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DSC THERMOPHYSICS ON SOME MEDIUM CHAIN THALLIUM(I) *n*-ALKANOATES: PHASE TRANSITIONS, THERMAL FUNCTIONS AND HEAT CAPACITY *

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ABSTRACT

Four members of the series of anhydrous thallium(I) *n*-alkanoates with medium chain-length (*n*-octanoate, *n*-nonanoate, *n*-undecanoate and *n*-tridecanoate) have been prepared, purified, and studied by differential scanning calorimetry between 200 and 500 K. Their polymorphic and mesomorphic behaviour has also been investigated by polarization microscopy.

The temperatures and enthalpy changes for the phase transitions have been measured and the corresponding entropy changes calculated.

Heat capacity measurements by DSC between 300 and 500 K are also reported.

INTRODUCTION

The thallium(I) *n*-alkanoates, like other series of salts with organic cations or anions [1], show manifold polymorphism and liquid-crystal-like mesomorphism, as well as a somewhat complicated thermal behaviour.

We have recently studied the thermophysical properties of thallium(I) *n*-hexanoate, *n*-heptanoate, *n*-decanoate, *n*-dodecanoate and *n*-tetradecanoate [2–7]. The complete morphology of the heat capacity curve for each compound, from 5 K to about 500 K, was obtained by combining data from

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* Dedicated to Prof. E.F. Westrum, Jr., in honour of his contribution to calorimetry and thermal analysis, and on the occasion of his 70th birthday.

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both sub-ambient adiabatic calorimetry and DSC techniques. Several solid-to-solid phase transitions, in addition to the fusion and clearing ones, were found and their temperatures, enthalpies and entropies determined. Previous DSC work in our laboratories dealt with the lower members of the series up to *n*-heptanoate [8].

In order to obtain valid information on the thermal behaviour of the thallium(I) *n*-alkanoates series from a homogeneous set of data, and to extend the available information to sub-ambient temperatures, we have undertaken a thermophysical study of the *n*-octanoate, *n*-nonanoate, *n*-undecanoate and *n*-tridecanoate (hereafter Tl8C, Tl9C, Tl11C and Tl13C, respectively) by DSC.

Previous work on this series has been done by other investigators using polarization microscopy [9,10], DTA [11] and DSC [12]. However, these studies have been limited to temperatures higher than 300 K and there are no heat capacity data. Moreover, it should be pointed out that most of the Tl*n*C members display solid-to-solid phase transitions under 300 K.

EXPERIMENTAL

Sample preparation

The studied thallium(I) *n*-alkanoates were prepared by reacting Tl_2CO_3 (Fluka, > 99% molar purity) with the proper *n*-alkanoic acid (H*n*C, $n = 8$, 9, 11, Merck, certified purity > 99%, > 98% and > 98%, and $n = 13$, Fluka, > 98%, respectively; tested at the manufacturers by GC), both reactants being dissolved in dry methanol. In order to avoid the formation of acid soaps (or molecular complexes) [1,7] by coprecipitation of the salt with the acid, a slight excess of thallium(I) carbonate (about 5%) was used instead of the more normal way of preparing metallic alkanoates which is to use acid in excess [13]. After refluxing for a few hours, and separating the thallium carbonate excess, the solvent was removed, and the recovered solid washed with ethyl ether. Then, the salts were purified using repeated recrystallization from ethanol, and vacuum dried at room temperature. Purity control was followed quantitatively by DSC using fractional fusion techniques [14].

DSC

A Perkin–Elmer DSC-2C, connected to a Model 3600 Data Station and provided with the Intracooler-2 unit for sub-ambient temperatures, was used between 230 and 480 K. Its temperature scale for the region of interest was calibrated by measuring the melting points of the usual high-purity standards: *n*-undecane, *n*-tridecane, *n*-pentadecane, *n*-octadecane, indium, tin and *n*-octadecanoic and benzoic acids. The power scale was calibrated using high-purity indium (> 99.999 mol.%) as standard material.

The purity of each compound was determined on three or four samples each between 3 and 6 mg, weighed to ±0.002 mg with a Mettler SM-5 microbalance, at low heating rates and high sensitivities.

For the enthalpy transition determinations, four to six samples weighing 5–15 mg were generally recorded at 10 K min^{-1}. In the lower temperature regions (up to about 400 K), the samples were capsulated in solid pans. At higher temperatures, hermetically sealed volatile pans were used in order to minimize undesired decomposition effects. The estimated errors were ±0.5 K and about 2% for transition temperatures and enthalpies, respectively.

