Thermal Properties of Ethyl Undecanoate and Ethyl Tridecanoate by Adiabatic Calorimetry

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The heat capacity of ethyl undecanoate was measured between 110 K and 365 K; the compound crystallized in a metastable form, which recrystallized slowly to the stable crystalline state during heating. The triple-point temperature of the stable form was found to be (259.17 ± 0.04) K, and the enthalpy of fusion was (36.1 ± 0.1) kJ·mol^{-1}. The purity calculated from the fractional melting curve was 97.5 mol %. The metastable form crystallized at 251.3 K. The heat capacity of ethyl tridecanoate was measured between 175 K and 320 K; the compound also crystallized in a metastable form, which recrystallized during heating to the stable form. The triple-point temperature was found to be (272.4 ± 0.1) K, and the enthalpy of fusion was (40.7 ± 0.1) kJ·mol^{-1}.

Introduction

In a recent publication,[1] the available vapor pressure data of a series of methyl esters of the linear carboxylic acids were assessed. The consistency of the data was checked using the "arc-method", in which, by applying a linear contribution to the Clapeyron fit, irregularities in the data are easily spotted. When the vapor pressure measurements of van Bommel[2] on the ethyl esters were checked, the measurements of the two compounds mentioned in the title clearly did not show the expected correlation. This was probably due to impurities in the samples. New samples, of the highest quality available, were purchased. A new series of vapor pressure measurements did not improve the results, so it was decided to measure the purity by adiabatic calorimetry. In this article, we present the heat capacity data and the enthalpies of fusion of the two ethyl esters, ethyl undecanoate and ethyl tridecanoate. No heat capacity data were found for these compounds in the literature.

Experimental Section

Ethyl undecanoate ($C_{13}H_{26}O_2$, CAR RN: 627-90-7) was purchased from Sigma; the stated purity was "approx. 99 mass %". Ethyl tridecanoate ($C_{15}H_{30}O_2$, CAS RN: 28267-29-0) was purchased from Lancaster Synthesis; the stated purity was 99 mass %. The compounds were used as received.

The calorimeter used for ethyl tridecanoate, CAL V (laboratory indication), has been described.[3,4] Oxford Instruments calibrated the thermometer with a precision of 0.001 K using the ITS-90[5] temperature scale. The uncertainties of the heat capacity measurements were checked with *n*-heptane[6] and synthetic sapphire[7,8] and found to be within 0.2%. 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 calorimeter vessel was filled in a glovebox under a nitrogen atmosphere and evacuated for about 5 min before closing the measuring vessel. A helium pressure of about 1000 Pa 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. The temperature increase was generally about 2 K for each measurement outside the transition region.

For the measurements on ethyl undecanoate, CAL 8 was used.[9] This calorimeter was specially designed for small samples and was used because only a limited amount of material was available. This calorimeter was described recently; it uses about 0.5 g of sample. The measurement on *n*-heptane and synthetic sapphire showed that the accuracy of the heat capacity measurements was on the order of 0.5% and for latent heat effects such as the enthalpy of fusion it was on the order of 0.2%.

Ethyl undecanoate (molar mass 214.34 g·mol^{-1}) was measured in CAL 8. About 0.5 g was used. The experimental data are given in Table 1. First the sample was quickly cooled to about 140 K, and a measurement was made to 300 K. In this measurement, exothermic effects took place (Figure 1) between 200 K and 220 K and during the melting process between 255 and 259 K, indicating the transition to the stable crystalline form. The sample was cooled again to 160 K; this cooling was controlled by setting the control temperature of the shield regulation about 10 K below the vessel temperature without breaking the vacuum. The cooling curve is given in Figure 4. From this curve, it is clear that the compound crystallizes at 253.2 K with only a very small undercooling, implying that this temperature can also be taken as the melting temperature of the metastable form. This means that the double peak in the heat capacity curve given in Figure 2 is not caused by a solid−solid transition followed by melting, as it appears at first sight, but is caused by the melting of the metastable crystal form, whereas during the melting process recrystallization to the stable crystal form takes place. This recrystallization is slow and is not directly visible in the heat capacity curve but manifests itself in the positive temperature drift during the stabilization periods. After equilibrating for 36 h at 252 K, a measurement to 257 K was made. No exothermic effects occurred, indicating that the

