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THERMOTROPIC MESOMORPHIC CHANGES IN RACEMIC AND MESO LEAD(II) 9,10-DIHYDROXYOCTADECANOATES

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ABSTRACT

Data are presented for the heats and entropies of phase changes for the racemic and meso lead(II) 9,10-dihydroxyoctadecanoates. The total enthalpy change accompanying the transformation crystal → liquid phase is lower for the lead(II) 9,10-dihydroxyoctadecanoates than for the lead(II) octadecanoate. This suggests the solid phase of the former to be more disordered than that of the latter.

Optical examination under a polarising microscope suggests the phase sequence: solid I → mesophase → liquid for the racemic isomer, and solid I → solid II → mesophase → liquid for the meso isomer. The mesophase and solid II phase are absent on reheating the racemic and meso soaps respectively. The behaviour is interpreted in terms of subtle structural rearrangement of the liquid phase arising from extensive hydrogen bonding. The texture of the mesophases of the isomers is observed to be different and the mesophase of the meso soap is stable over a wider temperature range than that of its racemic counterpart. The behaviour is indicative of the effect of stereochemical configuration on the thermal properties of the soap.

INTRODUCTION

The properties of mesophases or liquid crystals have been under intense investigation in the last 20 years or more because of their wide technological application. For example liquid crystals are common materials in many electrically controlled devices such as digital wristwatches, pocket calculators, thermometers [1] and so on. Thus any system that is capable of exhibiting liquid crystallinity will continue to be a subject of research interest.

A series of investigations on the phase changes occurring on heating anionic surfactants (e.g. soaps) is available in the literature [2–8]. Data in a previous study [9] from our laboratory, have shown that for the lead(II) dodecanoate and lower chain length soaps, the phase sequece is crystal → $G_{(\text{smectic})} \rightarrow V_{2(\text{cubic isomorphous})} \rightarrow$ liquid while for tetradecanoate and above, the V_2 phase is absent and the G phase melts directly to the liquid. Recently, Amorin Da Costa et al. [10] reassigned the structure of the higher tempera-

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ture mesophase of lead(II) decanoate to be L_∞(Smectic A) and the lower temperature one to be ordered smectic. The number and temperatures of the phase transitions in some branched-chain sodium soaps have been found to differ considerably from those of their straight-chain counterparts [11,12]. The present study is interested in the effect, on phase changes, of substituting dihydroxy groups in the middle of the carbon chain of lead(II) carboxylates. Hence this report on the melting and mesophase behaviour of the racemic and meso lead(II) 9,10-dihydroxyoctadecanoates.

EXPERIMENTAL

Materials

All the fatty acids employed were B.D.H. grade and were stated to have a minimum 99% purity by G.L.C. assay. They were used without further purification. Lead(II) nitrate was AnalaR from B.D.H.

Preparation of acids and their lead carboxylates

The racemic 9,10-dihydroxyoctadecanoic acid was prepared by the oxidation of *cis*-9-octadecenoic (oleic) acid with hydrogen peroxide in methanoic (formic) acid. The meso 9,10-dihydroxyoctadecanoic acid was prepared by the oxidation of *trans*-9-octadecenoic acid (elaidic) acid with H_2O_2–HCO_2H. The racemic and meso lead(II) 9,10-dihydroxyoctadecanoates, $Pb(OH)_2A_2$ were prepared from the racemic and meso acids respectively by metathesis in alcohol solution. The details of preparation, purification and characterisation of the acids [13,14] and the soaps [14,15] have previously been reported.

Measurements

The temperatures of the phase changes and their enthalpies were measured with a Perkin-Elmer DSC 2 calorimeter, calibrated with indium metal. Samples of about 5–10 mg of the soaps were weighed and sealed in the standard aluminium crucibles. The scan speed for both the heating and cooling processes was 5 K $\min^{-1}$. Measurements were performed at least in duplicate on at least two separate samples. Peak areas were measured by cutting out and weighing.

