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Thermotropic polymorphism in liquid-crystalline lead(II) alkanoates

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Lead(II) carboxylates with even chain lengths from octanoate to octadecanoate have been investigated by differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction, and dilatometry, together with Raman, infrared, and ^{207}Pb N.M.R. spectroscopy. The reassignment of the high temperature mesophase as smectic A (L_α) for the octanoate to dodecanoate is confirmed. This phase is most stable for the decanoate. The intermediate temperature mesophase is a highly ordered three dimensional lamellar structure based on ionic layers. The alkyl chains in this phase are partially disordered (melted) through the introduction of gauche conformations and show decreased lateral interactions; however, they remain largely in an extended conformation due to the constraints imposed by the ionic network. Melting of the alkyl chains occurs therefore in more than one step. Re-cooling to the crystalline phase appears to result in a different polymorphic crystalline form (albeit still lamellar) from the original.

1. Introduction

In an earlier publication, new experimental data on lead(II) decanoate led to a reassignment of the thermotropic mesophases involved [1], compared to that proposed by Adeosun and Sime [2]. The reassignment was based on optical and X-ray diffraction studies, complemented by differential scanning calorimetry, as well as Raman and ^{207}Pb N.M.R. spectroscopy. It was observed that heating from the room temperature crystalline phase results in the formation of a highly ordered phase which appears crystalline in nature from X-ray studies, but which includes partial chain disordering based on the spectroscopic studies. Further heating results in the formation of a smectic A (L_α) mesophase characterized spectroscopically by considerable chain disorder and decreased lead-carboxylate interactions.

To clarify further the thermotropic behaviour of lead(II) alkanoates, and in particular to probe better the nature of the highly ordered intermediate phase, these studies were extended to the series of even chain length lead(II) carboxylates from octanoate to octadecanoate. An apparent difference in the room temperature crystalline phase between recrystallized and premelted samples was also investigated by spectroscopic studies. For the reader's convenience, we note that the crystalline phase is referred to as K, the intermediate phase as KM (to reflect the uncertainty in assigning this as a crystalline phase or a mesophase), and the smectic A phase as M, with I indicating the isotropic or liquid phase. The lead(II) carboxylates will frequently be referred to as C_8, C_{10}, etc., where the numeral refers to the number of carbon atoms in the alkanoate chain (including the carboxylate group). Each soap molecule contains two chains.

2. Experimental

The lead(II) carboxylates were prepared as described in [2], and purified by several recrystallizations from benzene. The degree of purity, as determined by elemental analysis, is given in the table for lead(II) decanoate (C_{10}) to hexadecanoate (C_{16}). Although some results in what follows are presented for lead(II) octanoate (C_8) and octadecanoate (C_{18}), they must be considered marginal since the elemental analyses of these products were not very satisfactory.

Elemental analyses of the lead(II) carboxylates.

	C (per cent)		H (per cent)		Pb (per cent)	
Sample	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
C_{10}	43·7	43·77	6·97	7·02	37·69	37·75
C_{12}	47·58	47·02	7·65	7·63	34·20	34·37
C_{14}	50·81	50·60	8·22	8·23	31·30	31·18
C_{16}	53·53	53·59	8·70	8·84	28·86	28·62

Polarizing optical microscopy, differential scanning calorimetry (D.S.C.), X-ray diffraction, and Raman spectroscopy were performed on all samples as described in [1]. In addition, Raman spectra of recrystallized and premelted C_{10} were determined in 1 mm melting point capillaries on a Spex 1403 double spectrometer using the 514·5 nm line of an argon-ion laser (Spectra-Physics model 164-05). ^{207}Pb N.M.R. spectra were recorded with a Varian XL 200 spectrometer at 41·827 MHz; they were obtained at various temperatures on deoxygenated samples in 10 mm diameter tubes. Infrared spectra were obtained with KBr discs on a Perkin-Elmer model 683 spectrometer. Dilatometry of C_{10} was also performed; the method is described in [3].

3. Results

3.1. *D.S.C. and optical studies*

The transition temperatures determined by D.S.C. (see figure 1) are in satisfactory agreement with literature values [2, 4]; differences that exist can probably be attributed to differences in sample purity. The shorter chain length carboxylates up to C_{12} show three ordered phases, identified in order of decreasing temperature as a smectic A (or a lamellar L_α) phase, a highly ordered phase (either crystalline or a highly ordered smectic), and a true crystalline phase at room temperature [1]. The high temperature smectic A phase is confirmed by the focal conic and homeotropic textures observed

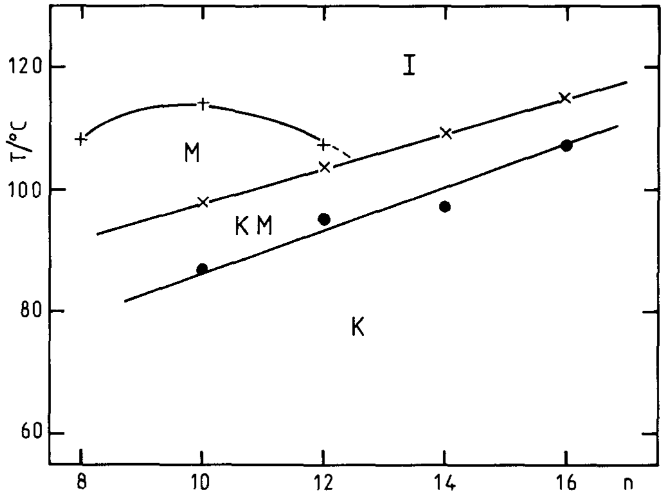

Figure 1. Transition temperatures of the lead(II) carboxylates as determined by differential scanning calorimetry.

by polarizing optical microscopy for each carboxylate C_8 to C_{12} (see also [1]). The homeotropic texture argues against this phase being smectic C, as assigned by Ellis [4] who claims that it shows a weak biaxiality. The C_{14} to C_{18} carboxylates form the highly ordered phase directly from the isotropic phase.

