BINARY PHASE DIAGRAMS OF SOME BIVALENT METAL CARBOXYLATE SYSTEMS

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ABSTRACT

Binary phase diagrams are presented for mixtures of lead(II), zinc(II), cadmium (II), manganese(II) and mercury(II) octadecanoates. Evidence is presented to show that addition of one metal carboxylate to another, of the same chain length, does not alter the degree of order of the hydrocarbon chains either in the solid or liquid phase.

INTRODUCTION

A lot of data have been reported in the literature on the thermal behaviour of several pure metal carboxylates[1-11]. Many of these compounds form mesophases before finally melting into the isotropic liquid phase, while some do not. Similar studies on binary mixtures of metal carboxylates and water, alcohol or simple inorganic salts have also been reported[12-19]. However, very few studies have been made on the thermal behaviour of binary mixtures of pure metal carboxylates, whereas a considerable amount of data exist in the literature on the thermal properties of binary mixtures of several non-amphiphilic systems[20].

Spegt and Skoulios[21, 22] have reported X-ray data on mixtures of some Group II metal carboxylates. They observed that, at high temperatures, a mixture of calcium and strontium octadecanoates gave X-ray diffraction patterns corresponding to a homogeneous hexagonal phase containing the two metals jointly, while mixtures of calcium and magnesium octadecanoates gave X-ray diffraction patterns corresponding to heterogeneous mixtures of the pure hexagonal phases of the individual soaps. Using the differential thermal analysis technique, Hagino[23] reported phase diagrams for a number of binary mixtures of even-chain-length sodium carboxylates from dodecanoate to octadecanoate.

In the work reported in this paper, we have studied the thermal behaviour of binary mixtures of lead(II), zinc(II), cadmium(II), manganese(II) and mercury(II) octadecanoates using the DTA technique, and phase diagrams have been constructed for these systems. The data could be useful, as mixtures of soaps are widely used in industry, especially as lubricants.

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EXPERIMENTAL

The soaps were prepared and purified as previously described[24]. The mixtures were made by weighing the appropriate amounts of the compounds into a quick-fit conical flask, evacuating the flask and melting the mixture on a hot-plate. The soaps dissolved readily in each other.

DTA measurements were made on a Mettler TA 2000 system at a scan speed of 1 K min^{-1}. Measurements were performed on at least four separate samples. Optical observations were made on a hot-stage polarising microscope.

RESULTS

Lead octadecanoate–zinc octadecanoate system (Fig. 1)

It has earlier been reported[9] that lead octadecanoate, on heating, passes through a G(smectic) phase before melting into the isotropic liquid phase, while zinc octadecanoate melts directly into the liquid phase[11]. Inspection of Fig. 1 shows that addition of small quantities of zinc octadecanoate to lead octadecanoate does not alter the phase sequence observed for lead octadecanoate. However, at about 0.2 mole fraction of zinc octadecanoate, a new phase appears. Optical observation suggested that this new phase is a structurally different G phase and has therefore been labelled G_2. This phase persists up to 0.8 mole fraction of zinc octadecanoate, above which the crystal melts directly to the liquid.
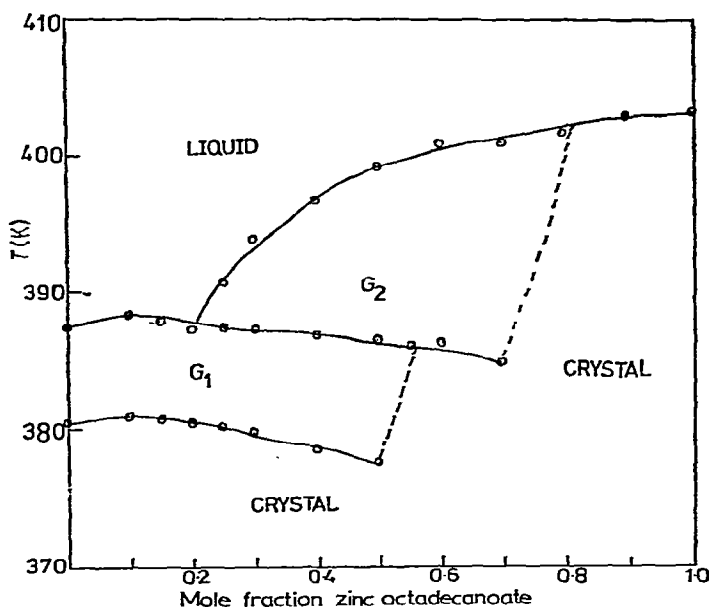