For the heat capacity determinations, four to six samples weighing 10–20 mg were scanned for each product in the temperature range of 300 to 500 K, using a heating rate of 10 K min^{-1}. Each scan was divided into approximately 30 K runs, overlapping each other to minimize base-line uncertainties. The estimated error of the heat capacities was about 2%.

Polarization microscopy

Optical observations of phase textures were made on a Galileo LN polarized-light microscope with a white light source and fitted with a Mettler FP52 + FP5 hot stage. The samples were examined sandwiched between microscope slides and cover-slips of Pyrex glass, previously cleaned, washed and both rubbed in one direction with acetone in order to avoid the homeotropic texture of the mesophase. In this manner it was found that heating to the isotropic phase followed by immediate cooling to the "neat" phase would produce the desired non-homeotropic condition. Pictures were recorded on regular film.

RESULTS AND DISCUSSION

DSC thermograms for Tl8C, Tl9C, Tl11C and Tl13C showed well-defined curves for each compound, in both the heating and cooling cycles. The purity of the four alkanoates was high enough to achieve reliable data. Table 1 gives the molar percent purities (eutectic impurities) and the corresponding fusion temperatures, which are compared with those from other authors [9–12], who did not report any figures for the purity of their samples.

Figures 1 and 2 show the recorded DSC thermograms for the four compounds studied. Figure 1 shows the lower temperature peaks for samples capsulated in solid pans. With the exception of the thallium(I) *n*-octanoate, which shows no hysteresis, the first and second scans present different patterns for the same operational conditions; this behaviour could be attributed to the possible occurrence of metastable forms. The behaviour

TABLE 1

Purities and temperatures of fusion of the thallium(I) *n*-alkanoates (Tl*n*C)

Compound	Purity [a] mol.%	T_f(K)		
		This work	Literature	Reference
Tl8C	99.79	411.0	411	9
			408.9	10
			403	11
			408.2	12
Tl9C	99.73	410.9	411	9
			411.8	10
			410	11
			409.7	12
Tl11C	99.86	404.2	404	9
			403.6	10
			401.9	12
Tl13C	99.86	397.9	398.5	12

[a] Mean values of four DSC determinations.

observed in the second scan was maintained during subsequent ones. Figure 2 shows the higher temperature peaks (the fusion and clearing peaks) with both the heating and cooling cycles for samples capsulated in volatile pans.

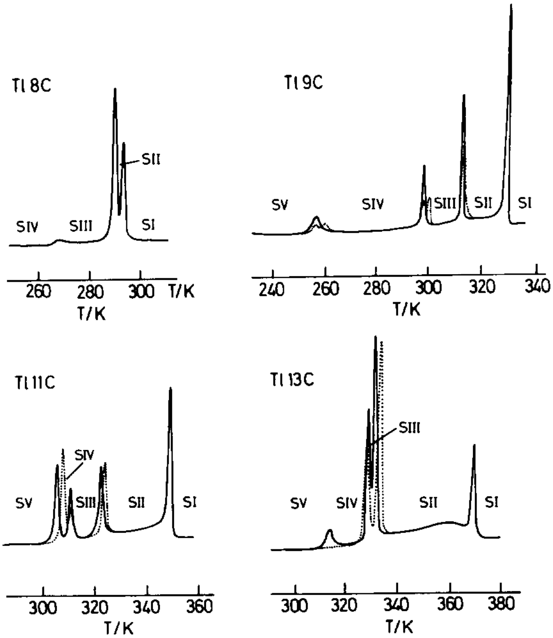

Fig. 1. Heating thermograms (solid pans) showing the solid-to-solid transitions of thallium(I) *n*-alkanoates (Tl*n*C). Dotted lines, first heating; continuous ones, second heating. SI–SV denotes the different solid phases.

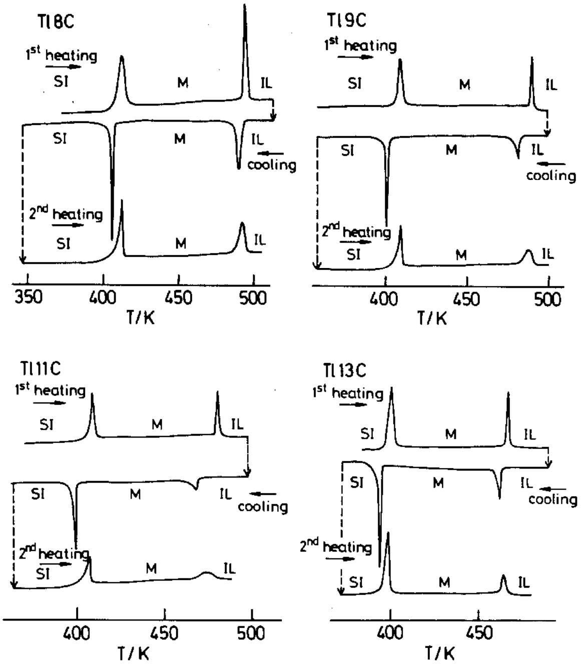

Fig. 2. Thermograms (volatile pans) showing the fusion and clearing transitions of thallium(I) *n*-alkanoates (Tl*n*C). M, mesophase; IL, isotropic liquid.