It is noteworthy that the transition temperatures of both the crystalline (K) to intermediate (KM) phases and the KM to smectic A (M) or isotropic (I) phases increase more or less linearly in temperature with increasing chain length for the carboxylates studied. In contrast, the M ↔ I transition shows a maximum for C_{10}, a chain length which presumably gives the smectic A phase its greatest stability. This stability can be related to the amphiphilic character of the molecules, one of the factors that determine smectic ordering in liquid crystals [5]. That is, a chain length of about ten carbon atoms apparently leads to the greatest incompatibility between the ionic head group and the non-polar hydrocarbon chains in lead(II) alkanoates, and hence the greatest smectic stability.

As is expected of disordered liquid-crystalline phases, the I ↔ M transition shows little or no supercooling. The KM → K transition shows about 10–15°C supercooling, consistent with the crystalline character of K. The relatively small supercooling of *c.* 3°C for the I/M ↔ KM transition indicates that the KM phase is not a classic crystalline phase. On the other hand, liquid crystal phases normally are not associated with significant supercooling. Possibly, a kinetic effect is induced by strong ionic interactions. Under normal light, the KM phase is translucent when pressed between glass microscope slides, and can be shared albeit with difficulty; these facts additionally argue against this phase being truly crystalline.

The enthalpy changes associated with the various transitions as a function of chain length are plotted in figure 2. Both the K → KM and KM → M/I transitions show a linear increase in enthalpy change with increasing chain length in the range studied; this indicates that these transitions involve disordering or melting of the aliphatic chains. Compared to a value of 270 J/g(CH_2) associated with complete melting of aliphatic chains from their fully crystalline state [6], the slopes of the K → KM and KM → M/I lines yield values of 135 and 180 J/g(CH_2), respectively. This can be

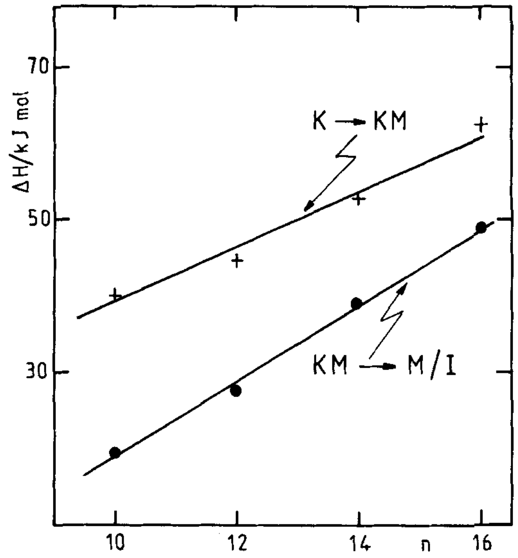

Figure 2. Enthalpies of transition of the lead(II) carboxylates as a function of the length of the aliphatic chain.

explained by supposing that partial melting occurs at the low temperature transition, and the remainder in the KM → M/I transition. As shown in the following subsections, this hypothesis is supported by spectroscopic studies (see also [1]). Extrapolation of the lines to zero methylene groups ($n = 2$) shows a small positive enthalpy change (8·4 J/g) for the K → KM transition and a larger negative one (−21 J/g) for the second transition. The implication is that there are minimal net enthalpic changes associated with the ionic interactions in the first transition, whereas there is a net improvement in these interactions in the second transition. (It should be noted that a transition from a crystalline to a rotator phase is excluded, since such a transition is associated with a considerably smaller variation in enthalpy change per carbon than that observed [7].)

It is worth mentioning that the M ↔ I transition (not represented in figure 2) is associated with a much lower enthalpy change (of the order of 1·5 J/g) than the other two transitions, consistent with the disordered smectic state of M.

3.2. *Raman spectral studies*

Temperature dependent changes were observed in the Raman spectra of all lead(II) soaps, C_8 to C_{18}. The most prominent changes are in the C–C (1000–1200 cm^{-1}) and C–H (2800–3000 cm^{-1}) stretching regions. Typical spectra for the decanoate have been given previously [1].

Raman spectral changes in the 1000–1200 cm^{-1} region are attributed to chain disordering [8–11], and show up mainly as a decrease in intensity of the band at *c.* 1128 cm^{-1}, assigned to the in-phase C–C stretching mode of the fully extended chain [12], as gauche bonds are introduced. In the Lippert–Peticolas band intensity analysis [11], the ratio of intensities of the bands at 1070–1100 cm^{-1} and *c.* 1128 cm^{-1} is taken as a measure of the change in concentration of gauche bonds. This ratio for the lead(II) soaps is shown as a function of temperature in figure 3. For C_8 and C_{10}, the biggest changes in intensity ratio occur at temperatures corresponding to the KM → M

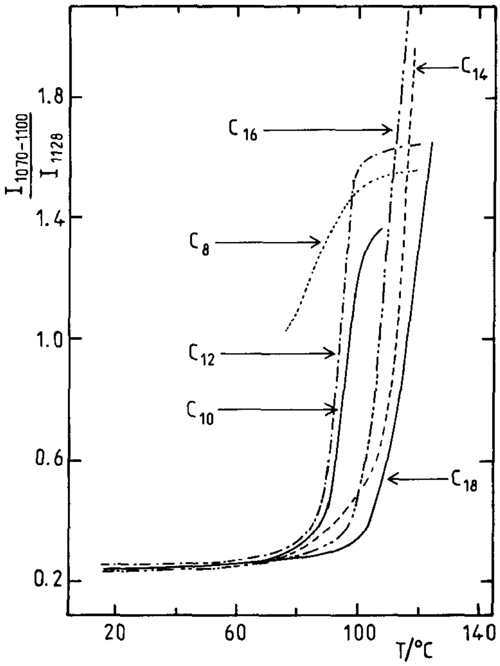

Figure 3. The Raman intensity of the band 1070–1100 cm^{-1} frequency region relative to the intensity of the band at 1128 cm^{-1} as a function of temperature in lead(II) octanoate (C_8), decanoate (C_{10}), dodecanoate (C_{12}), tetradecanoate (C_{14}), hexadecanoate (C_{16}) and octadecanoate (C_{18}).