Optical observations were made on Monoscop VI W. NR. 7016 microscope fitted with a heating stage and a cross polar. IR spectra of the samples were recorded as KBr discs on a Perkin-Elmer 683 spectrophotometer. Raman spectra of the samples were recorded on Cary Model 82.

RESULTS

Typical differential scanning calorimeter (DSC) curves for the racemic and meso lead(II) 9,10-dihydroxyoctadecanoates are shown in Fig. 1. The peaks labelled A, B, C are fairly broad relative to the peaks obtained for lead(II) octadecanoate [9] (which has the same number of carbon atoms as the $Pb(OH)_2A_2$). Both the elemental and IR spectral analyses [14] suggested that the samples were pure, and so the broad peaks are interpreted to be due to the influence of the dihydroxy groups. Thermogram (a) for the racemic $Pb(OH)_2A_2$ shows two phase transitions. On cooling the liquid, (curve not shown) an exothermic peak was obtained at 403 K, close to the solid I → mesophase transition temperature. Reheating of this sample an hour or any time after the initial heating produced (b) for which the solid melted directly to the liquid phase. The premelted sample behaved exactly as reheating a sample and produced (b). However, recrystallisation of the premelted sample in propan-1-ol (the same solvent used for recrystallising the crude product) reverted it to the initial solid (thermogram the same as (a)).

The meso $Pb(OH)_2A_2$ behaved almost identically to its racemic counterpart. In its case, three phase transitions are observed for the initial crystal, thermogram (c). The cooling process (curve not shown) produced two exothermic peaks. The reheated sample, curve (d), only showed two phase transitions. Again, recrystallisation of premelted meso soap produced the initial crystals and the thermogram was the same as (c).

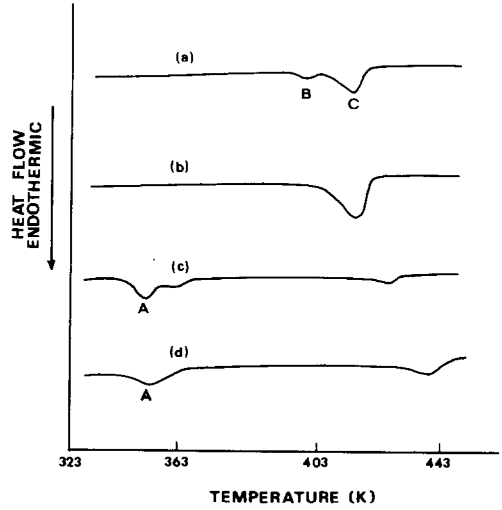

Fig. 1. DSC curves for the racemic and meso lead(II) 9,10-dihydroxyoctadecanoates, $Pb(OH)_2A_2$. (a) Pure racemic $Pb(OH)_2A_2$; (b) premelted racemic $Pb(OH)_2A_2$; (c) pure meso $Pb(OH)_2A_2$; (d) premelted meso $Pb(OH)_2A_2$.

TABLE 1

Temperatures [a] (K), enthalpies (kJ mol^{-1}) and entropies (J mol^{-1}) for phase transitions in racemic lead(II) 9,10-dihydroxyoctadecanoate

Sample treatment	Thermodynamic parameters							
	Solid I → mesophase			Mesophase → liquid			Solid → liquid	
	T	ΔH	ΔS	T	ΔH	ΔS	$\Delta H_{\mathrm{Total}}$	$\Delta S_{\mathrm{Total}}$
Heating	405	15.8 ± 0.8	39.0	412	49.4 ± 1.4	119.9	65.2 ± 2.2	158.9
	Solid I → liquid							
	T			ΔH			ΔS	
Cooling	403			-66.5 ± 1.0			-165.0	
Reheating	411			63.8 ± 2.9			155.2	

[a] Transition temperatures were measured at the start of the phase transitions.