A considerable undercooling effect (5–8 K at cooling rates 10 K min^{-1}) was always observed on forming both the mesomorphic and solid I phases for each compound. The second heating always produced a sharper fusion peak (due to an improved thermal contact); however, the clearing peak was broader and smaller and tended to decrease in area in the second and subsequent heating scans (due to thermal decomposition of the sample).

The designation of the different solid phases, mesophase and isotropic liquid is based on observation by polarizing microscopy, which is in agreement with that reported by previous authors [9–12]. The liquid crystalline mesophase (non-homeotropic) of all the samples exhibited a simple fan-shaped texture, which is only achieved after rapid cooling from the isotropic liquid. If the sample was heated from the solid phase or cooled slowly from the isotropic liquid, spontaneous formation of the homeotropic condition invariably resulted. Sometimes spherulitic domains were observed in the homeotropic texture during the cooling runs. Mesophases were also coloured, changing from low to high frequency colours with the decreasing temperature.

The mesophase has been identified as a homogeneous smectic A-like or "neat" structure [15,16] for all the samples studied. In Fig. 3 the typical fan-shaped texture for the Tl9C and Tl11C can be seen showing a decreasing size of the domains with the increasing number of carbons.

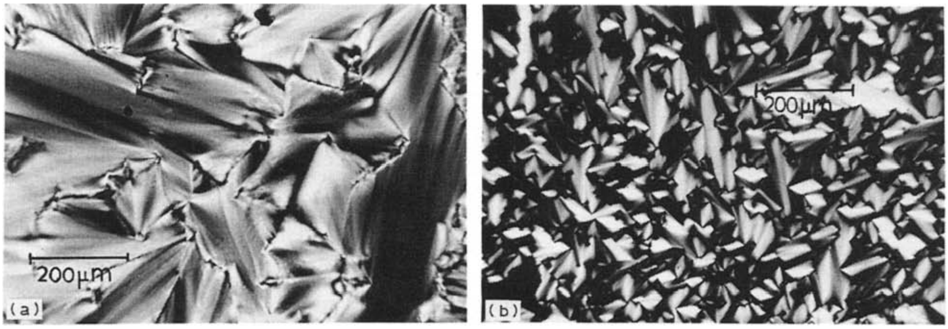

Fig. 3. Simple fan texture observed under crossed polars for the smectic A-like or "neat" phase of (a) thallium(I) nonanoate at 439 K and (b) thallium(I) undecanoate at 437 K.

The temperatures, enthalpies and entropies concerning all the transitions observed are presented in Table 2. Figure 4 summarizes the literature and present temperature data for comparison. While the entropy of fusion

TABLE 2

Thermal functions of the phase transitions of thallium *n*-alkanoates: Tl8C, Tl9C, Tl11C and Tl13C

Compound	Transition	T (K)	$\Delta H/R$ (K)	$\Delta S/R$
Tl8C	Solid IV–Solid III	268.7	20	0.07
	Solid III–Solid II	289.8	455	1.57
	Solid II–Solid I	294.3	260	0.88
	Solid I–Mesophase	411.0	682	1.66
	Mesophase–Isotropic Liquid	494.7	360	0.73
Tl9C	Solid V–Solid IV	259.3	125	0.48
	Solid IV–Solid III	299.8	188	0.63
	Solid III–Solid II	315.7	344	1.09
	Solid II–Solid I	332.2	834	2.51
	Solid I–Mesophase	410.9	728	1.77
	Mesophase–Isotropic Liquid	490.0	332	0.68
Tl11C	Solid V–Solid IV	306.2	404	1.32
	Solid IV–Solid III	312.4	255	0.82
	Solid III–Solid II	325.6	414	1.27
	Solid II–Solid I	351.1	848	2.42
	Solid I–Mesophase	404.2	734	1.82
	Mesophase–Isotropic Liquid	477.1	277	0.58
Tl13C	Solid V–Solid IV	315.0	95	0.30
	Solid IV–Solid III	328.1	581	1.77
	Solid III–Solid II	332.6	1120	3.37
	Solid II–Solid I	370.1	349	0.94
	Solid I–Mesophase	397.9	757	1.90
	Mesophase–Isotropic Liquid	464.7	225	0.48