transition, and indicate formation of 70–80 per cent of the total gauche bonds possible at these temperatures. For C_{14} to C_{18}, the main intensity changes occur for the KM → I transition. However, in all cases, there is evidence of some conformational disordering in the K → KM transition, with the gauche population increasing from *c.* 20 per cent of the maximum possible in C_8 to *c.* 50 per cent in C_{18}. This is consistent with the indications from the previous analysis of the enthalpic changes that there is partial melting of the aliphatic chains on heating to the KM phase. The rest of the melting occurs on entering the smectic A phase. As pointed out in [1], if there are no restrictions on the formation of gauche–gauche sequences, a maximum of about 34 per cent of the conformationally active bonds may adopt gauche conformations at 373 K. Combination of this with the Raman spectral results suggests average populations of the smectic A phase of C_8 and C_{10} of 1·7–1·9 gauche bonds per chain. In the KM phase of C_{18} there may be up to 2·6 gauche bonds per chain.

In the C–H stretch region (2800–3000 cm^{-1}), the most commonly used bands in conformational analysis are those at 2850 and 2880 cm^{-1} [8, 13, 14], which were assigned to the symmetric and antisymmetric stretching vibrations of the methylene groups [15]. The intensity ratio of these bands depends on both chain packing and conformational disorder [8]. The ratios of intensities are these bands for the lead(II) carboxylates are shown in figure 4. Although these intensity ratios show a similar sigmoidal temperature dependence to that observed in the C–C stretch region, the greatest intensity change in all cases in figure 4 corresponds to the lowest temperature transition. Thus, this K → KM transition appears to correspond to a loosening of the chain packing, with only limited conformational disordering in the hydrocarbons chains.

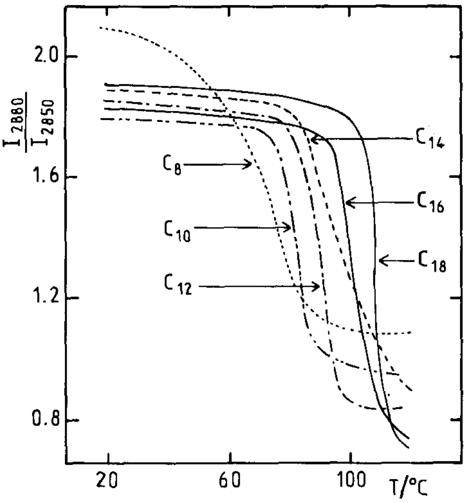

Figure 4. The Raman intensity of the 2880 cm^{-1} band relative to the intensity of that at 2850 cm^{-1} as a function of temperature in lead(II) octanoate (C_8), decanoate (C_{10}), dodecanoate (C_{12}), tetradecanoate (C_{14}), hexadecanoate (C_{16}) and octadecanoate (C_{18}).

3.3. *^{207}Pb N.M.R. spectra*

Natural abundance ^{207}Pb N.M.R. spectra were run of the lead(II) carboxylates, C_8 to C_{18} as a function of temperature. In all cases, a single signal with a near lorentzian lineshape was observed in the isotropic phase; its chemical shift is virtually independent of the length of the alkyl chain, but increases markedly with increasing temperature. Typical spectra of C_{10} have been shown in [1]. On cooling, changes in both chemical shift and linewidth occur at temperatures corresponding to the phase transitions.

For the C_8, C_{10} and C_{12}, the high temperature mesophase M gives isotropic signals of comparable linewidth to the liquid, whilst the KM mesophase gives only rather broad (*c*. 500 p.p.m.) signals. Such changes are consistent with results of a.c. impedance measurements [16], where relatively small conductance changes are observed between the liquid phase I and the mesophase M, whereas large changes are observed at temperatures corresponding to the M → KM transition. (n.b. in [16], as well as in [2], the mesophases KM and M are assigned G and V_2 structures, respectively, but since reassigned as noted in the Introduction.)

Measurements of C_{14}, C_{16} and C_{18} were hindered by supercooling. However, in all cases the isotropic signal of the liquid phase was lost on transition to the mesophase. Under the experimental conditions used, it was not possible to resolve the expected broad ^{207}Pb signal in this phase, possibly as a result of the decrease in relative metal content on increasing the chain length of the soap, and of instrumental problems associated with the long dead-time of the spectrometer. More detailed ^{207}Pb N.M.R. results on the various phases of these systems are reported elsewhere [17].

3.4. *X-ray diffraction*

From the X-ray diffraction results on all the carboxylates studied (C_8 to C_{16}), both the K and KM phases are crystal-like, showing numerous reflections at wide angles. The low angle reflection is complemented by many higher order reflections indicating that the crystal structure is of a lamellar nature (see [1]). The Bragg spacing of the KM phase is a little smaller than that of the K phase for all the carboxylates. An additional set of reflections is visible at intermediate angles upon formation of the KM phase that is not present for the K phase.

In the M phase, the low angle reflection, accompanied by second- and third-order reflections that indicate a lamellar structure, corroborates the smectic A assignment. Furthermore, there appears to be no variation in the spacing with temperature. A diffuse band corresponding to the spacing between disordered aliphatic chains expected at *c*. 4·5 Å is absent, probably because the lead ions are both strong absorbers and strong scatterers so that the X-ray patterns observed reflect mainly, if not exclusively, the ordering of these ions. The isotropic phase shows a strong, somewhat diffuse band which varies with chain length at low angles for all carboxylates.