The transition temperatures recorded in the optical microscope study confirmed completely those detected by DSC. The phase produced as a result of transition in (a), peak B, when viewed under cross polarisers was highly viscous. Cooling the liquid into the phase produced a typical mosaic texture of highly structured hexagonal packing, characteristic of smectic phase. The phase change of the meso $Pb(OH)_2A_2$ at the lower temperature (peak A in curve (c)) was a solid–solid transformation as this phase was not readily subject to mechanical deformation when the cover-slip on the microscope was perturbed. The higher temperature phase for this meso isomer was birefrigent and persisted over a fairly wide temperature range. Cooling the liquid into this phase revealed batonnets which transformed to a typical focal conic texture of smectic liquid phase. Either this phase cools directly to solid I or solid II supercools to solid I. A similar observation has been reported for laterally branched substances in which a phase observed on heating was lost on cooling, and the behaviour interpreted to mean the supercooling of the phase to the crystal [16]. Peak A of curve (d), the reheated meso sample, was a solid → mesophase transition. The texture of this mesophase was similar to the mesophase of the initial meso crystals.

The temperatures, enthalpies and entropies of these phase changes on heating, cooling and reheating are presented in Tables 1 and 2 for the racemic and meso soaps respectively. The highest error in the measurement of ΔH was not more than 5%, suggesting fairly reproducible runs.

DISCUSSION

The heats of solid → liquid transitions for the dihydroxy soaps (Tables 1 and 2) are much lower than that reported for lead(II) octadecanoate (119.5 kJ mol^{-1}) [9], while the melting temperatures to the liquid phase are higher

TABLE 2

Temperatures (K), enthalpies (kJ mol^{-1}) and entropies (J mol^{-1}) for phase transitions in meso lead(II) 9,10-dihydroxyoctadecanoate

Sample treatment	Thermodynamic parameters										
	Solid I → solid II			Solid II → mesophase			Mesophase → liquid			Solid I → liquid	
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	ΔH_{Total}	ΔS_{Total}
Heating	350	38.1 ± 1.5	108.9	358	15.0 ± 0.7	41.9	423	26.3 ± 0.8	62.2	79.4 ± 3.0	213.0
	Solid I → mesophase			Mesophase → liquid			Solid I → liquid				
	T	ΔH	ΔS	T	ΔH	ΔS	ΔH_{Total}	ΔS_{Total}			
Cooling	349	−10.6 ± 0.5	−30.4	423	−7.3 ± 0.4	−17.3	−17.9 ± 0.9	−47.7			
Reheating	352	29.4 ± 1.1	83.5	436	43.2 ± 2.0	99.1	72.6 ± 3.1	182.6			

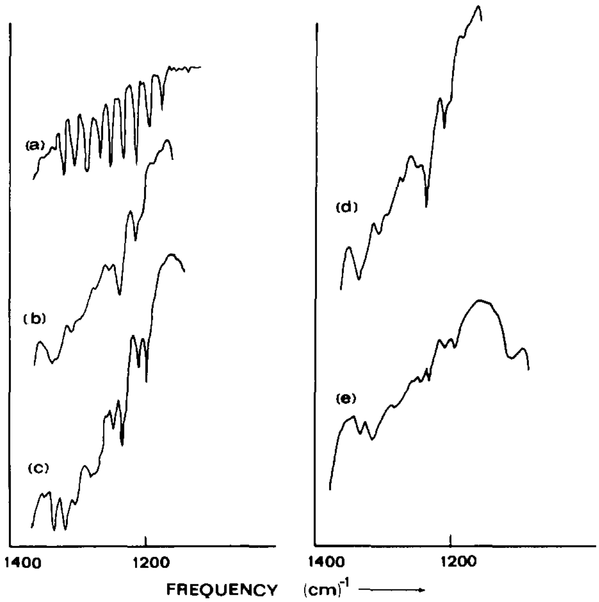

Fig. 2. IR spectra in the CH_2 rocking region. (a) Pure lead(II) octadecanoate; (b) pure racemic $Pb(OH)_2A_2$; (c) pure meso $Pb(OH)_2A_2$; (d) premelted racemic $Pb(OH)_2A_2$; (e) premelted meso $Pb(OH)_2A_2$.

