6.23	0.38	77.04	66.89	226.43	12030	318.10	260.01
6.63	0.58	79.82	69.05	226.49	19302	319.90	261.75
7.29	0.55	82.62	71.14	226.52	28650	321.70	263.65
7.59	0.66	85.42	73.21	226.55	39292	323.49	265.44
8.33	0.81	88.25	75.23	226.57	50753	325.27	267.34
8.65	0.92	91.08	77.20	226.58	66724	327.05	269.15
9.10	1.13	93.91	79.10	226.60	86529	328.82	270.96
9.46	1.19	96.73	80.88	226.61	106050	330.57	272.91
10.09	1.44	99.51	82.67	226.61	153451	332.33	274.59
10.57	1.65	102.14	84.69	226.62	253062	334.07	276.54
11.01	1.89	104.23	85.75	226.62	261244	335.80	278.19
11.61	2.15	106.71	87.38	226.62	380335	337.53	279.95
12.24	2.53	109.60	89.08	226.63	241729	339.25	281.70
12.62	2.70	112.49	90.67	226.63	77696	340.96	283.50
13.32	3.12	115.37	92.25	226.65	42937	342.67	285.12
14.01	3.62	118.27	93.81	227.08	898	344.38	286.83
14.38	3.82	121.17	95.17	228.77	199.21	346.07	288.48
15.17	4.52	124.07	96.95	231.33	200.08	347.76	290.00
15.92	4.85	126.98	98.46	233.87	200.96	349.45	291.14
16.31	5.23	129.89	100.30	236.40	201.97	351.13	293.81
17.15	5.89	135.80	103.15	238.93	202.98	352.80	295.37
17.97	6.66	138.70	104.42	241.44	204.05	354.46	297.12
18.36	6.91	141.60	105.91	243.95	205.10	356.11	298.70
19.26	7.71	144.52	107.35	246.44	206.25	357.76	300.28
20.11	8.58	147.44	108.76	248.93	207.41	359.40	301.88
20.52	8.90	150.37	110.18	251.40	208.63	361.04	303.33
21.47	9.86	153.30	111.54	253.87	209.48	362.67	304.61
22.38	10.90	156.23	113.01	256.32	210.68	364.30	306.24
22.79	11.23	159.17	114.37	258.77	212.05	365.92	307.65
23.78	12.33	162.10	115.77	261.21	213.48	367.53	309.09
24.74	13.49	165.04	117.15	263.63	214.83	369.14	310.41
25.15	13.90	167.98	118.55	266.05	216.37	370.75	311.57
26.19	15.07	170.92	119.95	268.45	217.89	372.35	312.82
27.20	16.11	173.86	121.36	270.84	219.48	373.95	314.30
27.62	16.44	176.80	122.79	273.22	221.05	375.55	315.42
28.71	17.58	179.74	124.24	275.58	222.79	377.14	316.68
29.78	18.83	182.69	125.71	277.94	224.39	378.73	317.95
30.17	19.25	185.63	127.24	280.28	226.11	380.31	319.24
31.78	21.20	188.57	128.81	282.61	227.76	381.89	320.17
35.16	25.36	191.51	130.44	284.93	229.63	383.47	321.16
38.00	28.31	194.46	132.06	287.23	231.51	385.05	322.12
40.50	31.13	197.40	133.63	289.53	233.35	386.63	322.81
42.88	33.91	200.34	135.37	291.81	235.25	388.21	323.86
45.33	36.72	203.28	137.57	294.08	237.16	389.79	324.17
47.82	39.53	206.22	139.93	296.34	239.12	391.37	324.97
50.34	42.36	209.15	142.67	298.59	241.17	392.95	325.81
52.89	45.17	212.07	145.66	300.82	243.13	394.53	326.66
55.47	47.75	214.98	150.00	304.88	246.88	396.11	327.44
58.09	50.26	217.85	158.73	305.73	247.71	397.70	327.86
60.73	52.78	220.62	179.49	307.09	249.04	399.28	329.13

[a] In $J \cdot K^{-1} \cdot mol^{-1}$ at temperatures in K.

cooling rate of about 4 $K \cdot h^{-1}$ was made before starting the heat capacity measurements in order to check for metastable solid phases.

After completion of the measurement, the data were combined in one file. For all compounds several runs were made and each temperature range was measured at least twice. With these four compounds no influence of the thermal history was found, and as the reproducibility of the calorimeter is better than the above stated accuracy, we give in the tables of experimental data those data which form a continuous set from the lowest to the highest measuring temperature. The heat capacity data in the melting region reach very high values, which are not suited for calculating the enthalpy of fusion. This calculation must be done with the enthalpy curve. We have included separate tables for the melting experiments in which the enthalpy data are also given. For the calculation of the purity a sigmoid baseline was constructed using as starting values for the heat capacity of the solid and the liquid linear fits. These fits are given in the tables which contain the measured enthalpies of fusion. The observed equilibrium temperatures in the melt are probably correct to a relative precision of 0.001 or 0.002 K, as sufficient time was taken to reach equilibrium to within this limit. Those data are also given together with the calculated reciprocal values of the melted fraction. The purity was calculated using the van't Hoff relation

$$(T_{\text{triple}} - T_{\text{eq}}) = \frac{RT_{\text{triple}}^2}{\Delta H_{\text{fus}}} \frac{x}{F}$$

in which T_{triple} is the triple point temperature, T_{eq} is the experimental equilibrium temperature in the melt at the melted fraction F, x is the impurity in moles, and ΔH_{fus} is the calculated enthalpy of fusion.

Between 4 K and 30 K the measurements were repeated three times and fitted to the low-temperature limit of the

Table 3. Experimental Enthalpy Increments for 1-Hexanol around the Melting Point

T / K	$H - H_{\text{start}}$ / $J \cdot mol^{-1}$	T / K	$H - H_{\text{start}}$ / $J \cdot mol^{-1}$	T / K	$H - H_{\text{start}}$ / $J \cdot mol^{-1}$
Exp 1		226.63	25175	226.49	19038
218.71	11620	226.63	26037	226.52	19896
221.44	12095	226.64	26899	226.55	20755
223.80	12630	226.65	27759	226.57	21615
225.34	13282	226.72	28612	226.58	22476
226.01	14051	227.49	29368	226.60	23338
226.27	14878	229.48	29956	226.61	24200
226.40	15723	232.03	30466	226.61	25062
226.47	16574	Exp 2		226.62	25924
226.52	17430	214.98	12896	226.62	26787
226.55	18288	217.85	13339	226.62	27650
226.57	19148	220.62	13806	226.63	28513
226.59	20008	223.11	14323	226.63	29375
226.60	20868	224.91	14939	226.65	30236
226.61	21730	225.81	15678	227.08	31040
226.61	22591	226.17	16492	228.77	31670
226.62	23452	226.33	17332	231.33	32179
226.62	24314	226.43	18183		