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Table 1. Experimental Data Series for Ethyl Undecanoate

T/K	C_p/J·K^{-1}·mol^{-1}	$H(T) - H(\text{start})$/J·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	$H(T) - H(\text{start})$/J·mol^{-1}	T/K	C_p/J·K^{-1}·mol^{-1}	$H(T) - H(\text{start})$/J·mol^{-1}
				series 1[a]				
139.88	207.52	8629	201.57	212.99	23 385	253.80	14892	55 259
143.35	212.19	9347	204.69	161.31	23 968	254.12	12654	59 599
146.22	216.66	9963	207.94	120.20	24 425	255.70	480	62 434
149.10	220.22	10 590	211.21	152.71	24 869	257.82	2171	64 633
151.98	223.45	11 231	214.35	206.94	25 433	258.64	18871	68 371
154.87	227.20	11 883	217.39	247.39	26 121	259.44	2260	72 131
157.77	230.26	12 544	220.36	278.18	26 901	261.58	419.55	74 286
160.66	236.92	13 219	223.29	297.94	27 746	264.49	420.55	75 509
163.55	242.00	13 912	226.21	309.76	28 631	267.39	421.02	76 732
166.44	242.39	14 613	229.11	318.55	29 544	270.29	422.21	77 953
169.36	239.53	15 314	232.01	328.11	30 481	273.18	423.35	79 176
172.28	242.64	16 018	234.90	342.23	31 450	276.07	424.79	80 399
175.19	244.71	16 727	237.78	363.87	32 464	278.95	425.66	81 623
178.11	247.80	17 445	240.62	402.06	33 551	281.82	425.14	82 843
181.02	251.81	18 176	243.39	477.14	34 768	284.68	426.82	84 063
183.93	254.69	18 912	246.01	650.51	36 235	287.54	428.33	85 284
186.85	258.17	19 659	248.31	1069	38 174	290.39	429.39	86 508
189.76	261.13	20 415	250.26	1451	40 594	293.24	430.72	87 732
192.68	263.19	21 180	251.84	2257	43 440	296.08	431.60	88 957
195.60	260.74	21 946	252.88	5347	46 917	298.92	433.20	90 185
198.55	246.06	22 694	253.45	10293	50 961			
				series 2[b]				
111.58	173.66	339	201.88	266.33	20 194	258.71	48322	64 790
113.84	175.94	740	204.18	269.86	20 811	258.78	41751	67 845
116.71	178.91	1248	206.47	268.45	21 427	258.87	27850	70 874
119.57	181.88	1764	208.75	272.25	22 043	259.64	994	73 091
122.42	185.27	2286	211.01	276.09	22 664	261.33	414.49	74 204
125.29	187.91	2821	213.26	279.59	23 289	263.28	418.61	75 019
128.15	190.48	3362	215.50	279.55	23 916	265.23	419.66	75 835
131.02	194.47	3914	217.73	283.48	24 543	267.18	419.56	76 652
133.86	198.69	4472	219.95	287.50	25 177	269.12	420.55	77 466
136.66	198.56	5029	222.16	290.42	25 814	271.06	421.01	78 282
139.44	201.64	5585	224.36	293.74	26 456	272.99	421.34	79 098
142.19	204.69	6143	226.54	297.69	27 101	274.93	422.40	79 914