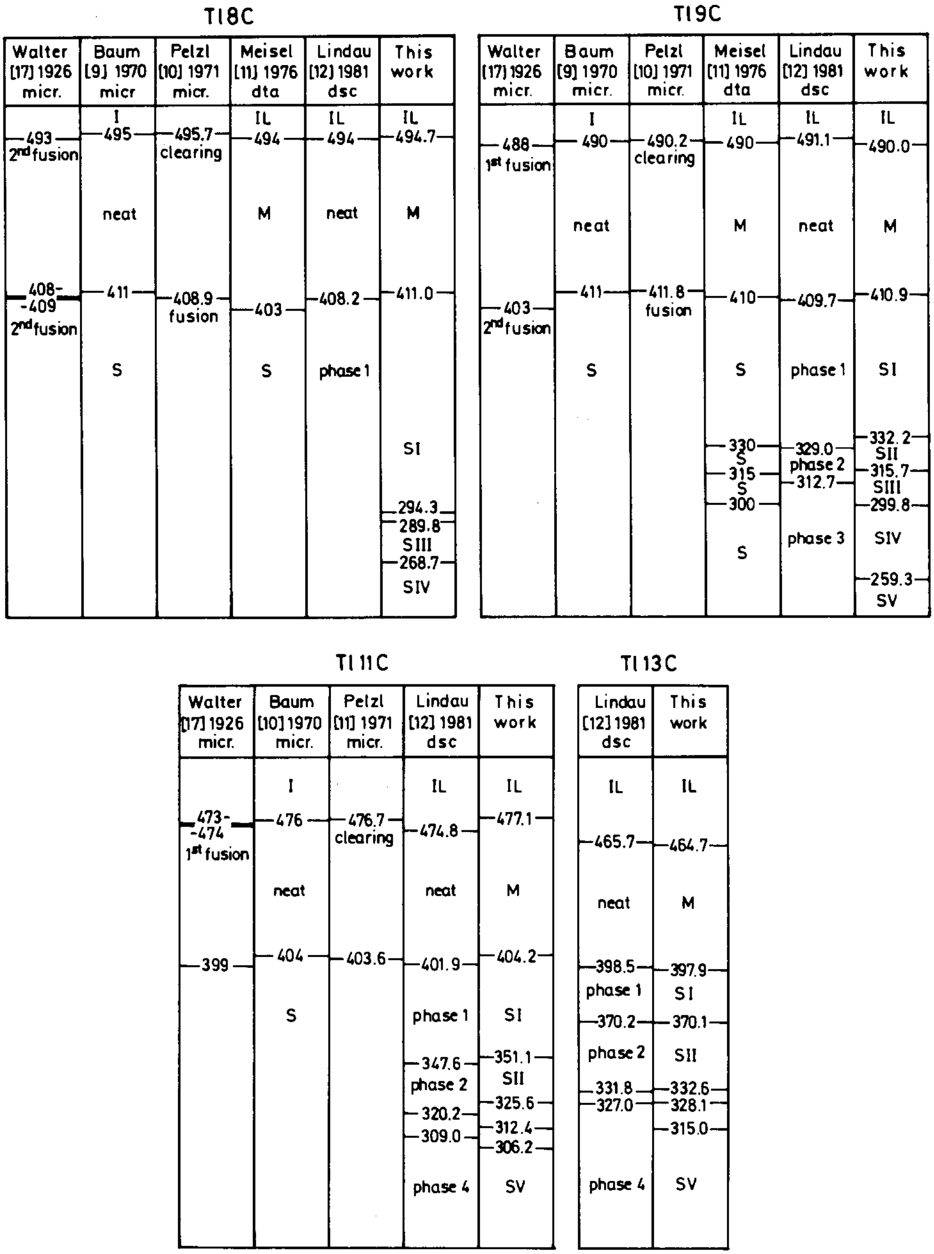

Fig. 4. Summary of the transition temperatures for the four thalium(I) *n*-alkanoates (Tl*n*C). Phase and transition designations according to the original papers: SI–SV, different solid phases; M, mesophase; IL, isotropic liquid. Experimental techniques: micr., microscopic observation; DTA, differential thermal analysis; DSC, differential scanning calorimetry.

increases with the chain length, the corresponding value for the clearing transition decreases, which suggests that the stability of the mesophase is lower for the longer chain homologues. This effect is also observed by comparing the mesophase temperature ranges with each other, defined as the difference between the clearing and the fusion temperatures. These values are 83.7, 79.1, 72.9 and 66.8 K for Tl8C, Tl9C, Tl11C and Tl13C, respectively.

