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PROPERTIES OF MOLTEN CARBOXYLATES

PART 4: A QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS STUDY OF MELTING AND MESOPHASE FORMATION IN SOME LEAD(II) CARBOXYLATES

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ABSTRACT

Data are presented for the heats of phase changes and specific heats for the even chain length lead(II) carboxylates from hexanoate to octadecanoate. Structures are proposed by analogy to the properties of 'fused' aqueous ampiphilic mesophases. Optical examination under a polarising microscope suggests the phase sequence

crystal → G (smectic) → V_2 (cubic isomorphous) → liquid

for the dodecanoate and lower chain length soaps. For tetradecanoate, and above, the V_2 phase is absent and the G phase melts directly to the liquid. The chain length dependence of the entropies of the crystal → G and G → V_2 or G → liquid transitions demonstrates that disordering of the hydrocarbon chain is a stepwise process. The entropy of the V_2 → liquid transition is consistent with the melting of a globular solid and may indicate an average micelle size of 4 carboxylate molecules. This leads to a model of the isotropic liquid consistent with the viscosity data previously presented[2].

INTRODUCTION

Previous papers in this series[1–3] have presented data for the conductance, density and viscosity of some molten carboxylates in the liquid phase. It was suggested that, even in the isotropic liquid, the molecules existed in clusters or aggregates with a central ionic core surrounded by disordered hydrocarbon chains[2,3]. Further evidence for aggregation in the melts could be obtained from entropy of fusion and specific heat data for the liquids. The existence of mesophases for the lead soaps was reported[1], but further study was postponed until a detailed thermodynamic analysis could be performed. This has been done using quantitative DTA, and the results are presented here. Mesophase formation in some molten divalent metal carboxylates has been studied by Spegt[4,5] and Luzzati[6,7] and co-workers. They have been able to propose various structures for these phases consistent with the X-ray data, but, as has been pointed out by Winsor, these must be regarded as assumed and not established structures[8]. No X-ray data are available for the lead carboxylates. There have been few studies of the thermodynamics of mesophase formation for pure ampiphilic systems. Vold[9] developed a quantitative differential calorimeter and measured the heats of phase changes in some long chain length sodium carboxylates, and, more recently, there have been two DSC studies of the low chain length sodium and potassium salts[10,11]. Studies for non-ampiphilic systems have been recently reviewed by Barrall[12]. In general, however, there has been little interpretation of the thermodynamic data in terms of the proposed mesophase structure.

EXPERIMENTAL

The preparation and purification of materials has been described elsewhere[1]. Measurements were performed with the Mettler TA 2000 system. For the determination of the heats of phase changes samples of between 10 and 20 mg were weighed on a Cahn electrobalance and sealed into the standard aluminium crucibles. The peaks were scanned at a heating rate of 0.5 K min^{-1}. Measurements were initially performed under nitrogen with pinholes in the crucible lids; however, it was found that identical results were obtained if the samples were completely sealed, the small quantities of oxygen trapped in the crucibles causing no appreciable decomposition. All samples were premelted at 390 K before the series of measurements was begun. Recrystallisation was in many cases a slow process and samples were always left overnight before rerunning. Similar effects have been noticed for sodium and potassium n-butanoate[11]. Measurements were made at least in duplicate on at least four (usually five) separate samples. Areas of the peaks were measured by cutting out and weighing.

Specific heats for the solid and isotropic liquid phases were obtained by the method of baseline displacement using samples of between 20 to 40 mg and scan speeds of either 3 or 5 K min^{-1}. The small temperature range of stability of the mesophases made this method impractical for them and a different method was devised. The sample was scanned isothermally at a given temperature until the baseline was steady. It was then heated very quickly (ca. 40 K min^{-1}) through a temperature jump of 1 or 2 K and then held isothermally at the new temperature until the baseline became steady. The heat flow equations to the sample crucible (s) and reference crucible (r) are

$$\frac{dq_s}{dt} = \frac{1}{R}(T_w - T_s) = C_{p_s}\frac{dT_s}{dt} \tag{1}$$

and

$$\frac{dq_r}{dt} = \frac{1}{R}(T_w - T_r) = C_{p_r}\frac{dT_r}{dt} \tag{2}$$

where T_w and R are the temperature of the furnace wall and the heat resistivity of the DTA cell, respectively, and the q's are the heats and the C_p's are the total effective specific heats of the sample and reference crucibles, contents and immediate surroundings.

