

## The phase behaviour of some mixtures of lead(II) carboxylates with phosphatidylcholines

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### Abstract

The phase behaviour of some binary mixtures of long-chain lead(II) carboxylates and phosphatidylcholines has been studied by DSC, optical microscopy, X-ray diffraction and multinuclear NMR. X-ray diffraction results confirm that all the soaps have the same lamellar layered structure in the solid, and that this is maintained on incorporation of phospholipids. With pure lead(II) decanoate, DSC and X-ray diffraction studies confirm that differences between recrystallized and premelted samples result from polymorphism. Didecylphosphatidylcholine (DDPC) was soluble in the liquid and  $L_{\alpha}$  liquid crystalline phase of lead(II) decanoate (PLC<sub>10</sub>) up to at least 10 wt%. In either the solid or the low temperature mesophase, phase separation occurs at lower concentrations. The C<sub>14</sub> (up to 10 wt%) and C<sub>18</sub> (up to 4 wt%) phosphatidylcholines also dissolve in the liquid phase of the corresponding chain length carboxylates, and miscibility is observed up to 4 wt% in the mesophase of the C<sub>14</sub> system. At higher phospholipid concentrations, optical observations confirm separation into two phases. The <sup>31</sup>P NMR spectra were run on these systems. In some cases spectra showed more than one peak, indicating different local environments for the phosphate group. The <sup>207</sup>Pb NMR spectra were run on the C<sub>14</sub> system and showed similar chemical shifts in the presence and absence of phospholipid, suggesting that Pb(II) does not bind to the phosphate. However, differences were observed in the bandshape of the <sup>207</sup>Pb NMR signal for the mesophase on incorporation of phospholipid, suggesting changes in the local dynamics. The <sup>13</sup>C NMR spectra and the longitudinal relaxation of a DDPC/PbC<sub>10</sub> mixture showed that at low temperature the choline methyl group signal is split in two, possibly as a result of phase separation. This is supported by DSC data.

### INTRODUCTION

The anhydrous long chain carboxylates of metal ions frequently exhibit one or more mesophases between the solid and the isotropic liquid [1–4]. The structures of these possess many similarities to phases observed in

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more complex systems, such as biological membranes, and have been used as models for them [2,5,6]. We have been interested in lead(II) carboxylates (represented here as  $\text{PbC}_n$ , where  $n$  is the carboxylate chain length), where two intermediate phases are observed for the shorter chain homologues (up to  $\text{C}_{12}$ ) and one for the longer chain members [7–11]. Although disagreement concerning the assignment of these phases exists [9–11], there is agreement that the low temperature phase for the shorter carboxylates, which is the only mesophase for the longer chain members, has a relatively ordered rigid structure, whereas the high temperature mesophase in the former compounds has a fluid lamellar liquid crystalline structure. Their structures have been suggested to be analogous to the gel and  $L_\alpha$  phases observed with phospholipids [6]. A number of reports exists on the phase behaviour of binary systems involving lead(II) carboxylates [12–16]. In this work we extend our study to some lead(II) carboxylate–phosphatidylcholine mixtures.

## EXPERIMENTAL

Preparation, purification and characterization of the lead(II) carboxylates have been described previously [7,10,11]. The synthetic phospholipids (Sigma) with 10 (DDPC), 14 (dimyristylphosphatidylcholine, DMPC) and 18 (distearylphosphatidylcholine, DSPC) carbon atoms were dried in a vacuum desiccator. They may still contain low concentrations (ca. 1:1 mole ratio) of chemically bound water. Mixtures of didecylphosphatidylcholine (DDPC) and lead(II) decanoate ( $\text{PbC}_{10}$ ) were prepared by adding solutions of the phospholipids in chloroform–methanol (1:1 by volume) and allowing the solvent to evaporate. Other mixtures were prepared by weighing. Homogenization of mixtures was achieved by several melting–cooling cycles in porcelain crucibles or Pyrex beakers. After each cycle, the solid was ground with a pestle and mortar. To confirm the composition of the mixtures, analysis of phospholipid phosphate was carried out using the method of Fiske and Subbarow [17].

Differential scanning calorimetry (DSC) was performed on 1–3 mg samples of freshly prepared mixtures in aluminium crucibles on a Perkin-Elmer DSC 7 Delta series apparatus using heating–cooling cycles normally at  $2.5^\circ\text{C min}^{-1}$ . Where there were difficulties with overlapping transitions, slower rates were used. Transition temperatures were normally determined by extrapolating the rising part of the peak traces to the baseline [18]. In the case of  $\text{PbC}_{18}$  this was not possible and the peak maximum was used. The estimated precision in these measurements is  $\pm 0.05$  K. Transition enthalpies were determined by numerical integration, and had a precision of  $\pm 0.1$  J  $\text{g}^{-1}$ . Optical observations were made on a Nikon Optiphot-Pol polarizing microscope, using a specially constructed heating stage [18]. X-ray patterns were obtained with a Philips diffractometer fitted with a

PW-1730 generator and a PW-1840 goniometer, using the copper  $K\alpha$  line filtered by nickel. Multinuclear nuclear magnetic resonance (NMR) measurements involved use of a Varian XL-200 spectrometer on freshly prepared samples using frequencies of 41.73 MHz ( $^{207}\text{Pb}$ ), 80.98 MHz ( $^{31}\text{P}$ ) and 50.31 MHz ( $^{13}\text{C}$ ). For  $^{13}\text{C}$  NMR measurements 1,4-dioxan was used as external reference. Longitudinal  $^{13}\text{C}$  relaxation times were obtained by a standard inversion–recovery technique as described elsewhere [19].

