Thermodynamics of thallium alkanoates

I. Heat capacity and thermodynamic functions of thallium(I) *n*-hexanoate [a]

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The sub-ambient heat capacity of thallium(I) *n*-hexanoate is characterized by transitions at 203.5 and 208.3 K which show $C_{p,m}/R$ maxima of about 400 and 2500 and $(\Delta S_m/R)$'s of 1.03 and 1.07. Both appear to be essentially first order and show typical under-cooling phenomena. The heat capacities are in excellent accord with the d.s.c. values of Fernandez-Martin, Lopez de la Fuente, and Cheda over the common range of super-ambient values. At $T = 298.15$ K the values of $\{S_m^\circ(T) - S_m^\circ(0)\}/R$, $\{H_m^\circ(T) - H_m^\circ(0)\}/R$, and $-\{G_m^\circ(T) - H_m^\circ(0)\}/RT$ are 39.06, 5880 K, and 19.33. Smoothed thermodynamic functions are tabulated through melting.

1. Introduction

Earlier related papers[1-4] describe the low-temperature thermophysics of several alkali-metal salts of *n*-alkanoic acids by equilibrium adiabatic calorimetry. Indeed, still other investigators have concerned themselves with the thermophysical properties of the alkali salts mainly by d.s.c. as has been succinctly summarized by Franzosini and Sanesi.[5] Although the analogous thallium(I) *n*-alkanoates display the same manifold mesomorphism as do the alkali salts, they have been relatively neglected except in some recent studies of super-ambient heat capacities,[6] thermal stability, structural properties, *etc.*[7-11]

This paper details the results of a similar study on thallium(I) *n*-hexanoate, denoted hereafter as Tl6C. This compound has been studied extensively in the super-ambient region by both thermal[6-8] and microscopic[7-8] methods which show that Tl6C exists in several different solid phases and a mesomorphic liquid phase before

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transforming to the isotropic liquid. The known phase transitions (see table 1) can be summarized[6] as:

Crystal III = Crystal II = Crystal I = Mesomorphic liquid = Isotropic liquid
T_{trs}:   389 K   412 K   422 K   500 K

The phase behavior below 300 K has not been investigated previously, however. In this paper, we report the existence of two new solid-to-solid transitions (presumably phase transitions) in Tl6C with transition behavior shown below.

Crystal V = Crystal IV = Crystal III
T_{trs}:   203.5 K   280.3 K

2. Experimental

The sample of Tl6C used in our study was a portion of a batch prepared at the Universidad Complutense, Madrid, Spain, and used for super-ambient d.s.c. studies.[6] The salt was obtained by reaction of purified *n*-hexanoic acid with thallium carbonate in methanol following the procedure of Meisel *et al.*[7] and
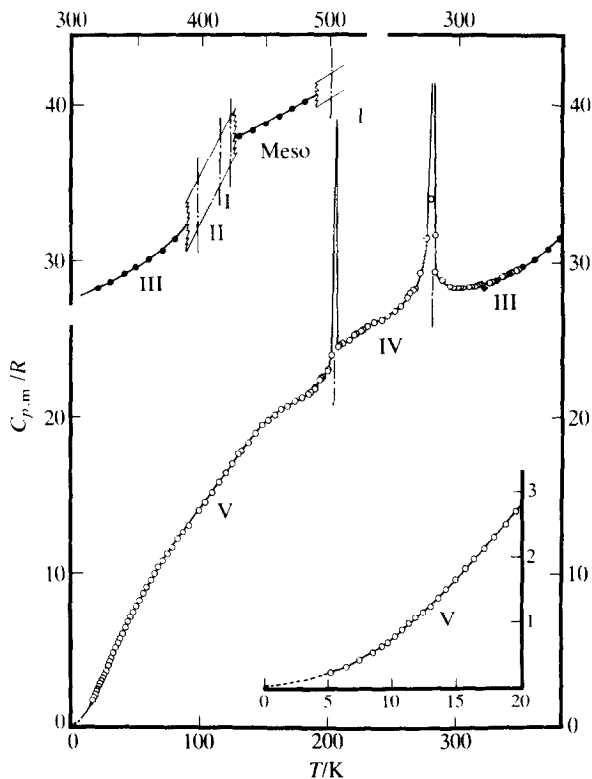

