

## **THERMAL BEHAVIOUR OF THE SYSTEM: LEAD(II) DECANOATE/ LEAD(II) OCTADECANOATE**

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### **ABSTRACT**

Differential scanning calorimetry is used to determine phase-transition temperatures, heats and entropies of phase changes for mixtures of lead(II) decanoate and lead(II) octadecanoate over a wide range of compositions. A phase diagram is also presented for the system.

Phase texture studies, by polarising light microscopy, suggest that the phase sequence, on addition of lead(II) octadecanoate up to 0.1 mole fraction, is the same as in pure lead(II) decanoate, i.e.

solid(K)  $\rightleftharpoons$  crystal I(C<sub>1</sub>)  $\rightleftharpoons$  smectic(SM)  $\rightleftharpoons$  isotropic liquid(I)

A new crystalline phase (C<sub>II</sub>) is observed at 0.2 mole fraction of lead(II) octadecanoate at ca. 349 K, is enhanced at 0.3 mole fraction, progressively reduced up to 0.6 mole fraction and finally disappears at 0.7 mole fraction of lead(II) octadecanoate.

The total entropy change per mole of hydrocarbon chain for conversion from K to I is virtually constant for mixtures containing 0.04–0.4 mole fraction of octadecanoate. This implies that the hydrocarbon chains in the mixtures are arranged in a similar manner in both the crystal lattice and the liquid phase. Above 0.5 mole fraction of octadecanoate, the data indicate some disordering of hydrocarbon chains in the liquid phase.

### **INTRODUCTION**

Thermotropic mesophases have been reported in the phase sequence for even chain-length lead(II) *n*-alkonates containing 12 carbon atoms or less per chain [1–4]. Subsequently, phase texture studies [2,4] have established the presence of a single mesophase, classified as a smectic mesophase (most probably a smectic C structure) in the phase sequence for this series of compounds. Other studies have focused on mesophase formation as a function of composition in binary mixtures of metal carboxylates [5–9]. For example, Spegt and Skoulios [8,9] have reported that, at high temperatures, a mixture of calcium and strontium octadecanoate gave X-ray diffraction patterns corresponding to a homogeneous hexagonal phase containing the two metals. In contrast, the mixture containing calcium and magnesium octadecanoate gave diffraction patterns that were interpreted as the heterogeneous mixtures of pure hexagonal phases of the individual soaps.

Whilst it has been reported [6] that the addition of lead oxide to lead(II) dodecanoate resulted in increased ordering of the hydrocarbon chains of the dodecanoate in the liquid phase, the addition of dodecanoate acid to lead(II) dodecanoate did not alter the degree of order of hydrocarbon chains either in the solid or liquid state [10]. Similarly, the addition of zinc octadecanoate ( $\text{ZnC}_{18}$ ) to lead(II) octadecanoate ( $\text{PbC}_{18}$ ) in the composition range 0.01–0.03 mole fraction, did not alter the degree of order of hydrocarbon chains in either the solid or liquid phases. Clearly, it would be of interest to see if small or large amounts of a long-chain *n*-alkonate ( $\text{PbC}_{18}$ ) in a shorter chain *n*-alkonate [lead(II) decanoate, ( $\text{PbC}_{10}$ )] would have a greater disruptive effect on the crystal structure and hence thermal behaviour of the shorter-chain compound than has been reported for mixtures of metal *n*-alkonates of similar shape and size.

In the present work, the techniques of differential scanning calorimetry (DSC), and hot-stage polarising light microscopy were used to investigate the thermal behaviour of mixtures of  $\text{PbC}_{10}/\text{PbC}_{18}$  from 0.04 to 0.9 mole fraction of octadecanoate.

## EXPERIMENTAL

The preparation and purification of lead(II) *n*-alkonates, of general formula  $(\text{CH}_3(\text{CH}_2)_n\text{COO})_2\text{Pb}$ ,  $n = 8 = \text{PbC}_{10}$ ,  $n = 16 = \text{PbC}_{18}$ , have been described elsewhere [11]. The melting points and C and H data for the anhydrous compounds were in excellent agreement with expected values.

The mixtures were prepared by weighing the desired amounts of the compounds into small flasks fitted with quick-fit stoppers with a vacuum tap. To assure a uniform mix, without thermal degradation, each mixture was melted under vacuum. The mixture was then cooled, ground up and remelted. This sequence was repeated several times before the samples were considered suitable for DSC study.

DSC measurements were performed using a Perkin–Elmer DSC-4-TADS system. For quantitative studies, samples of 2–10 mg were encapsulated in aluminium crucibles and scanned at  $1 \text{ K min}^{-1}$ . Measurements were made, at least in triplicate, on fresh samples in both a heating and cooling cycle.