Table 4. Equilibrium Temperatures in the Melt and the Reciprocal of the Melted Fraction of 1-Hexanol

experiment 1				experiment 2			
T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}
226.012	11.293	226.614	1.685	226.169	8.179	226.612	1.586
226.272	7.374	226.620	1.551	226.335	5.849	226.617	1.467
226.400	5.408	226.625	1.436	226.430	4.527	226.620	1.363
226.475	4.253	226.629	1.337	226.487	3.683	226.623	1.274
226.522	3.498	226.633	1.251	226.525	3.102	226.626	1.195
226.552	2.969	226.639	1.175	226.551	2.677	226.633	1.126
226.572	2.577	226.654	1.109	226.570	2.354	226.649	1.065
226.587	2.276	226.725	1.050	226.585	2.100	227.076	1.018
226.598	2.038	227.493	1.012	226.596	1.896	228.772	1.000
226.606	1.845	229.480	1.000	226.605	1.727	231.325	1.000

Table 5. Melting Experiments of 1-Hexanol[a]

experiment	triple point / K	ΔH_{fusion} / $J \cdot mol^{-1}$
1	226.69	16 723
2	226.70	16 735
mean value	226.70 ± 0.02	16 729 ± 35

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of fusion: $C_p(\text{solid}) = \{36.50 + 0.4890T\}$ $J \cdot K^{-1} \cdot mol^{-1}$ and $C_p(\text{liquid}) = \{103.88 + 0.4154T\}$ $J \cdot K^{-1} \cdot mol^{-1}$.

Table 6. Thermodynamic Properties at Selected Temperatures for 1-Hexanol Molar Mass = 102.18 g·mol^{-1}

T	$C^{\circ}_{p,m}$	S°_{m}	ΔH°_{m}
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}
10	1.41	0.49	3.7
20	8.47	3.33	48.6
30	19.07	8.73	185
40	30.56	15.83	435
50	41.99	23.89	798
60	52.09	32.47	1 270
70	61.11	41.18	1 837
80	69.18	49.88	2 489
90	76.46	58.46	3 218
100	83.02	66.85	4 015
110	89.30	75.07	4 878
120	94.61	83.08	5 798
130	100.4	90.87	6 773
140	105.1	98.48	7 800
150	110.0	105.9	8 876
160	114.8	113.2	10 000
170	119.5	120.3	11 171
180	124.4	127.2	12 390
190	129.6	134.1	13 659
200	134.3	140.8	14 978
210[a,b]	139.2	147.5	16 345
220[a,b]	144.1	154.1	17 762
226.70[a,b]	147.4	158.5	18 738
226.70[a,c]	198.1	232.3	35 473
230	199.6	235.2	36 133
240	203.4	243.8	38 147
250	207.9	252.2	40 204
260	212.8	260.4	42 305
270	218.9	268.6	44 463
280	225.9	276.7	46 687
290	233.7	284.7	48 984
298.15	240.8	291.3	50 917
300	242.4	292.8	51 364
310	251.9	300.9	53 835
320	261.9	309.0	56 403
330	272.3	317.3	59 073
340	282.5	325.5	61 847
350	291.9	333.9	64 721
360	302.4	342.3	67 696
370	311.0	350.7	70 764
380	319.0	359.1	73 914

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

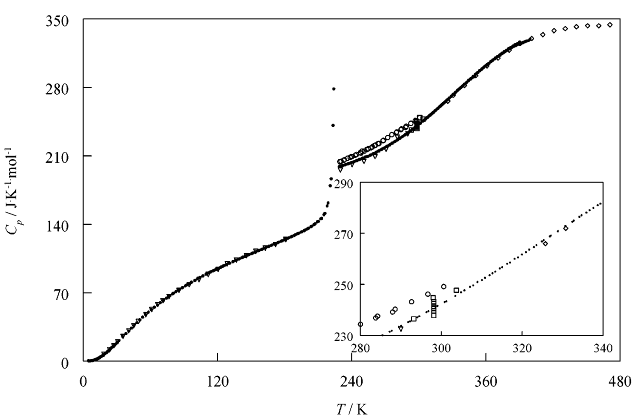

Figure 1. Experimental heat capacity values of 1-hexanol: (●) our data; (○) ref 10; (▽) data from ref 8; (◇) data from ref 9, these values were measured at 2 MPa; (■) data from NIST.[4] The inset gives an enlarged view of the data between 280 K and 340 K.

Debye heat capacity function $C_p = \alpha T^3$. The data set was interpolated for every degree, and the derived properties were calculated by numerical integration. The starting values of $S°$ and $H°(T) - H°(0)$ were calculated assuming that below 8 K the low-temperature limit of the Debye heat capacity function $C_p = \alpha T^3$ holds.

Table 7. Experimental Molar Heat Capacities[a] of 1-Heptanol

T	C_p	T	C_p	T	C_p	T	C_p
5.31	0.44	95.61	91.19	232.78	201.10	291.61	268.18
5.42	0.56	98.48	92.84	234.83	224.26	293.38	270.14
5.65	0.65	101.35	94.53	236.67	294.91	295.13	271.58
6.15	0.67	103.14	95.61	238.08	527.24	296.89	273.08
6.48	0.86	103.80	96.11	238.92	1349	298.63	274.82
7.31	1.19	105.60	97.26	239.30	3229	300.38	276.64
7.87	1.44	108.54	98.98	239.48	6098	302.11	278.13
8.68	1.85	111.44	100.70	239.59	10165	303.83	279.76
9.23	1.97	114.34	102.18	239.65	15473	305.55	281.48
10.13	2.56	117.25	103.89	239.70	22325	307.27	283.15
10.82	2.88	120.16	105.61	239.73	30787	308.97	284.94
11.98	3.13	123.07	107.23	239.75	44894	310.67	286.86
12.59	3.84	125.99	108.60	239.77	59712	312.17	287.58
13.88	5.66	128.91	110.24	239.78	76137	312.48	287.74
14.41	6.01	131.84	111.79	239.79	89416	313.47	289.53
15.57	7.38	134.77	113.19	239.80	118824	315.15	291.13
16.22	8.12	137.71	114.67	239.80	179459	316.82	292.75
17.55	9.78	140.65	116.31	239.81	211237	318.49	294.51
18.23	10.55	143.59	117.83	239.81	436948	320.15	296.14
19.79	12.66	146.51	119.01	239.81	$>10^7$	321.81	297.32
20.46	13.54	149.41	120.42	239.81	310201	323.47	298.29
22.10	15.64	152.27	121.98	239.81	253221	325.13	300.22
22.80	16.74	155.11	123.57	239.82	177250	326.77	304.10
24.52	18.91	157.93	125.00	239.83	79158	328.40	306.16
25.26	20.20	160.72	126.40	239.84	101942	330.02	307.87
27.06	22.51	163.48	127.87	240.21	897	331.64	309.45
27.82	23.98	166.23	129.28	241.56	234.91	333.25	311.37
29.69	26.33	168.95	130.67	243.49	235.74	334.86	313.07
30.49	27.89	171.65	132.10	245.41	236.40	336.46	315.09
32.23	29.87	174.34	133.48	247.33	237.15	338.06	316.80
34.64	33.16	177.00	135.02	249.24	238.27	339.65	318.31
36.93	36.15	179.64	136.57	251.15	239.26	341.23	320.04
39.27	39.19	182.25	138.29	253.05	240.26	342.81	321.74
41.68	42.23	184.85	139.84	254.94	241.30	344.38	323.31
44.12	45.22	187.43	141.46	256.83	242.37	345.95	325.06
46.61	48.18	189.99	143.11	258.71	243.50	347.51	326.69
49.13	51.12	192.54	144.77	260.59	244.66	349.06	328.33
51.68	53.98	195.06	146.54	262.46	245.74	350.62	329.86
54.27	56.79	197.57	148.40	264.33	246.95	352.17	331.49
56.89	59.48	200.05	150.08	266.19	248.18	353.71	333.02
59.54	62.05	202.53	151.80	268.04	249.42	355.25	334.62
62.21	64.76	204.98	153.71	269.89	250.62	356.78	336.30
64.91	67.35	207.41	154.84	271.74	251.77	358.30	337.67
67.61	69.71	209.83	157.69	273.58	253.30	359.82	372.26
70.34	72.23	212.23	159.75	275.41	254.82	361.11	251.89
73.09	74.58	214.61	161.90	277.24	256.14	362.30	354.74
75.86	76.67	216.96	164.20	279.06	257.48	363.71	342.83
78.64	78.77	219.30	166.60	280.87	259.09	365.22	344.07
81.44	81.34	221.62	169.38	282.68	260.54	366.73	345.59
84.25	83.31	223.92	172.57	284.48	261.95	368.24	346.84
87.07	85.42	226.20	176.32	286.27	263.46	369.74	347.99
89.91	87.09	228.44	181.33	288.06	265.02		
92.76	89.07	230.64	189.25	289.84	266.66		

