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A DIFFERENTIAL THERMAL ANALYSIS STUDY OF THE SYSTEM LEAD(II) DODECANOATE/DODECANOIC ACID

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ABSTRACT

Data are presented for the heats and entropies of phase changes for the system lead(II) dodecanoate/dodecanoic acid. A phase diagram has also been constructed for the system.

Optical observations using a hot-stage polarising microscope suggest that in mixtures containing very low acid concentration ($X_{acid} \leqslant 0.01$), the phase sequence is the same as in the pure soap, i.e. crystal → $G_{(smectic)}$ → $V_{2\ (cubic\ isomorphous)}$ → liquid. The V_2 phase disappears at higher acid concentrations. At high acid concentrations ($X_{acid} \geqslant 0.06$) a new phase transition occurs at temperatures very close to the melting point of the pure acid.

The total entropy change accompanying the transformation crystal → liquid phase is the same for all the compositions studied. This suggests that the addition of dodecanoic acid to lead dodecanoate does not alter the degree of order of the hydrocarbon chains either in the solid or liquid phase.

INTRODUCTION

In an earlier paper[1] we reported thermodynamic data on melting and mesophase formation in some lead(II) carboxylates. In particular, we showed that for pure lead dodecanoate, the phase sequence is crystal → $G_{(smectic)}$ → $V_{2\ (cubic\ isomorphous)}$ → liquid. We attempted a rationalisation of this phase sequence in terms of the *R* theory[2] of fused micellar phases, which was originally believed to be applicable only to 'fused' mesophases in which the amphiphilic layers were labile.

In an attempt to further test the applicability of the concepts of the *R* theory to non-aqueous carboxylate phases we have presented data on some soap systems in which perturbations of the intermolecular forces of the amphiphiles have been effected by the addition of polar and non-polar materials to the soap. In particular, we have modified the intermolecular forces within the ionic portion of the amphiphiles by the

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addition of lead oxide to lead dodecanoate[3]. It was observed that the addition of the smallest amount of lead oxide ($X_{PbO} = 0.005$) caused the disappearance of the V_2 phase and that the G phase broke down into three structurally different G forms. Similarly, we have modified the intermolecular forces within the lipophilic portion of the amphiphiles by the addition of hendecane to lead dodecanoate[3]. As in the case of the lead dodecanoate/lead oxide system, the addition of hendecane suppressed the formation of the V_2 phase and a new phase appeared at the high temperature region. The R theory was found to be adequate in explaining these observations.

It is the purpose of the present study to examine the effect of simultaneous perturbations of the intermolecular forces both within the ionic and the lipophilic portions of the amphiphiles on mesophase formation. This has been done by examining the effect of the addition of dodecanoic acid on the thermodynamics of mesophase formation of pure lead dodecanoate using quantitative DTA. In the lead dodecanoate/dodecanoic acid system the carboxylate head groups of the acid are incorporated into the ionic portion of the soap while the hydrocarbon chains of the acid are incorporated into the lipophilic portion of the soap.

EXPERIMENTAL

The preparation and purification of lead dodecanoate has been described elsewhere[4]. Dodecanoic acid was a B.D.H. product and was recrystallised from ethanol before use. The mixtures were made by weighing the appropriate amounts of the compounds into a quick-fit conical flask. The flask was then evacuated and the mixture melted on a hot plate. The acid dissolved readily in lead dodecanoate.

DTA measurements were made on a Mettler TA 2000 system. About 15–20 mg of the sample was weighed on a Cahn electrobalance, sealed into the standard aluminium crucibles of the Mettler TA 2000 analyser and scanned at a heating rate of 1 K min^{-1}. Measurements were performed in duplicate on at least four separate samples. The equipment was calibrated with indium metal and peak areas were measured by cutting and weighing.

Optical observations were made on a hot stage polarising microscope. IR spectra were recorded as KBr pellets on a pye unicam SP 1100 IR spectrophotometer.

