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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Amorim, A. M. , Costa, Da. , Burrows, H. D. , Geraldés, C. F. G. C. , Teixeira-dias, J. J. C. , Bazuin, C. G. , Guillon, D. , Skoulios, A. , Blackmore, E. , Tiddy, G. J. T. and Turner, D. L.(1986) 'Mesophase formation in lead(II) decanoate', *Liquid Crystals*, 1: 3, 215 – 226

**To link to this Article:** DOI: 10.1080/02678298608086510

**URL:** <http://dx.doi.org/10.1080/02678298608086510>

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## Mesophase formation in lead(II) decanoate

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(Received 11 December 1985; accepted 21 February 1986)

Structures of the thermotropic mesophases of lead(II) decanoate are reassigned following optical and X-ray diffraction studies. These results, and those of D.S.C., Raman and  $^{207}\text{Pb}$  N.M.R. spectroscopy, indicate formation of a lower temperature mesophase involving mainly increased lateral disorder, and a higher temperature  $L_s$  (smectic A) phase resulting from chain disordering and decreased lead-carboxylate interaction. Comparison of experimental thermodynamic data for the phase transitions with theoretical data in the literature indicates that the entropy change for the lower to higher mesophase transition is dominated by the increase in chain disorder.

### 1. Introduction

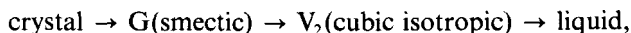
It has long been known [1, 2] that the long chain carboxylates of many divalent metal ions share with the alkali metal soaps the tendency to exhibit one or more liquid-crystalline phases between the solid and the isotropic liquid. Studies using X-ray diffraction [3–9], thermal analysis [2, 10–14] and optical observations using polarizing microscopes [10, 15] have helped in the elucidation of the structures of these thermotropic mesophases. Suggested structures include lamellae, disks, hexagons, and body-centred cubes [4–9, 16].

It is of interest to study both the macroscopic and the microscopic properties of such systems to obtain more detailed information on the mechanisms of the phase transitions. Investigation of the soaps of lead(II) is particularly attractive, as the shorter chain members exhibit two mesophases, whilst those with longer chains show only one. In addition, such systems are readily amenable to study by a variety of spectroscopic and other techniques. On the basis of optical studies, and in analogy with the behaviour of fused aqueous amphiphilic mesophases, Adeosun and Sime

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[10, 11] tentatively assigned the phase sequence



for the lead(II) carboxylates with chain lengths up to 12, whilst for the longer chain soaps the  $\text{V}_2$  phase was suggested to be absent. We have re-examined the phase behaviour for lead(II) decanoate, using optical and X-ray diffraction methods to identify the phases, and differential scanning calorimetry, Raman and  $^{207}\text{Pb}$  N.M.R. spectroscopy to obtain microscopic information on the processes occurring at the phase transitions. This chain length is of particular interest, as a number of detailed theoretical calculations have been made on disordering in decane systems [17–21].