[a] In J·K^{-1}·mol^{-1} at temperatures in K.

Results and Discussion

1-Hexanol. A sample of 6.5 g was used in CALV. The experimental data are given in Table 2; these are data for a continuous series from 8 K to 400 K. In Figure 1 the experimental data are plotted, together with the values reported by Kelley[8] and Kalowska et al.[10] and liquid heat capacity data reported by Fulem et al.[9] Also plotted are the values of the liquid heat capacity at and around 298.15 K given in the NIST[4] databank. The literature data correspond, within the error margin, with our results. In Table 3 the enthalpy increments in the melt around the two melting experiments are given. The calculated fractional melting data and the equilibrium temperatures in the melt are given in Table 4. The purities calculated from these experiments, using the $1/F$ range from 1 to 5, were respectively 99.82 mol % and 99.78 mol %. In Table 1 the

Table 8. Experimental Enthalpy Increments for 1-Heptanol around the Melting Point

T	$H - H_{start}$	T	$H - H_{start}$	T	$H - H_{start}$
K	J·mol^{-1}	K	J·mol^{-1}	K	J·mol^{-1}
Exp 1		239.803	27 092	234.828	17 706
213.594	11 262	239.805	27 902	236.667	18 178
215.567	11 581	239.808	28 712	238.083	18 728
217.539	11 904	239.809	29 523	238.918	19 386
219.509	12 231	239.810	30 333	239.301	20 127
221.478	12 562	239.812	31 144	239.485	20 905
223.443	12 897	239.819	31 953	239.589	21 698
225.406	13 238	239.840	32 760	239.654	22 498
227.365	13 585	240.167	33 511	239.698	23 302
229.313	13 939	241.435	34 086	239.729	24 109
231.243	14 303	243.354	34 540	239.751	24 917
233.148	14 680	245.274	34 993	239.767	25 727
235.008	15 079	247.189	35 446	239.779	26 537
236.741	15 521	249.100	35 900	239.789	27 348
238.143	16 052	251.004	36 355	239.797	28 159
238.989	16 704	252.903	36 810	239.803	28 970
239.359	17 447	254.797	37 266	239.807	29 782
239.524	18 227	Exp 2		239.810	30 593
239.613	19 020	212.227	13 712	239.811	31 405
239.669	19 821	214.605	14 094	239.812	32 217
239.707	20 625	216.965	14 479	239.815	33 028
239.734	21 430	219.304	14 866	239.819	33 840
239.753	22 237	221.625	15 256	239.826	34 651
239.767	23 045	223.924	15 649	239.835	35 462
239.778	23 854	226.197	16 045	240.214	36 204
239.787	24 663	228.439	16 446	241.556	36 768
239.794	25 472	230.640	16 854	243.487	37 222
239.799	26 282	232.782	17 272		

Table 9. Equilibrium Temperatures in the Melt and the Reciprocal of the Melted Fraction of 1-Heptanol

experiment 1				experiment 2			
T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}
239.524	6.210	239.803	1.563	239.485	6.386	239.807	1.563
239.613	4.918	239.805	1.462	239.589	5.025	239.810	1.462
239.669	4.060	239.808	1.374	239.654	4.129	239.811	1.373
239.707	3.453	239.809	1.295	239.698	3.499	239.812	1.294
239.734	3.002	239.810	1.226	239.729	3.034	239.815	1.223
239.753	2.654	239.812	1.163	239.751	2.676	239.819	1.160
239.767	2.378	239.819	1.106	239.767	2.393	239.826	1.104
239.778	2.154	239.840	1.055	239.779	2.164	239.835	1.052
239.787	1.968	240.167	1.016	239.789	1.975	240.214	1.014
239.794	1.811	241.436	1.000	239.797	1.816	241.557	1.000
239.799	1.678			239.803	1.680		

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

experiment	triple point (K)	ΔH_{fusion} (J·mol^{-1})
1	239.89	18 359
2	239.90	18 336
mean value	239.90 ± 0.02	18 348 ± 40

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of fusion: C_p(solid) = {42.20 + 0.5219T} J·K^{-1}·mol^{-1} and C_p(liquid) = {137.61 + 0.4028T} J·K^{-1}·mol^{-1}.

mean value is given; the almost exact correspondence between the calorimetric determined purity and the purity measured by analytical means is, in our opinion, due to the very low water content of 1-hexanol. It is to be expected that water does not form an eutectic system with the n-alcohols; we come back to this further on with the measurements of 1-octanol. Table 5 gives the results of the melting experiments and the linear fits of the heat capacity of the solid and liquid phase used as baselines for the calculation. The mean value of the enthalpy of fusion, (16 729 ± 35) J·mol^{-1}, is higher than the value reported by Kelley[8] of 15 380 J·mol^{-1}; the triple temperature found in this work, being (226.70 ± 0.01) K, is 0.9 K higher than the value reported by Kelley. These differences are not within the reported error margins and are probably due to a difference in purity. For the calculation of the entropy and enthalpy increments from 0 K, the relation $C_p = \alpha T^3$ was used to calculate the starting values for a numerical integration at 8 K; α was found to be 1.39 × 10^{-3} J·K^{-4}·mol^{-1}. The results are given in Table 6.