## RESULTS

### *X-ray diffraction of lead(II) carboxylates and their mixtures with phospholipids*

The X-ray diffraction spectra of the solid phase of  $\text{PbC}_{10}$ ,  $\text{PbC}_{14}$ ,  $\text{PbC}_{18}$  and their mixtures with phospholipids of the same chain length were recorded. In all cases good diffraction patterns were observed, with the main peaks assigned to the  $00n$  reflections from the lead atom planes. Typical data for the  $\text{PbC}_{10}$  system are given in Fig. 1, and all data are summarized in Table 1. For convenience, data on DMPC are also included. For the pure carboxylates, results were in general in agreement with available literature data [9–11,20–22] and suggest a layered lamellar structure with the carboxylates in an all-*trans* configuration [9]. For  $\text{PbC}_{18}$ , the

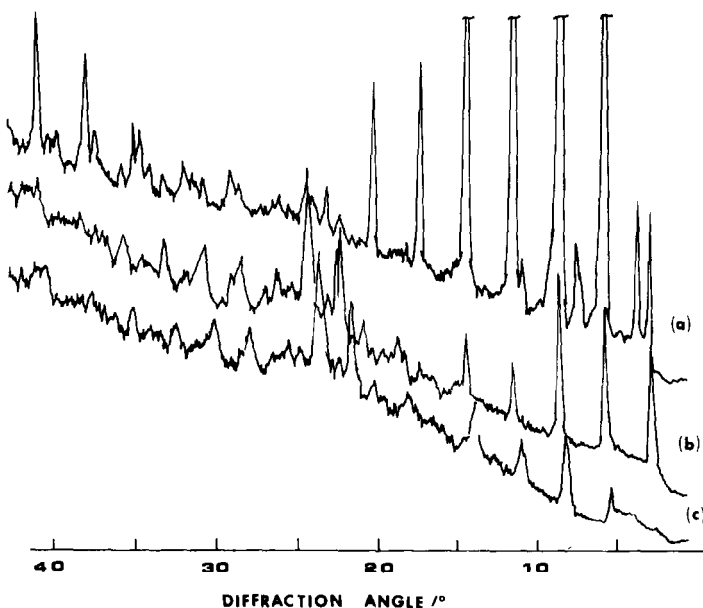


Fig. 1. X-ray diffractogram at room temperature for (curve a) premelted  $\text{PbC}_{10}$ ; (curve b) recrystallized  $\text{PbC}_{10}$ ; (curve c) 4 wt% DDPC- $\text{PbC}_{10}$ .

TABLE 1  
X-ray diffraction data ( $d/n, \text{\AA}$ )<sup>a</sup> for lead(II) carboxylate-phospholipid mixtures

PbC <sub>10</sub>	4% DDPC-PbC <sub>10</sub>	PbC <sub>14</sub>	5% DMPC-PbC <sub>14</sub>	PbC <sub>18</sub>	8% DSPC-PbC <sub>18</sub>	DMPC
Recrystallized	Premelted					
30.65 (0.91)	32.70 <sup>c</sup> (0.14)	41.64 (0.07)	42.44 (0.98)	50.37 <sup>c</sup> (0.17)	50.48 <sup>c</sup> (0.13)	55.87 (0.77)
		19.97 (0.50)	20.34 (0.86)	24.80 (0.38)	25.08 (0.39)	18.02 (0.05)
15.28 (0.83)	16.35 (0.33)	13.34 (1.00)	13.59 (1.00)	16.79 (1.00)	16.66 (0.63)	13.71 (0.27)
		9.97 (0.56)	10.16 (0.43)	12.58 (0.63)	12.62 (0.31)	9.32 (0.10)
		8.01 (0.75)	8.07 (0.50)	10.06 (0.89)	10.06 (0.40)	9.04 (0.08)
10.13 (1.00)	10.67 (0.61)	6.68 (0.35)	6.74 (0.25)	8.34 (0.46)	8.40 (0.21)	6.23 <sup>d</sup> (0.14)
		5.72 (0.41)	5.76 (0.28)	7.16 (0.60)	7.19 (0.23)	
		5.01 (0.21)	5.07 (0.17)	6.28 (0.30)	6.28 (0.12)	
7.64 (0.37)	8.01 (0.32)			5.58 (0.38)	5.60 (0.19)	
6.10 (0.38)	6.34 (0.44)			5.03 (0.21)		
5.09 (0.13)						

<sup>a</sup> Relative intensities are given in parentheses. In addition to the reflections reported here, a large number of bands was observed for  $d/n < 5 \text{\AA}$ .

<sup>b</sup> Shoulder.

<sup>c</sup> Because of the breadth of this reflection, values are calculated from higher order reflections.

<sup>d</sup> Maximum of a broad peak.

001 reflection was very broad, and it was difficult to determine the maximum. Ellis and De Vries [22] have suggested that, for lead(II) carboxylate having more than twelve carbon atoms, there is a change in lamellar structure from a bilayer to a monolayer molecular organization with respect to the metal planes. These structures are equivalent to the Y and X type multilayer observed with Langmuir–Blodgett films [23]. However, high resolution  $^{207}\text{Pb}$  [24] and  $^{13}\text{C}$  [25] NMR spectra on our solid samples are not consistent with this, and suggest that all three lead(II) carboxylates have the same Y-type lamellar structure. Further, in the X-ray patterns, at least 11 orders of the  $00n$  reflections are observed, as expected from this structure. With lead(II) decanoate, differences in the thermal behaviour of recrystallized and premelted samples have been observed [10], and have been attributed to polymorphism in the solid phase [11]. Differences observed in the X-ray diffraction pattern of recrystallized and premelted samples support this.

The diffraction patterns for lead(II) carboxylate–phospholipid mixtures were similar to those of pure soaps, with the only significant reflections being those from the lead atom planes. This is not surprising considering the strong scattering and absorbance of X-rays by  $\text{Pb}^{2+}$ . However, long spacings, corresponding to the distances between lead planes, appeared to be somewhat larger in the mixtures for  $\text{C}_{10}$  and  $\text{C}_{14}$ , with the effect being most pronounced for  $\text{PbC}_{10}$ –DDPC (Fig. 2).