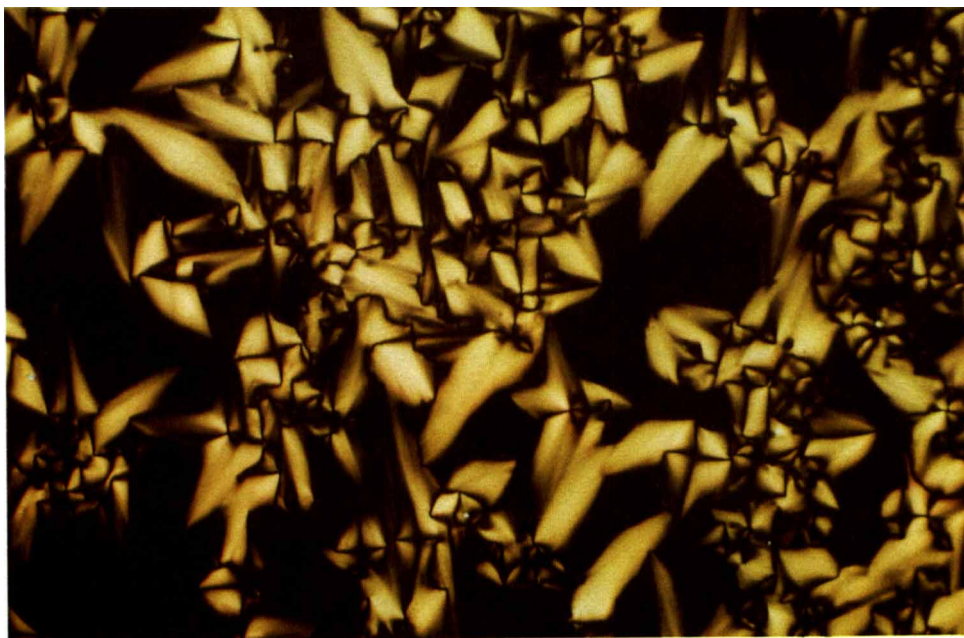
## 2. Experimental

Lead(II) decanoate was prepared as described [10], purified by repeated recrystallizations from benzene, and its purity checked by lead, carbon and hydrogen elemental analysis. (Found: C, 43.77; H, 7.02; Pb, 37.75 per cent; calculated for  $\text{PbC}_{20}\text{H}_{38}\text{O}_4$ : C, 43.70; H, 6.97; Pb, 37.75 per cent.)

Optical observations were made on a Leitz microscope fitted with a Mettler FP 52 hot stage (Strasbourg), and on a Zeiss microscope fitted with a Leitz hot stage (Port Sunlight). X-ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically using monochromatic copper  $K_\alpha$  radiations and a Guinier focusing camera equipped with a bent quartz monochromator. The set-up for variable temperature X-ray diffraction has been described in detail elsewhere [7]. Differential scanning calorimetry (D.S.C.) was performed at both Strasbourg and Port Sunlight using Perkin–Elmer DSC-2 calorimeters. Thermograms of samples in sealed aluminium pans were recorded over the temperature range 300–420 K in a nitrogen atmosphere at a scanning rate of  $2.5 \text{ K min}^{-1}$ . The values of the transition enthalpy were calibrated using a standard sample of indium ( $\Delta H = 28.4 \text{ J g}^{-1}$ ). Raman spectra were recorded of samples in 1 mm melting point capillaries on a Cary 82 Raman spectrometer with a Spectra-Physics argon–ion laser (model 164-05) whose output at 514.5 nm was adjusted to provide 200–250 mW at the sample. Scattered light was collected at  $90^\circ$  to the incoming laser light. Details of temperature measurements and evaluation of band intensities have been described elsewhere [22].  $^{207}\text{Pb}$  N.M.R. spectra were run on a Bruker CPX 200 spectrometer (Southampton) and a Varian XL 200 spectrometer (Coimbra), both operating at 41.857 MHz. Similar results were obtained with the two instruments, although rather better spectra were obtained at Southampton for the low temperature mesophase, probably as a result of the wider spectral window and higher intensity of the r.f. pulse used. N.M.R. spectra were obtained at various temperatures ( $\pm 1 \text{ K}$ ) of deoxygenated samples of pure soaps contained in 10 mm diameter tubes.

## 3. Results

On heating lead(II) decanoate a highly viscous mesophase I was observed to form at  $\approx 358 \text{ K}$ , to transform to a second mesophase II at  $\approx 369 \text{ K}$ , and finally to form a liquid phase at 386–387 K. Observations using an optical polarizing microscope showed that both mesophases were anisotropic. The higher temperature mesophase (cf. figure 1(a)) shows both the focal conic and the homeotropic textures that are characteristic of a lamellar  $L_\alpha$  (smectic A) phase. This disagrees with the previous assignment of a cubic isotropic  $\text{V}_2$  structure to this phase [10]. Figure 1(b) indicates



(a)



(b)

Figure 1. Mesophases II (a) and I (b) of lead(II) decanoate viewed with (a) microscope with crossed polars. The optical textures were observed for previously melted samples.

that the lower temperature mesophase is a highly ordered one. When first descending into this mesophase, the optical micrograph is very grainy. (N.b.  $L_x$  is identical to  $G$  in Winsor's nomenclature [16]. The correspondence between the different nomenclatures for amphiphile mesophases is discussed in [23], also given is the smectic nomenclature [24, 25] of the phase.)

