Thermochimica Acta, 19 (1977) 275–285
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

PROPERTIES OF MOLTEN CARBOXYLATES
PART 5. A QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS STUDY OF MESOPHASE FORMATION IN THE SYSTEMS LEAD(II)DODECANOATE/LEAD(II) OXIDE AND LEAD(II)DODECANOATE/HENDECANE

S. O. ADEOSUN, W. J. SIME AND S. J. SIME*
Chemistry Department, University of Ife, Ile-Ife, Nigeria (Africa)

(Received 26 August 1976)

ABSTRACT

Measurements have been made of the temperatures and enthalpy changes of phase transitions in the systems lead dodecanoate/lead oxide and lead dodecanoate/hendecane. The data have been discussed in terms of the *R* theory of amphiphylic mesophases. The concepts of the *R* theory are shown to be useful in the interpretation of phase transitions in molten carboxylate systems.

INTRODUCTION

In a previous paper in this series[1] data were presented for the thermodynamics of phase transitions of the lead(II) n-alkanoates. Liquid crystal phases were found between the crystalline and amorphous liquid phases, and, following a suggestion of Winsor[2], an attempt was made to classify these phases in terms of the *R* theory of aqueous amphiphylic mesophases, as opposed to the quasi-crystalline structures suggested from X-ray diffraction measurements for some other divalent metal carboxylates[3,4].

The *R* theory interprets the structures of mesophases in terms of a balance between the intermolecular forces tending to make the amphiphylic portion of the lamella ($\bar{C}$) become convex toward its lipophylic environment ($\bar{O}$) and those tending to make it become convex towards its polar environment ($\bar{W}$). The ratio of these tendencies, *R*, can be written, following Winsor's notation[1], as

$$R \rightarrow [(A\bar{C}\bar{O} - A\bar{O}\bar{O})/(A\bar{C}W - A\bar{W}\bar{W})]$$

where $A\bar{X}\bar{Y}$ represents the energy of interaction per unit area of interface at the $\bar{X}/\bar{Y}$ interface. As originally proposed, the *R* theory was held to be applicable only to 'fused' mesophases in which the amphiphylic layers were 'labile'[2]. There has been some discussion in the literature as to whether the polar

---

*To whom all correspondence should be addressed.

groups are 'fused' or 'crystalline' in the mesophases of pure carboxylates, and hence, as to whether the *R* theory is applicable to them[1]. However, this appears to be more a problem of semantics than of science. The concept of 'lability' of a phase is difficult to quantify. Thermodynamically a phase is stable until the free energy of the phase change is negative. This free energy is a direct function of the strength and nature of the intermolecular forces within the phase. The *R* theory, in considering the effects of composition and temperature on these forces, and the dominance of one or the other type of interaction within an amphiphylic system, would seem to be useful, at least in qualitative terms, in the discussion of the structures of all amphiphylic mesophases.

It is the purpose of this work to test the applicability of the concepts of the *R* theory to non-aqueous carboxylate phases by making systematic perturbations of the intermolecular forces by the addition of polar and non-polar materials as structurally similar to the soap as possible. In particular, using lead dodecanoate as the carboxylate, $(ACW-AWW)$ has been decreased by the dissolution of lead(II)oxide, and $(ACO-AOO)$ has been increased by the addition of hendecane (the hydrocarbon of the same chain length as the hydrocarbon portion of dodecanoic acid). We have studied the thermodynamics of mesophase formation as a function of composition using quantitative DTA.