Table 11. Thermodynamic Properties at Selected Temperatures for 1-Heptanol Molar Mass = 116.20 g·mol^{-1}

T	$C^{\circ}_{p,m}$	S°_{m}	ΔH°_{m}
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}
10	2.48	0.95	7.0
20	12.93	5.34	76.8
30	26.94	13.18	275
40	40.12	22.80	612
50	52.11	33.07	1074
60	62.51	43.51	1649
70	71.92	53.88	2322
80	80.02	64.01	3082
90	87.15	73.88	3920
100	93.74	83.41	4826
110	99.85	92.65	5796
120	105.5	101.6	6822
130	110.8	110.2	7904
140	116.0	118.6	9037
150	120.7	126.8	10221
160	126.0	134.8	11456
170	131.2	142.6	12742
180	136.1	150.2	14079
190	141.4	157.7	15466
200[a,b]	146.6	165.1	16906
210[a,b]	151.8	172.4	18398
220[a,b]	157.0	179.5	19942
230[a,b]	162.2	186.6	21539
239.90[a,b]	167.4	193.6	23170
239.90[a,c]	234.2	270.1	41518
240	234.3	271.1	41294
250	238.7	280.1	43890
260	244.3	289.5	46304
270	250.7	298.9	48778
280	258.9	308.1	51326
290	266.7	317.4	53954
298.15	274.0	324.9	56157
300	275.7	326.6	56666
310	285.7	335.8	59473
320	296.3	345.0	62383
330	307.2	354.3	65400
340	318.2	363.6	68528
350	329.0	373.0	71763
360	339.2	382.4	75104

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

1-Heptanol. We started cooling from room temperature to a temperature below the melting point to assess the thermal behavior. The cooling curve showed an undercooling of ~2.8 K at a cooling rate of 1.8 K·h^{-1}. The data series were combined and are presented in the same way as those for 1-hexanol. The temperatures and the heat capacity values are given in Table 7. The relative enthalpy increments as a function of temperature in the melting range are given in Table 8. A linear fit of the heat capacity of the solid, made between 150 K and 170 K, was used to calculate the enthalpy of fusion. This fit and a linear fit of the heat capacity of the liquid phase are given together with the result of the calculation of the enthalpy of fusion in Table 10. The enthalpy of fusion was found to be (18 348 ± 40) J·mol^{-1}, and the triple point temperature was (239.90 ± 0.02) K. The fractional melting curve was calculated by constructing a sigmoid baseline using these fits as starting values for the heat capacity. The calculated 1/F values of the two measurement series in the melt are given in Table

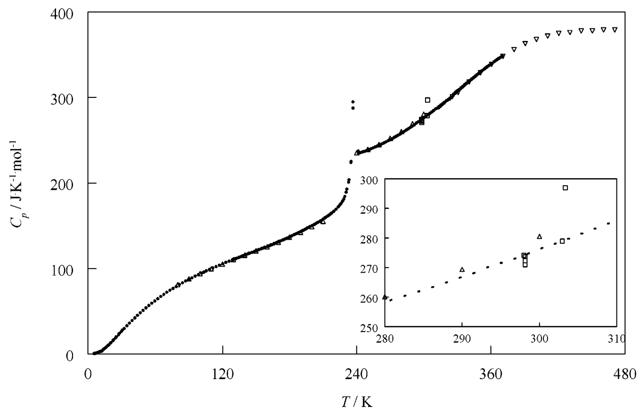

Figure 2. Experimental heat capacity values of 1-heptanol: (●) our data; (■) ref 4; (▽) data from ref 9; (△) ref 11. The inset gives an enlarged view of the data between 280 K and 310 K.

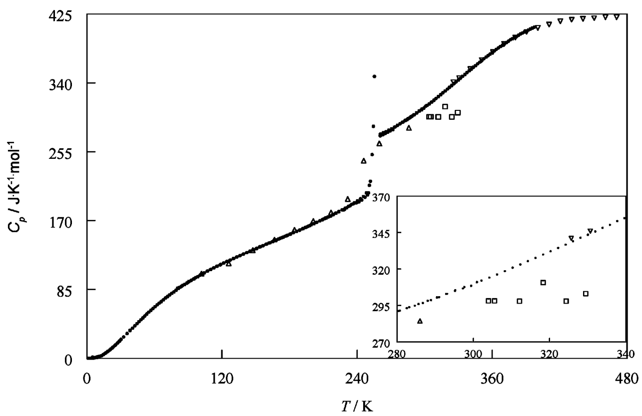

Figure 3. Experimental heat capacity values of 1-octanol: (●) our data; (■) ref 4; (▽) data from ref 9; (△) ref 12. The inset gives an enlarged view of the data between 280 K and 340 K.

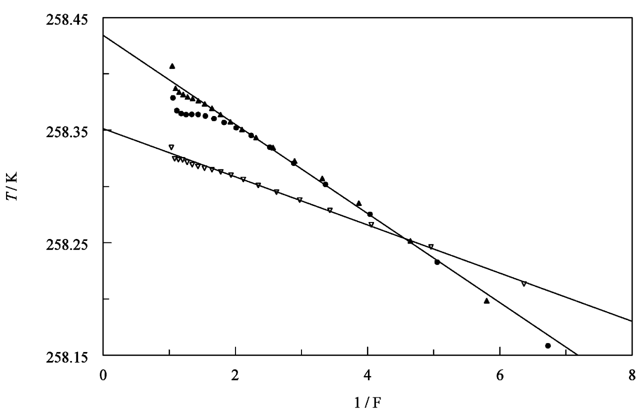

Figure 4. Fractional melting experiments of 1-octanol: (●, ▲) measurements on the sample reported in this work; (▽) measurement of a sample with a water content of 0.5 wt %.