144.90	207.94	6703	228.71	302.05	27 752	276.86	423.50	80 731
147.59	211.29	7266	230.87	307.08	28 409	278.79	424.54	81 549
150.26	213.75	7832	233.01	312.10	29 073	280.72	424.74	82 368
152.89	217.30	8401	235.14	318.94	29 745	282.65	425.25	83 187
155.51	220.97	8974	237.26	327.12	30 428	284.57	425.82	84 005
158.10	224.09	9550	239.36	337.32	31 125	286.49	426.92	84 826
160.67	229.12	10 132	241.44	349.15	31 839	288.42	427.56	85 647
163.21	233.25	10 720	243.49	366.65	32 574	290.34	427.60	86 467
165.73	236.15	11 312	245.51	390.29	33 339	292.25	429.47	87 289
168.24	230.57	11 897	247.49	425.06	34 147	294.17	430.48	88 114
170.74	232.17	12 475	249.42	480.50	35 017	296.09	431.30	88 940
173.23	234.76	13 056	251.26	571.99	35 982	298.00	431.45	89 767
175.70	236.78	13 638	252.97	727	37 090	299.92	432.30	90 594
178.15	239.40	14 222	254.50	1039	38 419	301.84	434.20	91 424
180.59	242.15	14 809	255.75	1661	40 066	303.75	436.09	92 258
183.01	244.19	15 398	256.70	2825	42 085	305.67	436.86	93 094
185.42	245.75	15 987	257.35	4810	44 446	307.58	437.94	93 930
187.81	248.17	16 577	257.78	7790	47 065	309.50	438.69	94 769
190.18	251.89	17 171	258.08	11784	49 851	311.41	439.51	95 609
192.55	256.43	17 772	258.29	16860	52 743	313.32	440.63	96 451
194.90	257.21	18 376	258.44	23291	55 703	315.24	441.69	97 295
197.24	257.78	18 978	258.55	30126	58 705	317.15	443.16	98 144
199.56	262.12	19 583	258.64	38815	61 737	319.06	444.40	98 991
				series 3[c]				
292.35	429.73	87 323	318.35	443.44	98 676	342.69	459.47	109 665
293.82	430.15	87 954	320.22	444.36	99 506	344.57	461.00	110 530
295.74	431.35	88 781	322.09	445.90	100 338	346.45	462.31	111 399
297.65	432.04	89 606	323.96	447.60	101 173	348.34	463.75	112 271
299.55	433.51	90 429	325.83	448.49	102 010	350.22	465.10	113 147
301.45	434.67	91 253	327.70	449.50	102 850	352.11	466.34	114 027
303.35	436.03	92 077	329.57	450.40	103 692	354.00	467.34	114 910
305.23	437.30	92 902	331.44	451.66	104 536	355.90	468.59	115 797
307.12	438.29	93 727	333.31	453.33	105 383	357.80	469.50	116 687
309.00	438.55	94 551	335.19	455.41	106 234	359.70	471.05	117 581
310.87	439.73	95 375	337.06	456.14	107 088	361.60	472.21	118 479
312.74	440.36	96 198	338.94	456.81	107 945	363.51	473.69	119 381
314.61	441.72	97 023	340.81	458.35	108 803	365.42	475.18	120 288
316.48	441.83	97 849						