FIGURE 1. Heat capacity of thallium(I) *n*-hexanoate with phase designations. ○, This work; ●, reference 6 by d.s.c.

recrystallized from (ethanol + ether). Infrared spectroscopic determinations showed no traces of water or free acid. A d.s.c. purity determination using fractional-fusion techniques yielded 99.97 moles per cent.[6] No detectable thermal anomaly is evident at the ice point nor at the melting temperature of hexanoic acid (271.15 K). This further attests to the purity of the sample.

The sample loaded into the gold-plated copper calorimeter W–62 had a mass of 53.480 g, corresponding to an amount-of-substance factor of 5.9746 with the molar mass of 319.52 g·mol^{-1} on the basis of the 1978 IUPAC relative atomic masses. The buoyancy corrections were calculated assuming a density of 3.0 g·cm^{-3}. No crystallographic information on density is available for Tl6C or adjacent members of the homologous series. The closest member of the series for which the density is available is thallium acetate which has a density of 3.6 g·cm^{-3}. Following evacuation, 3.1 kPa of purified helium was added to the calorimeter to promote thermal equilibration; the calorimeter was then sealed via a screw cap which pressed a gold gasket against the circular knife edge of the calorimeter.

TABLE 1. Literature transition temperatures, enthalpies, and entropies of thallium(I) n-hexanoate

Transition	T/K	$\Delta_{trs}H_m/R$ K	$\Delta_{trs}S_m/R$	Reference
II-to-III	397.9	25	0.06	6
	397.6	24	0.05	7
	395	21	0.055	8
I-to-II	415.0	79	0.19	6
	410.4	96	0.22	7
	412	90	0.22	8
I-to-meso	425.0	553	1.30	6
	421.7	420	1.0	7
	418	540	1.32	8
meso-to-l	499.8	474	0.95	6
	500.3	420	0.83	7
	500	400	0.80	8
$\sum \Delta_{trs}S^\circ_{m,i} = \Delta^{II}_{III}S^\circ_m + \Delta^{I}_{II}S^\circ_m + \Delta^{meso}_{I}S^\circ_m + \Delta^{l}_{meso}S^\circ_m =$			$\begin{cases} 2.5 \\ 2.1 \\ 2.40 \end{cases}$	6 7 8

The calorimetric measurements were made in the Mark X cryostat described previously.[1] The intermittent-heating adiabatic equilibrium method was utilized. The programming, data logging, and calorimetry were done by automated computerization as described elsewhere.[12]

The adiabatic calorimetric results are seen to be in excellent agreement in the overlap region. Despite the fineness of division of the sample, its heat capacity represented 60 to 70 per cent of that of the (calorimeter + heater + thermometer + sample) ensemble over most of the temperature range but approached 95 per cent near 10 K.

3. Results

The experimental heat capacities are given in table 2 and plotted in figure 1. These results are listed in chronological order. Within a series, the temperature interval of
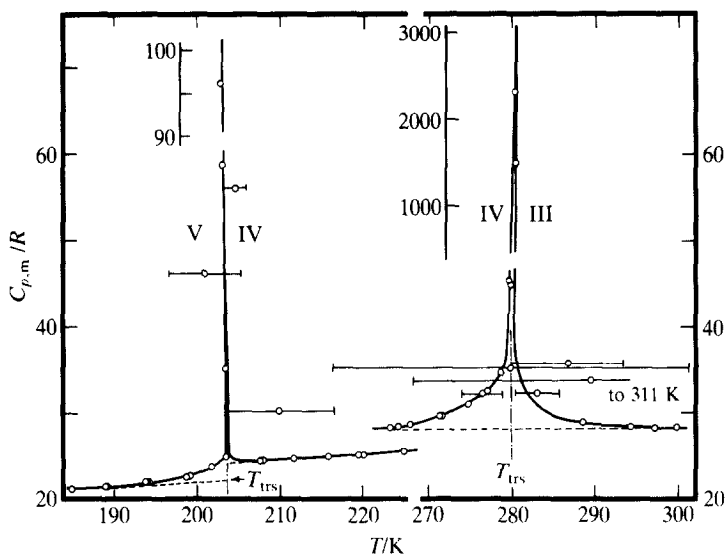
FIGURE 2. Sub-ambient transitions in thallium(I) *n*-hexanoate. Note adjuvant scales for peak values and phase designations. Horizontal bars indicate temperature increments of enthalpy-type determinations. Lattice heat-capacity contributions are indicated by dashed lines.