TABLE 3

Molar heat capacities of thallium(I) octanoate, nonanoate, undecanoate and tridecanoate ($R = 8.3144$ J mol^{-1} K^{-1})

T (K)	C_p/R			
	Tl8C	Tl9C	Tl11C	Tl13C
305	35.4	—	—	—
310	35.3	47.3	—	—
315	35.0	—	—	—
320	34.9	—	—	—
325	34.9	55.4	—	—
330	35.0	61.9	—	—
335	35.1	—	—	—
340	35.3	42.4	—	—
345	35.8	41.3	—	85.8
350	36.0	41.2	—	89.8
355	36.2	41.2	—	96.5
360	36.4	41.5	50.9	103.8
365	36.6	41.7	51.6	102.6
370	36.9	42.1	51.3	—
375	37.0	42.4	51.7	—
380	37.3	42.6	52.0	58.8
385	37.5	42.9	52.2	59.6
390	37.7	43.3	52.8	61.5
395	38.0	43.5	—	—
400	38.2	44.2	—	—
405	38.4	—	—	—
410	—	—	64.4	75.0
415	—	—	65.0	75.1
420	—	—	65.5	75.3
425	—	—	66.2	76.1
430	48.4	53.4	66.9	76.4
435	49.1	53.8	67.1	77.2
440	49.5	54.0	67.3	78.0
445	49.9	54.8	67.2	78.4
450	50.3	55.1	67.8	79.0
455	50.7	55.9	68.3	79.4
460	51.2	57.1	68.8	79.8
465	52.0	57.3	—	—
470	52.4	57.7	—	—
475	52.7	58.7	—	—
480	53.1	59.2	—	—
485	53.5	60.3	—	—
490	54.1	—	—	—

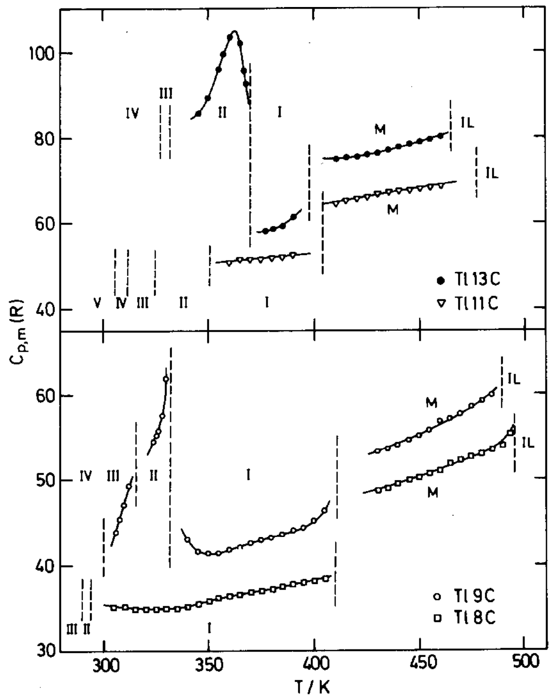

Fig. 5. Heat capacity curves for the different solid phases and mesophases of thallium(I) *n*-alkanoates (Tl*n*C); broken vertical lines represent the transition temperatures.

As is obviously expected, the overall entropy change associated with all the steps from the fully ordered crystalline state to the isotropic melt, increases with increasing chain length. However, this happens by means of an increase in the entropy change associated with the solid-to-solid phase transitions; effectively, the sum of $\Delta S_{\text{fusion}} + \Delta S_{\text{clearing}}$ is almost constant and equal to $(2.40 \pm 0.05)R$. This might suggest that the solid-to-solid transitions are associated with the disordering of hydrocarbon chains in the crystalline lattice, as a "partial melting". X-ray diffraction studies would elucidate this question.

The experimental molar heat capacities obtained for the four thallium(I) *n*-alkanoates are given in Table 3 at 5 K intervals within the temperature range 300–500 K. No measurements were taken at temperatures above the clearing point because decomposition of the samples in volatile pans begins near this limit, nor in the areas where phase transitions took place because of the lack of equilibrium inherent in the dynamic method employed.

The heat capacity measurements are plotted against temperature in Fig. 5; vertical lines denote transition temperatures and Roman numbers show the existing range of the different solid phases. These is a broad hump in the C_p/R vs. T curve for the solid II phase of the *n*-tridecanoate. This has also been observed, always in the solid II phase, in other members of the thallium(I) series [3,4].

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