[a] Series 1: metastable crystal to the liquid phase. [b] Series 2: annealed crystal to the liquid phase. [c] Series 3: liquid phase.

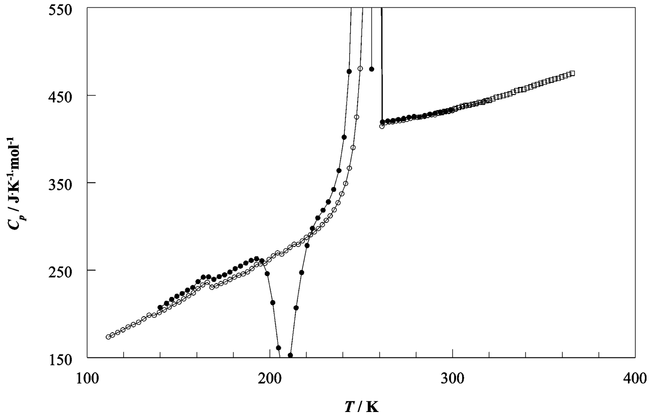

Figure 1. Experimental heat capacity data of ethyl undecanoate: ●, first run; ○, second run after equilibration close to the melting point.

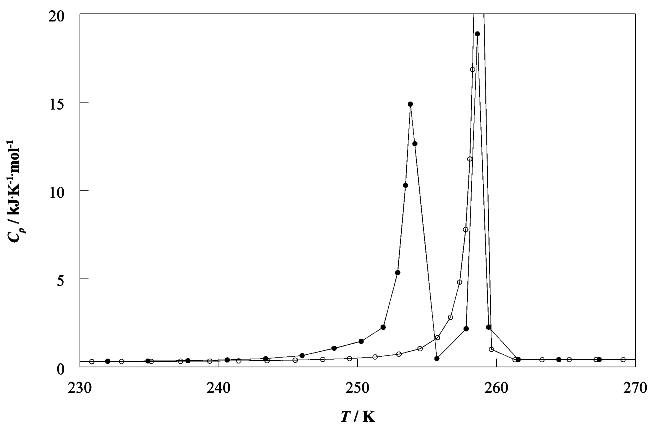

Figure 2. Enlarged view of Figure 1 around the melting point. In the first run, given by ●, the melting process takes place in two steps.

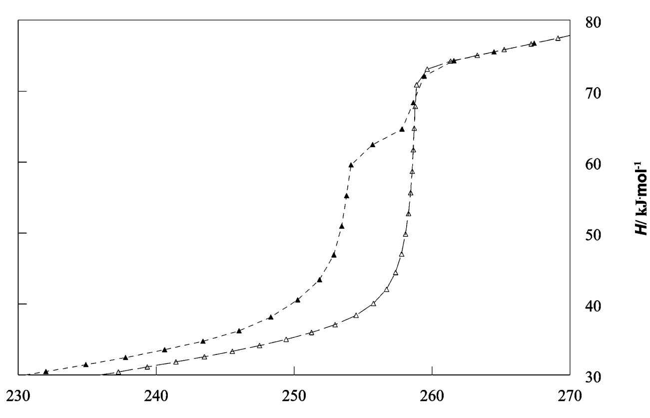

Figure 3. Enthalpy curves of ethyl undecanoate around the melting point: ▲, first run; △, second run with the annealed sample.

product had transformed completely to the stable crystalline form. The next measurement was made from 110 K to 320 K (series 2 in Table 1 and given in Figure 1). The enthalpy curves of the quenched and the annealed compound are given in Figure 3. The curves were shifted so that the enthalpies in the liquid phase corresponded at 300 K. From the measurement on the annealed sample, the enthalpy of fusion was calculated to be (36.0 ± 0.1) kJ·mol^{-1}. The calculation was made between 200 K and 264 K; the heat capacity of the solid used was $C_{p,s}$(170 K to 200 K) = {50.45 + 1.0604T/K} J·K^{-1}·mol^{-1}, and that of the liquid was $C_{p,l}$(263 K to 280 K) = {323.79 + 0.3595·T/K} J·K^{-1}·mol^{-1}. The enthalpy of fusion was calculated by constructing a sigmoid baseline. In the first calculation, the aforementioned fits were used to calculate the enthalpy increment of the solid and liquid only, thus without the fusion process, the difference in total enthalpy being the first approximation of the enthalpy of fusion. Then the melted fractions were calculated by constructing a new baseline using the contributions of the solid and liquid phases to the heat capacity, and a new enthalpy of fusion was found. This process was repeated until a stable baseline was found. Three iterations were needed. The triple-point temperature was found to be (259.17 ± 0.04) K, and the calculated purity according to the van't Hoff plot was 97.5 mol %. The error margin in the triple-point

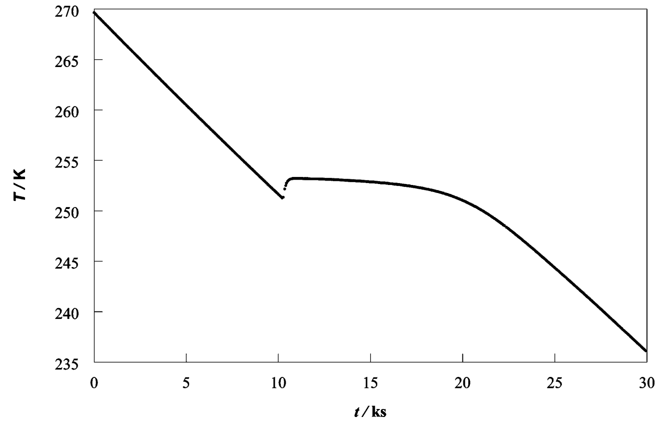

Figure 4. Cooling curve of ethyl undecanoate. Crystallization started at 251.3 K, and the temperature rose to 253.2 K. The cooling rate just before crystallization was 1.8 × 10^{-3} K·s^{-1}.