TABLE 2. Molar heat capacities of thallium *n*-hexanoate ($R = 8.3144 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series 1		319.52	28.524	Series IV		13.60	1.325	44.11	7.042	142.90	18.469
184.98	21.079	324.70	28.709	194.50	21.930	14.24	1.453	46.32	7.386	147.97	19.061
189.17	21.465	329.89	28.854	198.88	22.585	14.91	1.590	48.59	7.728	153.05	19.521
194.27	21.960	335.06	29.048	201.78	23.742	15.62	1.730	50.97	8.072	158.17	19.748
199.36	22.705	340.25	29.292	203.09	58.698	16.36	1.874	53.48	8.419	163.30	20.021
202.74	96.2	345.45	29.507	203.47	350	17.14	2.032	56.10	8.897	168.46	20.140
210.04	30.34	Series II		203.56	248	17.96	2.197	58.84	9.135	173.61	20.449
219.57	25.109	265.65	28.280	204.64	56.1	18.82	2.372	61.79	9.514	178.74	20.747
225.13	25.459	289.53	33.642	207.71	24.353	19.72	2.571	64.77	9.885	183.87	21.029
230.28	25.714	313.55	28.398	211.78	24.562	20.68	2.739	67.91	10.236	189.00	21.453
235.45	25.948	Series III		215.93	24.882	21.67	2.949	71.28	10.592	194.07	21.960
240.65	26.210	263.35	27.907	220.20	25.105	22.71	3.158	74.82	10.973	200.95	46.207
245.83	26.427	267.82	28.694	225.03	25.445	23.80	3.378	78.55	11.330	207.92	24.453
251.00	26.737	271.77	29.663	Series V		24.95	3.605	82.46	11.800	279.82	35.19
256.14	27.135	274.76	30.109	7.61	0.33	26.15	3.841	86.57	12.240	304.02	28.262
261.26	27.677	277.09	32.494	7.82	0.37	27.42	4.090	90.78	12.639	309.30	28.356
266.36	28.420	278.76	34.677	8.59	0.49	28.74	4.344	99.83	13.501	314.43	28.417
271.43	29.650	279.94	96.8	9.20	0.61	30.13	4.612	104.75	14.036	319.62	28.530
276.41	32.172	280.32	2300	9.70	0.66	31.59	4.885	109.73	14.613	324.83	28.707
279.60	146	280.37	1450	10.25	0.75	33.13	5.172	114.74	15.269	330.04	28.911
286.83	35.71	283.06	32.24	10.78	0.85	23.43	5.467	119.75	15.897	335.24	29.131
297.24	28.339	288.62	28.986	11.31	0.892	36.42	5.771	124.78	16.470	340.41	29.338
303.76	28.267	294.37	28.460	11.85	1.002	38.19	6.074	129.82	17.096	345.56	29.531
308.96	28.363	299.85	28.268	12.40	1.111	40.05	6.386	132.67	17.312		
314.24	28.385			12.98	1.208	42.00	6.708	137.84	17.854		

TABLE 3. Enthalpy and entropy of 203.5 K and 280.3 K transitions in thallium(I) n-hexanoate