EXPERIMENTAL

The preparation and purification of the carboxylates have been described elsewhere[5]. Lead(II)oxide was Hopkin–Williams general purpose grade and was dried under vacuum at 393 K for 14 h and stored in a dessicator over silica gel before use. Hendecane was prepared by the following reaction sequence.

$$\mathrm{CH_3(CH_2)_{10}CO_2^- + Ag^+ \rightarrow CH_3(CH_2)_{10}CO_2Ag} \qquad \text{(A)}$$

$$\mathrm{CH_3(CH_2)_{10}CO_2Ag + Br_2 \rightarrow CH_3(CH_2)_9CH_2Br + AgBr + CO_2} \qquad \text{(B)}$$

$$\mathrm{CH_3(CH_2)_9CH_2Br + Mg \rightarrow CH_3(CH_2)_9CH_2MgBr \xrightarrow{[H^+]} CH_3(CH_2)_9CH_3} \qquad \text{(C)}$$

The experimental procedures used for stages A and B were exactly as described by Luttringhaus and Schade[6]. Standard Grignard procedures were used for stage C[7]. The final product was distilled at atmospheric pressure and the fraction collected between 460 and 475 K (literature b.p. = 468 K). Both infrared and n.m.r. spectra were consistent with the desired product.

The mixtures were made by weighing out the desired amounts into small flasks fitted with quick-fit stoppers with a vacuum tap. In the case of the lead oxide mixtures the flasks were evacuated before melting to prevent decomposition of the soap. It was often necessary to cool, grind and remelt the mixtures several times before all the lead(II)oxide would dissolve. Up to

0.3 mole fraction of lead oxide could be dissolved in the soap without causing appreciable decomposition. In the case of the hendecane mixtures the flasks were not evacuated to prevent the hendecane from distilling to the cooler sides of the flask. However, hendecane dissolved easily in the lead dodecanoate and no visible decomposition of the soap occurred.

DTA measurements were made using the Mettler TA2000 system, calibrated with indium metal. Samples of about 10 to 20 mg of the soap mixtures were weighed on a Cahn electrobalance and sealed in the standard aluminium crucibles. Samples were premelted and always left overnight before calorimetric runs. The scan speed was 0.5 K $\min^{-1}$ except for the broad phase change (F) for which 3 K $\min^{-1}$ was used. Measurements were performed at least in duplicate on at least two separate samples. Peak areas were measured by cutting out and weighing.

Optical observations were made on an improvised polarising microscope fitted with a Koffler block heating stage. IR spectra were recorded as KBr discs on a Perkin-Elmer 457 grating spectrophotometer.

RESULTS OF THE $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$ SYSTEM

Typical DTA curves for the mixtures are presented in Fig. 1. The following general points are noteworthy.

(a) The addition of even the smallest amount of PbO ($X_{PbO} = 0.005$) caused the disappearance of the V_2 phase of the pure soap.

(b) The addition of PbO caused the appearance of two new phases within the normal G phase range (peaks C and D). Optical examination shows no visible difference in texture between these phases. However, attempts to move the cover slips with respect to each other showed the lower temperature phase to be considerably more viscous and less easily deformable.

(c) The addition of PbO up to $X_{PbO} = 0.14$ caused a decrease in the temperature of the G to liquid phase transition (peak E).

(d) Above $X_{PbO} = 0.16$ a new phase appears at higher temperatures which changes to the liquid phase over a relatively wide temperature range (peak F). Optical examination of this phase under crossed polarisers showed long rod-like batonnets.

Detailed examination of the DTA curves allowed the construction of a phase diagram as shown in Fig. 2. It is difficult to decide on the precise behaviour of the lower temperature phases (corresponding to phase changes B, C and D) at higher PbO composition. As seen below the heat of these transitions becomes small and irreproducible, and so hard to detect. However, optical observation does show a phase with a G texture at about 370 K, and it seems probable that these phases can be extrapolated as shown in Fig. 2. Heat and corresponding entropy values for the various changes are shown in Table 1. As the major contribution to the entropy change is the dis-