RESULTS

Typical DTA curves of the mixtures are shown in Fig. 1. The peaks are labelled A, B, C and D. Detailed examination of the DTA peaks together with optical observations on a hot stage polarising microscope allowed the construction of a phase diagram for the system (Fig. 2). The phase diagram for the low acid concentration region has been expanded in Fig. 3.

It can be observed that the addition of up to 0.01 mole fraction of acid to lead dodecanoate does not cause the disappearance of the V_2 phase (peak D). However, the V_2 phase disappeared at higher acid concentrations. At 0.06 mole fraction of acid

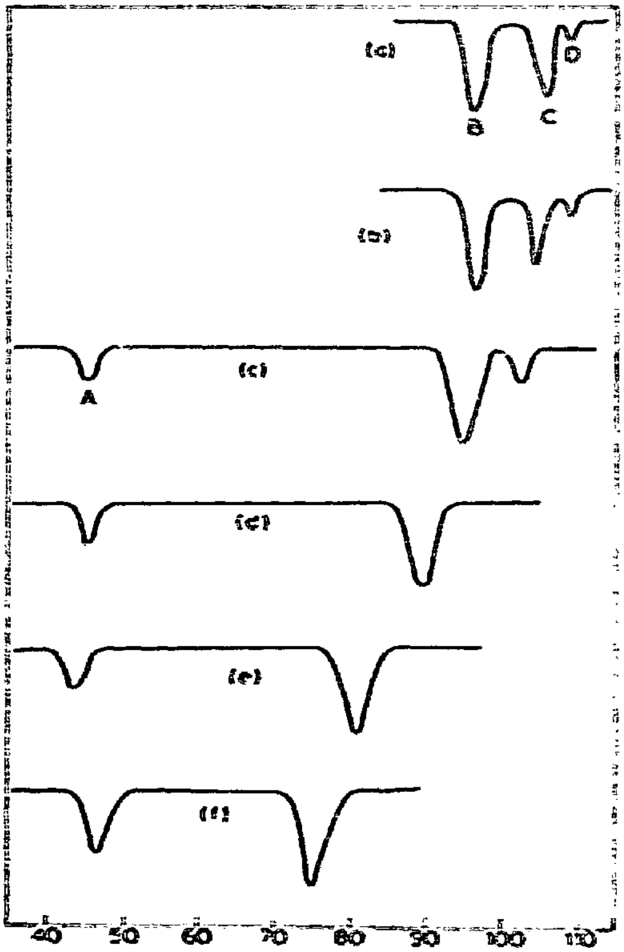

Fig. 1. DTA curves for $Pb(CH_3(CH_2)_{10}CO_2)_2$–$CH_3(CH_2)_{10}COOH$ mixtures.
(a) Pure $Pb(CH_3(CH_2)_{10}CO_2)_2$; (b) $X_{CH_3(CH_2)_{10}COOH} = 0.011$;
(c) $X_{CH_3(CH_2)_{10}COOH} = 0.102$; (d) $X_{CH_3(CH_2)_{10}COOH} = 0.299$;
(e) $X_{CH_3(CH_2)_{10}COOH} = 0.507$; (f) $X_{CH_3(CH_2)_{10}COOH} = 0.756$.
Scan speed; 1 K min^{-1}. Ordinate: ΔT. Abscissa: temperature (°C)

and above, a new peak appeared at the low temperature region. This is labelled peak A in Fig. 1. Optical observation suggests that this phase change is a solid → solid transition. It is interesting to note that the temperature of this phase transition is very close to the melting point of the acid.

At 0.18 mole fraction of acid and above, the *G* phase disappeared and the second solid phase passed directly into the liquid. It is noteworthy that while the temperatures of the solid I → solid II phase transition were essentially constant, the transition temperatures into the isotropic liquid decreased with increase in acid concentration.

The data on enthalpy and entropy changes for the different phase transitions are presented in Table 1. The values are calculated per mole of hydrocarbon chain present in the mixture since the major contribution to the entropy change is the disordering of the hydrocarbon chains. The errors in these values are within ± 2%.