Fig. 1. Lead octadecanoate–zinc octadecanoate binary phase diagram.
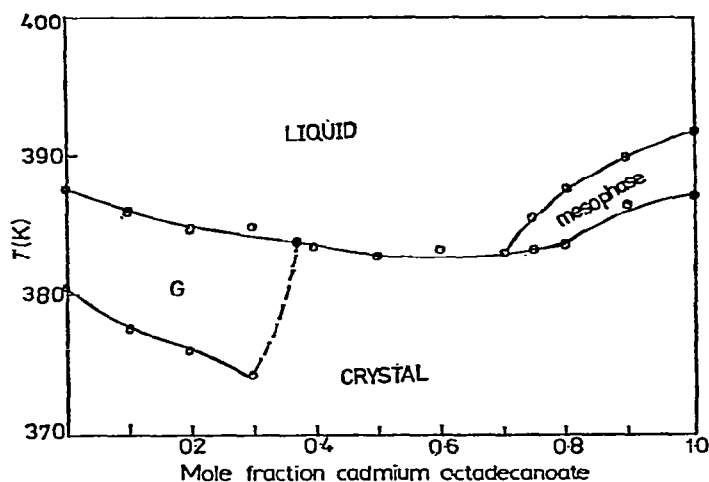
Fig. 2. Lead octadecanoate–cadmium octadecanoate binary phase diagram.

Lead octadecanoate–cadmium octadecanoate system (Fig. 2)

Addition of small amounts of cadmium octadecanoate does not alter the phase sequence abserved for pure lead octadecanoate. However, between 0.4 and 0.7 mole fractions of cadmium octadecanoate the G phase disappears and the crystal melts directly into the liquid phase. Above 0.7 mole fraction of cadmium octadecanoate a new mesophase appears. This is described simply as "mesophase" in Fig. 2, as optical observation did not help in classifying the phase. It has been reported that pure cadmium octadecanoate undergoes the phase sequence, crystal → mesophase → liquid[11].

Lead octadecanoate–manganese octadecanoate system (Fig. 3)

The phase sequence at all compositions is the same, i.e. crystal → G(smectic) → liquid.
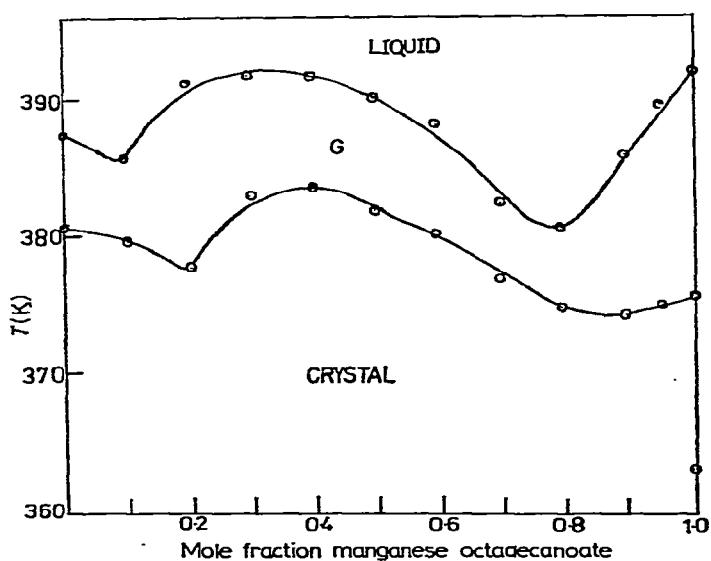

Fig. 3. Lead octadecanoate–manganese octadecanoate binary phase diagram.