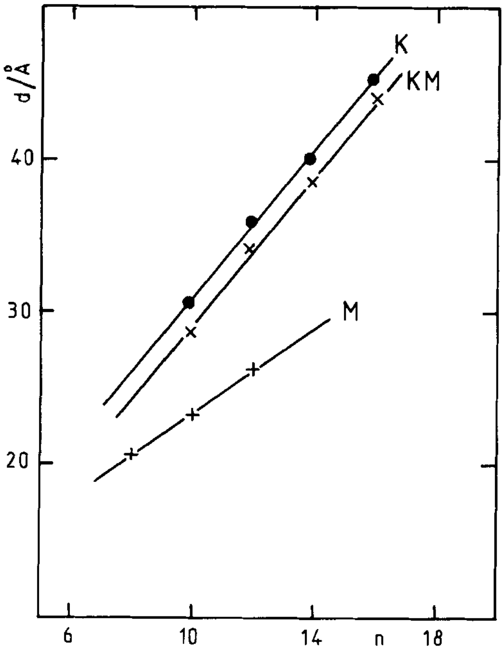

Figure 5. Lamellar spacings in the K, KM and M phases as a function of the length of the aliphatic chain at 25, 95 and 105°C respectively.

The lamellar spacings are plotted as a function of chain length, *n*, in figure 5. In all cases, there is a linear increase of *d* with *n*, in the range of *n* examined. The rate of increase for both the K and KM phases is 1·25 Å/CH_2. This value corresponds to that expected from crystalline aliphatic chains in their most extended configuration. This indicates that the aliphatic chains are in their fully extended conformation in both phases, which would seem to contradict the introduction of partial disorder of the aliphatic chains in the KM phase. However, as will be shown in the following Discussion, it is possible to resolve this apparent contradiction. The variation of *d* with *n* in the M phase is 0·7 Å/CH_2. Although no lamellar spacing can be assigned to the I phase, the centre of the diffuse band (reflecting groups of associated molecules and hence a molecular length) is seen to vary with *n* similarly to *d* in the M phase.

3.5. *Dilatometry and molecular areas*

Dilatometric experiments were performed on the C_{10} carboxylate only. The results are shown in figure 6, as a plot of the molar volume V as a function of temperature T. First, it is clear that the transition temperatures, as well as the observations regarding supercooling, corroborate the D.S.C. results. Secondly, the coefficients of expansion for each phase are noteworthy. The value of $3{\cdot}5 \times 10^{-4}\,K^{-1}$ for the K phase is typical of a crystalline phase and $8.0 \times 10^{-4}\,K^{-1}$ for the M phase is consistent with a disordered smectic phase [6], whereas $4{\cdot}7 \times 10^{-4}\,K^{-1}$ for the KM phase is an intermediate value.

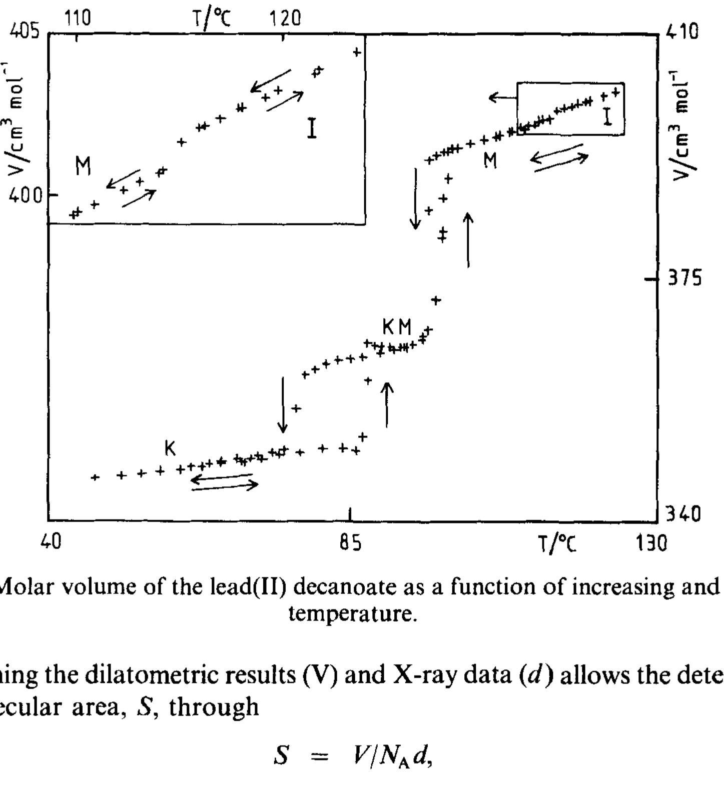

Figure 6. Molar volume of the lead(II) decanoate as a function of increasing and decreasing temperature.

Combining the dilatometric results (V) and X-ray data (d) allows the determination of the molecular area, S, through

$$S = V/N_A d,$$

where N_A is the Avogadro constant. The value of 19 Å^2 found for the molecular area in the K phase is typical of a crystalline structure where the molecules are orthogonal to the lamellar planes. The high value of 29 Å^2 for the M phase is consistent with a disordered smectic phase where S is normally greater than 22–23 Å^2. This value also agrees very well with the value of 30 ± 2 Å^2 previously estimated from calcium and rubidium soaps in [1]. Once again, the KM phase shows an intermediate value, 21·5 Å^2, supporting the deduction that the aliphatic chains are incompletely melted.

4. Discussion concerning the KM and smectic A phases

The apparent crystalline structure of the KM phase observed by X-ray diffraction can be attributed to the three dimensional order at the level of the ionic head groups in this phase. On the other hand, as indicated by both Raman studies and the results of enthalpic analysis, there is partial disorder of the aliphatic chains in the form of gauche bonds. It is likely that these gauche bonds predominate near the chain ends opposite the ionic heads; for, the molecular area available to the chains near the ionic head groups is strictly limited on account of the lateral spacing imposed by the ionic interactions. That there are more gauche bonds in C_{18} than in C_8 is consistent with this supposition.