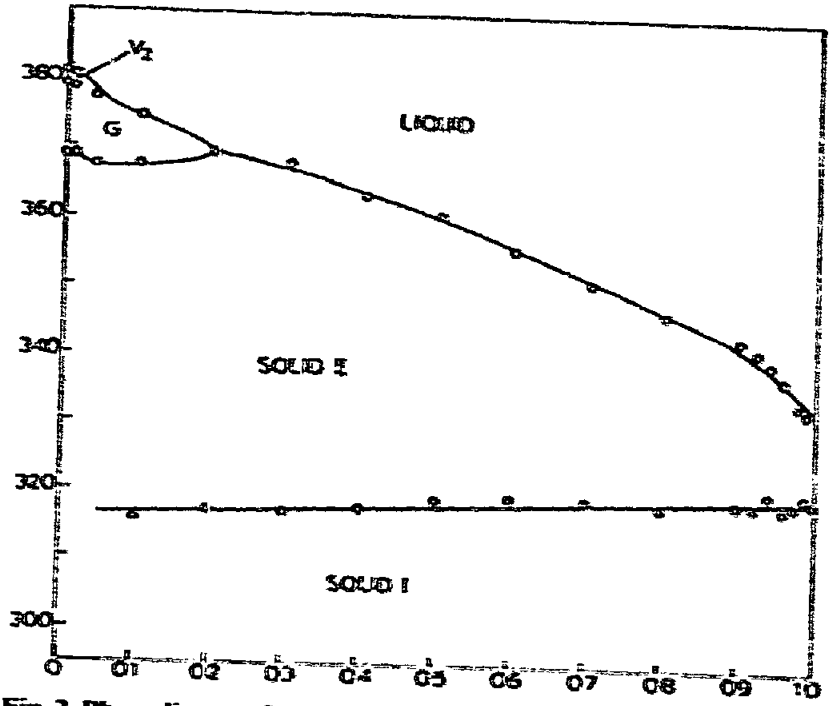

Fig. 2. Phase diagram for Pb(CH$_3$(CH$_2$)$_{10}$CO$_2$)$_2$/CH$_3$(CH$_2$)$_{10}$COOH system. Ordinate: temperature (K). Abscissa: $X_{CH_3(CH_2)_{10}COOH}$.