Cadmium octadecanoate–zinc octadecanoate system (Fig. 4)

Addition of up to 0.8 mole fraction of zinc octadecanoate to cadmium octadecanoate does not alter the phase sequence observed for pure cadmium octadecanoate, i.e. crystal → mesophase → liquid. The structure of the mesophase could not be classified by optical observation. However, at higher mole fractions of zinc octadecanoate the crystal melts directly into the liquid phase.
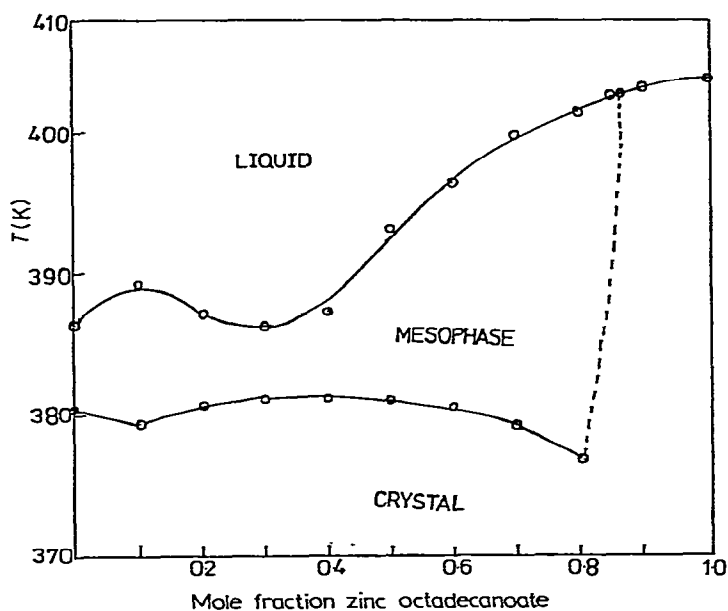

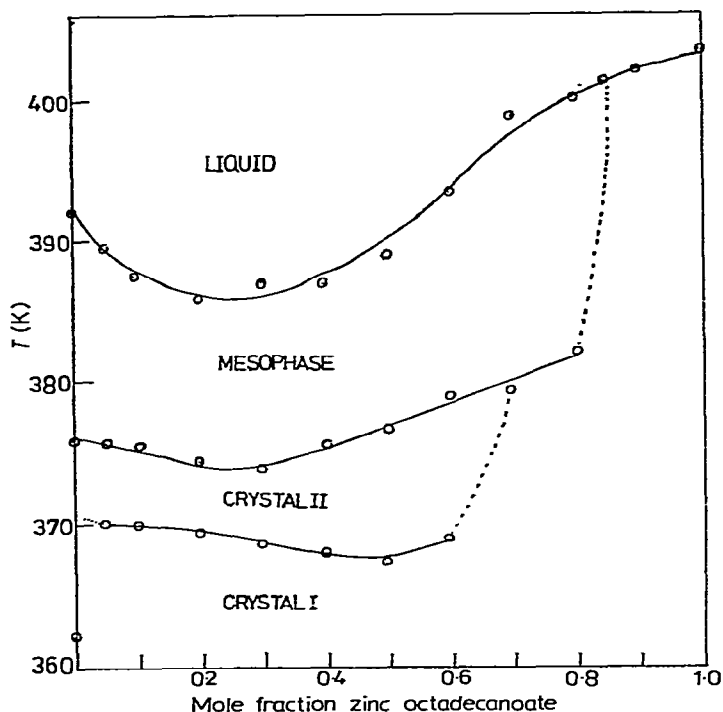Fig. 4. Cadmium octadecanoate–zinc octadecanoate binary phase diagram.

Fig. 5. Manganese octadecanoate–zinc octadecanoate binary phase diagram.