Table 12. Experimental Molar Heat Capacities[a] of 1-Octanol

T	C_p	T	C_p	T	C_p	T	C_p
5.51	0.55	71.67	76.25	199.21	164.61	292.88	303.04
7.65	1.13	73.56	78.27	201.74	166.06	295.28	305.54
8.67	1.38	75.46	80.21	204.25	167.79	297.66	307.64
9.45	1.79	77.36	82.12	206.75	169.44	300.98	311.08
9.60	1.87	79.26	83.98	209.24	171.15	302.16	312.05
10.46	2.27	81.17	86.12	211.71	172.75	304.21	314.16
10.49	2.20	81.87	87.31	214.16	174.25	306.25	316.36
10.59	1.99	83.09	87.87	216.60	175.77	308.28	318.62
11.31	2.15	84.00	88.68	219.03	177.39	310.30	320.94
12.02	2.64	85.01	89.74	221.44	179.06	312.31	323.19
12.51	2.70	86.87	91.24	223.84	180.79	314.32	325.48
13.25	3.26	86.93	91.20	227.87	183.03	316.31	327.65
14.41	4.33	88.86	92.89	228.80	183.89	318.29	329.87
14.41	4.32	89.71	93.73	230.74	185.62	320.27	332.17
15.01	4.91	90.79	94.84	233.70	188.03	322.24	334.52
16.12	5.91	92.55	96.12	236.61	190.47	324.20	336.75
16.18	5.98	92.72	96.30	239.31	191.90	326.16	339.10
16.80	6.56	94.66	97.76	241.65	193.09	328.10	341.40
18.08	7.79	95.39	98.32	244.20	195.39	330.05	343.52
18.11	7.82	96.60	99.48	247.12	198.75	331.98	345.75
18.86	8.63	98.25	100.63	249.34	201.65	333.90	348.22
20.26	10.18	98.55	100.87	250.05	204.14	335.82	350.30
20.30	10.22	100.49	102.53	251.91	218.67	337.73	352.81
21.07	11.09	101.11	103.05	254.58	286.37	339.63	354.92
22.52	12.79	103.98	105.11	256.63	581	341.53	356.95
22.57	12.84	106.86	107.33	257.68	2273	343.41	359.19
23.36	13.82	109.74	109.46	258.02	6629	345.29	361.35
24.83	15.65	112.63	111.55	258.16	13069	347.17	363.47
24.89	15.73	115.53	113.50	258.23	23718	349.03	365.55
25.62	16.68	118.43	115.45	258.28	39681	350.89	367.72
26.95	18.46	121.34	117.43	258.30	57715	352.74	369.80
27.01	18.51	124.25	119.33	258.32	78273	354.59	371.63
27.60	19.36	127.17	121.24	258.33	101445	356.43	373.69
28.73	20.88	130.09	123.10	258.35	143850	358.26	375.61
28.79	20.93	133.02	124.93	258.35	253752	360.09	377.59
29.30	21.67	135.94	126.61	258.36	295671	361.91	379.46
30.29	23.20	138.87	128.39	258.36	472686	363.73	381.30
30.34	23.31	141.81	130.27	258.36	627225	365.54	383.13
32.64	26.31	144.74	131.98	258.36	4113967	367.34	384.79
35.67	30.50	147.68	133.74	258.36	1824897	369.14	386.39
38.25	34.45	150.60	135.43	258.36	2139584	370.94	387.90
40.52	37.31	153.50	137.26	258.36	795376	372.73	389.69
42.56	40.16	156.36	138.96	258.37	333952	374.51	391.32
44.44	42.82	159.19	140.67	258.38	66333	376.30	393.10
46.21	45.20	162.00	142.31	258.92	965	378.07	394.44
47.94	47.59	164.78	143.89	260.72	276.51	379.85	395.86
49.70	49.95	167.54	145.46	263.26	278.28	381.62	397.23
51.47	52.30	170.28	147.16	265.79	279.96	383.38	398.77
53.25	54.69	172.99	148.67	268.30	281.74	385.15	400.21
55.05	57.19	175.69	150.31	270.80	283.47	386.92	401.56
56.86	59.30	178.37	151.92	273.30	285.37	388.68	402.87
58.68	61.44	181.04	153.46	275.79	287.38	390.44	404.11
60.51	63.66	183.69	155.20	278.27	289.49	392.19	405.29
62.35	65.86	186.32	156.65	280.73	291.59	393.95	406.53
64.20	68.03	188.93	158.14	283.19	293.87	395.70	407.67
66.06	70.11	191.53	159.84	285.63	296.00	397.45	408.64

[a] In J·K^{-1}·mol^{-1} at temperatures in K.

9. The calculated purities were respectively 99.79 mol % and 99.76 mol %. The value calculated for α in the relation $C_p = \alpha T^3$ was $\alpha = 2.5 \times 10^{-3}$ J·K^{-4}·mol^{-1} from the data between 5 K and 8 K and was used for calculating the starting values of the numerical calculation of the enthalpy and the entropy. The resulting thermodynamic data are given in Table 11. Near the melting point the thermodynamic functions are extrapolated according to the functions given in Table 10. In Figure 2 the experimental heat capacity data are given together with some selected literature data. The correspondence is good; the enthalpy of fusion can be compared to the value given by Parks et al.,[11] of 18 175 J·mol^{-1}. The difference between that and our value is probably caused by a different choice of baseline. Our value for the absolute entropy at 298.15 K corresponds to the value reported by Parks et al. to within 0.3%.

1-Octanol. The experimental data series between 5 K and 400 K are given in Table 12. In Figure 3 all data are plotted together with some literature values. Two melting experiments were performed; the results are given in Table 15 together with the linear fits of the heat capacity of the solid and liquid phase used to calculate the enthalpy of fusion. In Table 13 the data around the melting point are given with the enthalpy increments. The derived thermodynamic properties were calculated by numerical integra-

Table 13. Experimental Enthalpy Increments for 1-Octanol around the Melting Point

T	$H - H_{start}$	T	$H - H_{start}$	T	$H - H_{start}$
K	$J \cdot mol^{-1}$	K	$J \cdot mol^{-1}$	K	$J \cdot mol^{-1}$
Exp 1		258.367	24 304	258.198	28 343
250.045	144	258.379	25 558	258.252	29 432
251.907	544	258.919	26 696	258.285	30 526
254.583	1 214	260.722	27 560	258.307	31 620
256.628	2 034	263.260	28 264	258.323	32 714
257.676	3 069	Exp 2		258.334	33 810
258.019	4 249	226.780	17 948	258.343	34 906
258.158	5 477	229.544	18 457	258.351	36 003
258.233	6 732	232.289	18 969	258.357	37 100
258.275	7 991	235.016	19 483	258.364	38 198
258.302	9 243	237.723	19 999	258.369	39 297
258.321	10 495	240.414	20 519	258.373	40 396
258.335	11 749	243.086	21 041	258.376	41 497
258.345	13 003	245.737	21 567	258.378	42 598
258.352	14 258	248.362	22 098	258.379	43 697
258.357	15 513	250.941	22 636	258.382	44 795
258.360	16 768	253.387	23 203	258.384	45 893
258.363	18 023	255.528	23 834	258.387	46 991
258.364	19 279	257.030	24 604	258.407	48 085
258.364	20 535	257.703	25 355	258.974	49 060
258.364	21 792	257.950	26 198	260.638	49 796
258.365	23 049	258.111	27 262	262.865	50 409