Phase textures were determined using a Leitz Polarising Light Microscope fitted with a Mettler FP-2 heating stage (scan rate  $2 \text{ K min}^{-1}$ ). Samples for phase-texture determination were sandwiched between a microscope slide and cover slip. Prior to a run, both slide and coverslip were cleaned in acetone and allowed to dry. Their contact surfaces were then rubbed, in the same direction, with soft tissue to help obtain good textures. Room-temperature microscopic examination of the samples, under polarised light, showed them to be crystalline in all cases.

## RESULTS AND DISCUSSION

Each sample was examined on heating and cooling the calorimeter between ambient and a temperature in excess of the melting point of the mixtures (303–394 K). Transition temperatures were obtained from the DSC heating curves only and were taken as the maxima in these curves.

A wide variety of DSC curves were observed for the different mixtures as illustrated in Fig. 1. For  $\text{PbC}_{10}$ , three first-order transitions are obtained at 359.0, 371.4 and 384.2 K. The phases are birefringent and exhibit enantiotropic phase behaviour. Crystalline transitions were identified by their microscopic textures (Fig. 2), their resistance to mechanical deformation and by their tendency to supercool. The smectic phase was identified by the typical fan texture observed for this phase (Fig. 3) and by the negligible

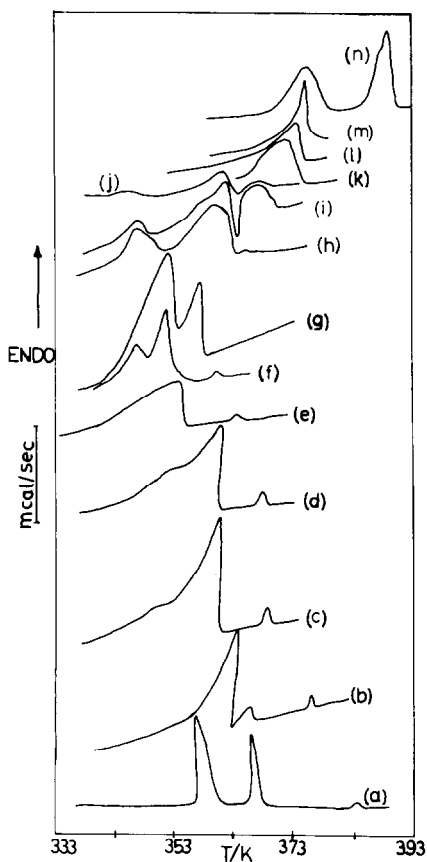


Fig. 1. DSC heating curves for the mixtures. (a) Pure  $\text{Pb}(\text{CH}_3(\text{CH}_2)_8\text{CO}_2)_2$ . (b)  $X_{\text{PbC}_{18}} = 0.04$ . (c)  $X_{\text{PbC}_{18}} = 0.08$ . (d)  $X_{\text{PbC}_{18}} = 0.10$ . (e)  $X_{\text{PbC}_{18}} = 0.12$ . (f)  $X_{\text{PbC}_{18}} = 0.20$ . (g)  $X_{\text{PbC}_{18}} = 0.30$ . (h)  $X_{\text{PbC}_{18}} = 0.40$ . (i)  $X_{\text{PbC}_{18}} = 0.50$ . (j)  $X_{\text{PbC}_{18}} = 0.60$ . (k)  $X_{\text{PbC}_{18}} = 0.70$ . (l)  $X_{\text{PbC}_{18}} = 0.80$ . (m)  $X_{\text{PbC}_{18}} = 0.90$ . (n) Pure  $\text{Pb}(\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2)_2$ .

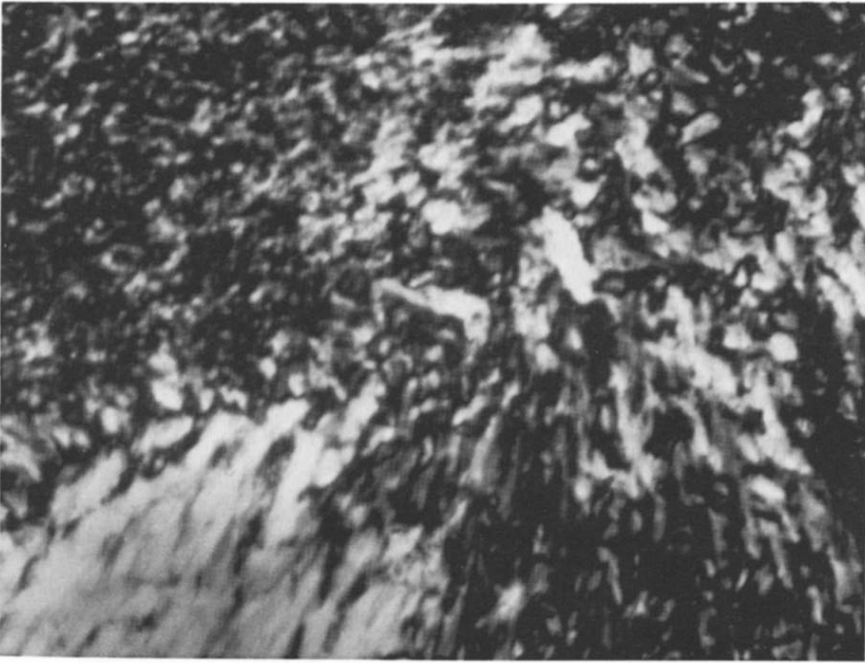
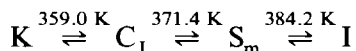