Writing

$$C_{p_s} = C'_{p_s} + C_{p_r}$$

and subtracting eqn (2) from eqn (1), one obtains

$$\frac{1}{R}\Delta T = C'_{p_s}\frac{\mathrm{d}T_s}{\mathrm{d}t} + C_{p_r}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} \tag{3}$$

where ΔT is $T_r - T_s$. Integrating from $t = 0$ to $t = \infty$ and noting that $\Delta T = 0$ for both one obtains

$$\frac{1}{R}\int_0^\infty \Delta T \mathrm{d}t = C'_{p_s}(T_f - T_i) = \mathrm{A}$$

where T_f and T_i are the final and intial temperatures, respectively and A is the area of the DTA signal. By performing runs with two crucibles of the same weight (including lid), one filled with the material of interest, and the other empty, it is easy to see that the difference in areas will be given by

$$\mathrm{A}_{\mathrm{filled}} - \mathrm{A}_{\mathrm{empty}} = C_{p_m}(T_f - T_i)$$

where C_{p_m} is the specific heat of the material in the crucible.

The method was tested using Analar Grade sodium nitrate as a standard. The specific heat of samples of this material was first measured in the range 500 to 570 K using the method of baseline displacement. The values agreed to within ±0.5% with the recent measurements of Dewing[13]. The specific heat at 550 K was then determined using the jump method. A value of 136±6 J mol^{-1} K^{-1} was obtained, compared to a value 137 found by Dewing. The method is, therefore, suitable to determine specific heats with a standard deviation of about ±5%. This error arises mainly from uncertainty in the value of the temperature jump, the manufacturers claiming a reproducibility in the furnace temperature of 0.1 °C. It is possible that the relative error could be reduced by increasing the jump distance. The jump method is not as accurate or as convenient as the method of baseline displacement for systems with large ranges of stability, but is useful for phases such as the mesophases studied here which exist over only a short temperature range.

Optical observations were made using an improvised polarising microscope fitted with a Kofler heating stage.

RESULTS

DTA curves for the materials studied are shown in Fig. 1, and their temperatures, heats and entropies of phase changes are shown in Table 1. Standard deviations have been omitted in all cases in which they were less than the ±2% expected of quantitative DTA. Errors were larger than 2% when two peaks overlapped and had to be separated graphically. In these cases the total heat effect was accurate to ±2%, but the separation introduced larger errors into the individual values, and

TABLE 1

THERMODYNAMIC DATA FOR PHASE CHANGES

Carbon chain length	*Crystal→G*			*G→V_2*			*V_2→liquid*		
	T (*K*)	ΔH (*kJ mol*$^{-1}$)	ΔS (*J K*$^{-1}$ *mol*$^{-1}$)	*T* (*K*)	ΔH (*kJ mol*$^{-1}$)	ΔS (*J K*$^{-1}$ *mol*$^{-1}$)	*T* (*K*)	ΔH (*kJ mol*$^{-1}$)	ΔS (*J K*$^{-1}$ *mol*$^{-1}$)
6	335.9	6.02±.46	18.0±1.3	338.5	15.8±0.5	46.4±1.3	350.2	1.3±0.1	3.8±0.4
8	352.5	30±1	89±4	356.2	7.9±0.4	24.7±1.6	381.2	1.2	3.1
10	354.9	32.7	92.0	367.4	20.0	54.4	385.2	1.0	2.7
12	365.2	48.3	132	377.2	29.8	79.1	381.2	0.9	2.5
14	372.7	59.1	159	382.7	41.6	109 } G→liquid			
16[a]	373.4	55±3	147±8	384.2	46.4	121			
18	381.2	62.6	164	387.2	56.9	147			

[a] A second smectic phase is formed at 380.6 K; $\Delta H = 40 \pm 4$ kJ mol^{-1}, $\Delta S = 10 \pm 10$ J mol^{-1} K^{-1}.

the resulting standard errors are shown in Table 1. The specific heats of the solid phases were considerably temperature dependent, as may be seen in Fig. 2. Closer to the melting points some deviations from linearity were observed, but as they could be an artifact due to a small concentration of impurity depressing the phase change temperature, the data have been omitted. No significant temperature dependence was observed for the specific heats of the liquids or of the mesophases over the narrow temperature range in which they were studied. The standard errors for the specific heats of the liquids and solids were within ±2%. Those of the mesophases were within ±4%.