Manganese octadecanoate–zinc octadecanoate system (Fig. 5)

Manganese octadecanoate exhibits the phase sequence, crystal → mesophase → liquid[25]. The structure of the mesophase could not be classified by optical observation. Inspection of Fig. 5 shows that addition of zinc octadecanoate to manganese octadecanoate causes the appearance of a new phase on the low temperature side of the DTA curve. This phase is not a mesophase but a crystalline phase, as it was not readily subject to mechanical deformation when pressed between coverslips on a hot-stage microscope. This phase is labelled crystal II.
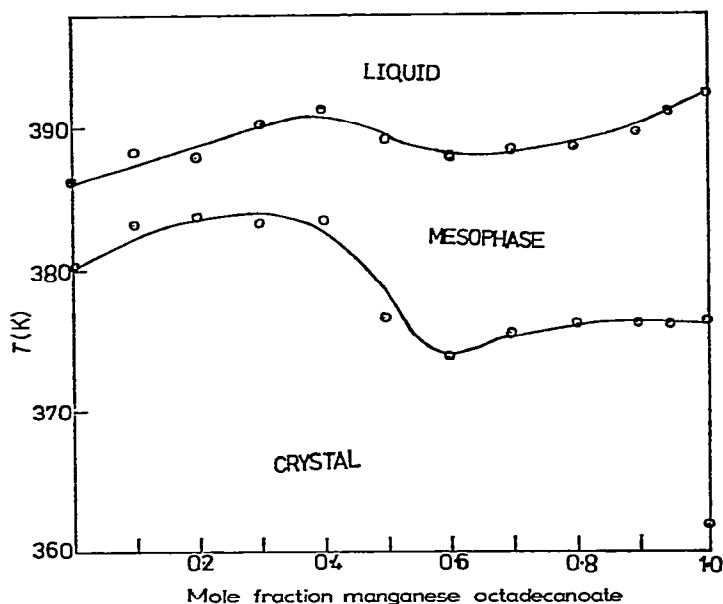

Fig. 6. Cadmium octadecanoate–manganese octadecanoate binary phase diagram.

Cadmium octadecanoate–manganese octadecanoate system (Fig. 6)

The phase sequence observed at all compositions of the mixtures is the same as that for the pure compounds.

Lead octadecanoate–mercury octadecanoate system (Fig. 7)

Addition of small quantities of mercury octadecanoate to lead octadecanoate does not alter the phase sequence observed for pure lead octadecanoate. However, between 0.4 and 0.9 mole fractions of mercury octadecanoate, a new laminar G phase is observed. This has been labelled G_2. At higher mole fractions of mercury octadecanoate, the system melts directly to the liquid. It should be noted that in an earlier paper[10] we reported that mercury octadecanoate shows a solid → solid phase transition at 355 K before finally melting at 393.2 K, whereas in the present study we observed that mercury octadecanoate melted directly at 392.1 K. This discrepancy might be due to the fact that while premelted samples were used in the present study, the samples used in the earlier work were not premelted. Vold et al.[7] have shown that

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the nature of phases exhibited by lithium hexadecanoate depends on the thermal history of the compound.
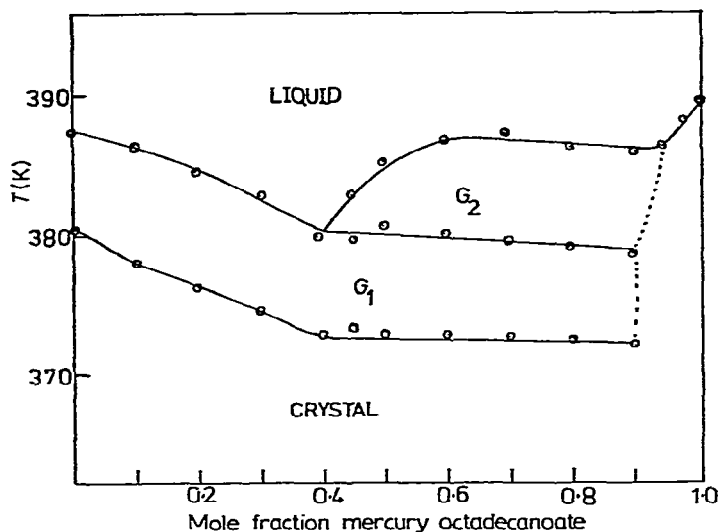

Fig. 7. Lead octadecanoate–mercury octadecanoate binary phase diagram.