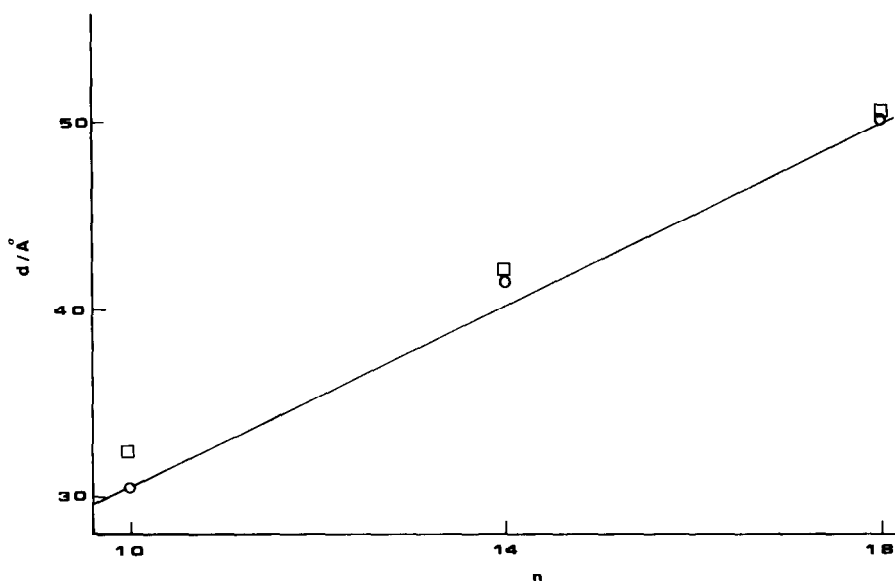


Fig. 2. Long spacings as a function of chain length for pure lead(II) carboxylate (circles) and lead(II) carboxylate–phospholipid mixtures (squares). The straight line is the least squares plot for pure carboxylates using data from this and previous studies [9,11,20–22].

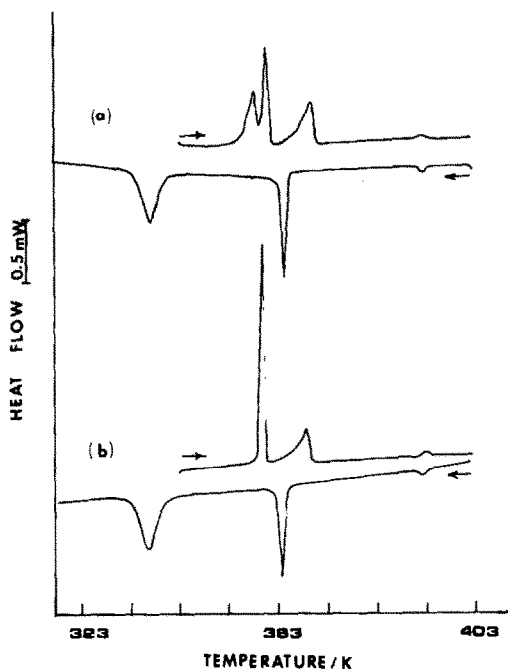


Fig. 3. DSC curves for (a) heating and cooling recrystallized  $\text{PbC}_{10}$ ; (b) second heating and cooling of  $\text{PbC}_{10}$  sample.

### *DSC and optical studies*

Pure  $\text{PbC}_{10}$ ,  $\text{PbC}_{14}$  and  $\text{PbC}_{18}$ , and mixtures with phosphatidylcholines of the same chain length, were studied by DSC on both heating and cooling cycles (Figs. 3–6). As previously noted [10], differences were observed for recrystallized and premelted samples of  $\text{PbC}_{10}$ . The broad peak previously reported for the solid  $\rightarrow$  mesophase I transition on first heating [10] was resolved into two very close peaks (Fig. 3), confirming the previous suggestion [11] that this is, in fact, a double transition. For all other studies, premelted samples were employed. Transition temperatures and enthalpies for the pure lead(II) carboxylates were in good agreement with literature data [7,9–11]. Results for these and mixtures are summarized in Table 2. With the low temperature transitions in the  $\text{C}_{10}$  system, and with  $\text{PbC}_{18}$ –DSPC, the overall enthalpy changes are given because of the somewhat complex phase behaviour at high phospholipid concentrations. Full thermodynamic data are given elsewhere [18].

For  $\text{PbC}_{10}$ –DDPC mixtures (Fig. 4) at low concentration of phospholipid ( $< 4$  wt%) the same number of transitions was observed as in pure  $\text{PbC}_{10}$ , although the transition temperatures decreased. At higher DDPC concentration, an additional peak was observed at ca. 357 K and, although the transition temperature for the mesophase I  $\rightarrow$  mesophase II and mesophase

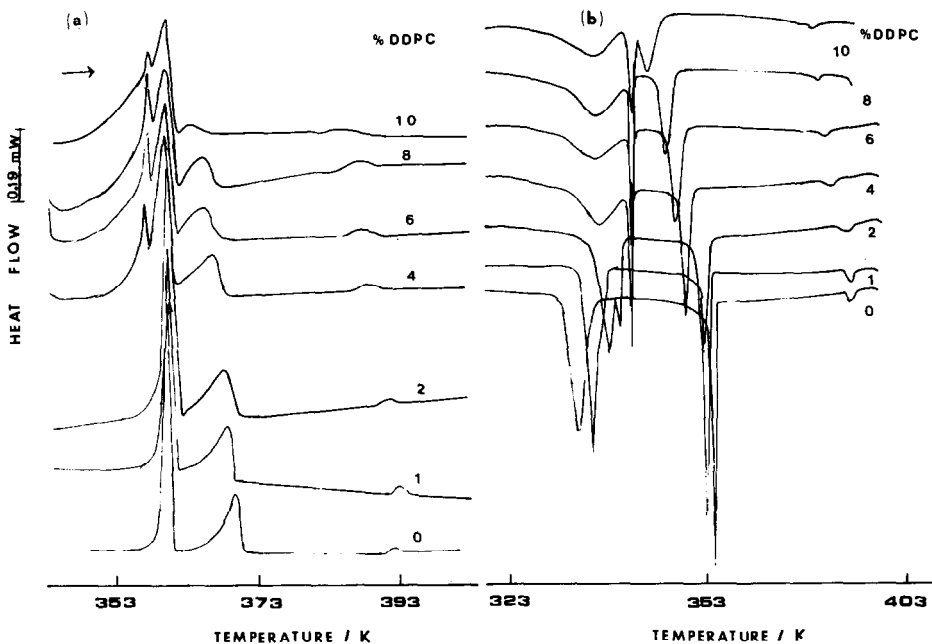


Fig. 4. DSC traces for (a) heating; (b) cooling  $\text{PbC}_{10}$ -DDPC mixtures.