Table 14. Equilibrium Temperatures in the Melt and the Reciprocal of the Melted Fraction of 1-Octanol

experiment 1				experiment 2			
T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}
258.019	9.910	258.360	1.677	258.111	7.692	258.369	1.648
258.158	6.728	258.363	1.548	258.199	5.803	258.373	1.537
258.233	5.052	258.364	1.256	258.252	4.646	258.376	1.440
258.275	4.037	258.364	1.437	258.285	3.869	258.378	1.355
258.302	3.364	258.364	1.340	258.307	3.313	258.380	1.279
258.321	2.882	258.365	1.182	258.323	2.896	258.382	1.211
258.335	2.521	258.367	1.116	258.334	2.572	258.384	1.150
258.345	2.240	258.379	1.057	258.343	2.313	258.387	1.095
258.352	2.014	258.919	1.015	258.351	2.101	258.407	1.046
258.357	1.830	260.722	1.000	258.357	1.925	262.865	1.000
				258.364	1.775		

Table 15. Melting Experiments of 1-Octanol[a]

experiment	triple point K	ΔH_{fusion} $J \cdot mol^{-1}$
1	258.43	25 137
2	258.43	25 132
mean value	258.43 ± 0.02	25 135 ± 40

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of fusion: C_p(solid) = {34.94 + 0.6507T} $J \cdot K^{-1} \cdot mol^{-1}$ and C_p(liquid) = {93.92 + 0.7001T} $J \cdot K^{-1} \cdot mol^{-1}$.

tion, starting with fitting the heat capacities up to 8 K to the function $C_p = \alpha T^3$; α was found to be 1.38×10^{-3} $J \cdot K^{-4} \cdot mol^{-1}$, and the thermodynamic properties are given in Table 16. The calculated $1/F$ values of the two measurement series in the melt are given in Table 14. The triple point temperature was (258.43 ± 0.02) K, and the enthalpy of fusion was (25135 ± 40) $J \cdot mol^{-1}$. In Figure 4 the equilibrium temperatures in the melt are plotted against the reciprocal of the melted fraction. The purity calculated from this curve was 99.82 mol %. In the same figure the measurement on a sample containing 0.5 wt % water is given. The measurements on this sample were not used after we found the high water content, but it is interesting to see that, while the triple point is, as expected, lower than the triple point of the more pure sample, the purity calculated from this measurement is even better than that of the pure sample. This confirms that water does not form

Table 16. Thermodynamic Properties at Selected Temperatures for 1-Octanol Molar Mass = 130.33 $g \cdot mol^{-1}$

T	$C^{\circ}_{p,m}$	S°_{m}	ΔH°_{m}
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot mol^{-1}$
10	2.14	0.46	3.5
20	9.90	3.71	54.9
30	22.74	10.00	214
40	36.64	18.40	509
50	50.35	28.03	944
60	63.04	38.37	1 512
70	74.50	48.96	2 201
80	84.76	59.59	2 998
90	94.02	70.15	3 895
100	102.1	80.45	4 874
110	109.7	90.56	5 935
120	116.5	100.4	7 067
130	123.0	110.0	8 265
140	129.1	119.3	9 525
150	135.1	128.4	10 847
160	141.2	137.4	12 228
170	147.0	146.1	13 668
180	152.9	154.7	15 167
190	158.8	163.1	16 726
200	165.1	171.4	18 346
210	171.7	179.6	20 029
220	178.1	187.7	21 777
230	184.6	195.8	23 590
240	191.1	203.8	25 469
250[a]	197.6	211.7	27 413
258.43[a,b]	203.1	218.4	29 102
258.43[a,c]	274.9	315.6	54 234
260	276.0	317.3	54 666
270	283.0	327.8	57 461
280	290.6	338.3	60 338
290	300.0	348.7	63 292
298.15	308.1	357.1	65 772
300	310.1	359.0	66 343
310	320.6	369.4	69 495
320	331.9	379.7	72 757
330	343.5	390.1	76 135
340	355.3	400.5	79 629
350	366.7	411.0	83 239
360	377.5	421.5	86 960
370	387.1	432.0	90 785
380	396.0	442.4	94 702
390	403.8	452.8	98 702

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

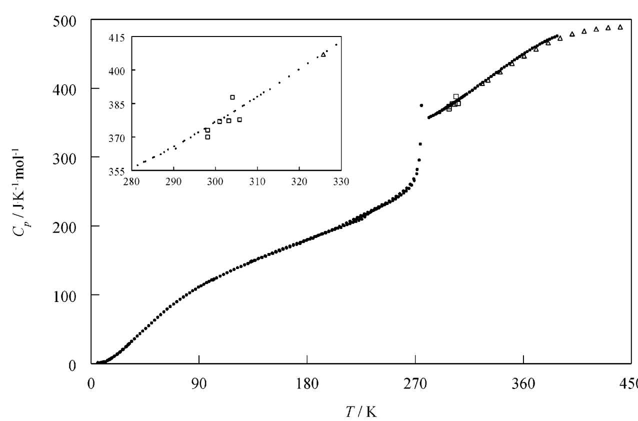

Figure 5. Experimental heat capacity values of 1-decanol: (●) our data; (■) ref 4; (△) data from ref 9. The inset gives an enlarged view of the data between 280 K and 330 K.

a eutectic system with the alcohol and that the calorimetric purity determination of the n-alcohols can be performed only on very dry samples.

1-Decanol. The cooling curve showed an undercooling of the crystallization of 0.8 K. The continuous set of experimental data between 5 K and 388 K is given in Table