For all the compounds, the first phase formed was highly viscous and, viewed under crossed polarisors, cooling into the phase produced bâtonnets which at lower temperatures extended into a typical fan texture[14]. The higher temperature phases of the soaps of dodecanoic and lower chain length acids were optically isotropic. However, at the transition temperature to the lower phase, hexagonal patterns appeared, identical to those described for the V_2 phase by Winsor[15]. The second phase shown by DTA for the hexadecanoate caused no visible difference in texture which is fan-like above and below the transition temperature. As neither author has

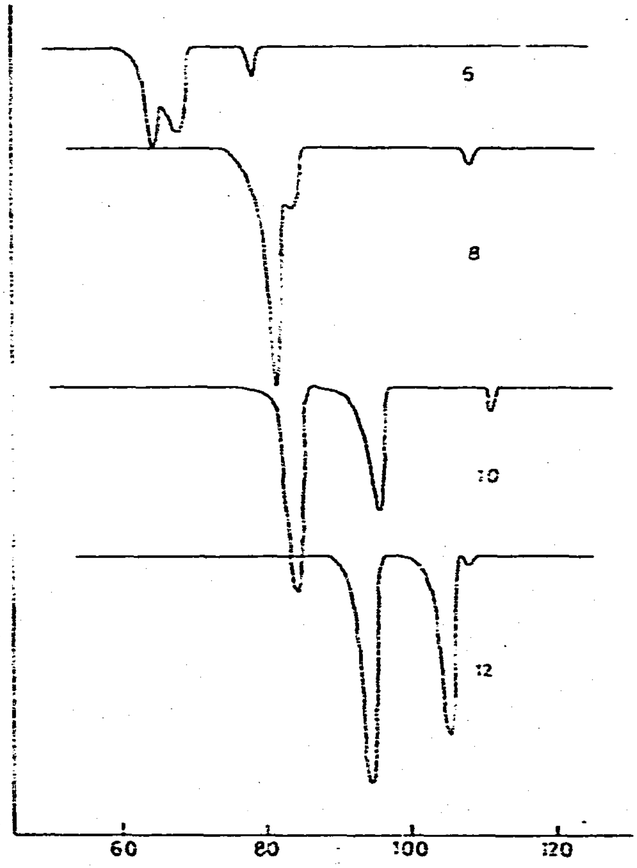

Fig. 1a (See legend on p. 356).