Fig. 2. Texture of crystalline phase at 345 K for 0.1 mole fraction mixture.



Fig. 3. Texture of smectic phase at 368.4 K for 0.1 mole fraction mixture.

supercooling observed in the DSC curve on cooling into this phase. For pure  $\text{PbC}_{10}$ , the transition at 359 K has been identified as a solid (K) to crystal I ( $C_1$ ) transition, while those at 371.4 K and 384.2 K were identified as the  $C_1$  to smectic ( $S_m$ ) and  $S_m$  to isotropic (I) transitions respectively [2]. The suggested phase sequence:



differs, in several respects, from the tentative scheme proposed by Adeosun and Sime [1]. In their work, the transition on the low temperature side was reported to be a K to  $S_m$  transition and on the high temperature side, a cubic to I transition. The evidence for their phase sequence was inconclusive, as those authors admitted, and are now considered to be in error [2,3]. For pure  $\text{PbC}_{18}$ , only crystalline polymorphism was observed [2].

Figure 1 shows that at 0.04–0.1 mole fractions of  $\text{PbC}_{18}$  the phase sequence  $\text{K} \rightleftharpoons C_1 \rightleftharpoons S_m \rightleftharpoons \text{I}$  is unchanged. However, the K to  $C_1$  transition decreases with increasing concentrations of  $\text{PbC}_{18}$ . This transition has been ascribed, by Amorim daCosta et al. [3], to C–H stretching vibrations leading to a substantial decrease in lateral order on forming  $C_1$ . Clearly, the addition of  $\text{PbC}_{18}$  results in increased lateral order. An extra transition at ca. 337 K is observed in the DSC cooling curve (not shown) between the  $C_1$  to K transition. This transition could result from the formation of a new crystalline structure, or might indicate the expected increase in sample thickness as the sample is cooled from  $C_1$  to K. Unfortunately, no new texture was observed on microscopic examination of this transition, even when  $C_1$  was slowly cooled to K. On the addition of 0.2 mole fraction of  $\text{PbC}_{18}$ , a new crystalline phase, crystal II ( $C_{II}$ ), appears at ca. 349 K, is enhanced at 0.3 mole fraction of  $\text{PbC}_{18}$  and is progressively reduced at 0.4, 0.5 and 0.6 mole fractions of  $\text{PbC}_{18}$  at slightly lower temperatures. Interestingly, the occurrence of a structurally different phase has been reported at low mole fractions of lead oxide in  $\text{PbC}_{12}$  [6] and, indeed, the presence of such phases has been predicted by Winsor [12]. Though  $C_{II}$  could not be separated texturally from the other crystalline phases, a new transition was observed on cooling into this phase. The  $S_m$  phase disappears ca. 0.7 mole fraction of  $\text{PbC}_{18}$  and at this composition only the K to I transition at 377 K was observed. Thereafter the transition temperatures for fusion increased with increasing  $\text{PbC}_{18}$  concentration up to 0.9 mole fraction. The transition at ca. 382 K for 0.9 mole fraction of  $\text{PbC}_{18}$  is also present in pure  $\text{PbC}_{18}$  as a premelting transition.

Detailed examination of the DSC curves allowed the construction of a phase diagram as shown in Fig. 4. The  $S_m$  phase extends over a wide range of composition and breaks down at a concentration approaching 0.7 mole fraction of  $\text{PbC}_{18}$ . As it was not possible to determine the boundary of this phase with any certainty, an extrapolated boundary is shown.