for the former soaps than that for the latter (397–399) [15]. The higher melting points for the dihydroxy soaps are likely to be due to the presence of hydrogen bonding. The IR spectra confirm the existence of extensive hydrogen bonding in these soaps, as broad peaks were observed at 3500–3200 cm^{-1}. The low enthalpy of solid → liquid transitions for both the racemic and meso $Pb(OH)_2A_2$ would suggest that the hydrocarbon chains of the soaps are either more disordered in the solid phase or are more ordered in the liquid phase than that of lead(II) octadecanoates. To qualitatively test the degree of order of the carbon chain in the solid phase of the dihydroxy soaps and lead octadecanoate, IR spectra were recorded as KBr discs between 1400 and 1100 cm^{-1}, Fig. 2. It has been reported that in this region a series of bands occur as a result of the rocking of the CH_2 groups in the crystal lattice [17,18]. These bands broaden on heating as the chains are free to twist [19]. Figure 2 shows that on a relative basis broadening of the hydrocarbon chains of the dihydroxy soaps occurs (spectra (b), (c), (d), (e)) at room temperature, suggesting that the solid phase is more disordered in them than in lead(II) octadecanoate, spectrum (a). Thus the dihydroxy groups must be playing a role similar to the double bonds, in the middle of the anion, in which they impose some degree of rigidity on the soap molecules thereby preventing close packing in the solid phase [20].

A striking feature of the quantitative result is the approximately constant value of the enthalpy for the conversion of solid → liquid or vice versa

(Table 1) on heating, cooling and reheating the racemic $Pb(OH)_2A_2$ even when the number of phases differs. This would suggest some subtle rearrangement of the crystal structure on heating. The same trend holds for the meso product except that the cooling process produced extremely low total enthalpy change ($\simeq -18$ kJ mol^{-1}). The total enthalpy change for solid II → liquid of this soap (41.3 kJ mol^{-1}, Table 2) on heating is very close to the heat change (43.2 kJ mol^{-1}) for mesophase → liquid on reheating. It thus appears that solid II phase is relatively unstable. This view is reinforced by the closeness of the solid I → solid II transition temperature (350 K) and solid II → mesophase temperature (358 K). The behaviour may partly explain the absence of solid II phase on reheating the sample.

The temperature at which a mesophase appears in racemic $Pb(OH)_2A_2$ (405 K) is much higher than that of the meso isomer (358 K). On the other hand, the mesophase in the meso $Pb(OH)_2A_2$ is stable over a wider temperature range than that of its racemic counterpart. These behaviours coupled with the difference in the total entropies (solid → liquid) of the isomers indicate the effect of stereochemical configuration on phase transitions. The observation of the effect of stereochemical configuration on melting temperatures has been discussed in an earlier report [14]. It is even tempting, from the result of the optical examination to tentatively assign the mesophase of the racemic $Pb(OH)_2A_2$ as a smectic B phase and that of the meso $Pb(OH)_2A_2$ as a smectic A phase. While evidence from the optical microscopy study is not sufficient for complete identification of phases, the difference in the texture of the mesophases of the racemic and meso isomers, which is obvious from this technique, further strengthens the idea that the stereochemistry of the soaps plays a significant role in their thermal behaviours.

The complete explanation for the difference in the sequence of phase changes on heating and reheating a sample of the soap is not immediately clear. The results of both the IR and Raman spectra were not very effective in providing a clear picture of the behaviour. The X-ray diffraction spectral analysis indicates that the degree of crystallinity is higher in the premelted solid sample than the original crystal, as sharper peaks were observed for the former. On melting, the soap molecules probably exist as small micellar aggregates, similar to the aggregates of the molten, straight chain metal carboxylates [9,21], and because of greater flexibility in the molten than the solid state, the hydrogen bond in the molten phase could adopt a different configuration from that in the solid state. If the soap resolidified in this new orientation, then some subtle structural rearrangement may occur and this may account for the difference in the thermal behaviour of the initial and premelted crystals. It is noteworthy that the premelted solid reverts to the original crystals on recrystallisation in propan-1-ol, indicating that the structural adjustment probably is of a physical nature.

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