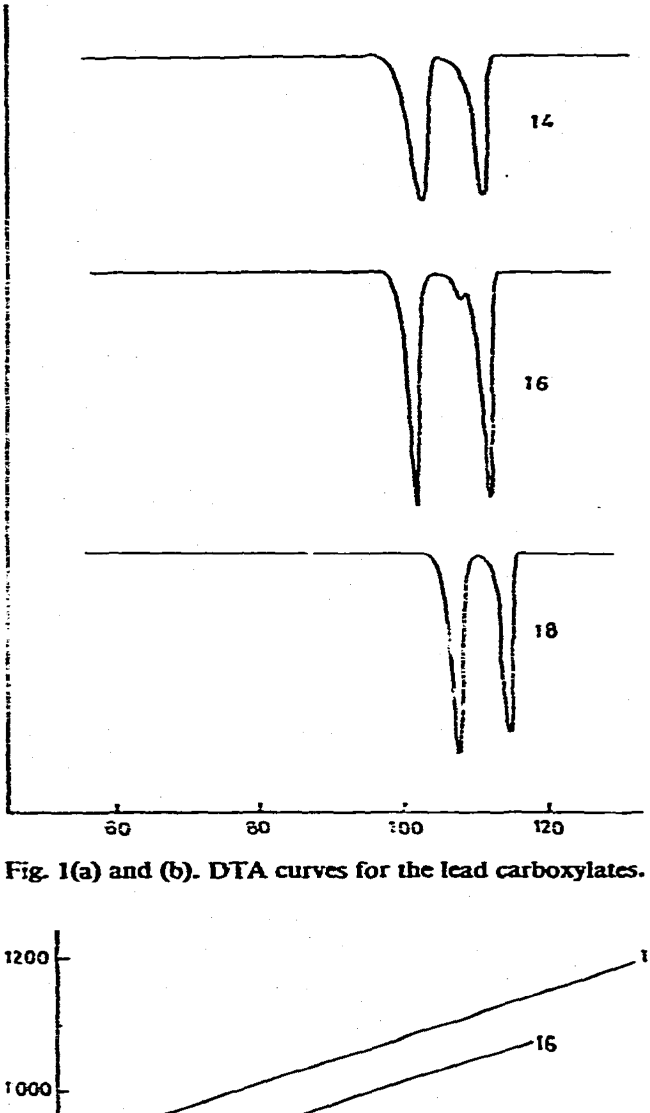

Fig. 1(a) and (b). DTA curves for the lead carboxylates. Scan speed, 0.5 K min^{-1}. Ordinate, t (°C).

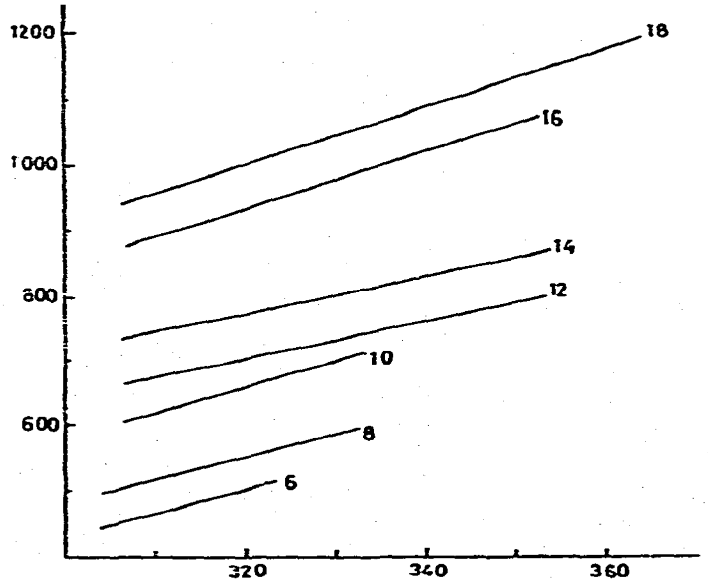

Fig. 2. Molar heat capacities of the solid carboxylates. Abscissa, C_p (J mol^{-1} K^{-1}); ordinate, T (K).

TABLE 2

SPECIFIC HEATS OF LIQUIDS AND MESOPHASES

Carbon chain length	*Phase*	*Mesophase*		*Liquid*	
		C_p ($J\ mol^{-1}\ K^{-1}$)	*Temp. range (K)*	C_p ($J\ mol^{-1}\ K^{-1}$)	*Temp. range (K)*
6	V_2	586	341–345	602	413–493
8	V_2	749	360–375	766	413–493
10	G	820	357–360	837	413–453
	V_2	870	372–376		
12	G	1160	366–374	1080	413–473
14	G	1420	374–379	1320	413–473
16	G	1750	375–377	1420	413–473
18	G	2320	383–385	1440	413–453

experience in the optical examination of liquid crystals, no more detailed investigation was attempted.

DISCUSSION

X-ray studies of mesophase formation in a series of divalent metal carboxylates have led to several interesting structures being proposed[4], and these structures have

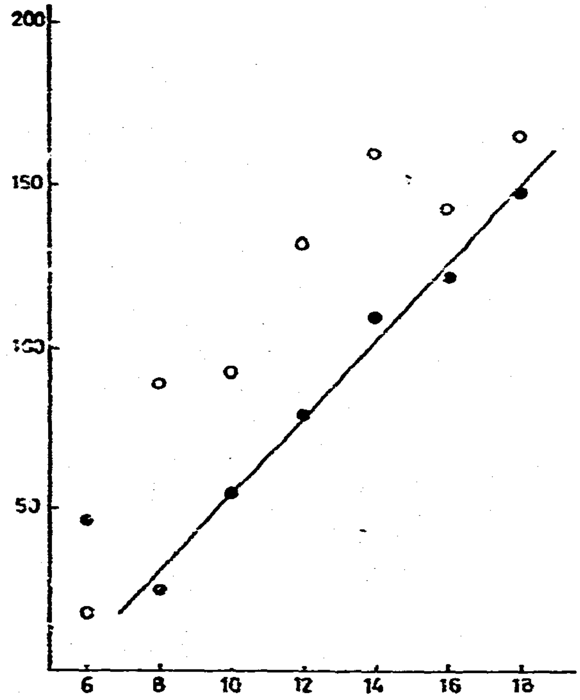

Fig. 3. Entropy of phase transitions. ⊙, crystal to G; ●, G to V_2 or G to liquid. Abscissa, ΔS ($J\ mol^{-1}\ K^{-1}$); ordinate, chain length.