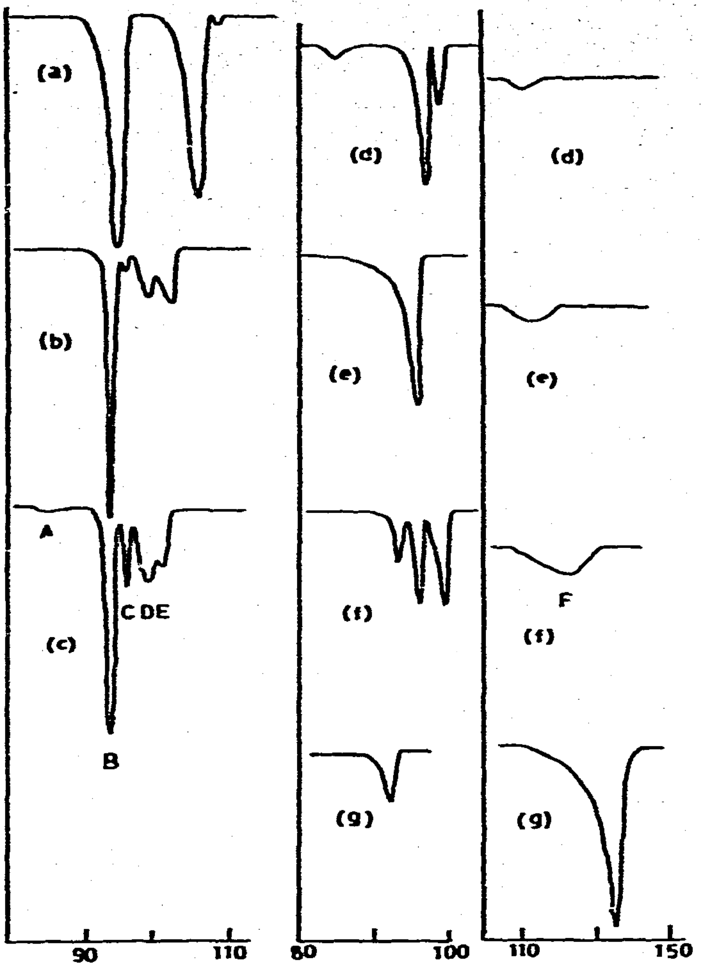

Fig. 1. DTA curves for $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$ mixtures. (a) Pure $Pb(CH_3(CH_2)_{10}CO_2)_2$; (b) $X_{PbO} = 0.051$; (c) $X_{PbO} = 0.098$; (d) $X_{PbO} = 0.148$; (e) $X_{PbO} = 0.183$; (f) $X_{PbO} = 0.213$; (g) $X_{PbO} = 0.296$. The region between 80 and 110 °C was scanned at 0.5 K min^{-1}; that between 100 and 150°C, at 5 k min^{-1}. Abscissa: temperature (°C).

ordering of the aliphatic chain, these values are quoted per mole of hydrocarbon chain present in the mixture. The values for the individual transitions A, B, C and D were not reproducible from sample to sample or on reruns on the same sample, as is demonstrated by their large standard errors. However, the sum of heats was reproducible, and this is also shown in Table 1. Solid and liquid specific heats, measured by the method of baseline displacement, are shown in Fig. 5.

DISCUSSION

The results of the optical examination lead us to propose that the new phases occurring at low X_{PbO} are structurally different G phases. The occur-