II  $\rightarrow$  liquid transitions continued to decrease with increasing concentration of phospholipid, the temperature of the solid  $\rightarrow$  mesophase I transition remained constant. On cooling, the liquid  $\rightarrow$  mesophase II and mesophase II  $\rightarrow$  mesophase I transition again showed decreases in transition temperatures with increasing phospholipid concentration, suggesting that DDPC and  $\text{PbC}_{10}$  are miscible in the liquid and the mesophase II up to the highest concentration studied. However, two effects are apparent on the low temperature transition(s). Firstly, incorporation of even small amounts of phospholipids greatly decreases the supercooling on the mesophase  $\rightarrow$  solid transition. This is reasonable, as DDPC may provide nucleation sites for crystallization. Secondly, at DDPC concentration  $> 2$  wt%, the transition splits into two, and above ca. 4 wt% of phospholipid the temperatures of the two transitions remain relatively constant. It is probable in this case that separation into lead(II) carboxylate-rich and DDPC-rich phases occurs, and that the new low temperature transition corresponds to a process within the DDPC-rich phase.

With  $\text{PbC}_{14}$ /DMPC mixtures (Fig. 5), the same number of transitions was observed on heating as in the pure carboxylate for phospholipid concentrations of up to 8 wt%. At higher concentrations there were indications of a new weak peak around 353 K, the solid  $\rightarrow$  mesophase transition was replaced by two peaks, and the mesophase  $\rightarrow$  liquid transition broadened considerably. On cooling, a progressive decrease in the

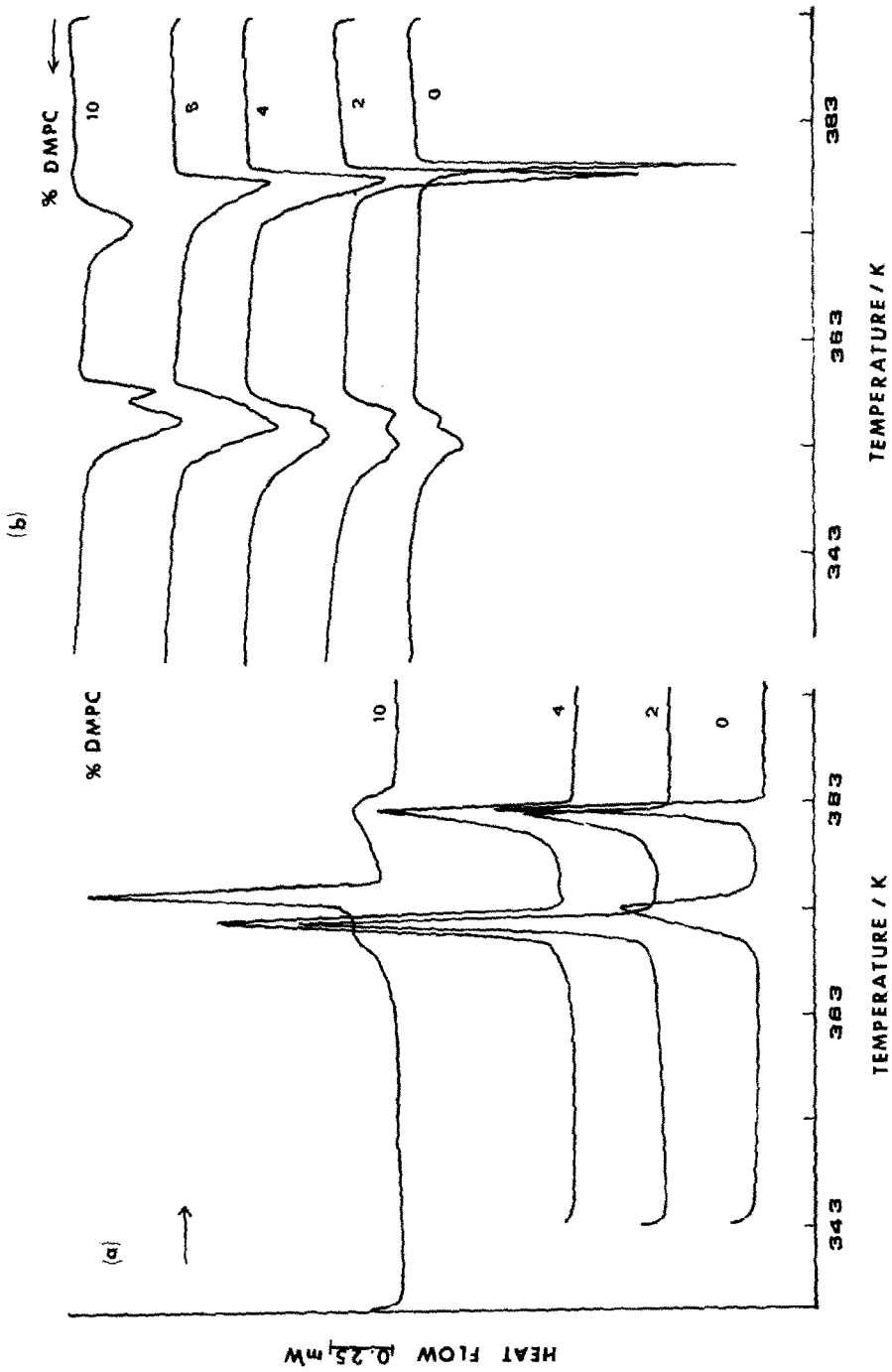


Fig. 5. DSC traces for (a) heating; (b) cooling  $\text{PbC}_{14}$ -DMPC mixtures.