It should be pointed out that partial disorder in the KM phase is consisted with the facts that the lamellar spacing is slightly decreased and that the molecular area is slightly increased in this phase compared to the K phase. Furthermore, the existence of disorder is not in contradiction with the result that the chains appear to be fully extended in this phase. For, the change in d with n ($\delta d/\delta n$) is actually a change in the molar volume, since

$$\delta d/\delta n = (\delta V/\delta n)/S,$$

where S may be considered constant with n. That $\delta d/\delta n$ equals 1·25 Å/CH_2 in both the K and KM phases is possible, since $\delta V/\delta n$ and S both have slightly larger values in the KM phase compared to the K phase.

It is also pertinent to discuss the possibility of chain tilting in the KM and M phases, as postulated by Ellis [4]. In fact, since the ionic head group is rather short and thus cannot be considered to be tilted significantly, any tilting must be the aliphatic chains. However, the concept of chain tilting is applicable only in the case of extended chains, not in the case of disordered chains. For the M phase, even if the first carbons nearest the ionic head group are more extended (i.e. have fewer gauche bonds) and the possibility of their being tilted may then be considered in order to account for the reported weak birefringence (but not observed by us), it seems unwarranted to call this chain tilting. Certainly, determination of a tilt angle based on the d spacing and a calculated molecular length that supposes a fully extended chain is completely unwarranted.

As for the KM phase, the relatively large tilt angle (77°) calculated by Ellis is not consistent with the S value determined from our X-ray and dilatometric. The tilt angle determined, again based on a fully extended chain, would require an S value of 47 Å^2, more than twice as large as the experimental value. Moreover, a tilted chain could show a change in d spacing per methylene group that is less than the experimentally determined value of 1·25 Å/CH_2.

5. Polymorphism in the crystalline phase

From a close inspection of the transitions with a polarizing optical microscope, it appears that the first heating (recrystallized samples) behaves differently from subsequent heatings (premelted samples) for the C_{10}, C_{12} and C_{14} carboxylates: that is, the K → KM transition is not detected on first heating whereas it is subsequently. For the C_{16} and C_{18} carboxylates, this transition is apparent directly on the first heating. Significantly, the same transition as detected by D.S.C. is somewhat lower in temperature (*c.* 2°C for C_{10}) and higher in enthalpy change (*c.* 8 J/g for C_{10}) for the first heating compared to the second heating; the peak itself is also less sharp on first heating. This may indicate that the crystalline phase obtained after one heating is in a metastable state. The vibrational spectra of these systems may help clarify these observations. Cursory X-ray diffraction patterns do not show major differences; however, the long exposure times required and the lack of resolution of the numerous diffraction peaks preclude a detailed analysis of the crystalline phase by this method.

Infrared spectra of recrystallized and premelted samples of lead(II) decanoate in KBr discs are shown in figure 7. The spectrum of the recrystallized sample is identical

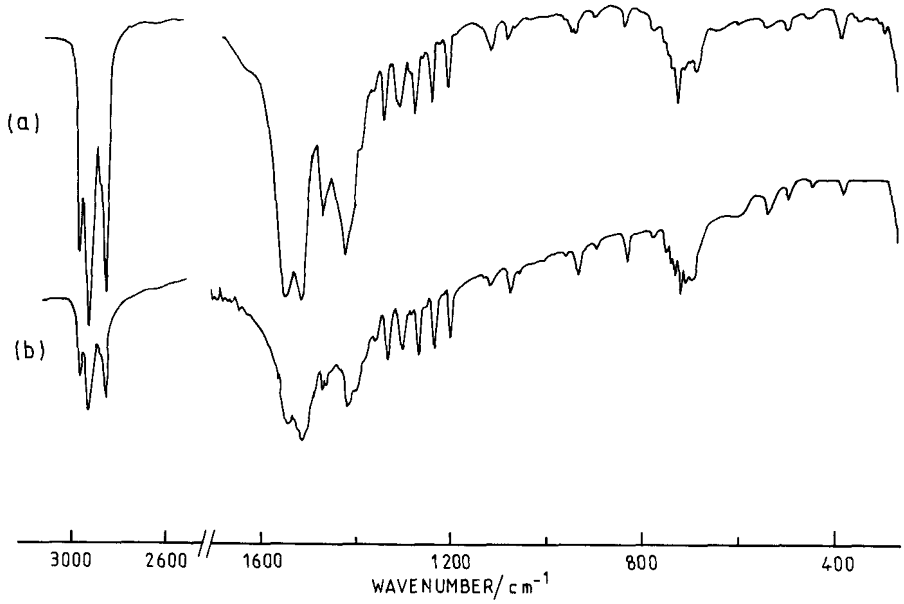

Figure 7. Infrared spectra of lead(II) decanoate: (*a*) recrystallized sample; (*b*) premelted sample.

to that previously reported for this compound [18, 19]. No significant differences are apparent between the spectra of recrystallized and premelted samples in the 2800–3000 cm^{-1} (C–H stretch [12]) the 1000–1350 cm^{-1} (predominantly CH_2 wagging modes [12, 18]) or the 300–600 cm^{-1} regions. However, there are marked changes in intensity of the progressions from 680–750 cm^{-1} and 1385–1550 cm^{-1}. In addition, a doublet at 930–940 cm^{-1} in the recrystallized sample is replaced by a single band at 930 cm^{-1}, and a single band at 1470 cm^{-1} has become a doublet in the premelted sample.

Modifications in similar spectral regions are observed in the Raman spectra (see figure 8). The band at 218 cm^{-1} in the recrystallized sample is replaced by two peaks at 230 and 246 cm^{-1}. There seems to be slight additional modifications in the 300–700 cm^{-1} region, although these are poorly resolved in the spectra obtained. The band at 924 cm^{-1} is replaced by one at 938 cm^{-1} in the premelted sample, and there are significant changes in the relative intensities of the 1044 and 1060 cm^{-1} bands as well as in the progression from 1364 to 1484 cm^{-1}. In the 2700–3000 cm^{-1} region, the only notable changes involve two small peaks at 2862 and 2956 cm^{-1} for the recrystallized sample, which are lost for the premelted sample.