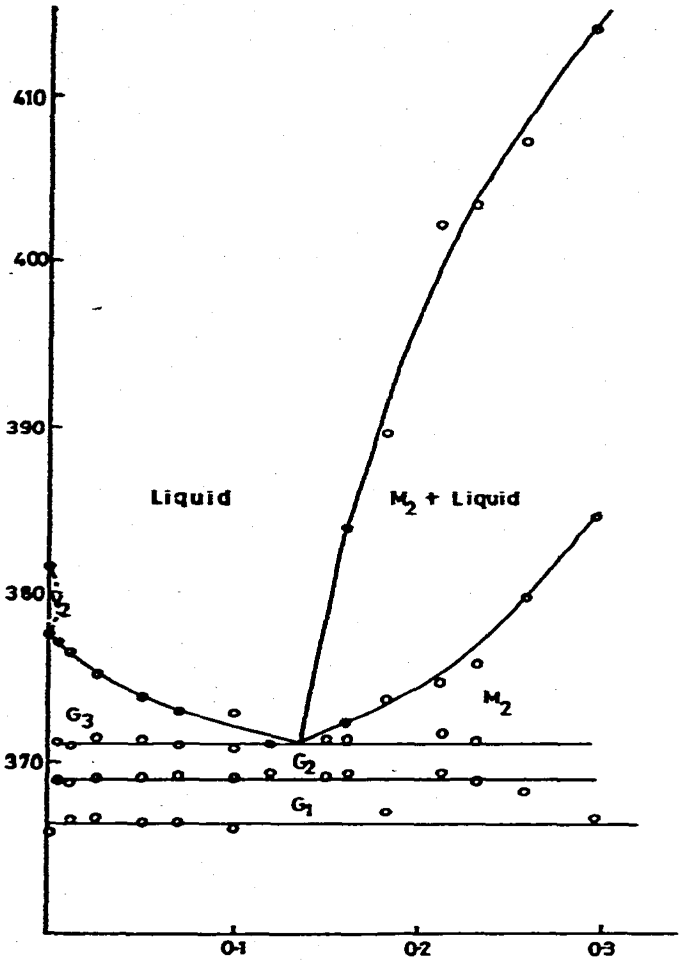

Fig. 2. Phase diagram for $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$. Abscissa: X_{PbO}; ordinatie: T(K).

TABLE 1

THERMODYNAMICS OF PHASE TRANSITIONS IN THE SYSTEM $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$
ΔH(kJ mol^{-1} hydrocarbon); ΔS(J K^{-1} mol^{-1} hydrocarbon).

Phase change	*A*		*B*		*C*		*D*	
X_{PbO}	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
0.0297	1.7±1.9	4.6	12.3±8.2	34	6.5±4.6	18	2.7±0.6	7.3
0.0512	1.7±1.5	4.6	11.5±5.4	32	6.5±3.3	18	4.0±0.4	10.7
0.0711	2.1±2.1	5.9	6.1±4.4	17	9.0±3.8	24	4.8±0.8	13
0.0983	3.8±1.3	10.5	2.7±3.8	7.5	10.0±2.9	27	5.9±1.9	16
0.1216	4.4±0.4	12.3	—	—	14.6±2.1	40	5.4±1.7	15
0.1480	1.5±1.0	4.2	2.3±3.1	6.3	13.2±3.3	36	2.5±2.5	6.7
0.1618	2.7±0.8	7.5	1.5±2.1	4.0	11.7±1.5	32	4.8±1.3	13
0.2126	2.9±0.4	8.2	—	—	12.3±0.4	33	0.6±0.4	1.7
0.2323	2.1±0.8	5.9	—	—	9.8±1.5	27	—	—
0.2576	1.5±1.9	4.2	0.8±0.4	2.3	7.9±0.6	22	—	—
0.2956	0.6±0.6	1.7	0.4±0.4	1.0	3.3±0.8	9	—	—

TABLE 1 *(continued)*

Phase change X_{PbO}	*E* ΔH	ΔS	*F* ΔH	ΔS	*Total* $A+B+C+D$ ΔH	ΔS	*Grand total* ΔH	ΔS
0.0297	9.6 ±0.3	26	—	—	23 ±2	63	33±2	89
0.0512	7.8 ±0.3	21	—	—	24 ±2	64	31±1	85
0.0711	5.6 ±0.7	15	—	—	22 ±3	60	28±3	74
0.0983	4.4 ±1.9	12	—	—	22 ±2	61	27±1.9	73
0.1216	0.08±0.12	0.2	—	—	24 ±0.6	67	24±0.6	67
0.1480	—	—	—	—	19 ±2.5	53	19±1	53
0.1618	—	—	0	0	21 ±1	56	20±1	56
0.2126	—	—	1.7±0.2	4.4	16 ±0.5	43	18±0.2	48
0.2323	—	—	3.6±0.8	9.0	12 ±2	32	15±3	41
0.2576	—	—	3.4±0.2	8.6	11 ±2	28	14±1	37
0.2956	—	—	6.3±0.4	15	4.6±0.6	12	11±0.6	27

rence of such phases has been predicted by Winsor[2]. The poor reproducibility of the heats of the individual phase changes, whilst the total remains reproducible is unusual. It may imply that owing to kinetic factors not all the material in the solid phase for example undergoes the transition to the first *G* phase, some of it remaining and undergoing a phase transition directly to the second *G* phase. Thus the total entropy change for solid to liquid remains constant, but the different degrees of conversion at different stages give rise to the irreproducibility of the individual values.