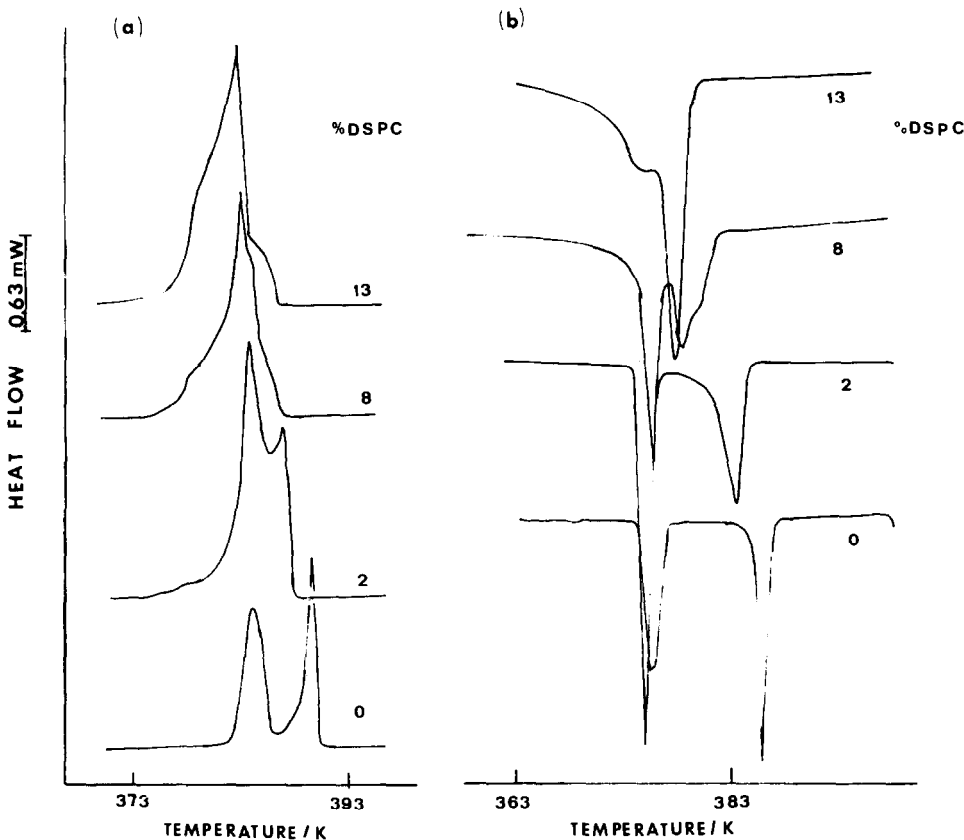


Fig. 6. DSC traces for (a) heating; (b) cooling  $\text{PbC}_{18}$ -DSPC mixtures.

liquid  $\rightarrow$  mesophase transition temperature was observed, and in both pure  $\text{PbC}_{14}$  and the mixture the lowest energy transition gave two peaks. The most dramatic changes occurred with  $\text{PbC}_{18}$ -DSPC mixtures (Fig. 6). Already at ca. 2 wt% of phospholipid the two transitions observed on heating the pure carboxylate were replaced by a complex series of overlapping transitions in the range 370–390 K. On cooling, it was possible to resolve the liquid  $\rightarrow$  mesophase and mesophase  $\rightarrow$  solid transition at a DSPC concentration of 2 wt%, and both of these showed decreased transition temperatures on incorporation of the phospholipid.

To attempt to clarify the phase changes occurring in these systems, samples were observed through crossed polars on an optical microscope. With  $\text{PbC}_{10}$ -DDPC mixtures up to 10 wt% of phospholipid, there was no evidence of any phase separation in the isotropic liquid phase or in the mesophases. The texture observed for mesophase I was similar to that reported for pure  $\text{PbC}_{10}$  [10]. Although mesophase II showed similarities to this phase in the pure carboxylate [10], the texture was rather more granular, and it was possible to distinguish two domains having singular

TABLE 2

Transition enthalpies observed on heating lead(II) carboxylate–phospholipid mixtures

Phospholipid (wt%)	$\Delta H$ (J g <sup>-1</sup> )	$\Delta H$ (J g <sup>-1</sup> )
<i>PbC</i> <sub>10</sub> – <i>DDPC</i>	<i>solid</i> → <i>mesophase II</i> <sup>a</sup>	<i>mesophase II</i> → <i>liquid</i>
0	85.4	1.8
1	77.5	–
2	80.9	1.8
4	84.4	1.7
6	85.5	1.7
8	88.7	1.5
10	73.0	1.9
<i>PbC</i> <sub>14</sub> – <i>DMPC</i>	<i>solid</i> → <i>mesophase</i>	<i>mesophase</i> → <i>liquid</i>
0	83.2	64.2
2	78.7	46.5
4	73.4	46.6
6	67.9	35.6
8	66.1	40.9
10	62.7	20.2
<i>PbC</i> <sub>18</sub> – <i>DSPC</i> <sup>a</sup>		
0	164.4	
2	158.4	
4	148.4	
8	147.9	
13	135.8	

<sup>a</sup> Overlapping transitions not resolved.

arrangements of points. This is similar to the observations reported for disordered smectic phases in which the average orientation of the long axis deviates from the normal to the bilayer plane [26]. Ellis [9] has previously proposed a smectic C structure for this phase, in which there is chain tilting. We have given reasons why this is unlikely in the pure carboxylate [11]; however, some local distortion is probably necessary to incorporate the relatively large phospholipid molecule.

With *PbC*<sub>14</sub>–*DMPC* mixtures up to 10 wt% of phospholipid, there was no evidence for phase separation in either the isotropic liquid or the mesophase. However, at higher phospholipid concentration phase separation does occur, and on heating above ca. 385 K the carboxylate melts to give an isotropic phase, incorporated in which is a second anisotropic phase. As the temperature increases, aggregation of particles of the second phase occurs up to about 440 K, when melting of this second phase starts. This continues up to 460 K, when the separated phase has completely melted. On cooling, the second phase gives anisotropic textures. Finally, the mixtures solidify, and a rather complex texture is observed, probably corresponding to a mixture of various structures [18].