Table 17. Experimental Molar Heat Capacities[a] of 1-Decanol

T	C_p	T	C_p	T	C_p	T	C_p
5.55	0.74	60.70	75.26	183.30	182.52	280.00	20176
5.64	1.03	63.34	79.18	186.25	184.33	280.86	657
5.67	1.07	66.01	82.81	189.19	186.23	282.91	358.86
6.16	0.68	68.71	86.35	192.14	188.22	285.35	361.01
6.50	0.83	71.43	89.88	195.09	190.24	287.77	363.22
6.70	0.84	74.18	93.36	198.03	192.29	290.19	365.86
7.37	1.13	76.92	96.71	200.98	194.46	292.59	368.37
8.64	1.81	79.58	99.90	203.92	196.69	294.99	371.16
8.65	1.58	82.14	102.85	206.87	199.08	297.37	373.68
8.66	1.55	84.63	105.79	209.82	201.58	299.75	376.70
9.87	2.12	87.05	108.08	212.77	204.11	302.11	378.70
10.31	2.28	89.41	111.02	215.71	206.65	304.46	381.48
10.43	2.39	91.72	113.03	218.67	209.39	306.80	384.26
11.82	2.42	93.98	115.26	221.62	212.04	309.13	386.97
12.00	2.50	96.19	117.42	224.58	214.79	310.82	388.98
12.05	2.55	98.36	119.35	227.54	217.31	311.49	389.98
13.67	4.40	100.49	121.62	230.49	219.67	312.97	391.42
13.94	4.68	101.87	121.58	233.44	222.38	315.26	394.31
14.01	4.72	102.58	122.70	236.40	225.04	317.54	397.13
15.31	5.87	104.62	124.55	239.36	227.79	319.81	400.16
15.69	6.24	107.54	127.13	242.32	230.74	322.06	403.05
15.79	6.38	110.43	129.59	245.27	233.10	324.31	405.72
17.19	7.90	113.33	132.08	248.22	235.90	326.55	408.55
17.63	8.42	116.23	134.43	251.18	239.43	328.78	411.36
17.72	8.50	119.13	136.64	254.13	243.00	331.01	414.11
19.32	10.35	122.04	139.24	257.07	246.84	333.22	416.89
19.82	11.05	124.95	141.17	260.01	250.80	335.43	419.70
19.92	11.18	127.87	143.57	262.94	255.03	337.63	422.74
21.51	13.16	130.80	145.30	265.85	260.57	339.82	424.33
22.06	13.96	132.92	147.40	268.73	268.46	342.00	428.23
22.16	14.08	133.72	148.63	271.55	282.12	344.17	430.82
23.80	16.35	134.15	148.38	274.26	318.87	346.33	433.27
24.42	17.26	136.23	150.01	276.39	655	348.48	435.92
24.51	17.38	136.65	150.07	277.87	912	350.63	438.60
26.20	20.08	139.18	152.21	278.91	1692	352.77	441.15
26.87	20.79	139.59	152.88	279.45	5009	354.89	443.71
26.96	20.96	142.11	154.39	279.66	11149	357.01	446.07
28.69	23.90	142.53	154.20	279.76	20788	359.13	448.66
29.40	24.78	145.04	156.43	279.82	35838	361.23	451.07
29.49	24.89	145.48	155.88	279.85	56015	363.33	453.17
30.92	27.38	147.97	158.42	279.88	82149	365.43	455.63
31.28	28.13	148.43	158.53	279.89	107988	367.51	458.20
31.93	28.92	150.91	160.36	279.90	150593	369.59	459.67
33.77	32.15	151.37	159.91	279.91	165853	371.67	461.76
36.14	36.01	153.85	162.66	279.92	272961	373.74	463.90
38.42	40.02	156.78	164.70	279.93	352824	375.81	465.88
40.75	43.50	159.72	166.73	279.93	568545	377.87	467.86
43.12	47.25	162.67	168.67	279.93	1458445	379.92	469.67
45.52	51.05	165.61	170.56	279.93	1425403	381.97	471.19
47.96	55.00	168.56	172.56	279.93	724242	384.02	473.13
50.44	59.06	171.50	174.48	279.94	620954	386.07	474.36
52.95	63.07	174.45	176.31	279.94	952075	388.12	476.04
55.50	67.11	177.40	178.37	279.94	273491		
58.09	71.13	180.35	180.39	279.95	106784		

[a] In $J \cdot K^{-1} \cdot mol^{-1}$ at temperatures in K.

17. In Table 18 the data of the two melting experiments are given. The calculated fractional melt data of these series are given in Table 19. The results of the melting experiments and the linear fits of the heat capacity of the solid and liquid phase used in the calculation are given in Table 20. The purity calculated from the fractional melting experiments is 99.78 mol % using values of $1/F$ up to 5. As the curve of the equilibrium temperature in the melt against the reciprocal of the melted fraction is not linear above this value, the use of the model assuming eutectic behavior between the main component and the impurity is questionable. However, the value calculated for the purity does correspond very well to the value found by analytical means. The triple point temperature (at $1/F = 0$) was found to be (280.00 ± 0.02) K, and the mean enthalpy of fusion was 33670 $J \cdot mol^{-1}$, which is quite different from the value given in the NIST Databook[4] of 37 660 $J \cdot mol^{-1}$. In Figure 5 the experimental data are given together with literature data. The inset gives the data range around 298.15 K and the literature data mentioned in the NIST Databook. No large deviations were found; the correspondence with the data given by Fulem[9] is good even considering that these data were measured under a pressure of 2 MPa.

Table 18. Experimental Enthalpy Increments for 1-Decanol around the Melting Point

T	$H - H_{start}$	T	$H - H_{start}$	T	$H - H_{start}$
K	$J \cdot mol^{-1}$	K	$J \cdot mol^{-1}$	K	$J \cdot mol^{-1}$
Exp 1		279.890	46 372	265.854	26 161
242.169	24 428	279.900	47 512	268.731	26 922
244.489	24 960	279.908	48 652	271.553	27 699
246.795	25 495	279.915	49 793	274.255	28 509
249.091	26 031	279.921	50 934	276.391	29 469
251.374	26 570	279.927	52 075	277.870	30 605
253.642	27 110	279.931	53 217	278.910	31 857
255.896	27 653	279.934	54 359	279.445	33 244
258.139	28 199	279.936	55 500	279.657	34 718
260.368	28 748	279.939	56 641	279.760	36 220
262.582	29 300	279.941	57 784	279.818	37 735
264.783	29 856	279.943	58 926	279.853	39 256
266.966	30 417	279.946	60 067	279.876	40 779
269.125	30 983	279.949	61 209	279.892	42 306
271.249	31 558	279.951	62 350	279.904	43 833
273.314	32 148	279.954	63 492	279.914	45 360
275.215	32 781	279.959	64 633	279.921	46 889
276.652	33 537	279.966	65 772	279.926	48 417
277.732	34 390	280.257	66 836	279.930	49 946
278.642	35 287	281.456	67 657	279.932	51 475
279.207	36 276	Exp 2		279.933	53 005
279.486	37 342	242.316	20 426	279.934	54 535
279.633	38 444	245.268	21 110	279.937	56 064
279.721	39 562	248.223	21 803	279.939	57 594
279.777	40 689	251.179	22 506	279.942	59 124
279.815	41 820	254.128	23 217	279.952	60 652
279.843	42 956	257.069	23 938	279.997	62 171
279.863	44 094	260.007	24 668	280.862	63 470
279.879	45 233	262.940	25 410	282.909	64 452

Table 19. Equilibrium Temperatures in the Melt and the Reciprocal of the Melted Fraction of 1-Decanol

experiment 1				experiment 2			
T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}
279.633	6.651	279.934	1.611	279.657	6.674	279.932	1.549
279.721	5.468	279.937	1.527	279.760	5.164	279.933	1.447
279.777	4.632	279.939	1.452	279.818	4.198	279.934	1.358
279.815	4.013	279.941	1.384	279.853	3.532	279.937	1.279
279.843	3.537	279.943	1.322	279.876	3.047	279.939	1.209
279.863	3.161	279.946	1.265	279.892	2.678	279.942	1.146
279.879	2.857	279.949	1.213	279.904	2.388	279.952	1.089
279.891	2.605	279.951	1.165	279.914	2.155	279.997	1.039
279.900	2.395	279.955	1.121	279.921	1.963	280.862	1.008
279.908	2.215	279.959	1.080	279.926	1.803	282.909	1.000
279.915	2.061	279.966	1.042	279.930	1.666		
279.921	1.926	280.257	1.012				
279.927	1.808	281.457	1.000				
279.931	1.704						

Table 20. Melting Experiments of 1-Decanol[a]

	triple point	ΔH_{fusion}
experiment	K	$J \cdot mol^{-1}$
1	280.00	33 522
2	280.00	33 817
mean value	280.00 ± 0.02	33 670 ± 150

[a] The following linear fits of the heat capacity were used to calculate the enthalpy of fusion: $C_p(\text{solid}) = \{14.01 + 0.8933T\}$ $J \cdot K^{-1} \cdot mol^{-1}$ and $C_p(\text{liquid}) = \{51.63 + 1.0832T\}$ $J \cdot K^{-1} \cdot mol^{-1}$.