Confirmation of a lamellar structure for mesophase II came from X-ray diffraction (cf. figure 2). A sharp reflection, along with second- and third-order reflections, all equally spaced, were observed at low Bragg angles. The spacing did not vary in the temperature range of this phase. A diffuse band at larger angles, that is typically observed for disordered alkyl chains and that corresponds to a Bragg spacing of  $4.5 \text{ \AA}$  was not apparent. However, this is not unexpected given the very high absorbance of X-rays by lead, together with the relatively weak diffraction of X-rays by alkyl chains compared to that of lead ions.

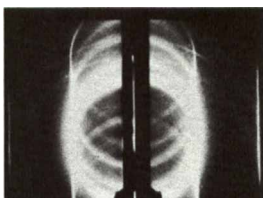


Figure 2. X-ray pattern of mesophase II of lead(II) decanoate.

It is possible to estimate the molecular area,  $S$ , of lead(II) in mesophase II at a particular temperature (e.g. 378 K) using density measurements as functions of alkyl chain length,  $n$ , for the related rubidium [5] and calcium [6] soaps at 583 K and 448 K, respectively. Molar volumes obtained from this data are linear functions of  $n$ , from which values for  $n = 10$  can be obtained easily. Assuming an average thermal expansion coefficient of  $0.8 \times 10^{-3} \text{ K}^{-1}$ , [26, 27], we estimate volumes of  $713 \text{ \AA}^3$  per two molecules for rubidium (a monoalkylated soap) and  $650 \text{ \AA}^3$  per molecule for calcium at 378 K. As the ionic radius of  $\text{Pb}^{2+}$  is roughly an average of that of  $\text{Ca}^{2+}$  and  $\text{Rb}^+$ , it is reasonable to fix the volume per molecule of lead(II) decanoate at this temperature at  $c. 680 \text{ \AA}^3$  per molecule. We note that the volume per molecule calculated at 387 K for the liquid phase of lead(II) decanoate from literature data [26] is  $665 \text{ \AA}^3$  per molecule. Since the Bragg spacing,  $d$ , of the low angle reflection is  $23.0 \text{ \AA}$ , the molecular area ( $S = V/d$ ) is estimated to be  $30 \pm 2 \text{ \AA}^2$ . This value is in perfect agreement with those usually found for disordered smectic liquid crystals [28], and lends further support to the idea that mesophase II of lead decanoate is of  $L_x$  type. During the preparation of this manuscript, we learnt that Ellis has also been studying the mesophases of long chain lead carboxylates [29], and concludes similarly that mesophase II has a lamellar structure.

The X-ray diffraction pattern of mesophase I suggests a highly ordered, crystal-like structure. The primary low angle reflection indicated a Bragg spacing of  $28.6 \text{ \AA}$ . There were at least ten higher-order reflections, indicating a lamellar layering. The X-ray pattern of the crystal phase showed a similar lamellar layering whose Bragg spacing is slightly larger ( $30.5 \text{ \AA}$ ). Ellis has shown [29] that this is consistent with the expected arrangement of all-trans carboxylate chains orthogonal to the planes containing the  $\text{Pb}^{2+}$  ions.

Enthalpies and transition temperatures† for phase transitions in lead(II) decanoate.

	Solid → mesophase I			Mesophase I → mesophase II			Mesophase II → liquid		
	Heating	Cooling	Reheating	Heating	Cooling	Reheating	Heating	Cooling	Reheating
$\Delta H/\text{kJ mol}^{-1}$	40.6	-34.4	35.7	20.1	-21.5	19.7	1.1	-1.3	1.1
$T/\text{K}$	357.1	347	359.5	369.5	367	368.5	386.7	388	387.4

† Transition temperatures were measured at the start of the phase transitions.

Both the ordered mesophase I and the crystal phase showed many reflections at higher angles, not all at the same positions. For the mesophase they were relatively weak; for the crystal phase some were intense. From a study in progress of the lead soaps,  $n = 8-18$ , it seems possible that the low-temperature mesophase is a highly-ordered smectic type, such as smectic E. Certainly from the X-ray data there are no indications of any significant hydrocarbon disordering in this phase.

