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DSC THERMOPHYSICS ON SOME LOWER THALLIUM(I) *N*-ALKANOATES *

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ABSTRACT

Five of the lower members of thallium(I) *n*-alkanoates were synthesized and recrystallized until their purity, as determined by DSC, was considered appropriate to undertake thermodynamic studies on the polymorphic and mesomorphic transitions they exhibit and thermodynamic data are reported. Heat capacity measurements by DSC are also given between 320 and 500 K.

INTRODUCTION

Thermal behaviour of alkali *n*-alkanoates has received much attention during the last few years due to the mesomorphism they exhibit, so that many authors [1–5] have measured the thermodynamic parameters related to their phase transitions and their thermal decomposition has been also studied. While this is so for Li, Na, K, Rb and Cs derivatives, the corresponding thallium(I) *n*-alkanoates have been less investigated, even when they also exhibit a similar behaviour. These thallium(I) salts may offer additional interest, due to the fact that they could present other transitions at low temperatures, a point that has been now observed by Westrum [14] in the hexanoate member of the series.

Some work [6–10] has, however, been carried out by other authors on the

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thermal stability, thermodynamic data acquisition or texture and structural parameters of these compounds. Nevertheless there is a complete lack of data in the literature concerning their heat capacities which could be also very useful to obtain information about the thermodynamic parameters. For this reason, the present report deals with the DSC heat capacity determinations on several members of the thallium(I) alkanoates from room temperature up to that of transition to isotropic liquid. The thermodynamic characterization of their phase transitions has been also carried out by DSC, laying special emphasis on the purity aspects.

EXPERIMENTAL

Materials

Thallium(I) alkanoates were prepared by heterogeneous reaction of *n*-fatty acids (Fluka, puriss) with thallium(I) carbonate (Fluka, puriss) in dry methanol, following the procedure of Meisel et al. [10]. The salts were recrystallized from an ethanol–ether mixture and vacuum-dried. The absence of water and free acid was assessed by IR spectroscopy.

Purity

The purity was determined by DSC [13] with a Perkin–Elmer DSC-2, whose temperature display was previously calibrated by the melting point of several high purity ($> 99.9\%$) substances (gallium, benzoic and stearic acids, indium and tin). Three or four samples between 2 and 6 mg, weighed to ± 0.002 mg with a Perkin–Elmer AR-2 Autobalance, were capsuled in solid pans for each salt and scanned through its solid–liquid or solid–mesophase transition, depending on the thermal behaviour of the substance, at a heating rate of 0.625 K min^{-1} and 0.5 mcal s^{-1} full scale sensitivity.

The transition enthalpies were determined by planimetry using a high purity indium ($> 99.999\%$) as reference ($\Delta H_f = 3.267$ kJ mol^{-1}).

Transition data

The method was the same as above but samples ranged between 10–20 mg and the heating rate and sensitivity were 10 K min^{-1} and 10 mcal s^{-1} full scale, respectively. At this scanning speed the mesophase–liquid transition always took place with decomposition and weight losses but, as assessed by TG (Perkin–Elmer Thermogravimetric System TGS-2), it was retarded by capsuling the sample into hermetically sealed volatile pans and pertinent data could be obtained thus (see Tl6C thermogram in Fig. 1). The estimated