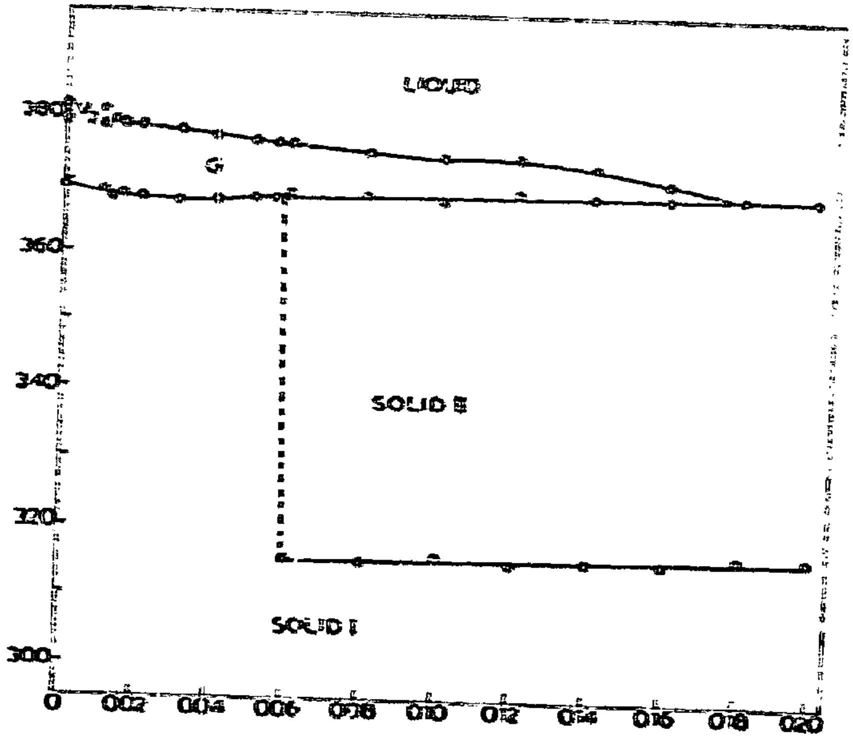

Fig. 3. Phase diagram for Pb(CH$_3$(CH$_2$)$_{10}$CO$_2$)$_2$/CH$_3$(CH$_2$)$_{10}$COOH system in the region of low concentration of CH$_3$(CH$_2$)$_{10}$COOH.
Ordinate: temperature (K). Abscissa: $X_{CH_3(CH_2)_{10}COOH}$.

TABLE 1

THERMODYNAMIC DATA FOR PHASE CHANGES IN THE SYSTEM LEAD DODECANOATE/DODECANOIC ACID

Phase change	*A*		*B*		*C*		*D*			
$X_{\text{Dodecanoic acid}}$	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH_{Total}	ΔS_{Total}
0	—	—	24.2	66.0	14.8	39.4	0.5	1.3	39.5	106.7
0.011	—	—	24.1	65.4	14.7	38.9	0.4	1.1	39.2	105.4
0.019	—	—	24.6	66.8	14.3	37.8	—	—	38.9	104.6
0.041	—	—	24.5	66.7	14.1	37.4	—	—	38.6	104.1
0.102	1.3	4.1	28.4	77.1	9.6	25.6	—	—	39.3	106.8
0.159	2.6	8.3	30.7	83.4	4.5	12.1	—	—	37.8	103.8
0.199	3.5	11.0	34.2	92.7	—	—	—	—	37.7	103.7
0.252	5.7	18.0	32.2	87.3	—	—	—	—	37.9	105.3
0.301	5.3	16.7	32.2	87.5	—	—	—	—	37.5	104.2
0.349	8.7	27.4	27.9	76.3	—	—	—	—	36.6	103.7
0.399	8.4	26.4	28.4	78.1	—	—	—	—	36.8	104.5

ΔH values are expressed in kJ (mole of hydrocarbon chain)$^{-1}$ while ΔS values are expressed in J K^{-1} (mole of hydrocarbon chain)$^{-1}$. Errors in the values are within ± 2%.

DISCUSSION

It has been shown that the concepts of the *R* theory are useful, at least in qualitative terms, in the interpretation of phase transitions in amphiphilic mesophases[3]. The *R* theory interprets the structures of mesophases in terms of a balance between the intermolecular forces which tend to make the amphiphilic portion of the lamellae ($\overline{\text{C}}$) become convex towards its lipophilic environment ($\overline{\text{O}}$) and those tending to make it become convex towards its polar environment ($\overline{\text{W}}$). According to Winsor[2], the ratio, *R*, of these tendencies can be expressed as

$$R \rightarrow [(A_{\overline{\text{C}}\overline{\text{O}}} - A_{\overline{\text{O}}\overline{\text{O}}})/(A_{\overline{\text{C}}\overline{\text{W}}} - A_{\overline{\text{W}}\overline{\text{W}}})]$$

where $A_{\overline{\text{X}}\overline{\text{Y}}}$ is the energy of interaction per unit area of interface at the $\overline{\text{X}}/\overline{\text{Y}}$ interface. For a given $\overline{\text{O}}$ and $\overline{\text{W}}$, *R* will increase with the ratio $A_{\overline{\text{C}}\overline{\text{O}}}/A_{\overline{\text{C}}\overline{\text{W}}}$.