Enthalpies and transition temperatures for the phase transitions in lead(II) decanoate were determined for heating, cooling, and reheating using D.S.C. (cf. table).  $\Delta H$  values for mesophase I  $\rightarrow$  II, and mesophase II  $\rightarrow$  liquid transitions, and for the reverse of these processes, are in good agreement with the results obtained by Adeosun and Sime using differential thermal analysis [10]. Slight differences in the transition temperatures between our study and theirs come from the different ways used to determine the phase transition. The largest difference, however, occurs for the solid  $\rightarrow$  mesophase I transition. On heating a fresh sample of lead(II) decanoate the enthalpy and transition temperature for this process were higher than reported earlier [10]. On cooling, considerable super-cooling was observed for this transition, accompanied by some loss (15–20 per cent) in the enthalpy change, whilst on reheating both the transition temperature and  $\Delta H$  were close to the values reported by Adeosun and Sime, who took their measurements on premelted samples [10]. These results were quite reproducible using D.S.C. at Strasbourg and Port Sunlight. In addition, on the first heating, the sample gave a broad peak for this transition whilst on reheating this peak was fairly sharp (figure 3). At present a convincing, thermodynamically acceptable explanation of these observations eludes us.

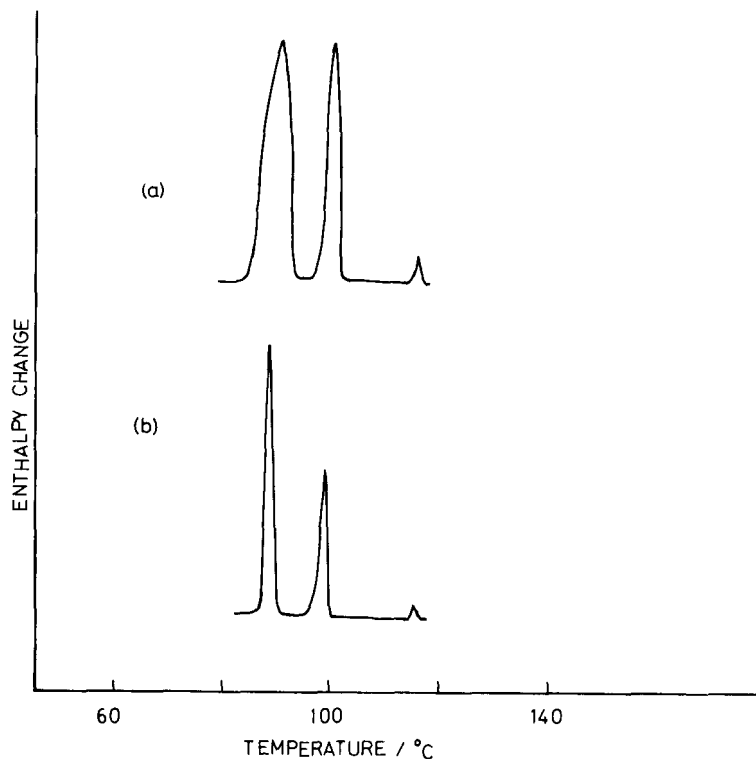


Figure 3. D.S.C. curves for lead(II) decanoate: (a) on initial heating; (b) on reheating the same sample.

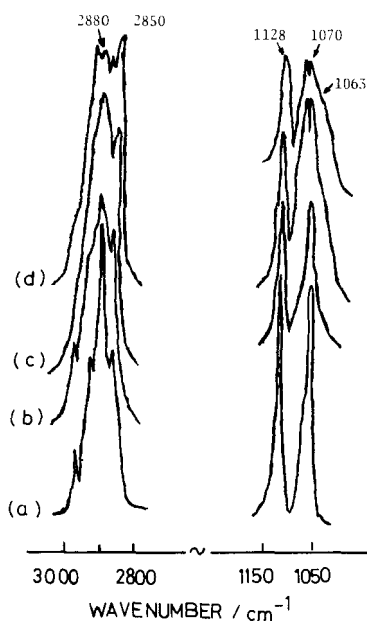


Figure 4. The 2800–3000  $\text{cm}^{-1}$  and 1000–1150  $\text{cm}^{-1}$  regions in the Raman spectra of lead(II) decanoate: (a) 295 K (solid); (b) 359 K (mesophase I); (c) 373 K (mesophase II); (d) 388 K (liquid).