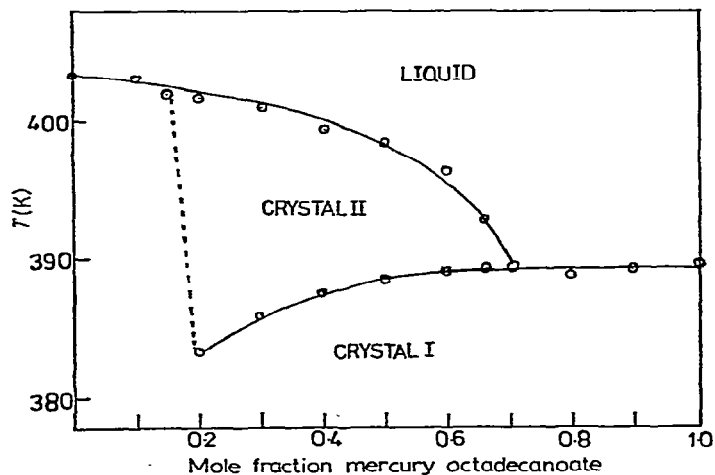Fig. 8. Zinc octadecanoate–mercury octadecanoate binary phase diagram.

Zinc octadecanoate–mercury octadecanoate system (Fig. 8)

It is noteworthy that while both zinc octadecanoate and mercury octadecanoate melt directly into the liquid phase, a new crystalline phase is observed in the mixtures between 0.2 and 0.7 mole fractions of mercury octadecanoate. This new phase is labelled crystal II.
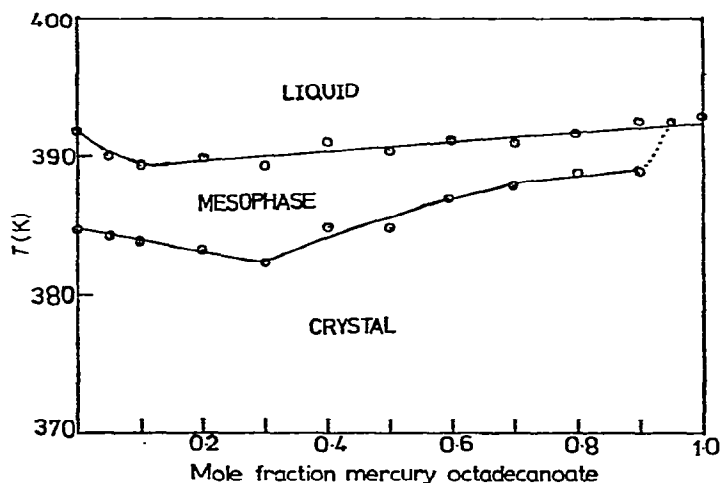
Fig. 9. Cadmium octadecanoate–mercury octadecanoate binary phase diagram.

Cadmium octadecanoate–mercury octadecanoate system (Fig. 9)

The phase sequence, crystal → mesophase → liquid, observed for pure cadmium octadecanoate, persists up to 0.9 mole fraction of mercury octadecanoate. The structure of the mesophase could not be classified from optical observations.
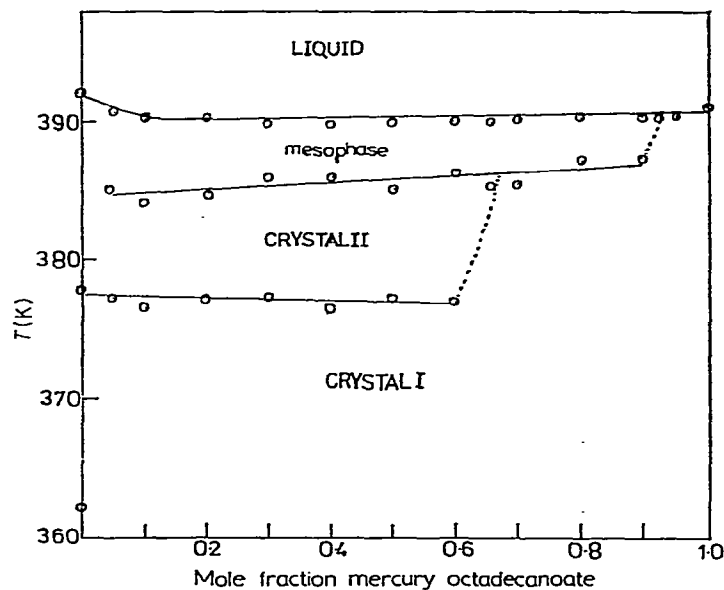
Fig. 10. Manganese octadecanoate–mercury octadecanoate binary phase diagram.

