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²⁰⁷Pb N.M.R. of lead(II) soaps in solid, liquid-crystalline and liquid phases

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²⁰⁷Pb N.M.R. data are reported for a number of even chain length lead(II) carboxylates (soaps) at various temperatures. At room temperature, the solid lead(II) decanoate and tetradecanoate show similar spectra, with a single metal ion site, and modest shielding anisotropy. As the temperature is increased, the soaps (hexanoate to octadecanoate) all form a highly ordered smectic phase, which gives a very broad ²⁰⁷Pb signal of linewidth comparable to that of the solid phase. At higher temperatures, the hexanoate to dodecanoate soaps form a lamellar L_α (smectic A) phase, whilst the longer chain length carboxylates melt directly to the liquid phase. Both the lamellar L_α and liquid phase give fairly sharp, isotropic signals, whose chemical shifts and linewidths are strongly temperature dependent. Possible explanations for this effect include paramagnetic contributions to the shielding tensor from low-lying electronic states of Pb(II), and contributions to the observed signal from different coordination species produced in the lead(II) carboxylate system. Although there are discrete changes in chemical shift at the phase transition, the magnitudes observed in all the phases are similar, suggesting that there are no dramatic changes in the metal coordination environment.

1. Introduction

The heavy metal soaps enjoy considerable industrial importance in lubricating greases, paint driers, polymer stabilizers, etc [1]. In addition, these long chain carboxylates of divalent metal cations share with the alkali metal carboxylates the tendency to form one or more mesophases between the solid and isotropic liquid [2]. We have been particularly interested in the phase behaviour of straight chain lead(II) carboxylates, where the soaps with twelve or less carbon atoms per chain show two mesophases, whilst longer chain members show only one [3-6]. The initial structural assignment [3] of G (lamellar) and V_2 (cubic isotropic) structures to the mesophases has been shown to be in error [4, 5], and we favour assignment to highly ordered smectic and lamellar L_α (smectic A), respectively [4, 6]. A somewhat different view has been presented by Ellis [5].

Metal ion N.M.R. spectroscopy is potentially a powerful technique for studying the behaviour of the polar region of these amphiphilic systems. For example, ²³Na spectroscopy of long chain sodium carboxylates [7, 8] has provided valuable information on the anisotropic motion of sodium and carboxylate ions in the mesophases, and unrestricted motion in the isotropic melt. ²⁰⁷Pb is an attractive nucleus for N.M.R. studies (21.11 per cent natural abundance, $I = \frac{1}{2}$, 9.13×10^{-3} times as

sensitive as ^1H for equal numbers of nuclei), and the chemical shifts of this species have been shown to be strongly dependent on the local environment [9–11]. In our preliminary report [4] we observed isotropic ^{207}Pb N.M.R. signals in the high temperature mesophase and liquid of lead(II) decanoate, whilst the low temperature mesophase was found to give a broad spectrum, whose linewidth (*c.* 480 p.p.m.) suggested substantial chemical shift anisotropy. Further, both the chemical shift and linewidth of the isotropic ^{207}Pb N.M.R. spectra were found to be temperature dependent. We have extended this study to the other even chain length lead(II) carboxylates from hexanoate to octadecanoate, and also report here the high resolution ^{207}Pb N.M.R. of solid lead(II) decanoate and tetradecanoate, systems which show rather different phase behaviour [3, 5, 6].

2. Experimental

The preparation, purification and characterization of the lead(II) carboxylates have been described elsewhere [3, 4, 6]. $\text{Pb}(\text{ClO}_4)_2$ was prepared by dissolving lead(II) oxide in perchloric acid.

^{207}Pb N.M.R. of mesophases and liquids were run on a Varian XL 200 spectrometer operating at 41.857 MHz. Some preliminary experiments were run on a Bruker CXP 200 spectrometer at the University of Southampton, England [4]. The only significant difference was that rather better spectra were obtained for the low temperature mesophase on this instrument. Spectra were obtained at various temperatures (± 1 K) of deoxygenated samples contained in 10 mm diameter tubes. Samples were melted into the liquid phase and spectra recorded on cooling. Chemical shifts were determined relative to tetramethyllead, using $1 \text{ mol dm}^{-3} \text{ Pb}(\text{ClO}_4)_2$ in water at 25°C as a secondary reference [12].