Raman spectra were obtained for lead(II) decanoate at various temperatures up to 393 K. Figure 4 shows the spectra obtained for the C–C (1000–1200  $\text{cm}^{-1}$ ) and C–H (2800–3000  $\text{cm}^{-1}$ ) stretching regions for the solid, mesophases and liquid. Three main bands are observed in the 1000–1200  $\text{cm}^{-1}$  region: a band at about 1063  $\text{cm}^{-1}$  ascribed to methylene rocking, a band at  $\approx 1128 \text{ cm}^{-1}$  assigned to in-phase C–C stretching mode of the fully extended chain, and a band at about 1070  $\text{cm}^{-1}$ , which is a combination of skeletal stretching and methylene rocking [30]. The 1128  $\text{cm}^{-1}$  band is known to undergo a reduction in intensity as gauche bonds are introduced into the hydrocarbon chain, and various methods [31, 32] and intensity references [32–34] have been used to estimate their concentration. We have used the Lippert–Peticolas band intensity analysis [34], where the ratio of the intensities of the central band in this region and the band at  $\approx 1128 \text{ cm}^{-1}$  is taken as a measure of the change in concentration of gauche bonds (figure 5). A gradual disordering of the chain structure, following a sigmoidal curve, is observed on heating. Quantitatively, taking the C–C intensity ratio to be almost linearly related to the concentration of trans bonds which can form gauche conformations in the liquid phase [31],  $\approx 20$  per cent of the possible gauche conformations are formed on going from solid to mesophase I, whilst the mesophase I  $\rightarrow$  II transition leads to a further 60 per cent increase in this conformation. Of the seven possible gauche bonds in each chain, simple Boltzmann statistics, using an energy difference of 2.1  $\text{kJ mol}^{-1}$  between the gauche and trans states [20, 35] and placing no restrictions on the possibility of gauche–gauche sequences, indicate a maximum gauche population of  $\approx 34$  per cent at 373 K. Combination of this with the Raman results suggests an average of *c.* 1.9 gauche bonds per chain. This value is slightly higher than the figures obtained from molecular dynamics calculations [19], or from Gruen's single-chain model [20], but in those cases gauche–gauche sequences were suppressed. From models, molecular lengths of  $27(\pm 2) \text{ \AA}$  can be determined for



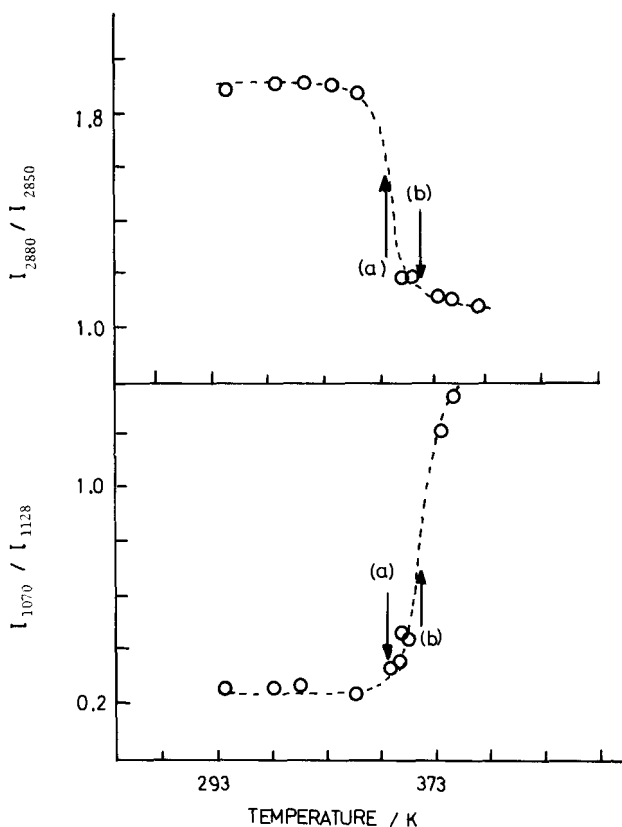


Figure 5. The 2880 versus 2850  $\text{cm}^{-1}$  and 1070 versus 1128  $\text{cm}^{-1}$  relative Raman band intensities as a function of temperature in lead(II) decanoate. Arrows at (a) and (b) correspond to the solid  $\rightarrow$  mesophase I and mesophase I  $\rightarrow$  II transitions as determined by D.S.C.