Solid *n*-alkane derivatives normally exist as fully extended chains, with an all-trans configuration of the methylene groups [20]. A band at *c.* 1128 cm^{-1}, assigned to the in-phase C–C stretching mode of the fully extended chain, decreases in intensity as gauche bonds are introduced [8]. In our previous report [1], and in the studies of the conformational changes observed on heating, the ratio of the band at *c.* 1070 cm^{-1} to this band has been used as a measure of chain disordering. In the premelted sample, it was not possible to resolve the 1070 cm^{-1} band. However, the intensity ratios of the 1062 (CH_2 rock) to *c.* 1128 cm^{-1} bands are identical in the recrystallized and premelted samples, indicating that the observed effects do not result from any conformational differences.

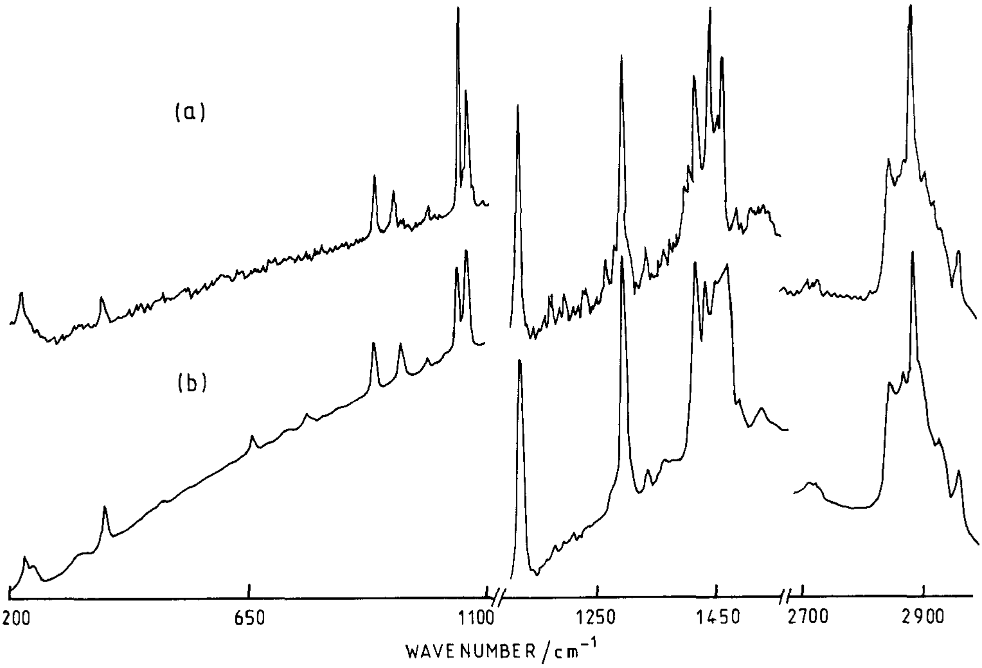

Figure 8. Raman spectra of solid lead(II) decanoate: (*a*) recrystallized sample; (*b*) premelted sample.

Changes in chain packing are, however, known to affect vibrational spectra significantly [21]. In the infrared spectra, the dominant vibrations in the 680–750 cm^{-1} regions are the CH_2 rocking modes, which are strongly dependent on the crystallographic structure [22, 23]. Similarly, strong intermolecular effects are observed with the CH_2 bending modes in the 1370–1480 cm^{-1} region [23]. In contrast, the C–H stretching and CH_2 wagging modes seem to be less sensitive to such changes.

The normal crystal systems of *n*-alkanes are orthorhombic, monoclinic and triclinic [7, 23], and occasionally hexagonal [7, 24]. In the hexagonal and triclinic structures, where the planes of hydrocarbon chains are parallel, only single bending and rocking modes are observed, whereas in orthorhombic and monoclinic structures these bands are split [22, 23]. The effect is most noticeable at low temperatures, but can be seen at room temperature in the 720 cm^{-1} band of the rocking progression [21, 22]. As noted previously [18], a large amount of splitting and overlapping is observed with the bands in the 700–1000 cm^{-1} region of the lead(II) soaps, such that detailed assignment is difficult. The 720 cm^{-1} band is suggested to be split into components at 720 and 730 cm^{-1}. Both components are observed in recrystallized samples. However, the intensity of the 730 cm^{-1} component is greatly enhanced in the latter case.

In the Raman spectra, the bands in the 200–380 cm^{-1} region are due to external modes, which would be expected to be strongly affected by changes in crystal structure. Although the presence of a broad band at 230 cm^{-1} has been suggested to imply the existence of random gauche conformers in the chains of alkane derivatives [25], and a transition is observed in this region in the premelted sample, we believe that this interpretation is not correct in view of the absence of changes in intensity in the somewhat more sensitive band at *c.* 1128 cm^{-1}. It may be noted that solid *n*-decane shows its main longitudinal acoustic mode at 231 cm^{-1} [26], and that reduction of the extended carbon chain length, such as would occur with the introduction of gauche bonds in the chain, would shift this band to higher energies [27].

Changes in intermolecular packing would be expected to modify the crystalline CH_2 twist (1044 cm^{-1}) and wag (1180–1270 cm^{-1}) bands, and the C–H bending progression (1360–1480 cm^{-1}) [25]. Differences in these regions are observed between the spectra of recrystallized and premelted samples. Considering the bending region, the major changes in the premelted sample are dramatic increases in intensity of the bands at 1404 and 1420 cm^{-1}, tentatively assigned to CH_2 symmetric and antisymmetric (adjacent to $-CO_2^-$) deformations [28], and a decrease in intensity in the band at 1438 cm^{-1}, which is probably due to the antisymmetric deformation of the methylene groups which are not adjacent to the carboxylate [28]. Such changes are consistent with differences in crystal structure between the two samples, and are in accord with the effects of chain packing observed on the symmetric and antisymmetric CH_2 bending modes of crystalline polyethylene, and related compounds [29].