A striking feature of the quantitative results is the decrease in the total enthalpy change for the conversion of solid to liquid per mole of hydrocarbon chain (Fig. 3). This implies that either there is considerable disorder of the carbon chains in the solid phase of the mixtures, or that they are much more ordered in the liquid phases. To obtain a qualitative feel for the amount of disorder of the carbon chain in the solid phase, IR spectra were recorded as KBr discs between 1400 and 1000 cm^{-1}. In this region, a series of bands occurs which have been assigned to the rocking of the CH_2 groups in the crystal lattice[8,9]. It is well established that, on heating, these bands broaden as the chains become free to twist and flex[11]. Thus, if addition of PbO caused considerable loosening of the packing of the hydrocarbon chain, resulting in increased rotational disorder, broadening of these bands would be expected. As can be seen from Fig. 4 slight broadening occurs at room temperature. A more sensitive test of increased freedom of the hydrocarbon chain is the measurement of the specific heats of the samples. Figure 5 shows the specific heat per mole of mixture as a function of PbO content. The solid line corresponds to the predictions of simple additivity. It is seen that there is a slight increase above additivity for the solid phase, but hardly sufficient to account for the considerable changes in $\Delta H(c \rightarrow l)$. The occurrence of the broad transition (A) at around 358 K may indicate some premelting disordering of the hydrocarbon

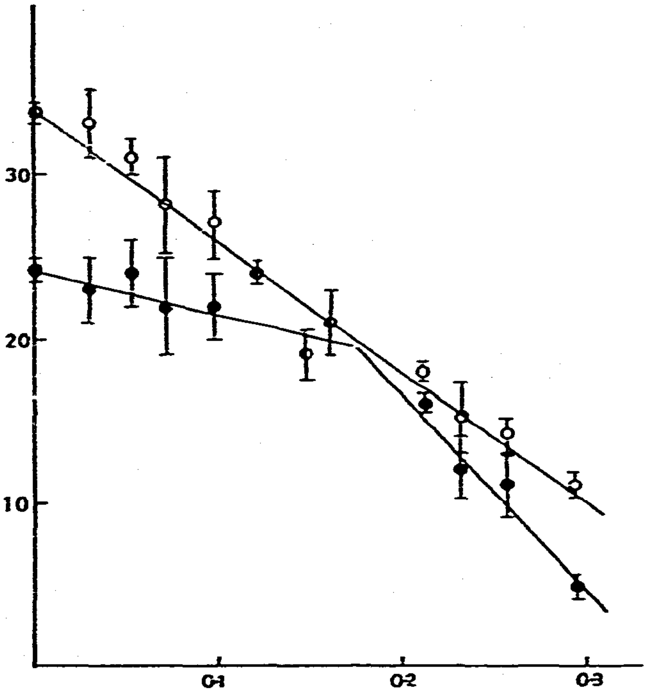

Fig. 3. Heats of phase changes in the $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$ system. Abscissa: X_{PbO}; ordinate: ΔH(kJ(mole of hydrocarbon chain)$^{-1}$). ● Total ΔH for peaks A, B, C and D; ◐ superposition of the two summations; ○ total for all phase changes.

chain caused by a disturbance of the lattice structure resulting from the addition of PbO, but the value of the heat for this transition is included in the data in Fig. 3. It thus seems established that addition of PbO leads to considerable ordering of the hydrocarbon chain in the liquid phase itself.