High-resolution high-power-decoupling, cross-polarization, magic-angle-spinning (HPD, CP, MAS) ^{207}Pb N.M.R. spectra of the solids were recorded at ambient temperature on a Bruker CXP 200 spectrometer operating at 41.868 MHz. The chemical shifts are referenced to neat tetramethyllead. About 7400 transients were recorded, with contact time of 5 ms and recycle time of 10 s. Further details of high resolution ^{207}Pb solid N.M.R. measurements are given elsewhere [13].

3. Results

^{207}Pb N.M.R. spectra of even chain length lead(II) carboxylates from hexanoate to octadecanoate were recorded at various temperatures on cooling from the isotropic liquid. Typical spectra of melt and mesophases for lead(II) decanoate have already been presented [4]. The liquid phase in all cases showed a single sharp (linewidth *c.* 30 p.p.m.) isotropic signal, whose chemical shift and linewidth were strongly temperature dependent. The chemical shifts were fitted to the empirical relationship

$$\delta = \delta_0 + aT.$$

Values of δ_0 and a obtained by linear regression, and of the correlation coefficient (r) are presented in the table. For comparison, the chemical shifts for all the liquid phases calculated at 383 K (δ_{383}) are also included. The values of δ_{383} seem to increase slightly from hexanoate to decanoate, and then to be independent of chain length for the decanoate to hexadecanoate soaps, indicating similar chemical environments for the Pb(II) nucleus in the liquid phases. The value for the octadecanoate appears anomalously low, possibly due to problems with the chemical shift reference at high

Table. Temperature dependence of the chemical shift in the ²⁰⁷Pb N.M.R. spectra of liquid and lamellar L_α phases of lead(II) carboxylates.†

Lead(II) carboxylate	Lamellar L _α phase				Liquid phase				
	Temperature range/K	δ ₀ /p.p.m.	a/p.p.m. K ⁻¹	r	Temperature range/K	δ ₀ /p.p.m.	a/p.p.m. K ⁻¹	r	δ ₃₈₃ /K
Hexanoate	338-349	- 3757	4.226	0.990	348-392	- 3592	3.596	0.999	- 2215
Octanoate	358-379	- 3502	3.433	0.962	378-404	- 3599	3.552	0.990	- 2238
Decanoate	366-384	- 4122	5.060	0.999	386-394	- 3889	4.273	0.995	- 2252
Dodecanoate	374-378	- 3307	2.900	0.943	378-387	- 3455	3.121	0.987	- 2259
Tetradecanoate					381-394	- 3894	4.287	0.986	- 2252
Hexadecanoate					379-390	- 3486	3.204	0.978	- 2259
Octadecanoate					384-434	- 3701	3.971	0.994	- 2180

† See the Results section for the significance of the symbols.

temperatures. The average variation of the chemical shift for the liquid phase of the lead(II) carboxylates with temperature was 3.7 ± 0.5 p.p.m. K^{-1} . For comparison, the variation in the ^{207}Pb chemical shift of aqueous solutions of lead(II) perchlorate over the range 21–90°C was found to be only 0.13 p.p.m. K^{-1} .