Considering, finally, the changes in the 880–1000 cm^{-1} region, the main vibrations expected here are rocking modes [25], which are known to be strongly dependent on crystal structure [23]. The band at c. 886 cm^{-1}, tentatively assigned to the terminal CH_3 group, is unchanged; but the band at 924 cm^{-1} is virtually lost in the premelted sample, whilst the intensity of the band at 938 cm^{-1} increases dramatically. Detailed interpretation of these changes is not possible at the moment, but they are consistent with the general picture of the formation of different polymorphic structures of lead(II) decanoate that depend on whether the material has been recrystallized or cooled from the melt.

Such polymorphism at room temperature is not uncommon in systems such as *n*-alkanes [7], fatty acids [30], and glycerides [31]; and it also seems to occur in silver(I) soaps [18]. One possible cause of such polymorphism is the presence of impurities. Although the lead(II) decanoate was made from the purest grade acid commercially available (stated as 99 per cent), gave good elemental analysis, showed similar behaviour on further recrystallization, and, for premelted samples, gave both temperatures and enthalpies of phase transitions in reasonably good agreement with previous studies [2, 4], the presence of substoichiometric quantities of impurities cannot be ruled out. Impurity effects appear to be fairly common in *n*-alkanes [7], where small quantities of isomers, or hydrocarbons with slightly different chain lengths can significantly affect both phase transitions and structures. Whilst such impurities may change the overall phase behaviour, it is difficult to see how they could lead to effects like the considerable supercooling observed on the mesophase → solid transition. A second kind of impurity effect is observed with cadmium(II) arachidate [32], where trace amounts of water have been shown to facilitate chain disordering. However, in this case both exothermic and endothermic peaks would be expected in the D.S.C. trace [32], and the presence of free acid, from hydrolysis of the carboxylate, is expected to show up in the infrared spectrum. Neither effect was observed here.

A more likely factor causing polymorphism is a kinetic effect; that is, formation of the crystalline structure on cooling is faster than formation of the original structure. Such an effect has been observed with various fatty acids, including ultra pure oleic acid [33]. Support of this kinetic interpretation comes from the Raman spectrum of the solid sample taken two weeks after melting, which shows small, but detectable, differences from that of the premelted sample. The most notable of these are a small increase in intensity of the c. 1044 cm^{-1} band relative to the 1060 cm^{-1} band, intensity changes in the 1400–1490 cm^{-1} region, and the reappearance of the weak band at 2862 cm^{-1}. Although the spectrum did not completely revert to that of the recrystallized sample, the changes are certainly consistent with a very slow ($t_{1/2}$ of several weeks) reconversion process. It is also worthy of note that the signal-to-noise ratio on this spectrum is very much lower than the premelted sample, which again may be related to slow structural changes occurring within this phase.

A possible criticism of this explanation is that any metastable form so produced should have a lower transition temperature than the more stable form, whereas the transition temperature observed on reheating is, in fact, higher than on first heating. Results on the lowest temperature phase transitions of unbranched saturated fatty acids [34, 35] provide a possible solution to this dilemma. In these systems, a low temperature solid → solid transition is normally observed, which is irreversible for even chain length acids, but reversible for odd-numbered carbon chains [34]. The enthalpy for this transition is stearic acid (4·3 $\mathrm{kJ\,mol^{-1}}$), which has 18 carbon atoms, is remarkably close to the difference in enthalpy observed for the K → KM transition on first heating and on reheating of lead(II) decanoate (4·9 $\mathrm{kJ\,mol^{-1}}$ [1]), where there are 20 carbon atoms in the molecular unit. The broad transition observed on heating recrystallized lead(II) soaps may, then, actually be a double transition, with the initial part being only very slowly reversible on cooling. Speculation on the nature of such processes is probably premature, although the intermediacy of some kind of rotator phases [36, 37], or the presence of small concentrations of conformational defects [38], not detected in the Raman spectra, may be important.

6. Thermodynamics of the phase transitions

Allowing for differences in the lowest temperature phase transition between fresh and premelted samples [1], there is reasonable agreement between the results obtained independently at Strasbourg and Port Sunlight, and those of Adeosun and Sime [2] and Ellis [4] on the enthalpies and entropies of the phase transitions of the lead(II) carboxylates. It has been shown previously [1] that the experimental entropy for the K → KM phase transition in lead(II) decanoate is in good agreement with that predicted from a molecular dynamics simulation of chain disordering [39].

An alternative approach to the understanding of phase transitions is to separate the entropy and enthalpy changes into their most important contributions, introduce reasonable theoretical estimates for each of these, and then determine if the recombination of these terms adequately fits the observed experimental data. Such decompositions have been extensively used in both polymer and bilayer membrane systems, most notably by Nagle, and are critically reviewed in [40] and [41]. The analysis is restricted to the overall change from solid to isotropic liquid, and lead(II) decanoate in particular is considered. The enthalpy can be separated as

$$\Delta H(\text{solid} \rightarrow \text{liquid}) = \Delta U_{\text{conf}} + \Delta U_{\text{vdW}} + \Delta U_{\theta} + P(\Delta V),$$