It is tempting to tentatively assign the new phase formed at higher temperatures and lead oxide compositions as an M_2 phase, i.e., a regular array of infinitely extended cylindrical micelles with polar groups pointing inwards surrounded by 'molten' hydrocarbon tails. The batonnets observed are similar to those recorded for the M phase by Rosevear[12], but this is not sufficient evidence for complete identification. The change from this phase to the liquid phase is not sharp and takes place over a range of temperatures, particularly at lower PbO compositions. This coexistence of phases is a common occurrence in aqueous amphiphylic systems[2]. If this identification of this phase is correct, it leads to an interesting picture of the liquid phase as changing from small, essentially spherical micelles in the pure lead dodecanoate (similar to the V_2 phase preceding melting[1]) to long cylindrical micelles with the addition of PbO. This is consistent with the decrease in entropy of fusion, as it is probable that a cylindrical arrangement must place greater spacial restrictions on the first few carbon atoms of the aliphatic chain than a spherical arrangement. (A cylindrical micellar structure for the molten cadmium carboxylates has been

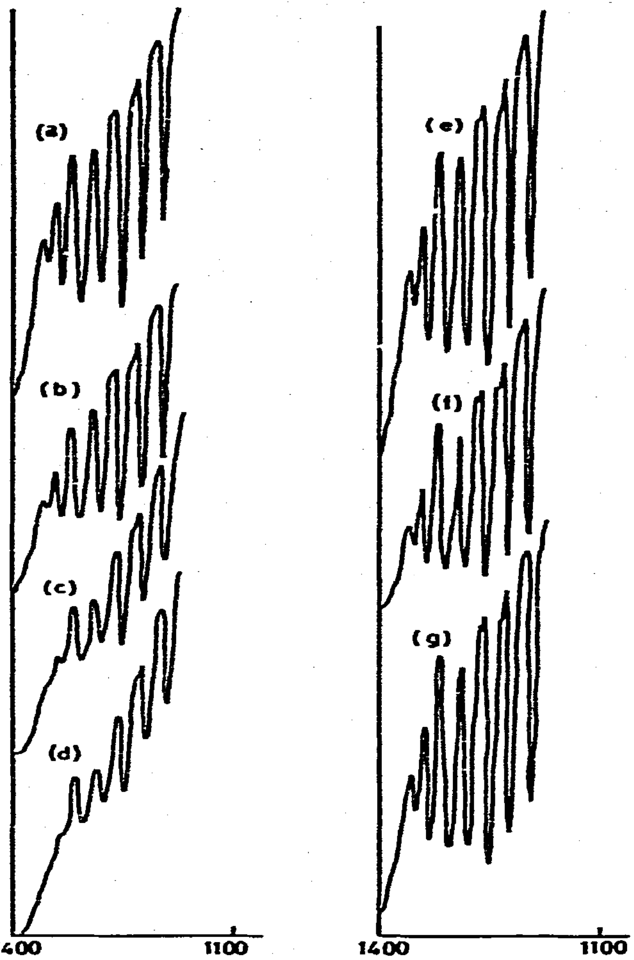

Fig. 4. IR spectra in the CH$_2$ rocking region. Abscissa: frequency (cm^{-1}). (a) Pure Pb(CH$_3$(CH$_2$)$_{10}$-CO$_2$)$_2$; (b) $X_{PbO}=0.1$; (c) $X_{PbO}=0.2$; (d) $X_{PbO}=0.3$; (e) $X_{CH_3(CH_2)_{14}CH_3}=0.1$; (f) $X_{CH_3(CH_2)_{14}CH_3}=0.2$; (g) $X_{CH_3(CH_2)_{14}CH_3}=0.3$.

proposed based upon conductance, viscosity and density data[10]. Similar measurements are planned for the PbO/Pb(CH$_3$(CH$_2$)$_{10}$CO$_2$)$_2$ system.)