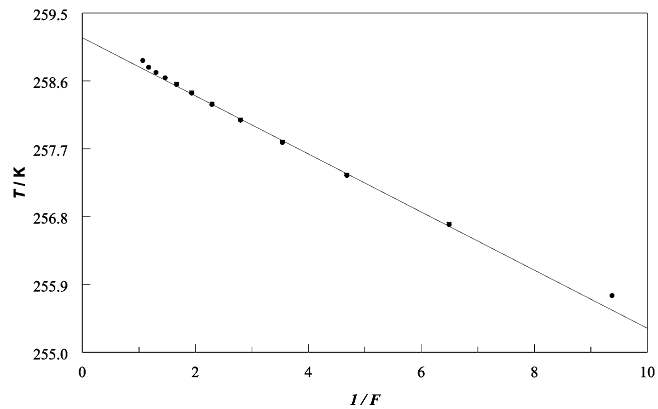

Figure 5. Equilibrium temperature in the melt against the reciprocal of the melted fraction for ethyl undecanoate. ●, Data points calculated from the run with the annealed sample. Calculated purity, 97.5 mol %; triple-point temperature, 259.17 K; and enthalpy of fusion, 36.05 kJ·mol^{-1}.

Table 2. Reciprocal of the Melted Fraction (1/*F*) and the Equilibrium Temperatures (T_{eq}) in the Melt of Ethyl Undecanoate

1/F	T_{eq}/K
9.375	255.754
6.491	256.695
4.680	257.347
3.540	257.784
2.799	258.079
2.294	258.287
1.935	258.438
1.668	258.553
1.464	258.642
1.303	258.713
1.174	258.781

Table 3. Experimental Data Series for Ethyl Tridecanoate

T	C_p	$H(T) - H(\text{start})$	T	C_p	$H(T) - H(\text{start})$	T	C_p	$H(T) - H(\text{start})$
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}
series 1[a]			271.90	40 847	44 512	226.72	334.00	13 085
176.54	281.19	0	271.96	57 663	47 127	229.65	338.41	14 073
177.15	283.11	171	272.00	76 091	49 749	232.57	342.70	15 066
178.94	285.04	680	272.03	92 057	52 375	235.47	347.41	16 065
181.89	288.42	1528	272.06	100 985	55 004	238.34	352.35	17 071
184.84	291.56	2383	272.08	98 382	57 633	241.19	357.30	18 083
187.78	294.94	3246	272.11	85 465	60 261	244.03	362.39	19 102
190.73	298.28	4119	272.15	65 481	62 885	246.84	368.11	20 129
193.68	301.62	5004	272.20	42 791	65 502	249.63	374.08	21 164
196.62	305.04	5897	272.28	24 659	68 103	252.40	380.86	22 211
199.57	308.53	6800	273.17	1079	70 300	255.15	387.34	23 269
202.51	312.04	7714	275.34	486.33	71 853	257.88	398.08	24 339
205.46	315.60	8639	278.01	487.34	73 153	260.57	413.23	25 429
208.41	319.25	9574	280.68	488.58	74 453	263.19	439.48	26 546
211.35	323.04	10 519	283.33	489.10	75 752	265.70	495.53	27 717
214.30	326.79	11 477	285.99	489.40	77 051	267.99	628.88	28 995
217.25	330.79	12 447	288.64	490.72	78 351	269.83	1076	30 497
220.19	334.71	13 428	291.29	492.03	79 651	270.96	2812	32 352
223.14	338.31	14 419	293.93	493.00	80 951	271.50	6749	34 508
226.10	341.95	15 424	296.56	494.67	82 253	271.75	13133	36 803
229.05	345.12	16 439	299.20	496.00	83 557	271.90	21540	39 153
232.00	347.77	17 463	301.82	497.42	84 861	271.99	32070	41 530
234.97	349.71	18 497	304.44	498.94	86 167	272.05	43573	43 920
237.95	350.93	19 540	307.06	500.72	87 474	272.10	49770	46 317
240.94	351.32	20 592	309.67	502.48	88 783	272.15	57072	48 717
243.95	351.20	21 648	312.27	503.98	90 094	272.19	60 211	51 119
246.97	350.67	22 708	314.87	505.99	91 407	272.23	66 847	53 523
250.01	349.28	23 772	317.47	507.58	92 722	272.26	67 665	55 928
253.09	346.31	24 842	320.06	509.22	94 039	272.30	68 212	58 333
256.20	343.21	25 915	series 2[b]			272.34	55 061	60 736
259.34	342.53	26 992	203.72	303.18	5757	272.39	41 856	63 134
262.48	350.24	28 078	204.30	304.48	5931	272.46	27 902	65 521
265.53	387.68	29 202	206.07	306.99	6475	272.58	16 184	67 886
268.28	550.06	30 472	209.03	310.71	7389	273.13	1987	70 029
270.21	1448	32 146	211.98	314.26	8310	274.84	493.67	71 597
271.15	4663	34 322	214.92	318.07	9241	277.28	486.51	72 794
271.52	10682	36 777	217.87	321.89	10 185	279.73	487.34	73 987
271.71	18329	39 325	220.82	325.88	11 141	282.18	488.17	75 179
271.83	27817	41 909	223.77	329.74	12 108	284.62	489.23	76 373