Abrupt changes in both chemical shift and lineshape were observed close to the phase transitions. As with the thermal behaviour [3, 5, 6] differences were observed between the shorter and longer chain length compounds. In the hexanoate to dodecanoate the ^{207}Pb N.M.R. signal was replaced by another isotropic signal of comparable lineshape, corresponding to a high temperature mesophase to which we have assigned a lamellar L_α (smectic A) structure [4, 6]. In most cases we observed co-existence of the liquid and L_α mesophase signals over a temperature range of 2–3 K. We believe that this is due to supercooling and sample inhomogeneity. At lower temperatures, the L_α mesophase signal was replaced by a broad signal of the ordered smectic phase. Observed linewidths for this phase were typically about 500 p.p.m. With the tetradecanoate to octadecanoate, the isotropic signal of the liquid phase was replaced by the broad signal of this ordered smectic phase. Chemical shifts as a function of temperature for the liquid and L_α phases of the hexanoate and decanoate, and for the liquid phase of the tetradecanoate are shown in figure 1, whilst data for the temperature dependence of the chemical shift of the L_α phase of the hexanoate to dodecanoate are included in the table. Also included in figure 1 are the weighted average chemical shifts of the broad ^{207}Pb N.M.R. signal observed for the low temperature mesophase of lead(II) decanoate as a function of temperature. Whilst it was difficult to obtain reliable values for the other systems due to baseline problems, the magnitudes of the ^{207}Pb chemical shift for this ordered smectic phase in all the lead(II) carboxylates appear very similar.

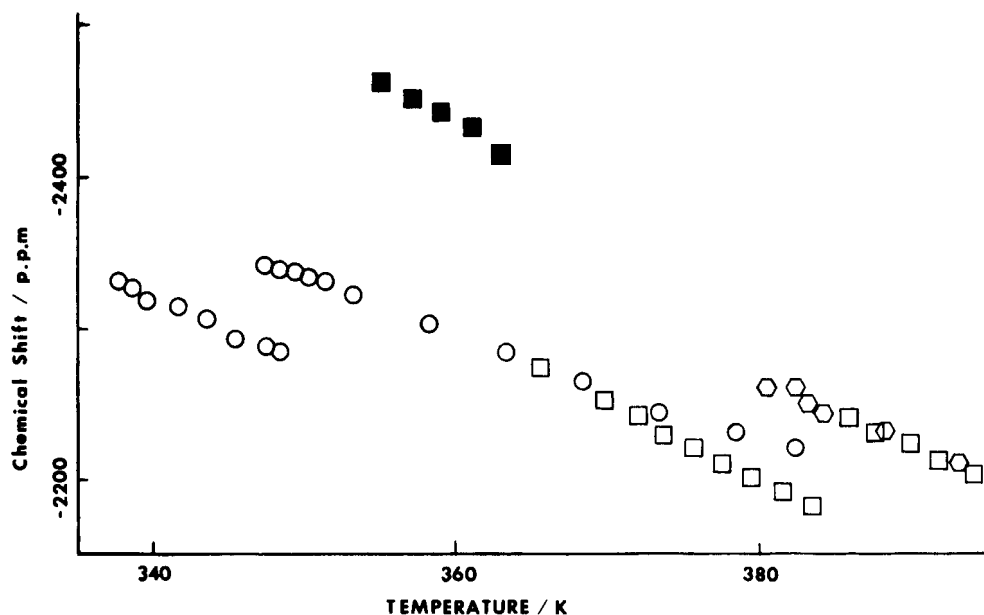


Figure 1. Chemical shift of isotropic ^{207}Pb N.M.R. signals of lead(II) hexanoate (circles), decanoate (squares) and tetradecanoate (hexagons) as a function of temperature. The solid squares correspond to the weighted average chemical shift of the broad signal for the low temperature mesophase of lead(II) decanoate.

The fact that near Lorentzian lineshapes are observed in the liquid and L_x phases indicates rapid isotropic motion of the cation which averages out the dipolar interactions of the lead nuclei and chemical shift anisotropies. This is similar to what is observed in the isotropic melts of sodium [7, 8] and thallium(I) [14] carboxylates. Support for such motion comes from a.c. impedance measurements on these systems [15], where activation energies for conductance in the two phases are found to be very similar.