TABLE 1

Thermodynamic data <sup>a</sup> for phase transition in the lead(II) decanoate/lead(II) octadecanoate system

$X_{\text{PbC}_{18}}$	K $\rightarrow$ C <sub>I</sub>		K $\rightarrow$ C <sub>II</sub>		K $\rightarrow$ S <sub>m</sub>		C <sub>I</sub> $\rightarrow$ S <sub>m</sub>	
	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$
0	19.3	53.7					9.1	24.4
0.04	21.7	59.9					1.7	4.6
0.08	0.7	2.0			21.3	59.2		
0.10	0.6	1.7			22.3	62.1		
0.12					20.8	59.3		
0.20								
0.30								
0.40			6.7	19.4				
0.50			4.4	12.5				
0.60			1.2	3.5				
0.70								
0.80								
0.90								
1.00	27.9 <sup>b</sup>	73.1 <sup>b</sup>						

<sup>a</sup>  $\Delta H$  values are expressed in kJ (mole of hydrocarbon chain)<sup>-1</sup>;  $\Delta S$  values in J K<sup>-1</sup> (mole of hydrocarbon chain)<sup>-1</sup>. Errors are within  $\pm 3\%$ .

<sup>b</sup> K  $\rightarrow$  C<sub>I</sub><sup>\*</sup> values for pure PbC<sub>18</sub>.

These results point to a similarity of crystal structures within the composition range 0.04–0.12 mole fraction of PbC<sub>18</sub>. Indeed, the thermodynamic data (given in Table 1) suggest some similarity in the thermal behaviour of mixtures up to at least 0.4 mole fraction PbC<sub>18</sub>. For these mixtures, the total

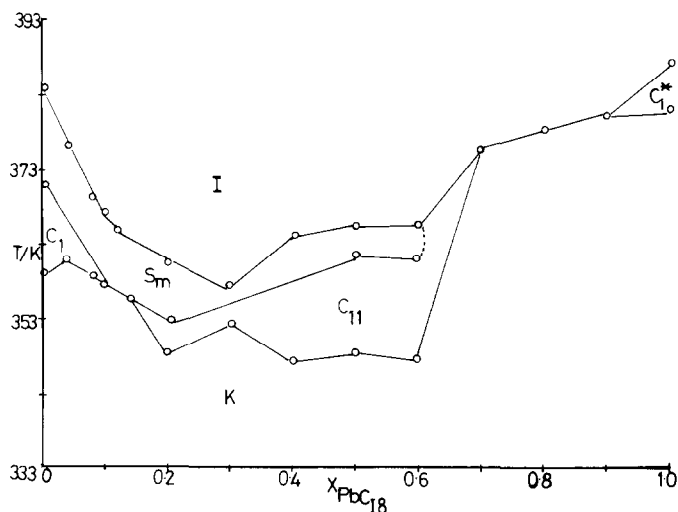


Fig. 4. Phase diagram for  $\text{Pb}(\text{CH}_3(\text{CH}_2)_8\text{CO}_2)/\text{Pb}(\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2)_2$ . X, mole fraction; C<sub>I</sub><sup>\*</sup>, crystal I for pure PbC<sub>18</sub>.

$C_{II} \rightarrow S_m$		$K \rightarrow I$		$S_m \rightarrow I$		$C \rightarrow I$		$\Sigma\Delta H$	$\Sigma\Delta S$
$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$	$\Delta H$	$\Delta S$		
				0.4	1.1			28.8	79.2
				0.6	1.4			24.0	65.9
				0.5	1.4			22.5	62.6
				0.5	1.3			23.4	65.1
				0.4	1.0			21.2	60.3
				0.5	1.3			23.9	67.9
								22.1	66.4
15.2	42.6			0.2	0.4			22.1	62.4
23.3	64.4			13.9	38.1			41.6	115.0
7.5	20.6			2.3	6.3			11.0	30.4
		13.6	36.1					13.6	36.1
		35.2	93.0					35.2	93.0
		18.0	47.1					18.0	47.1
						27.0	69.5	54.9	142.6

entropy change  $\Sigma\Delta S$  per mole of hydrocarbon chain, for conversion from K to I is virtually constant. As the main contribution to  $\Delta S$  is the stepwise disordering of hydrocarbon chains in the lattice with increasing temperature [1,2], it seems reasonable to suggest that  $PbC_{18}$  in the mixture up to 0.4 mole fraction alters, insignificantly, the degree of order of hydrocarbon chains either in the solid or liquid phase. This implies that hydrocarbon chains in the mixtures are arranged in the same manner in the crystal lattice as in the liquid phase. Beyond 0.5 mole fraction of  $PbC_{18}$ , no significant trends are discernable with increasing concentrations of  $PbC_{18}$ . Nevertheless, the data indicate either an increased disordering of hydrocarbon chains in the solid phases of the mixtures or an increased ordering in the liquid phases. The weight of evidence, from specific heat measurements as a function of composition of like systems [6] and this work, suggests no increase in rotational disorder resulting from a looser packing of hydrocarbon chains in the crystal lattice. It thus seems that these higher compositions of  $PbC_{18}$  lead to some ordering of hydrocarbon chains in the liquid phase itself.

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