With  $\text{PbC}_{18}$ -DSPC mixtures, phase separation is observed even at relatively low (ca. 4 wt%) concentrations of phospholipid. As with the  $\text{C}_{14}$  system, an anisotropic phase is observed within the isotropic liquid carboxylate phase above the melting point of the pure carboxylate. This persists up to about 450 K, above which it melts to give liquid droplets within the molten  $\text{PbC}_{18}$  [18]. The texture of this anisotropic phase is similar to that observed with diisobutylsilanediol [27], and is typical of smectic structure in which the interactions of polar groups are not regularly organized [28].

### Multinuclear NMR studies

To attempt to characterize further the phase behaviour, multinuclear NMR spectra were recorded for some of the mixtures. Proton decoupled

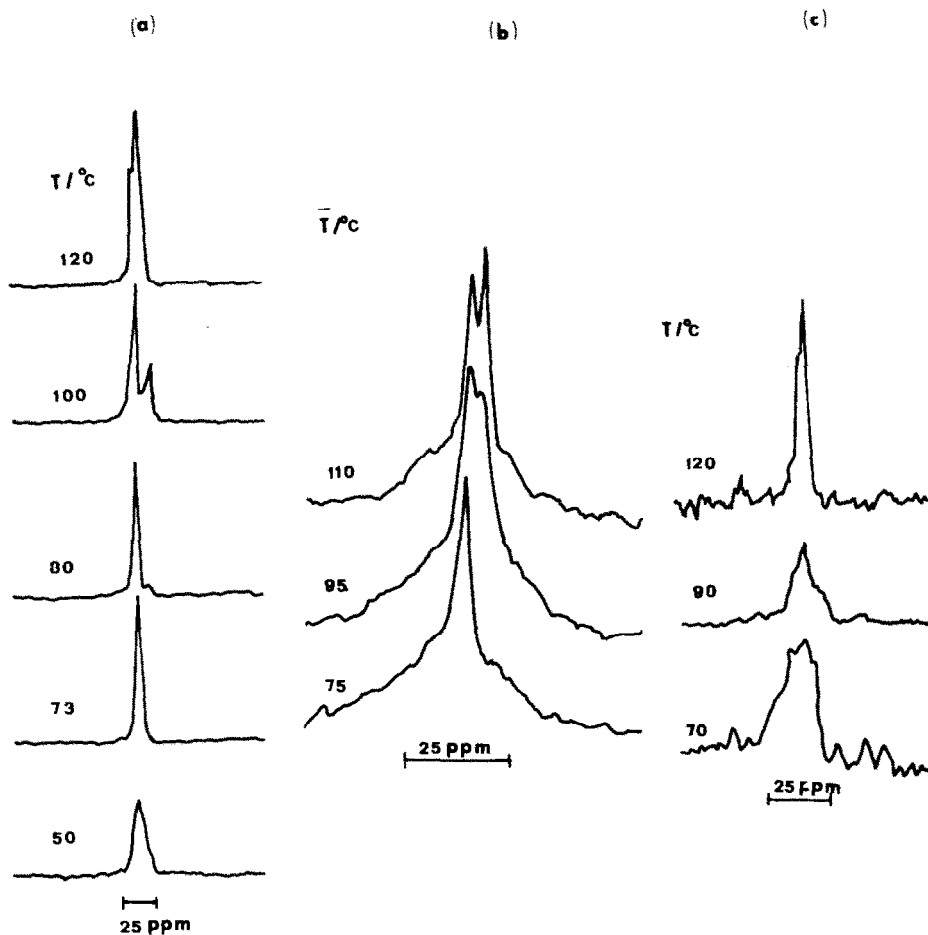


Fig. 7. Proton decoupled  $^{31}\text{P}$  NMR spectra at various temperatures for (a) 8 wt% DDPC- $\text{PbC}_{10}$ ; (b) 5 wt% DMPC- $\text{PbC}_{14}$ ; (c) 6 wt% DSPC- $\text{PbC}_{18}$ .

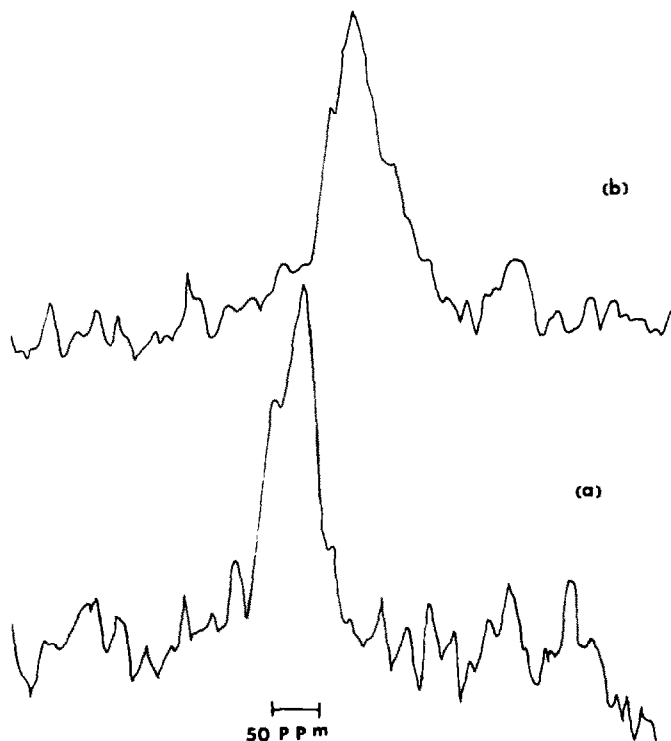


Fig. 8.  $^{207}\text{Pb}$  NMR spectra of 5 wt% DMPC- $\text{PbC}_{14}$ : (a) liquid at 125°C; (b) mesophase at 95°C.