[a] Series 1: Measurement of the metastable crystalline phase to the liquid phase. [b] Series 2: Measurement of the annealed crystalline phase to the liquid phase.

temperature was taken as twice the standard error calculated for the first coefficient of the linear fit. The small hump around 166 K is probably due to an impurity and will be the eutectic transition. The heat effect of this transition was not included in the calculation of the enthalpy of fusion. When integrated separately, the enthalpy of transition of the eutectic effect was 108 J·mol^{-1}. A likely candidate for the impurity is ethanol, whose melting point of 159 K is close to the transition temperature. This would give an impurity of 0.021 mol of ethanol in 0.9955 mol of ethyl undecanoate, leading to a purity for the ethyl undecanoate of 97.9 mol %, quite close to the measured value. The corrected enthalpy of fusion of ethyl undecanoate than becomes 36.16 kJ·mol^{-1}. The van't Hoff plot is given in Figure 5; the calculated values of the reciprocal of the melted fraction at the equilibrium temperatures in the melt are given in Table 2. Measurements of the heat capacity of the liquid phase were extended to 365 K (series 3). Reference 10 gives a value for the melting temperature of the stable phase of 258.5 K, 0.7 K lower than our value. For the metastable phase, a melting temperature of 253.9 K was reported. This value is close to the crystallization temperature, which we measured to be 253.2 K (Figure 4). The enthalpy of fusion of the stable phase was given, assuming that the value cited was in kcal·mol^{-1}, as 31.9 kJ·mol^{-1}, about 4 kJ lower than our value. Taking into account that this value was measured indirectly by using the freezing-point depression, the difference is reasonable.

Table 4. Reciprocal of the Melted Fraction (1/*F*) and the Equilibrium Temperatures (T_{eq}) in the Melt of Ethyl Tridecanoate

$1/F$	T_{eq}/K
12.558	270.963
7.852	271.496
5.520	271.752
4.212	271.896
3.391	271.988
2.834	272.052
2.432	272.104
2.129	272.149
1.893	272.190
1.704	272.228
1.549	272.264
1.420	272.299
1.311	272.339
1.219	272.389
1.138	272.460

Ethyl tridecanoate (molar mass 242.4 g·mol^{-1}) was measured in CAL V; 4.4 g was transferred to the calorimeter vessel in a glovebox under a nitrogen atmosphere. Before closing, the vessel was evacuated, and 1000 Pa of helium pressure was admitted to enhance the heat transfer in the vessel. The experimental data are given in Table 3. The sample was cooled to 175 K, and a continuous