Further structural information on these systems was obtained from solid-state N.M.R. High resolution HPD, CP, MAS ^{207}Pb N.M.R. spectra were obtained of lead(II) decanoate and tetradecanoate. The spectra were very similar, and indicated a single crystallographic site for the lead ion in both cases (though this statement must be seen in the light of the observed linewidths). Electron diffraction and microscope studies of the related lead(II) octadecanoate multilayers [16] have also indicated the presence of just one metal site. A typical ^{207}Pb N.M.R. spectrum for lead(II) tetradecanoate is shown in figure 2. The positions of the centre bands, identified by changing the speed of rotation, are found to be within experimental error the same, $\delta = -2138 \pm 5$ p.p.m. for the decanoate and tetradecanoate. The linewidths are substantial (≈ 700 Hz for the decanoate and ≈ 900 Hz for the tetradecanoate). A rough calculation using the Maricq-Waugh method [17] gave the shielding anisotropy, $\Delta\sigma$, for the tetradecanoate as 424 p.p.m. and the asymmetry, η , as 0.1 ($\sigma_{11} = 1906$, $\sigma_{22} = 1945$, $\sigma_{33} = 2562$ p.p.m.). The anisotropy is of a similar magnitude to that observed in the ordered smectic phase of the soaps, and in other lead(II) salts [18]. However, within the span of known shielding anisotropies for ^{207}Pb , the values here are modest.

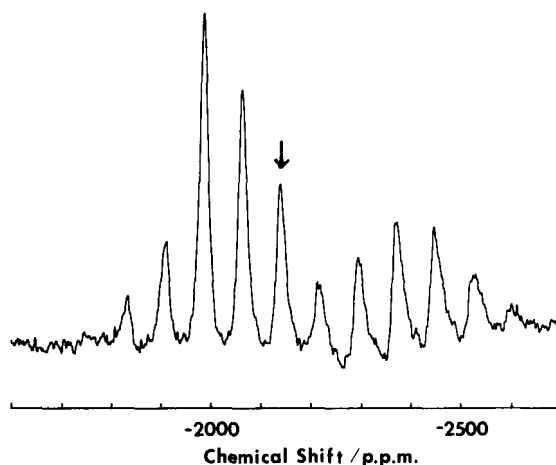


Figure 2. Cross-polarization magic-angle-spinning ^{207}Pb N.M.R. spectrum of lead(II) tetradecanoate, obtained with high-power proton decoupling at ambient probe temperature. Spectrometer conditions: number of transients 7440, contact time 5 ms, recycle delay 10 s, spinning speed 3.15 kHz, radiofrequency 41.868 MHz. The vertical arrow indicates the centre band.

4. Discussion

Combination of the present N.M.R. results with previous X-ray, thermal, Raman spectral and conductivity data [4, 6, 15, 19] provides a fairly coherent view of the phase transitions in the lead(II) carboxylates. In the solid phase the compounds have lamellar layer structures [4, 5], with the hydrocarbon chains being in the fully extended

all-trans conformation and the lead ions all being equivalent. On heating, an increase in lateral disordering starts to occur with the formation of the ordered smectic phase. However, the observed linewidths of the ^{207}Pb N.M.R. signals of this phase are only slightly less than those observed in the solid, which, together with a.c. impedance results [15], suggests that the motion of the metal ion is still highly restricted. Sample calculations [4] suggest that the observed width is dominated by chemical shift anisotropy. This behaviour is similar to that observed in the mesophases of thallium(I) soaps [14].

Onset of conformational disordering of the hydrocarbon chains occurs at a slightly higher temperature, as shown by Raman spectroscopy [4, 6], and leads to the formation of the L_α phase for the shorter chain length carboxylates, whilst the longer chain ones form the isotropic liquid directly. The equivalence of the ^{207}Pb N.M.R. signals in solid lead(II) decanoate and tetradecanoate suggests that the differences in thermal behaviour between the shorter and longer chain length lead(II) carboxylates do not stem from any differences in metal carboxylate structure, but are, rather, a result of balances between the headgroup and hydrocarbon interactions. Formation of the lamellar L_α phase in systems up to the dodecanoate may be associated with the somewhat lower flexibility of the hydrocarbon chain, and greater importance of metal-carboxylate interactions. It is worth noting that the temperature for the ordered smectic to lamellar L_α or liquid phase transition increases with chain length, whereas the L_α to liquid transition temperature shows a maximum at the decanoate ([20], with our reassignment of the phase structures), supporting the idea that more than one factor is involved.