The qualitative concepts of the *R* theory are easily applicable to the phase sequences and thermodynamic data observed. Addition of PbO to the soap increases the strength of the ionic interactions inside the polar part of the lamellae of the *G* phase tending to make them concave toward the polar region. Thermal disruption of the interaction of the hydrocarbon chains decreases the counterbalancing tendency, changing the value of *R* from unity, and the *G* phase breaks down at lower temperatures. The internal rearrangements to try and maintain a value of $R = 1$ lead to the formation of new distinct laminar *G* phases. The strong long-range ionic interactions brought about by the lead oxide will tend to make larger micellar aggregates stable in the liquid phase, and, as noted above, the formation of these aggregates will place spacial res-

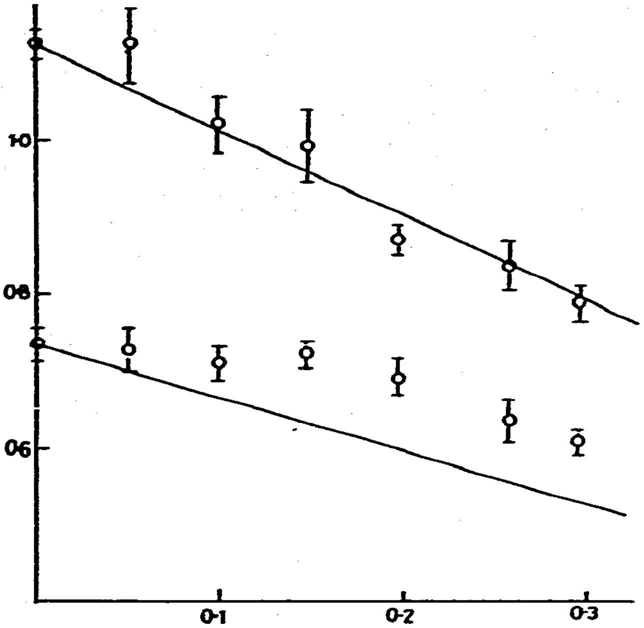

Fig. 5. Specific heats for $PbO/Pb(CH_3(CH_2)_{10}CO_2)_2$ mixtures. Upper line, liquid at 323 K; lower line, solid at 453 K; solid lines, the prediction of simple additivity; abscissa: X_{PbO}; ordinate: C_p(kJ(mole mixture)$^{-1}$ K^{-1}).

trictions on the first few carbon atoms of the chain, lowering the entropy of fusion, particularly of the G to liquid transition, as is observed. At higher PbO compositions the increased ionic interactions within the polar region are not thermally disrupted until higher temperatures, and the indefinitely extended micelles form a new M_2 phase. Increasing temperature decreases the average micellar size and the M_2 phase breaks down gradually to the liquid phase.

RESULTS OF THE $Pb(CH_3(CH_2)_{10}CO_2)_2/CH_3(CH_2)_9CH_3$ SYSTEM

The following observations were noteworthy.

(a) As in the case of the PbO system, the addition of hendecane suppressed the formation of the V_2 phase.

(b) The addition of hendecane caused the appearance of a new phase change at approximately 368.5 K (corresponding to phase change C in the PbO system).

(c) The temperature of the G to liquid phase transition decreased with increasing mole fraction of hendecane, reaching 369 K at $X = 0.3$. At this composition the crystal to G phase transition was broadening, indicating the formation of a mixture rather than a single phase, and no higher compositions were studied.

Heat and corresponding entropy values for the phase changes are reported in Table 2. As the division of the enthalpy between phase changes B and

TABLE 2

THERMODYNAMICS OF PHASE TRANSITIONS
IN THE $Pb(CH_3(CH_2)_{10}CO_2)_2/CH_3(CH_2)_9CH_3$ SYSTEM

$X_{hendecane}$	Total $B+C$		E	
	ΔH(kJ mol^{-1})	ΔS(J K^{-1} mol^{-1})	ΔH(kJ mol^{-1})	ΔS(J K^{-1} mol^{-1})
0	24.1±0.5	66	14.9±0.3	40
0.047	23.6±0.3	65	14.4±0.2	39
0.096	23.7±0.3	65	13.7±0.4	38
0.155	23.5±0.3	64	13.2±0.1	36
0.206	23.8±0.3	65	10.6±0.3	29
0.257	24.3±0.5	67	10.5±0.3	29
0.303	27.8±0.5	76	4.7±0.5	13

C were irreproducible (*B* usually small), only the sum has been tabulated. The data have been presented per mole of hydrocarbon chain present, regardless of whether it is as hendecane or as the dodecanoate ion.