$^{31}\text{P}$  NMR of mixtures of  $\text{PbC}_{10}$ -DDPC,  $\text{PbC}_{14}$ -DMPC and  $\text{PbC}_{18}$ -DSPC (Fig. 7) showed broadening of signals on passing from the liquid to the solid phase. Somewhat surprisingly, the spectra in some cases showed more than one peak. Although this may be due to some sample inhomogeneities with these rather viscous mixtures, it does suggest that there is more than one phosphorus site. Possibly, even though the samples appear on optical observation to give a single phase at these concentrations, there is formation of soap-rich and phospholipid-rich regions.

For  $\text{PbC}_{14}$ -DMPC, the  $^{207}\text{Pb}$  NMR spectra were recorded of the liquid and the mesophase (Fig. 8). For the liquid phase, both the chemical shift and the bandwidth were similar to that of pure  $\text{PbC}_{14}$  [24], indicating that at these concentrations the phospholipid does not greatly affect the liquid structure, nor bind significantly to  $\text{Pb(II)}$ . In contrast, although the  $^{207}\text{Pb}$  chemical shift of the mesophase was similar to that of pure  $\text{Pb}_{14}$  [23], the bandwidth ( $\Delta\nu_{1/2}$ ) was reduced from ca. 480 ppm to ca. 140 ppm. Chemical shift anisotropy (CSA) is one of the dominant factors in the bandwidth here [19], and some components of this would appear to be averaged out on the timescale of the NMR experiments, possibly as a result of changes in the local dynamics.

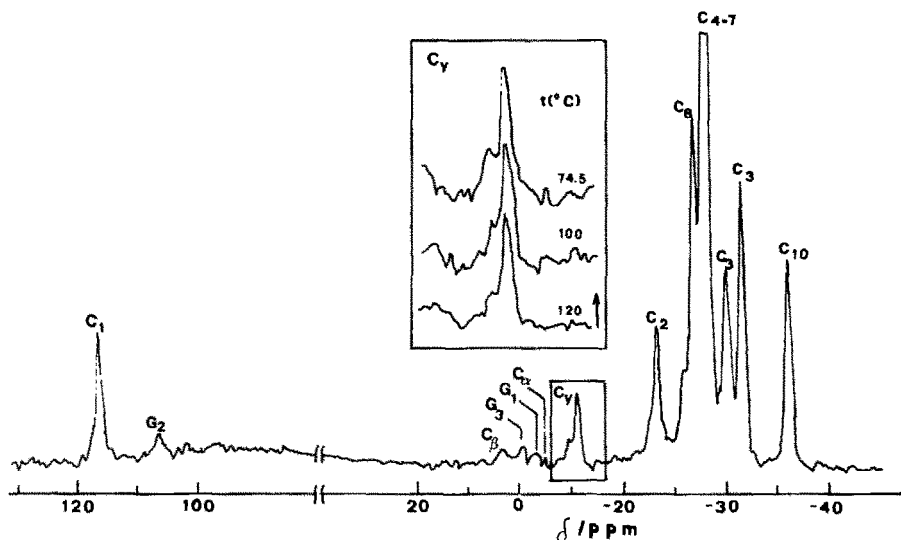


Fig. 9. Proton decoupled  $^{13}\text{C}$  NMR spectra of 8% DDPC- $\text{PbC}_{10}$  at  $100^\circ\text{C}$ . The numbers refer to carbon atoms in lead(II) decanoate starting from carboxylate group,  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{C}_\gamma$  correspond to the choline carbon atoms, and  $\text{G}_1$ ,  $\text{G}_2$  and  $\text{G}_3$  to the glycerol carbon atoms. Chemical shifts are relative to 1,4-dioxane ( $\delta = 67.4$  ppm relative to TMS [31]). Inset shows evolution of the  $\text{C}_\gamma$  signal as a function of temperature.

The  $^{13}\text{C}$  NMR spectra of a  $\text{PbC}_{10}$ -DDPC mixture were recorded (Fig. 9). The spectrum of the conglomerate is similar to that of molten lead(II) decanoate [19]. In addition, bands of the phospholipid were observed, and were assigned using literature data [29]. Of particular interest is the behaviour of the  $\text{C}_\gamma$  signal corresponding to three methyl groups linked to nitrogen in the choline part of the phospholipid. As the system cools into the mesophase this signal appears as two peaks, indicating that the methyl groups are not equivalent. Longitudinal  $^{13}\text{C}$  relaxation measurements on the choline methyl group at  $80^\circ\text{C}$  give a single component with  $T_1 = 2 \pm 1$  s, close to the value observed with sonicated dipalmitoyllecithin in  $\text{D}_2\text{O}$  at  $65^\circ\text{C}$  [29]. However, on cooling to  $74.5^\circ\text{C}$ , decay of the two components was observed with  $T_1$  values of  $0.015 \pm 0.004$  and  $0.53 \pm 0.04$  s for the low and high field components, respectively. Comparison with DSC results at these concentrations suggests that the components may result from DDPC in the carboxylate-rich and phospholipid-rich phases, with the shorter  $T_1$  value corresponding to a less mobile region. Considering the rigidity of the mesophase in the pure soap at these temperatures, this may well be the soap-rich region.

## DISCUSSION

Previous reports [12–14] have shown that molten long chain lead(II) carboxylates can dissolve a variety of substances, including acids, hydrocar-

bons, lead(II) oxide and lead(II) acetate. However, in many of these systems, the second component significantly affects the phase behaviour. For example, addition of small quantities of lead(II) oxide to lead(II) dodecanoate leads to loss of the high temperature mesophase and formation of one or more intermediate phases between the solid and the ordered smectic [12]. In this study, phospholipids are seen to be partially soluble or miscible with lead(II) carboxylates. A plot of the long spacings from the X-ray data on mixtures against chain length (Fig. 2) shows that the interplanar spacing increases on incorporation of the phospholipid, the biggest effect being for the C<sub>10</sub> system. The phospholipid headgroups are considerably larger than the lead(II) carboxylate moieties, and it is reasonable that an expansion of the lattice is necessary to incorporate these molecules. The balance between steric, hydrophobic and electrostatic interactions, makes changes most pronounced with the decanoate.