Designation	No. of detns	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{H_m^\circ(T_2)-H_m^\circ(T_1)}{R\ K}$	$\dfrac{H_m^\circ(210\ K)-H_m^\circ(180\ K)}{R\ K}$	$\dfrac{S_m^\circ(210\ K)-S_m^\circ(180\ K)}{R}$
			V-to-IV transition (203.5 K)			
Series I	6	183.35	216.60	964.9	872.6	
Series IV	8	192.07	209.72	605.4	871.7	
Series V	5	181.30	210.55	859.6	873.2	
Graphical integration:					872.0	4.433
				mean:[a]	872.5	
Lattice contribution:					663.9	3.396
				$\Delta_{trs}H_m^\circ/R$ K:	208.6	
				$\Delta_{trs}S_m^\circ/R$:		1.037

					$\dfrac{H_m^\circ(300\ K)-H_m^\circ(265\ K)}{R\ K}$	$\dfrac{S_m^\circ(300\ K)-S_m^\circ(265\ K)}{R}$
			IV-to-III transition (280.3 K)			
Series II	6	263.82	301.15	1355.0	1289.1	
Series III	1	268.12	310.90	1440.6	1220.2	
Series IV	12	265.40	302.46	1347.1	1288.9	4.575
Series V	1	258.37	301.27	1509.6	1290.0	
Graphical integration:					1288.6	4.526
				mean:[b]	1289.0	
Lattice contribution:					987.0	3.507
				$\Delta_{trs}H_m^\circ/R$ K:	302.0	
				$\Delta_{trs}S_m^\circ/R$:		1.068

[a] Average calculated omitting Series IV values and graphical integration.
[b] Mean calculated omitting Series III values and graphical integration.

each measurement may usually be estimated as twice the difference between adjacent mean temperatures. The results have been fitted to a series of orthogonal polynomials in regions of normal heat capacity. Appropriate integration of these polynomials yielded the thermodynamic functions. A tabulation of the smoothed values of $C_{p,m}/R$ and derived functions is given for selected temperatures in table 4. The heat capacities given in transition include those for the lattice with the enthalpy-of-transition and entropy-of-transition increments incorporated at the transition temperatures by the procedure followed in the previous papers of a related series.[1-3]

Two first-order transitions were observed in the heat-capacity curve defined by our measurements. The details of the heat-capacity peaks are shown in figure 2. Unlike the transformation behavior observed in some lower members of the alkali salts, reproducible heat capacities were obtained for both anomalies. The total enthalpy increments through the transition regions for the various series of determination are given in table 3.

TABLE 4. Smooth thermodynamic values at selected temperatures for thallium(I) *n*-hexanoate

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^\circ}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\ K}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
		Phase V		
0	0	0	0	0
5	0.093	0.031	0.117	0.008
10	0.711	0.264	1.97	0.067
15	1.600	0.714	7.67	0.203
20	2.601	1.310	18.15	0.402
25	3.616	2.000	33.70	0.651
30	4.593	2.764	54.25	0.938
35	5.513	3.524	79.54	1.251
40	6.376	4.318	109.29	1.585
45	7.184	5.116	143.21	1.933
50	7.927	5.912	181.0	2.291
60	9.288	7.480	267.2	3.026
70	10.470	9.003	366.2	3.772
80	11.519	10.470	476.2	4.518
90	12.527	11.885	596.4	5.258
100	13.575	13.258	726.9	5.990
120	15.89	15.93	1021.2	7.425
140	18.20	18.56	1362.7	8.829
160	19.84	21.11	1744.6	10.206
180 [a]	20.79	23.50	2151.3	11.55
	[20.79]	[23.50]	[2151.3]	[11.55]
190	21.50	24.65	2362.4	12.22
	[21.36]	[24.64]	[2361.5]	[12.21]
200	22.91	25.78	2583.6	12.86
	[22.05]	[25.75]	[2578.3]	[12.86]
203.5 [b]	(350)	(26.14)	(2655.9)	(13.09)
	[22.31]	[26.14]	[2655.9]	[13.09]
		Phase IV		
203.5 [b]	(350)	(27.18)	(2867.0)	(13.09)
	[24.10]	[26.14]	[2655.9]	[13.09]
210	24.45	27.94	3023.8	13.54
	[24.45]	[26.90]	[2814.4]	[13.50]
220	25.13	29.09	3271.8	14.22
240	26.15	31.33	3785.4	15.55
260	27.44	33.47	4319.8	16.61
270	29.23	34.53	4602.1	17.48
	[28.20]	[33.48]	[4391.2]	[17.22]
280	(91.8)	(36.21)	(5066.7)	(18.11)
	[28.20]	[34.51]	[4673.2]	[17.82]
280.3 [b]	(2300)	(35.58)	(4891.1)	(18.13)
	[28.20]	[34.54]	[4681.7]	[17.84]
		Phase III		
280.3 [b]	(2300)	(36.64)	(5190.6)	(18.13)
	[28.20]	[34.54]	[4681.7]	[17.84]
290	28.76	38.26	5648.1	18.78
	[28.20]	[35.50]	[4955.1]	[18.41]
298.15	28.26	39.06	5880.3	19.33
300	28.20	39.23	5932.7	19.45