DISCUSSION

The most striking feature of the quantitative results is that, with the exception of the highest concentration mixture, the enthalpy of the crystal to *G* phase transition per mole of hydrocarbon chain remains essentially constant at the value for the pure carboxylate. This implies that the hendecane chain is arranged in the crystal lattice and in the lamellae of the *G* phase of the soap in the same manner as the hydrocarbon portion of the dodecanoate anion. Complete ordering of the hydrocarbon chain in the solid is further supported by the lack of broadening of the CH_2 rocking modes for these mixtures (Fig. 4). The gradual decrease in enthalpy of the *G* to liquid transition implies, as in the case of the lead oxide system, that the hydrocarbon chain in the liquid is increasingly ordered with increasing hendecane composition. In terms of the *R* theory, similar arguments can be presented as for the PbO system to account for the observations. The addition of hendecane increases $\dot{A}C\dot{O}-\dot{A}O\dot{O}$, thus making the lamellae of the *G* phase tend to become concave towards the ionic portion.

CONCLUSION

From the foregoing discussion it is seen that the concepts of the *R* theory are useful in rationalising the mesophases formed by molten carboxylates when their intermolecular interactions are perturbed by the addition of structurally similar materials. X-ray studies of the mesophases formed by these systems would help confirm the suggested structures. Of interest in this respect are the powder pattern studies of Spegt and Skoulios[11] of the mesophases of the cadmium carboxylates. They report the formation of a phase structurally similar to the M_2 phase before the final melting point which occurs above 425 K for these compounds. However, in a recent publication, we have reported the preparation of cadmium carboxylates of established purity, which melt to the isotropic liquid at around 380 K, and have suggested that the materials used by Spegt and Skoulios were basic carboxylates. This suggestion is supported by the present study. We intend to study the mesophases formed by the cadmium carboxylates and by the cadmium carboxylate/cadmium oxide system in an effort to show that the high temperature phase reported by Spegt and Skoulios is a result of the addition of cadmium oxide, and hence that the mesophases of this system may also be rationalised in terms of the R theory.

REFERENCES

1 S. O. Adeosun and S. J. Sime, *Thermochim. Acta*, in press.
2 P. A. Winsor, in G. W. Gray and P. A. Winsor (Ed.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974.
3 P. Spegt and A. E. Skoulios, *Acta Crystallogr.*, 21 (1966) 892.
4 V. Luzzati and P. A. Spegt, *Nature*, 215 (1967) 701.
5 M. E. Ekwunife, M. U. Nwachukwu, F. P. Rinehart and S. J. Sime, *J.C.S. Faraday I*, 71 (1975) 1432.
6 A. Luttringhaus and D. Schade, *Ber.*, 74 (1941) 1565; quoted in *Organic Reactions*, Vol. IX, John Wiley, New York, 1957, p. 357.
7 M. S. Karash and O. Reinuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954.
8 R. G. Sinclair, A. F. McKay and R. N. Jones, *J.A.C.S.*, 74 (1952) 2572.
9 D. Chapman, *J.C.S.*, 2 (1962) 2310.
10 S. O. Adeosun, W. J. Sime and S. J. Sime, *J.C.S. Faraday I*, (1976).
11 P. A. Spegt and A. E. Skoulios, *Acta Crystallogr.*, 16 (1963) 301.
12 F. B. Rosevear, *J. Am. Oil Chem. Soc.*, 31 (1954) 628.