At low phospholipid concentrations, the temperatures of the mesophase I → II and mesophase II → liquid transitions in PbC<sub>10</sub>-DDPC (up to 10 wt% of phospholipid) and the mesophase → liquid transitions in PbC<sub>14</sub>-DMPC (up to 4 wt%) and PbC<sub>18</sub>-DSPC (up to 2 wt%) all showed a decrease with increasing phospholipid concentration. For ideal solutions, decrease in melting temperature ( $\Delta T_f$ ) can be predicted by

$$\Delta T_f = \frac{RT_f^2 \chi_s}{\Delta H_f} \quad (1)$$

where  $T_f$  and  $\Delta H_f$  are the transition temperature and enthalpy of the pure solvent and  $\chi_s$  is the mole fraction of solute [30]. Although this equation is strictly derived for melting, it was found that, using the appropriate transition temperatures and enthalpies, it predicted the lowering of the mesophase I → II transition in the C<sub>10</sub> system and the mesophase → liquid transition in the C<sub>14</sub> and C<sub>18</sub> systems fairly well (Fig. 10). Probably above 4 wt% of phospholipid for C<sub>14</sub> and 2 wt% of phospholipid for C<sub>18</sub>, phase separation occurs in the mesophase. The values predicted for the mesophase II → liquid transition in PbC<sub>10</sub>-DDPC were much lower than those observed if the experimental enthalpy change of  $\Delta H_f = 0.99 \text{ kJ mol}^{-1}$  was used (Fig. 10, solid line), and could only be reproduced if the higher value of  $\Delta H_f = 13 \text{ kJ mol}^{-1}$  was employed. Although the reason for this is not clear, it should be remembered that eqn. (1) is strictly derived for solid-liquid phase transitions, and its application to liquid crystal → liquid transitions is questionable.

Combination of thermal and optical data for the three systems allows one to suggest a tentative interpretation of the phase behaviour. For the C<sub>10</sub> system, PbC<sub>10</sub>-DDPC appears to be miscible in the liquid and the mesophase II up to at least 10 wt%. Above 4 wt% of phospholipid a new transition is observed at low temperature, and it is probable, that on

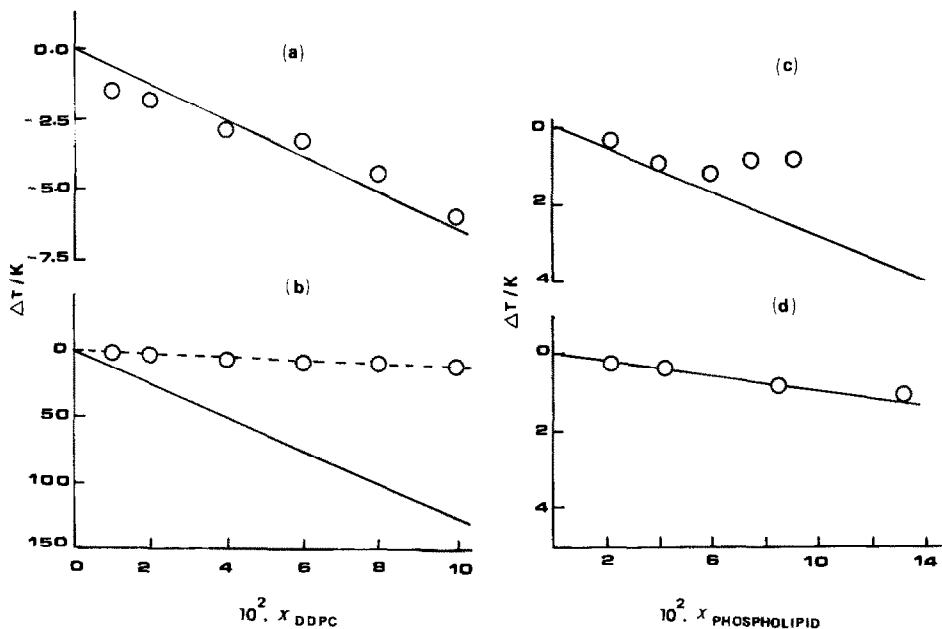


Fig. 10. Lowering of transition temperature as function of mole fraction of phospholipid for (a)  $\text{PbC}_{10}$ -DDPC mesophase I  $\rightarrow$  mesophase II; (b)  $\text{PbC}_{10}$ -DDPC mesophase II  $\rightarrow$  liquid; (c)  $\text{PbC}_{14}$ -DMPC mesophase  $\rightarrow$  liquid; (d)  $\text{PbC}_{18}$ -DSPC mesophase  $\rightarrow$  liquid. Circles are experimental data, lines are calculated by eqn. (1). For (b) the broken line corresponds to calculations using  $\Delta H_f = 13 \text{ kJ mol}^{-1}$ . For (d), the line corresponds to calculations using the total enthalpy change for the solid  $\rightarrow$  liquid transition.

cooling to the solid, separation into  $\text{PbC}_{10}$ -rich and phospholipid-rich zones occurs. With  $\text{PbC}_{14}$ -DMPC, the phospholipid dissolves in the liquid phase up to ca. 10 wt% ( $\chi = 0.1$ ). At higher concentrations, phase separation occurs, and in the mesophase separation into carboxylate-rich and phospholipid-rich zones occurs at around 4 wt% of phospholipid. With  $\text{PbC}_{18}$ -DSPC, phase separation in the liquid phase occurs at around 4 wt%, and in the mesophase at even lower concentrations.

Both the size and the chemical bonding of the lead(II) carboxylate and phospholipid contribute to the partial solubilities observed in these systems. It is of interest that the solubility is highest in the shortest chain length homologue, and that the phospholipid dissolves without significantly affecting the bulk structure of mesophase I (assigned as ordered smectic) or mesophase II (given an  $L_\alpha$  structure [10]). This lends support to the suggestion [6] that these phases may serve as models for the gel and  $L_\alpha$  structures present in phospholipid dispersions and biological membranes.

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