The observation of an isotropic signal in the ^{207}Pb N.M.R. spectrum of the L_α phase can be compared with the behaviour of the corresponding phases in the metal ion N.M.R. spectrum of other carboxylates. With the L_α (smectic A) phase of sodium soaps [7, 8], quadrupolar splitting and second-order quadrupolar shift of the central transition of the ^{23}Na N.M.R. spectra are observed, in spite of the apparently rapid ion motion. However, symmetry effects are suggested to be important, and simulated spectra indicate negligible chemical shift anisotropy in this phase. In contrast, with the neat or modified neat phases of certain thallium(I) soaps considerable chemical shift anisotropy is observed [14]. Thallium(I) and lead(II) are isoelectronic, and such differences seem surprising. One possible explanation is that these lamellar phases in the lead(II) and thallium(I) soaps actually have somewhat different structures. More than one L_α phase has been reported for the potassium palmitate-water system [21], with the phases differing in the axes about which the molecule is suggested to rotate [22]. We should remember, however, that the L_α description refers to the intra- and intermolecular arrangement of the hydrocarbon chain, and that the metal ion properties are also strongly dependent on the structure of the metal-carboxylate region. Where the metal ion has rapid motion on the N.M.R. time scale, as in the sodium soaps [7, 8], no chemical shift anisotropy is observed. The a.c. impedance results for lead(II) carboxylates [15] suggest relatively high mobility for the charge carrier in this phase, which may explain the isotropic ^{207}Pb N.M.R. signal observed here. In contrast, thallium(I)-oxygen bonds are known to have considerably greater covalent character than alkali metal-oxygen bonds [23], and it is possible that the observed chemical shift anisotropy is associated with the decreased mobility of Tl^+ .

Given the strong temperature dependence of the spectra in these systems, the ^{207}Pb chemical shifts of the solids, mesophases and liquids are fairly similar, suggesting that the Pb^{2+} coordination environment does not change dramatically during the phase

transitions. The values (typically about -2200 p.p.m.) can be contrasted with those of lead(II) acetate and other short chain carboxylates in solution, where much smaller chemical shifts are observed [9, 12, 24]. In these cases the spectra are strongly concentration dependent due to complexation equilibria, but with lead(II) acetate in acetic acid a value of $\delta = -1519$ p.p.m. has been reported [9]. These differences probably reflect changes in coordination geometry round the metal ion on going from the shorter chain to longer chain carboxylates.

In both the liquid and lamellar L_α phase, the frequency of the ^{207}Pb N.M.R. signal increases linearly with temperature (deshielding effect). Although a strong temperature dependence of the chemical shift seems to be common in ^{207}Pb N.M.R. spectroscopy [9], the magnitude of this effect is much greater in the long chain carboxylates than in systems such as lead(II) perchlorate. A temperature dependence of the same sign and similar magnitude has been observed for various cobalt(III) complexes [25], and can be rationalized in terms of a temperature dependence of the dominant paramagnetic contribution to the shielding tensor through a temperature induced change of the mean excitation energy of the low-lying (e.g. $6s6p$) electronic states of Pb(II) due to the thermal motion of the ligands [26]. An alternative explanation is that the effect of temperature on the dissociation equilibria of the lead(II) carboxylates is involved, and that, as with the lead(II) carboxylate equilibria in solution [12, 24], we are looking at the average ^{207}Pb N.M.R. signal of different coordination species. Conductivity measurements on molten lead(II) carboxylate confirm the existence of such equilibria [19], although from the reported thermodynamic data the dissociation constant for molten lead(II) carboxylates is fairly small. From the data of Adeosun and Sime [19] an average dissociation constant of 0.02 ± 0.02 mole fraction at 383 K can be calculated. The observed temperature dependence of the chemical shift probably reflects a combination of these factors.

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