lead(II) decanoate having two gauche conformations per chain, and having the two chains on opposite sides of the lead atom, as has been suggested for Langmuir–Blodgett multilayers of lead(II) stearate [36]. This is somewhat larger than the  $d$  spacing for this phase obtained from X-ray diffraction (23.0 Å). However, as has been discussed previously [37],  $d$  spacings observed for smectic A phases are frequently about 10 per cent less than molecular lengths.

Temperature dependent intensity changes are also observed in the 2800–3000  $\text{cm}^{-1}$  frequency range. This is a complex and congested Raman spectral region, where the assignment of the different bands has been frequently revised and has not yet been uniformly adopted. However, the most commonly used bands here for conformational analysis are those at 2850 and 2880  $\text{cm}^{-1}$  [22, 30, 38], which are assigned to the symmetric ( $\nu_s$ ) and antisymmetric ( $\nu_{as}$ ) stretching vibrations, respectively, of the methylene groups [39]. The value of the peak height ratio,  $I_{\nu_{as}}/I_{\nu_s}$ , is found to depend on both the lateral packing of the extended chains and on the conformational disorder [31]. The change in the intensity ratio  $I_{2880}/I_{2850}$  as a function of temperature is also presented in figure 5. The sigmoidal curve shows a gradual disordering on heating, similar to that indicated by the variation of the  $I_{1070}/I_{1128}$  ratio. However, as the arrows indicate, the inflexion points of the two S-shaped curves do not correspond to the same phase transition. The inflexion point for the C–H stretching

intensity ratio curve corresponds to the solid  $\rightarrow$  mesophase I transition, the first step in the disordering process, whilst that for the C–C stretching intensity ratio curve occurs at the transition from mesophase I to mesophase II. These results suggest that mesophase I formation is accompanied by a substantial decrease in lateral order, but only a limited conformational change of the hydrocarbon chain.

It is expected that further information on these phase transitions may be obtained from metal–ion N.M.R. Natural abundance (21.11 per cent)  $^{207}\text{Pb}$  N.M.R. spectra were run of lead(II) decanoate for various temperatures between room temperature and 393 K. The chemical shift and lineshape of the  $^{207}\text{Pb}$  N.M.R. signal vary with temperature, with abrupt changes close to the phase transitions; typical spectra are shown in figure 6. In the isotropic melt a near lorentzian lineshape is observed, which indicates that dipolar interactions of the lead nuclei and chemical shift anisotropies are averaged out by isotropic motions of the cations. Mesophase II also gives an isotropic signal of comparable linewidth. In contrast, mesophase I gives a broad signal distributed over a very wide frequency range ( $\approx 20$  kHz). Close to the lower phase transition temperature the spectrum displays a hint of a powder pattern. With  $^{207}\text{Pb}$  ( $I = \frac{1}{2}$ ) such a powder pattern could, in principle, result either from residual dipolar interactions or from chemical shift anisotropy. However, whilst the spectra were not simulated, sample calculations using the van der Waals contact distance for  $\text{Pb}^{2+}$  ( $3.82 \text{ \AA}$  [40]) indicate maximum linewidths due to residual dipolar interactions which were about a tenth of those observed here. Therefore such a spectrum is likely to be the result of chemical shift anisotropy. Anisotropies of 53–56 p.p.m. have been observed for lead(II) nitrate in crystals and powders [41, 42], whilst values between 200 and 900 p.p.m. have been observed with lead(II) salts of lower crystallographic symmetry [41]. These values are to be compared with the observed width of  $\approx 480$  p.p.m. for the mesophase I signal.