Our results on the lead dodecanoate/dodecanoic acid system can be rationalised in terms of the *R* theory. Addition of small quantities of dodecanoic acid ($X_{\text{acid}} \leqslant 0.01$) to pure lead dodecanoate does not significantly alter the intermolecular attractions responsible for $A_{\overline{\text{C}}\overline{\text{O}}}$ and $A_{\overline{\text{C}}\overline{\text{W}}}$. Thus the ratio $A_{\overline{\text{C}}\overline{\text{O}}}/A_{\overline{\text{C}}\overline{\text{W}}}$ remains essentially the same as in the pure soap and hence the phase sequence in the system lead dodecanoate/lead dodecanoic acid at very low acid concentration remains the same as for the pure soap, i.e. crystal → $G_{(\text{smectic})}$ → $V_{2(\text{cubic isomorphous})}$ → liquid. However, at higher concentrations of the acid the intermolecular attractions responsible for $A_{\overline{\text{C}}\overline{\text{O}}}$ become bigger due to increased van der Waals forces between the hydrocarbon chains. On the other hand the intermolecular attractions responsible for $A_{\overline{\text{C}}\overline{\text{W}}}$ are not significantly different from those in the pure soap since the carboxylate head groups of the acid are in an environment of similar ions, i.e. carboxylate head groups of the soap. It is assumed here that the repulsive forces between the hydrogen ions of the acid and the lead ions of the soap make little contribution to A_{cw}. The result is that the ratio, R, will tend to increase and the stability of the lamellar (G) phase could be maintained only by some internal rearrangement that would restore the value of R to unity. Beyond the limits where such rearrangement is energetically possible, the phase breaks down thus passing into the isotropic liquid. At high acid concentration ($X_{acid} \geqslant 0.18$) the ratio R becomes much greater than unity thus making the G phase unstable and the solid phase passes directly into the liquid phase.

One aspect of our results that is worthy of note is that the V_2 phase persists in lead dodecanoate/dodecanoic acid mixtures containing up to about 0.01 mole fraction of the acid. Also, the temperatures of the phase transitions in these mixtures are similar to those in the pure soap. This result contrasts with the behaviour of the lead dodecanoate/lead oxide and lead dodecanoate/hendecane systems where the smallest addition of lead oxide or hendecane resulted in the disappearance of the V_2 phase. The practical implication of this result is that DTA technique is not very useful in detecting acid contaminants in metal carboxylates when the acid concentration is extremely low, unlike the case of metal oxide contaminants. It is also important to note that the IR spectra of the soap/acid mixtures containing up to 0.01 mole fraction of acid, do not show the characteristic acid peak at 1700 cm^{-1}, which again demonstrates the limitation of IR spectroscopy in detecting the presence of excess acid in metal carboxylates when the acid concentration is very low.

Inspection of the phase diagram in Fig. 3 shows that a new phase transition occurs on the low temperature side at about 0.06 mole fraction of acid and above. The temperatures of this phase transition are very close to the melting point of pure dodecanoic acid. Optical observation suggests that this phase change is a solid → solid transition as the new phase is not readily subject to mechanical deformation. The enthalpy change accompanying this phase transition (Table 1) increases roughly with increase in acid concentration. It is therefore tempting to speculate that this new phase change corresponds to the melting of excess acid that is not incorporated into the amphiphilic system. However, careful optical observation clearly showed that there was no melting and that the phase change is a solid → solid transformation.

One notable feature of the phase diagram shown in Fig. 2 is the apparent lack of a eutectic point. In a DTA study of the liquid–liquid and liquid–solid equilibria of some binary systems of alkali metal stearates and some fatty acids[5], eutectic points were observed with eutectic compositions very close to 1.0 mole fraction of the acid. For example in the sodium stearate/succinic acid system, the eutectic point occurred at 0.989 mole fraction of succinic acid while in the potassium stearate/succinic acid system a eutectic point occurred at 0.994 mole fraction of the acid. It is noteworthy that these authors did not present data on any binary system containing a metal carboxylate and its corresponding fatty acid as has been done in the present study.