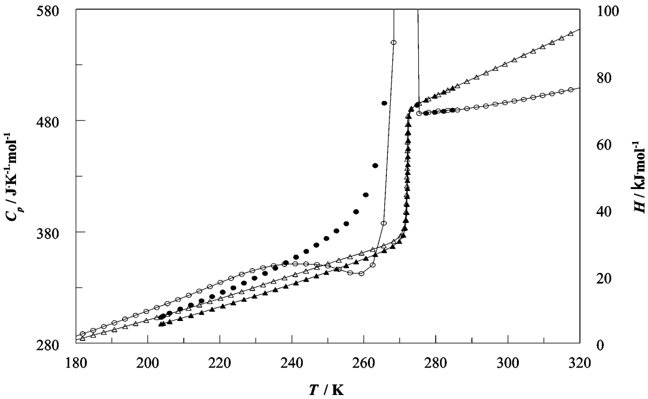

Figure 6. Experimental heat capacity data for ethyl tridecanoate. ○, Heat capacity and △, enthalpy of the first measurement. ●, Heat capacity and ▲, enthalpy after relaxation close to the melting point.

measurement to the liquid phase was made. Between 240 K to 260 K, an exothermic effect took place (Figure 6). Next, the sample was cooled again to 150 K, heated to 269 K, and stabilized overnight at this temperature. Series 2 was measured after cooling the annealed sample to 200 K. No exothermic effects were found in this series.

Calculation of the Enthalpy of Fusion. The calculation was made between 220 K and 278 K. First the heat capacity of the stable solid phase was fitted between 200 K and 220 K. This gave $C_{p,s}$(200 K to 220 K) = {43.85 + 1.27665T/K} J·K^{-1}·mol^{-1}. The heat capacity of the liquid phase was fitted between 275 K to 300 K, the fit result being

$$C_{p,l}(275\ \mathrm{K\ to\ 300\ K}) = \{401.74 + 0.3079T/\mathrm{K}\}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The enthalpy of fusion was calculated using the same procedure as for ethyl undecanoate. The enthalpy of fusion was found to be (40.7 ± 0.1) kJ·mol^{-1}. In Figure 7, the equilibrium temperatures in the melt are plotted against the reciprocal of the melted fraction. Using the van't Hoff relation for the calculation of the impurity level, thus assuming that the impurity formed an eutectic system with the main component, resulted in a purity of 99.3 mol %, the triple-point temperature being (272.4 ± 0.1) K. The assumption that the system is eutectic seems to be reasonable because a large part of the plot in Figure 2 is linear; however, the increase in temperature near the end of the melting process might indicate that the impurity does form a solid solution with the main component. It is for this reason that we have given a larger error margin for the triple-point temperature. The melting temperature of the stable form of ethyl tridecanoate was reported by van Bellinghen[10] to be 272.3 K, and for the metastable form he found a value of 269.7 K. We did not measure the melting temperature of the metastable phase. For the enthalpy of fusion of the stable form, he reported 10.20 cal; if we assume that this should be kcal, then his value (42.6 kJ·mol^{-1}), measured indirectly by the use of the freezing-point depression, is close to our value.

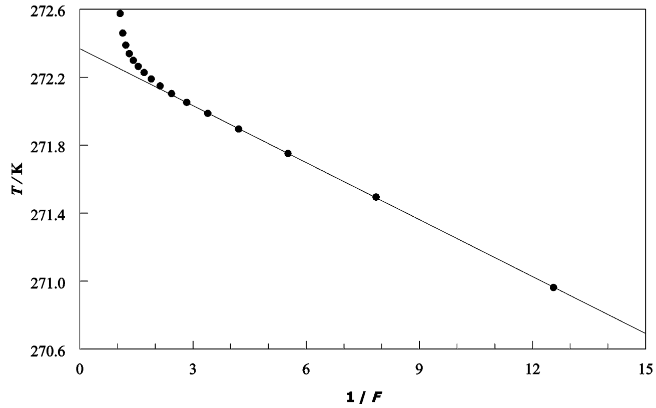

Figure 7. Equilibrium temperature in the melt against the reciprocal of the melted fraction for ethyl tridecanoate. ●, Data points calculated from the measurement series on the annealed sample. Calculated purity, 99.3 mol %; triple-point temperature, 272.4 K; and enthalpy of fusion, 40.7 kJ·mol^{-1}.

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