Manganese octadecanoate–mercury octadecanoate system (Fig. 10)

A new crystalline phase, i.e. crystal II, appears between 0.05 and 0.6 mole fractions of mercury octadecanoate. Between 0.6 and 0.9 mole fractions of mercury octadecanoate the phase sequence is the same as for pure manganese octadecanoate, i.e. crystal → mesophase → liquid. The system melts directly to the liquid at higher mole fractions of mercury octadecanoate.

DISCUSSION

The phase diagrams presented in Figs. 1–10 show that the phases observed in mixtures of pure metal carboxylates depend crucially on the nature of the cations involved. We had earlier[9,][11] explained mesophase formation in some metal carboxylates in terms of the R-theory of fused micellar phases. The R-theory[26] explains structures of mesophases in terms of a balance between the intermolecular forces which tend to make the amphiphilic portion of the lamellae become convex towards its lipophilic environment and those tending to make it become convex towards its polar environment. It is reasonable to expect that the intermolecular forces within the ionic portion of binary mixtures of metal carboxylates would depend on the type and composition of the ions present in the system. Hence, the phase sequence observed for a binary mixture of metal octadecanoates would depend on the nature and composition of the cations present.

It has been reported[17] that addition of lead oxide to lead dodecanoate results in greater ordering of the hydrocarbon chains of the soap in the liquid phase. On the other hand, addition of dodecanoic acid to lead dodecanoate does not alter the degree of order of the hydrocarbon chains either in the solid or liquid states[19]. In order to examine the effect of addition of one metal carboxylate on the degree of order of the hydrocarbon chains of another metal carboxylate of the same chain length, we have measured the heat and entropy changes which accompany the phase transitions in the system lead octadecanoate/zinc octadecanoate. The data are presented in Table 1. The values are quoted per mole of hydrocarbon chain present in the mixture, as the major contribution to the entropy change is the disordering of the hydrocarbon chains[9].

TABLE 1

THERMODYNAMIC DATA FOR PHASE CHANGES IN THE SYSTEM LEAD OCTADECANOATE/ZINC OCTADECANOATE

Phase change	$Crystal \rightarrow G_1$		$G_1 \rightarrow liquid$		$G_1 \rightarrow G_2$		$G_2 \rightarrow liquid$			
X_{zinc} octadecanoate	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH_{Total}	ΔS_{Total}
0	31.3	82.0	28.4	73.5					59.7	155.5
0.01	31.1	81.6	26.6	68.6					57.7	150.2
0.05	29.7	77.7	29.2	75.3					58.9	153.0
0.10	29.6	77.9	28.8	73.0					58.4	150.9
0.15	27.7	72.7	29.6	76.2					57.3	148.9
0.20	24.3	63.8	33.9	87.6					58.2	151.4
0.25	20.9	54.9			22.9	59.1	13.7	35.0	57.5	149.0
0.30	20.5	53.9			25.8	66.7	11.5	29.2	57.8	149.8

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 $\pm$ 3%.

The most significant feature of the results in Table 1 is that the change in entropy does not vary significantly with the concentration of zinc octadecanoate in the mixture. This suggests that addition of zinc octadecanoate to lead octadecanoate does not alter the degree of order of the hydrocarbon chains either in the solid or liquid phase, which implies that the hydrocarbon chains of the two soaps are arranged in the same manner in the crystal lattice as well as in the liquid phase. It is reasonable to expect that other binary mixtures of bivalent metal carboxylate systems would behave similarly, since the entropy change accompanying the disordering of the ionic portions of the amphiphiles makes little contribution to the overall entropy change[9].

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