The most striking feature of the quantitative results summarised in Table 1 is the approximately constant value of the total enthalpy change as well as the total

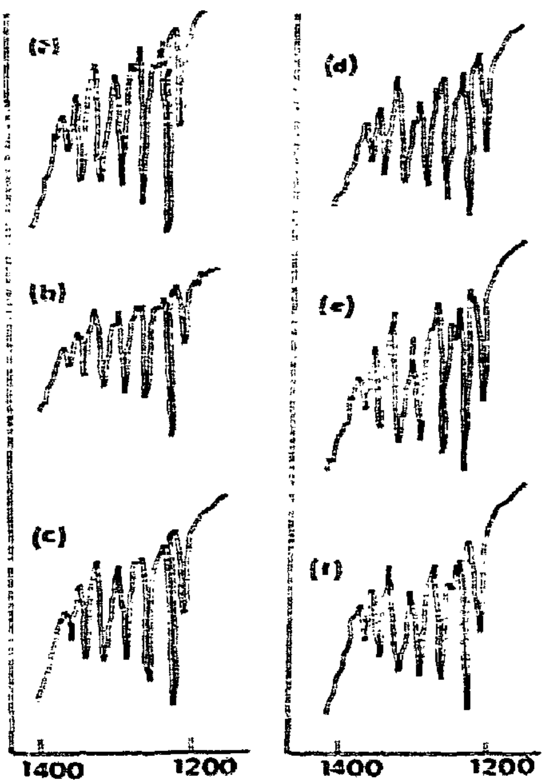

Fig. 4. IR spectra of $Pb(CH_3(CH_2)_{10}CO_2)_2$ $CH_3(CH_2)_{10}COOH$ mixtures in the CH_2 rocking region. Abscissa: frequency (cm^{-1}).
(a) Pure $Pb(CH_3(CH_2)_{10}CO_2)_2$; (b) $X_{CH_3(CH_2)_{10}COOH} = 0.011$;
(c) $X_{CH_3(CH_2)_{10}COOH} = 0.100$; (d) $X_{CH_3(CH_2)_{10}COOH} = 0.199$;
(e) $X_{CH_3(CH_2)_{10}COOH} = 0.301$; (f) $X_{CH_3(CH_2)_{10}COOH} = 0.355$.

entropy change for all the compositions studied. This implies that addition of dodecanoic acid to lead dodecanoate does not alter the state of order of the hydrocarbon chains either in the solid or liquid phase. This result contrasts with our earlier results on the lead dodecanoate/lead oxide and lead dodecanoate/hendecane systems[3] where a steady decrease in the total entropy change with increase in lead oxide or hendecane concentration was observed. We demonstrated that the decrease in the total entropy change with increase in concentration of hendecane or lead oxide was as a result of greater order of the hydrocarbon chains in the liquid phase of the mixtures.

In an attempt to show that the degree of order of the hydrocarbon chains in lead dodecanoate is not altered in the crystal phase on the addition of dodecanoic acid IR spectra of the mixtures were recorded as KBr pellets between 1400 and 1100 cm^{-1}. It has been reported that in this region a series of bands occur as a result of the rocking of the CH_2 groups in the crystal lattice[6,7]. These bands broaden on heating as the chains are now free to twist[8]. Thus if addition of dodecanoic acid causes a loosening of the packing of the hydrocarbon chains thus resulting in increased disorder, a broadening of these bands would be observed. Figure 4 shows the IR spectra of some of the mixtures and the pure soap between 1100 and 1400 cm^{-1}.

It is clear from this figure that there is no broadening of the bands in this region in any of the mixtures. Thus, it seems established that addition of dodecanoic acid to lead dodecanoate does not alter the degree of order of the hydrocarbon chains either in the crystal or in the liquid phase. This probably suggests that the hydrocarbon chains of the acid are arranged in the crystal lattice and in the liquid phase in the same manner as the hydrocarbon portion of the dodecanoate anion.

A more sensitive method of demonstrating increased order or disorder in the crystal or liquid phase of the mixtures is to measure the specific heats of the mixtures both in the crystal and liquid phases and compare the values with those calculated on the basis of simple additivity, as was done for the lead dodecanoate/lead oxide system[3]. An attempt was made to measure the specific heats of the mixtures by the method of baseline displacement using the DTA equipment. Unfortunately, we were unable to obtain reproducible values.

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