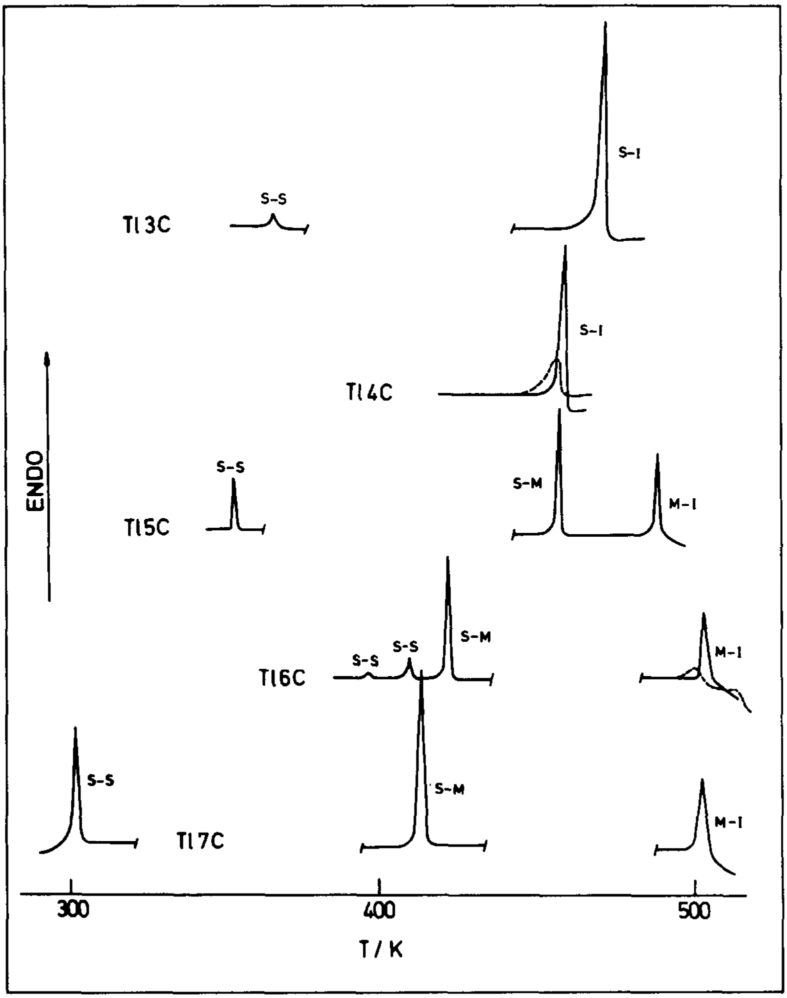

Fig. 1. Heating DSC-grams of the thallium(I) *n*-alkanoates from propanoate to heptanoate.

standard error was ±0.5 K and 2–5% for transition temperatures and enthalpies, respectively.

Heat capacity

Four to six samples of about 10–20 mg were scanned for each product in the temperature interval 320–500 K, using a heating rate of 10 K min^{-1} and a sensitivity of 2 mcal s^{-1} full scale. Solid or volatile aluminium pans were used, according to the tested temperature range. Each scan was divided into runs of approximately 30 K, overlapping each other to minimize base-line uncertainty. Synthetic sapphire was used as external standard [11,12]. The estimated error of these values was ~ 2%.

RESULTS AND DISCUSSION

Thermal behaviour and thermodynamic data

As can be seen in Table 1, the purity of the alkanoates was high enough to achieve reliable data. The corresponding transition temperatures are also given, for comparison with those with other authors [6–10] who did not report any figures for the purity of their compounds. Endothermic peaks of the DSC heating thermograms are given in Fig. 1, where the phase transition involved is indicated according to characterizations made by previous authors [7–10] and confirmed in our work by thermal microscopy (polarizing microscope equipped with Mettler FP5 + FP52 system). This technique showed how much the thermal behaviour of the lower members, Tl3C and Tl4C, can be altered by the presence of moisture, due to the appearance of new

TABLE 1

Purity and fusion temperatures (literature and experimental) of the compounds investigated

Compound	% Purity molar	T_f (K)		
		This work	Literature	Ref.
Tl3C	99.45	468.0	461	6
			459	8
			468	10
			462.4	7
Tl4C	99.85	456.7	455	6
			450	8
			459	10
			451.9	7
Tl5C	99.86	455.0	448	6
			454	8
			454.2	9
			455	10
			453.0	7
Tl6C	99.97	425.0	425	6
			422	8
			422.2	9
			418	10
			421.7	7
Tl7C	99.89	420.7	416	6
			416	8
			416.0	9
			419	10
			413.7	7

mesomorphic phases (lyotropism); therefore these compounds must be handled in a dry atmosphere.

The effect shown in the Tl4C thermogram was exhibited by all the compounds when fused twice. The sharper peak at the highest temperature corresponded to the solid–mesophase transition of the compound recrystallized from the solvent, while the broader and smaller one was due to the material solidified from the melt. By analogy with other compounds it is assumed that during the resolidification after melting the sample would develop some lattice defects, about which some kind of motion of the hydrocarbon chain could occur at lower temperatures.

Temperature, enthalpy and entropy concerning all the transitions observed are shown in Table 2. Although it should be confirmed by the study of a large number of members of the homologous series, an odd–even effect on the transition temperatures was observed.

The thermodynamic parameters obtained agreed variably with those reported by other authors, ours being generally higher, which is attributed to purity; as it is well known, small impurities may affect the phase transition parameters, especially in the case of mesomorphic ones, and it is presumed that our samples were the purest.

No analysis of the entropy contribution per CH_2-group was attempted since low temperature transitions have already been observed [14] on Tl6C in addition to those reported here; an odd–even effect was, however, apparent.