TABLE 4—continued

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^\circ}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\,K}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
320	28.50	41.06	6500	20.75
340	29.27	42.81	7078	21.99
360	30.2	44.51	7672	23.20
380	31.5	46.1_7	8288	24.2_9
397.9 [b]	(>35)	(47.6_5)	(8863)	(25.3_7)
	[32.2]	$[44.8_9]$	[8170]	
Phase II				
397.9 [b]	(>35)	(47.7_1)	(8888)	(25.3_7)
	[33.9]	$[44.8_9]$	[8170]	
400	34.0	47.8_9	8959	25.4_9
410	35.0	48.7_4	9304	26.0_5
415.0 [b]	(>40)	(49.1_7)	(9480)	(26.3_3)
	[35.3]	$[46.3_6]$	[8762]	
Phase I				
415.0 [b]	(>40)	(49.3_5)	(9559)	(26.3_3)
	[36.1]	$[46.3_6]$	[8762]	
420.0	36.5	49.7_9	9741	26.6_0
425.0 [b]	(>200)	(50.2_3)	(9928)	(26.8_7)
	[37.6]	$[47.2_3]$	[9131]	
Mesomorphic phase				
425.0 [b]	(>200)	(51.5_3)	(10481)	(26.8_7)
	[37.6]	$[47.2_3]$	[9131]	
440	38.4	52.8_5	11051	27.7_3
460	39.4	54.5_8	11829	28.8_6
480	40.4	56.2_7	12625	29.9_0
499.8 [b]	(>100)	(57.9_3)	(13430)	(31.0_6)
	[41.2]	$[53.6_3]$	[12063]	
Isotropic liquid				
499.8 [b]	(>100)	(58.8_8)	(13904)	(31.0_6)

[a] Values in [ ] refer to lattice estimates.

[b] Assuming the transition to be isothermal. All values in parentheses ( ) of thermodynamic functions except heat capacities are based on that assumption.

Insufficient results were available to calculate by corresponding states or other methods the lattice heat capacity necessary to obtain values for the $\Delta_{trs}H_m^\circ$ and $\Delta_{trs}S_m^\circ$. Consequently, the lattice heat-capacity curve was estimated by inspection of the regions of normal heat capacity around each transition and extrapolated to the transition temperature. Significant excess heat capacity appears to be present for a large temperature region below both first-order peaks; hence, the large ranges given in table 3.

The enthalpies and entropies of transition in the two transformation regions were obtained as the difference of the appropriate integrations of the hand-drawn $C_{p,m}/R$ curve and the estimated lattice heat-capacity curve. The $\Delta_{trs}H_m^\circ$ and $\Delta_{trs}S_m^\circ$ values are much larger than observed for the other solid-to-solid phase transitions, $i.e.$

I-to-II and II-to-III (compare table 1). Some of the excess might come from our choice of the lattice contribution, resulting in apparent broadening of the transition regions, but even more conservative estimates of the transition region still give large values. The magnitude of the transition properties suggests that a significant degree of rearrangement occurs within the crystal at the III-to-IV and IV-to-V transformations. Detailed crystallographic studies of these two phases would be valuable.

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