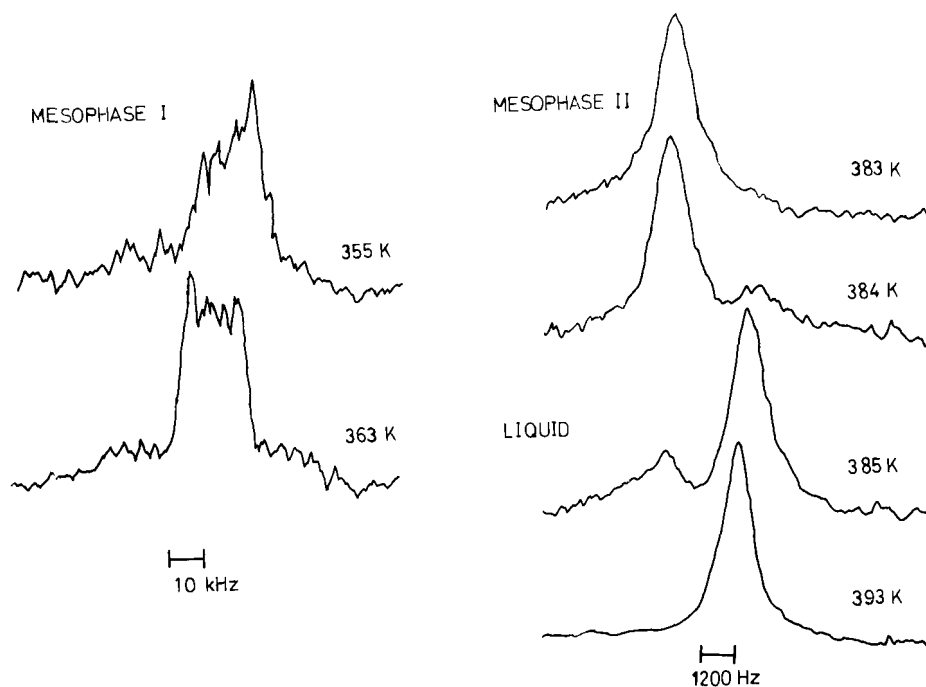


Figure 6.  $^{207}\text{Pb}$  N.M.R. signals for lead(II) decanoate at various temperatures.

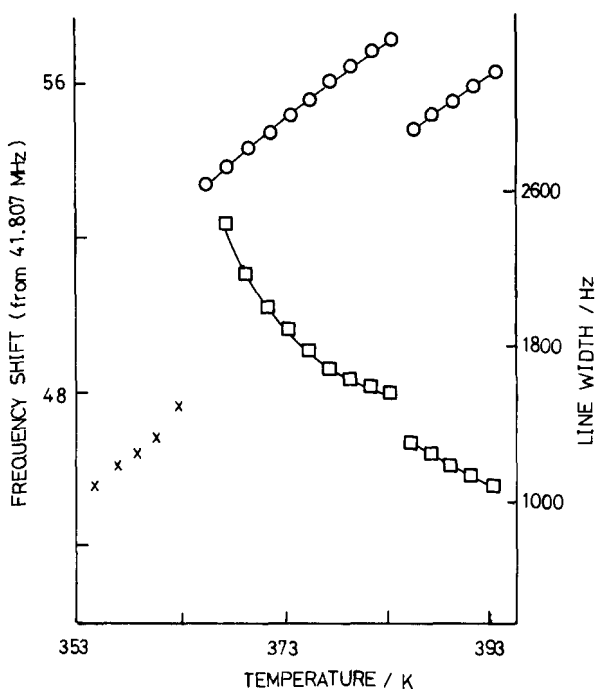


Figure 7. Line frequency (circles) and linewidth (squares) of  $^{207}\text{Pb}$  N.M.R. signals of lead(II) decanoate as a function of temperature. Crosses in the low temperature region correspond to the weighted average frequency of powder type spectra for mesophase I.