where ΔU_{conf} and ΔU_{vdW} are the energy changes resulting from intramolecular conformational disordering and decrease in van der Waals forces respectively, and ΔU_{θ} incorporates all other energy terms (such as changes in electrostatic interactions). The $P(\Delta V)$ term can be considered to be negligible compared with the other contributions [40]. Raman spectral results on lead(II) decanoate suggest the formation of 1·9 gauche conformations per chain in the melting process [1]. Combining this result with an energy difference of 2·1 $\mathrm{kJ\,mol^{-1}}$ between trans and gauche conformers [41] gives $\Delta U_{\text{conf}} = 8{\cdot}0\,\text{kJ}\,\text{mol}^{-1}$. The change in van der Waals interactions can be estimated [41] using Salem's treatment [42] of the interaction between parallel hydrocarbon chains, and experimental data for the cohesive energy density in polyethylene. Ignoring repulsive terms, Nagle and Goldstein [41] estimated $\Delta U_{\text{vdW}} = 3{\cdot}0\,\text{kJ}\,(\text{mol}\,\text{CH}_2)^{-1}$ from Billmeyer's analysis of the enthalpy of sublimation of crystalline polyethylene [43]. From latent heat data, Bunn [44] obtained $\Delta U_{\text{vdW}} = 2{\cdot}8\,\text{kJ}\,(\text{mol}\,\text{CH}_2)^{-1}$. For simplicity, the average of these can be taken, given $\Delta U_{\text{vdW}} = 52{\cdot}2\,\text{kJ}\,\text{mol}^{-1}$ for the change in van der Waals interactions in the hydrocarbon part of lead(II) decanoate on melting. The sum of this and the conformational term is

$$\Delta U_{\text{conf}} + \Delta U_{\text{vdW}} = 60{\cdot}2\,\text{kJ}\,\text{mol}^{-1}.$$

This can be compared with the experimental total enthalpy change for lead(II) decanoate of $61{\cdot}8\,\text{kJ}\,\text{mol}^{-1}$ [1]. While the good agreement is possibly fortuitous, it certainly supports the idea that the dominant process in the fusion of lead(II) decanoate is hydrocarbon chain melting. Changes in electrostatic interactions are relatively unimportant, in agreement with the results of extrapolation of enthalpy data shown in figure 2. This is not surprising considering the much smaller dependence of these terms on changes in intermolecular distances compared with the van der Waals dispersive interactions [45]. Comparison of results of similar calculations for other chain lengths with experimental data (see figure 9) supports the importance of chain melting in the overall fusion process. The biggest deviation is observed for Adeosun and Sime's result [2] on lead(II) hexadecanoate. However, the total enthalpy data for this was calculated using their reported observation of a second smectic phase at 380·6 K, with $\Delta H = 40\,\text{kJ}\,\text{mol}^{-1}$, whereas visual inspection of the published D.T.A. curve [2] suggests that the actual enthalpy change is very much less.

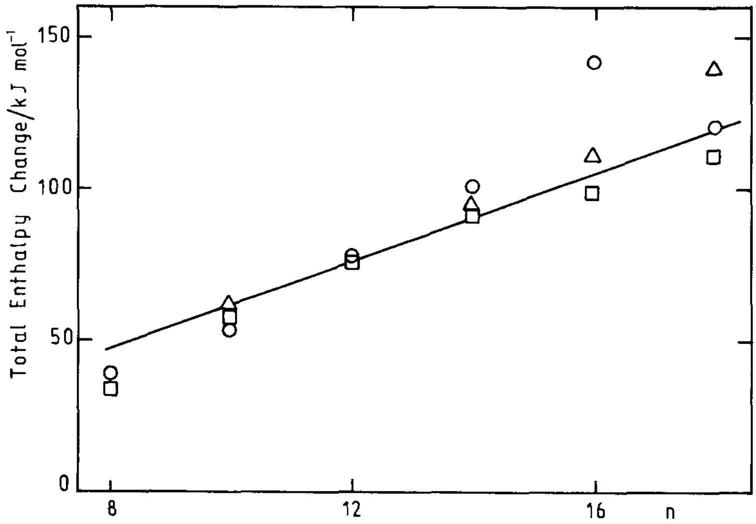

Figure 9. Total enthalpy change (solid → liquid) for even chain lead(II) carboxylates as a function of chain length: circles [2]; squares [4]; triangles ([1] and this work). The straight line is the theoretical slope for the changes of conformational and van der Waals energies on melting.

The statistical thermodynamic basis for the decomposition of entropy in these systems is more suspect than that of enthalpy, as the entropy changes for the processes occurring on chain fusion are essentially interdependent [41]. The same criticism does not apply to molecular dynamics calculations [39], where one is modelling the total change in conformation and packing of the chains. However, this can be circumvented by obtaining entropy changes from a free energy decomposition [41]. Using the terminology and values from [41]

$$\Delta S_c + \Delta S_x \approx 4{\cdot}06\,\mathrm{J\,K^{-1}\,(mol\,CH_2)^{-1}}$$

for the increase in entropy resulting from changes in conformation and excluded volume, and

$$\Delta S_v + \Delta S_0 \approx 5{\cdot}82\,\mathrm{J\,K^{-1}\,(mol\,CH_2)^{-1}}$$

for the effects of volume expansion and other processes, we obtain a total entropy change for melting a system with 18 methylene groups of 177·8 $\mathrm{J\,K^{-1}\,mol^{-1}}$. This compares well with the experimental total change (solid → liquid) of 171·2 $\mathrm{J\,K^{-1}\,mol^{-1}}$ in lead(II) decanoate [1].

7. Conclusions

The melting of the even chain length lead(II) carboxylates proceeds in more than one step. Heating from the initial lamellar crystalline phase results in a transition to another lamellar highly ordered phase which is characterized by partial disorder of the alkyl chains in the form of additional gauche conformations and decreased lateral interactions. The three dimensional order is imposed by a kind of framework of ionic layers formed by strong ionic interactions. The alkyl chains sandwiched between the ionic layers are constrained to remain largely extended. The three dimensional order of the ionic frame gives rise to a crystal-like X-ray diffraction pattern, where diffraction is caused principally by the lead ions. Further heating results in a transition directly to the isotropic phase for the longer chain length carboxylates. For C_8 to C_{12}, complete melting proceeds via a disordered smectic lamellar phase identified as smectic A (L_α), where the alkyl chains are completely disordered and where the remaining ionic interactions no longer impose a three dimensional order but still allow formation of a layer structure in two dimensions. This mesophase is apparently most stable for a chain length of ten carbon atoms. No evidence was found for chain tilting in any of the phases. Once the carboxylates are melted, D.S.C. data supported by infrared and Raman spectra analysis indicate that they do not return to the original crystalline form.

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