been revised and re-interpreted in terms of even more complex networks by later authors[5–7]. As has been discussed by Winsor[16], those engaged in X-ray diffraction studies have tended to assume that the mesophases were quasi-crystalline and ignore the classification of structures used in the description of 'fused' mesophases in mixed aqueous systems. In the absence of X-ray data for the lead soaps, it would seem more useful to try to interpret the structures of these compounds in terms of the R[16] theory and classify them using the same nomenclature as employed for aqueous ampiphilic mesophases than to speculate as to which of the rather specialised suggested X-ray structures may fit the data.

The optical observations of the first phase formed on melting are consistent with a smectic phase and we tentatively classify it as a G phase. A plot of the entropy change on forming this phase against chain length is shown in Fig. 3. Although there is no smooth trend, it is seen that the value is strongly chain length dependent, increasing with increasing chain length, as is consistent with the idea that the primary process is randomisation of the carbon chain. The lower than expected values for the hexadecanoate and octadecanoate may indicate a different crystal structure for the solid phase, or a higher degree of order in the G phase. In line with the general structure of G phases we picture these systems as consisting of lamellae of polar carboxylate groups surrounded by randomised carbon chains.

Optical observations of the other phase formed for the dodecanoate and lower soaps are consistent with the cubic isotropic phase V_2, which is pictured as consisting of more or less spherical micelles, polar parts inwards, surrounded by randomised aliphatic chains, arranged on a cubic lattice. Figure 3 also shows a plot of the entropy of formation of this phase from the G phase against carbon chain length. This is strongly chain length dependent, demonstrating that disordering of the aliphatic chain is not complete in the G phase. This is a sensible result in as much as one may imagine that some spacial restrictions must be made as regards the methylene groups close to the carboxylate head group to form a laminar layer that would be removed on the formation of smaller spherical micelles. The near linearity of ΔS with n (with the exception of the hexanoate) indicates the structural similarity of the G phase and of the V_2 and liquid phases for all the compounds. In terms of the R theory the change from the G to V_2 phase is caused by increasing thermal disruption of the interaction of the alkanoic chains which finally results in the structure becoming convex towards the ionic portion of the lamellae, and results in the formation of quasi-spherical micelles. A small globular aggregate will require little ordering of the alkanoic chain and one may expect this portion of the molecule to be completely 'molten' in the V_2 phase. This is supported by the values of the entropy changes for the V_2 to liquid transitions which are small, and in fact decrease slightly with increasing chain length. Globular solids in which rotational disordering has occurred below the melting point (plastic crystals) usually show molar entropies of fusion[17,18] between 8 and 12 J mol^{-1} K^{-1}. The observed molar entropy for the V_2 to liquid transition of approximately 3 J mol^{-1} K^{-1} may suggest that the micellar unit in the V_2 phase and in the liquid consists of approximately 3 or 4 molecules. The high rate of change of activation energy for viscous flow of the liquid lead carboxylates[2] with chain length led to the suggestion that these soaps consist of aggregates in the liquid phase. It is interesting to note that the observed rate of increase is between 3 and 5 times larger than would be predicted in the absence of aggregation, again suggesting micellar units of between 3 and 5 carboxylate molecules.

The large temperature dependence of the specific heats of the solid phase may indicate that some randomisation of the carbon chain occurs below the transition point. The specific heats of the G phases for the dodecanoate and above are all larger than the values for the solid or the isotropic liquid, the difference increasing with increasing chain length. This is consistent with the idea that internal structural variations take place within the mesophase to help keep the value of R unity and hence maintain the laminar structure. For the V_2 phases for which specific heats could be measured, the values are very close to those of the isotropic liquid, as would be expected if the only structural changes between the two phases is the loss of cubic symmetry.

Although the structural models proposed must be regarded as speculative, it is seen that an adequate description of mesophase formation in these systems can be given in terms of the R theory, and that this description leads to a proposed structure of the isotropic liquid consistent with the viscosity data.

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