Table 21. Thermodynamic Properties at Selected Temperatures for 1-Decanol Molar Mass = 158.28 g·mol^{-1}

T	$C^{\circ}_{p,m}$	S°_{m}	ΔH°_{m}
K	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·mol^{-1}
10	2.17	0.88	6.48
20	11.29	4.59	65.37
30	25.66	11.81	248
40	42.38	21.58	592
50	58.34	32.73	1 095
60	74.16	44.78	1 758
70	88.03	57.29	2 571
80	100.4	69.86	3 514
90	111.6	82.33	4 573
100	121.1	94.56	5 736
110	129.2	106.5	6 987
120	137.4	118.1	8 321
130	144.8	129.4	9 734
140	153.3	140.4	11 224
150	159.7	151.2	12 787
160	166.9	161.8	14 422
170	173.5	172.1	16 123
180	180.2	182.2	17 891
190	186.8	192.1	19 726
200	193.7	201.9	21 628
210	201.7	211.5	23 604
220	210.6	221.1	25 665
230	219.3	230.6	27 816
240	228.4	240.2	30 054
250	237.3	249.7	32 383
260[a,b]	246.3	259.1	34 801
270[a,b]	255.2	268.6	37 308
280[a,b]	264.1	278.1	39 904
280[a,c]	354.9	398.9	73 721
290	365.8	411.5	77 325
298.15	374.6	421.8	80 342
300	377.0	424.1	81 037
310	388.0	436.6	84 862
320	400.4	449.2	88 804
330	412.9	461.7	92 870
340	424.6	474.2	97 058
350	437.8	486.7	101 370
360	449.7	499.2	105 807
370	460.1	511.6	110 356
380	469.7	524.0	115 005

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

Thermodynamic properties resulting from numerical calculation are given in Table 21, α for the relation $C_p = \alpha T^3$ was calculated from the data between 5 K and 9 K to be 1.4×10^{-3} J·K^{-4}·mol^{-1}. The data were interpolated for every degree from 9 K on. Near the melting point, the thermodynamic functions were extrapolated according to the fits given in Table 20.

Correlation of the Liquid Heat Capacity Data. In the previous articles on the 1-alcohols, we presented correlation functions for the heat capacities of the liquid 1-alcohols. In the first article, concerning the heat capacity data of the alcohols with the number of carbon atoms in the chain of 18, 19, 20, and 22, a simple function with three variables could be used. After the data set was extended with the compounds with carbon numbers 12, 13, 15, and 17, the number of variables was increased to four. When we included the data presented in this article, again the number of variables had to be increased to obtain the best fit for the whole set. The following correlation function

$$C_{p,l}(n,T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = (a_0 + a_1 n + a_2 nT + a_3 T + a_4 T + a_5/T + a_6 T^2)$$

was fitted for all data measured on the compounds with the number of carbon atoms in the chain ranging from 6 to 22. The total number of data triplets, consisting of mean temperature, mean heat capacity over the measuring interval, and the number of carbon atoms in the chain (n), was $N = 702$. The correlation function found was

$$C_{p,l}(n,T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -3163.5 + 21.0156n + 0.04223nT + 9.89055T + 322705.7/T - 0.0093225T^2$$

The mean absolute percentage deviation of the function with the experimental data was 0.22%, and the standard deviation was 1.26 J·K^{-1}·mol^{-1}. The temperature dependence of the heat capacity of the pure liquid n-alcohols is quite complex, as described by Zábranský.[13] This is reflected in the number of parameters needed for the correlation function.

Correlation of the Entropy at 360 K and at 298.15 K. In Table 22 the experimental absolute entropy values at 360 K are given for the alcohols with carbon numbers 6, 7, 8, 9, 12, 13, 18, 19, 20, and 22. A linear fit as a function the number of carbon atoms in the molecules resulted in the correlation

$$S°(360\ \text{K},n) = (111.86 + 38.613n)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The standard deviation of this equation is 0.82 J·K^{-1}·mol^{-1}, and the maximum deviation is 0.36% for $n = 6$. Using the above-mentioned correlation for the heat capacity of the liquid phase, the absolute entropy at 298.15 K was also calculated. At this temperature the alcohols with carbon number 12 and higher are in the solid phase, so the

Table 22. Measured and Correlated Absolute Entropies of the Liquid 1-Alcohols at 289.15 K and 360 K[a]

compound	n[b]	S_{abs}(360 K) meas J·K^{-1}·mol^{-1}	S_{abs}(360 K) correlated J·K^{-1}·mol^{-1}	dev %	S_{abs}(298.15 K)[c] meas J·K^{-1}·mol^{-1}	S_{abs}(298.15 K) correlated J·K^{-1}·mol^{-1}	dev %
1-hexanol	6	342.3	343.5	−0.36	291.3	292.6	−0.43
1-heptanol	7	382.4	382.1	0.07	324.9	324.6	0.09
1-octanol	8	421.5	420.8	0.17	357.1	356.6	0.13
1-decanol	10	498.8	498.0	0.16	421.8	420.7	0.26
1-dodecanol	12	574.8	575.2	−0.08	484.3	484.8	−0.10
1-tridecanol	13	613.6	613.8	−0.04	516.5	516.8	−0.05
1-octadecanol	18	806.8	806.9	−0.01	676.9	677.0	−0.01
1-nonadecanol	19	845.8	845.5	0.04	709.3	709.0	0.05
1-eicsanol	20	885.1	884.1	0.11	742.0	741.0	0.13
1-docosanol	22	960.2	961.3	−0.12	804.0	805.1	−0.14

[a] The correlations are S_{abs}(360 K) = (111.86 + 38.613n) J·K^{-1}·mol^{-1} and S_{abs}(298.15 K) = (100.35 + 32.035n) J·K^{-1}·mol^{-1}. [b] Number of carbon atoms. [c] For the compounds with n = 12 to n = 22, the melting point is above 298.15 K; S_{abs}(298.15 K) of the hypothetical liquid was calculated from S_{abs}(360 K) using the correlation function for C_p(l).

correlation for the entropy is made for the hypothetical liquids at this temperature. The correlation found was

$$S_{abs}(298.15\ K) = (100.35 + 32.035n)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

The standard deviation of this fit was 0.86 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

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