The chemical shifts of the various phases, and the linewidths of the isotropic signals were found to be temperature dependent (figure 7). The variation in the linewidths within mesophase II and liquid indicates that motion of the cation in these phases decreases with temperature, and is faster in the liquid phase. However, the small differences of dipolar linewidths throughout mesophase II as compared to the isotropic melt implies that cation diffusion is still very rapid in the mesophase [43]. Such results are in good agreement with the a.c. impedance studies of Adeosun and Sime [44], where activation energies for conductance in the two phases were found to be very similar. In mesophase I, the observed broad signal in the  $^{207}\text{Pb}$  N.M.R. spectrum implies a low mobility of the  $\text{Pb}^{2+}$  ion, which agrees with the much lower conductance observed with this phase [44]. Indeed, it is suggested [44] that some fraction of the charge carriers in this phase may contain carboxylates bound to the metal ion.

#### 4. Discussion

As previously reported [10], lead(II) decanoate is found to exhibit two thermotropic mesophases between the solid and isotropic liquid. However, both optical and X-ray results of the present study indicate that a reassignment of these phases is necessary, and suggest that the higher temperature one has a  $L_x$  (smectic A) structure, while the lower temperature one seems to have an ordered smectic structure. The overall enthalpy change on going from solid to isotropic liquid ( $\approx 58.8 \text{ kJ mol}^{-1}$ ), after allowing for the number of hydrocarbon chains, is comparable to that of decane, decanoic acid, [45] and the decanoates of zinc(II) [12] and copper(II) [14], but is

somewhat greater than that of sodium decanoate [46]. However, the overall entropy change ( $149.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is only about 80 per cent of that observed on fusion of two moles of decanoic acid [47], suggesting that a certain order remains in the liquid phase of the soap. Viscosity measurements [48] confirm that the liquid still has lead decanoate aggregates.

It is convenient to consider the energy of interaction of amphiphilic molecules in terms of three contributions: the internal energy due to the particular sequence of trans and gauche conformations, the dispersive interaction, and the lateral pressure resulting from steric repulsion [17]. Both Raman spectroscopy and preliminary X-ray diffraction on mesophase I indicate relatively little chain disorder, whilst  $^{207}\text{Pb}$  N.M.R. and a.c. impedance measurements [44] suggest little fusion of the polar region in this phase. The main energetic contribution to the solid  $\rightarrow$  mesophase I transition is then due to a decrease in the London-van der Waals interaction between the hydrocarbon chains. This is not unreasonable considering the strong dependence of this term on the interchain distance [49]. For the mesophase I  $\rightarrow$  II transition, Raman spectroscopy indicates increasing chain disorder, whilst both  $^{207}\text{Pb}$  N.M.R. and a.c. impedance measurements [44] indicate that the  $\text{Pb}^{2+}$  cation has a mobility approaching that of the liquid phase. It should be noted that even in the liquid the overall degree of dissociation of the lead carboxylate bond is small [26]. The energetic cost of forming gauche conformations can be estimated fairly accurately [17, 20, 32], and for forming two gauche conformations per chain in this transition would require *c.*  $10 \text{ kJ mol}^{-1}$ . The extra change associated with this transition results presumably from both decreased dispersive and steric interactions. The conformational entropy change associated with this transition can also be estimated. The value calculated from molecular dynamics simulation [18] for two decanoate chains, and for the increase in gauche population given by Raman spectra is  $54.6 \text{ J K}^{-1} \text{ mol}^{-1}$ , which compares remarkably well with the observed entropy change from the mesophase I  $\rightarrow$  II transition ( $54.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ).

The mesophase II  $\rightarrow$  liquid transition is accompanied by relatively small  $\Delta H$  and  $\Delta S$  values, suggesting relatively minor structural changes. This appears to contradict the proposed spherical micellar structure for the melt [10, 48], and the lamellar  $L_x$  (smectic A) structure for mesophase II. An alternative structure for the micelles in the melt compatible with the thermodynamic data could involve small discs, as has been suggested in the  $L_2$  phase formed by melting the  $L_x$  phase in monoglyceride-water mixtures [50].

We are grateful to Dr. H. A. Ellis for communicating his results on lead(II) carboxylates prior to publication. The group at Coimbra is grateful to J.N.I.C.T. and I.N.I.C. for financial support. One of us (C. F. G. C. G.) thanks the British Council for a travel bursary, which enabled him to carry out some of the experiments at Southampton.

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