TABLE 2

Thermal functions of phase transitions of thallium(I) *n*-alkanoates from *n*-propanoate (Tl3C) to *n*-heptanoate (Tl7C)

Compound	Transition	T(K)	$\Delta H/R$(K)	$\Delta S/R$
Tl3C	solid II–solid I	364.8	38	0.10
	fusion	468.0	1260	2.70
Tl4C	fusion	456.7	925	2.03
Tl5C	solid II–solid I	353.0	253	0.72
	solid I–mesophase	455.0	686	1.50
	mesophase–isotropic liquid	488.0	367	0.75
Tl6C	solid III–solid II	397.9	25	0.06
	solid II–solid I	415.0	79	0.19
	solid I–mesophase	425.0	553	1.30
	mesophase–isotropic liquid	499.8	474	0.95
Tl7C	solid II–solid I	301.9	319	1.06
	solid I–mesophase	420.7	758	1.80
	mesophase–isotropic liquid	502.0	397	0.79

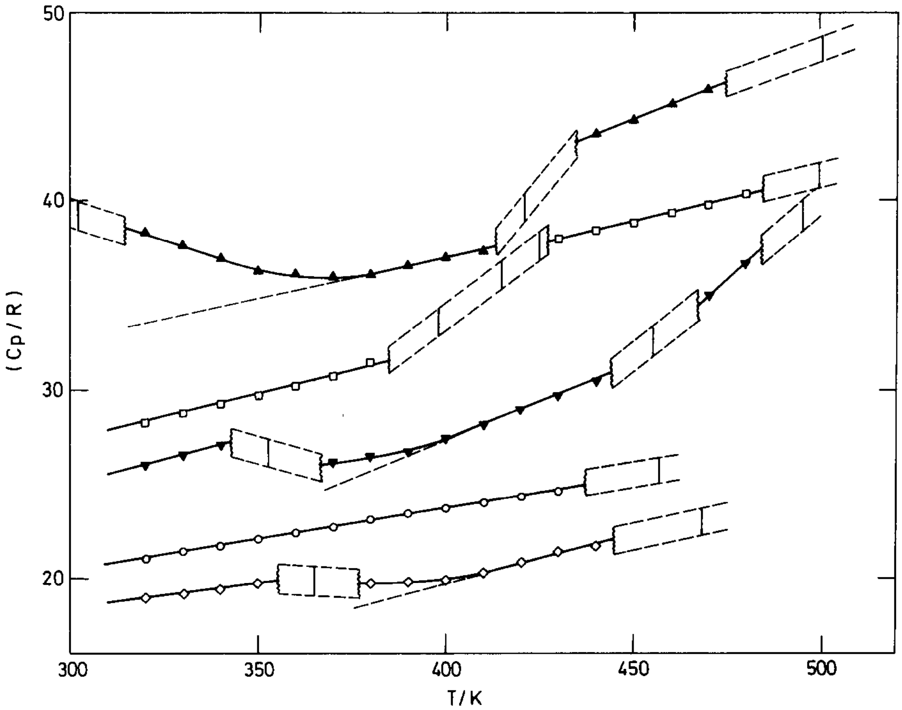

Fig. 2. Heat capacity (C_p/R) vs. temperature T (K) of the thallium(I) *n*-alkanoates. Experimental data: ◇, $n = 3$; ○, $n = 4$; ▼, $n = 5$; □, $n = 6$; ▲, $n = 7$. Transition intervals are framed and transition temperatures denoted by vertical lines.

TABLE 3

Heat capacities of thallium(I) *n*-alkanoates ($R = 8.31441$ J mol^{-1} K^{-1})

T (K)	C_p/R				
	Tl3C	Tl4C	Tl5C	Tl6C	Tl7C
320	19.0	21.1	26.0	28.3	38.3
330	19.2	21.4	26.5	28.8	37.7
340	19.4	21.7	27.1	29.3	36.9
350	19.7	22.1	–	29.7	36.3
360	–	22.4	–	30.2	36.2
370	–	22.7	26.2	30.8	36.0
380	19.7	23.1	26.4	31.5	36.1
390	19.8	23.4	26.7	–	36.3
400	19.9	23.7	27.4	–	37.0
410	20.3	24.0	28.2	–	37.3
420	20.9	24.3	28.9	–	–
430	21.4	24.5	29.6	38.0	–
440	21.7	–	30.3	38.4	43.6
450	–	–	–	38.8	44.3
460	–	–	–	39.3	45.1
470	–	–	35.0	39.8	35.9
480	–	–	36.7	40.4	–

Heat capacity

These data are plotted in Fig. 2, where worthy of mention is the fact that after the solid II–solid I transition of the odd members of the series, i.e., Tl3C, Tl5C and Tl7C, the C_p–T curve went down during a certain temperature interval; this was particularly noticeable for Tl7C.

Dash lines would represent the real pattern for 100% pure samples. Table 3 gives the heat capacity values at 10° intervals within the temperature range 320–500 K, with the exception of those zones where phase transitions took place. The data seem to be consistent within the series, but no comparison with other data is possible as none is found in the literature.

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