Thermochimica Acta, 25 (1978) 333–339
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF THE SYSTEM LEAD(II) DODECANOATE/ LEAD ACETATE

S. OLUYEMI ADEOSUN
Department of Chemistry, University of Ife, Ile-Ife (Nigeria)
(Received 16 September 1977)

ABSTRACT

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

Optical observation under a polarising microscope suggests that the phase sequence in this system is the same as in pure lead dodecanoate i.e. crystal → G (smectic) → V_2 (cubic isomorphous) → liquid.

The entropy of the V_2 → liquid transition in the mixtures is the same as for pure lead dodecanoate which suggests that addition of lead acetate to lead dodecanoate does not affect the state of aggregation of the soap in the liquid phase.

INTRODUCTION

In a previous paper[1], data were presented on heats of phase changes and heat capacities for the even chain length lead(II) carboxylates from hexanoate to octadecanoate inclusive. It was shown that these soaps pass through a number of mesophases before finally melting into the isotropic liquid. Further, it was shown that for the dodecanoate and lower chain length soaps, the phase sequence is crystal → G (smectic) → V_2 (cubic isomorphous) → liquid while for tetradecanoate and above, the phase sequence is crystal → G (smectic) → liquid.

It is well known that several amphiphilic systems are capable of incorporating into their polar regions a considerable amount of water, inorganic salts and water-soluble organic compounds. In a recent paper[2] thermodynamic data on mesophase formation in the system lead(II) dodecanoate/lead oxide were presented. It was observed that addition of lead oxide to lead dodecanoate resulted in the disappearance of the V_2 phase. Also it was observed that two new phases occurred within the normal G phase range and that, at high lead oxide concentration, a new phase appeared at the high temperature region which was tentatively classified as an M_2 phase. These results were rationalised in terms of the R theory of fused micellar phases[3].

In the present study, the effect of lead acetate on the thermal behaviour of lead dodecanoate has been examined. In the lead dodecanoate/lead acetate system, the ionic portion contains similar ions to those in pure lead dodecanoate i.e. lead and carboxylate ions. Also, the hydrocarbon portion is essentially the same in both cases. It would therefore be of interest to see how the addition of lead acetate affects mesophase formation in lead dodecanoate.

EXPERIMENTAL

Materials. The fatty acids were commercial samples and were used without further purification. Anhydrous lead acetate was prepared by dehydrating $Pb(CH_3CO_2)_2 \cdot 3H_2O$ in a vacuum oven at 390 K for 24 hours. The IR spectrum of the product showed that all the water of crystallisation had been removed. Elemental analysis of the sample gave satisfactory results. (Found (%): Pb, 64.05; C, 14.87; H, 1.82. Calc. (%): Pb, 63.71; C, 14.76; H, 1.85).

The preparation of lead(II) dodecanoate has been described in an earlier paper[4]. The lead dodecanoate/lead acetate mixtures were prepared by weighing the appropriate amounts of the two compounds into a Quickfit conical flask. The flask was evacuated and the mixture melted. The lead acetate dissolved readily in lead dodecanoate.

DTA measurements. About 15–20 mg of the sample was sealed into the standard aluminium crucible of the Mettler TA 2000 analyser and scanned at a heating rate of 1 K min^{-1}. Measurements were made in duplicate on at least three separate samples. The DTA equipment was calibrated with pure indium metal. Peak areas were measured by cutting and weighing. Specific heats were measured by the method of baseline displacement and optical observation of the melts was made using a polarising microscope to which a Kofler heating stage was attached.

RESULTS

Typical DTA curves for the mixtures are shown in Fig. 1. All the mixtures show three phase transitions. Peak A occurs at increasingly lower temperatures with increasing lead acetate concentration while peak C occurs at increasingly higher temperatures with increasing lead acetate concentration.

The first phase formed was highly viscous. Optical observation, on cooling into this phase, produced bâtonnets which at lower temperatures extended into a typical fan texture[5]. This is consistent with a *G* (smectic) phase which was observed earlier for the pure lead dodecanoate[1]. Optical observation on cooling from the isotropic liquid into the second phase showed the appearance of hexagonal patterns at the transition temperature to the lower phase. This phase is consistent with the V_2 (cubic isomorphous) phase described by Winsor[6] and which was reported for lead dodecanoate and lower chain length soaps[1]. A phase diagram for the lead dodecanoate/lead acetate system is presented in Fig. 2.

The enthalpy and entropy changes accompanying the different phase changes are summarised in Table 1. These values are quoted per mole of hydrocarbon chain

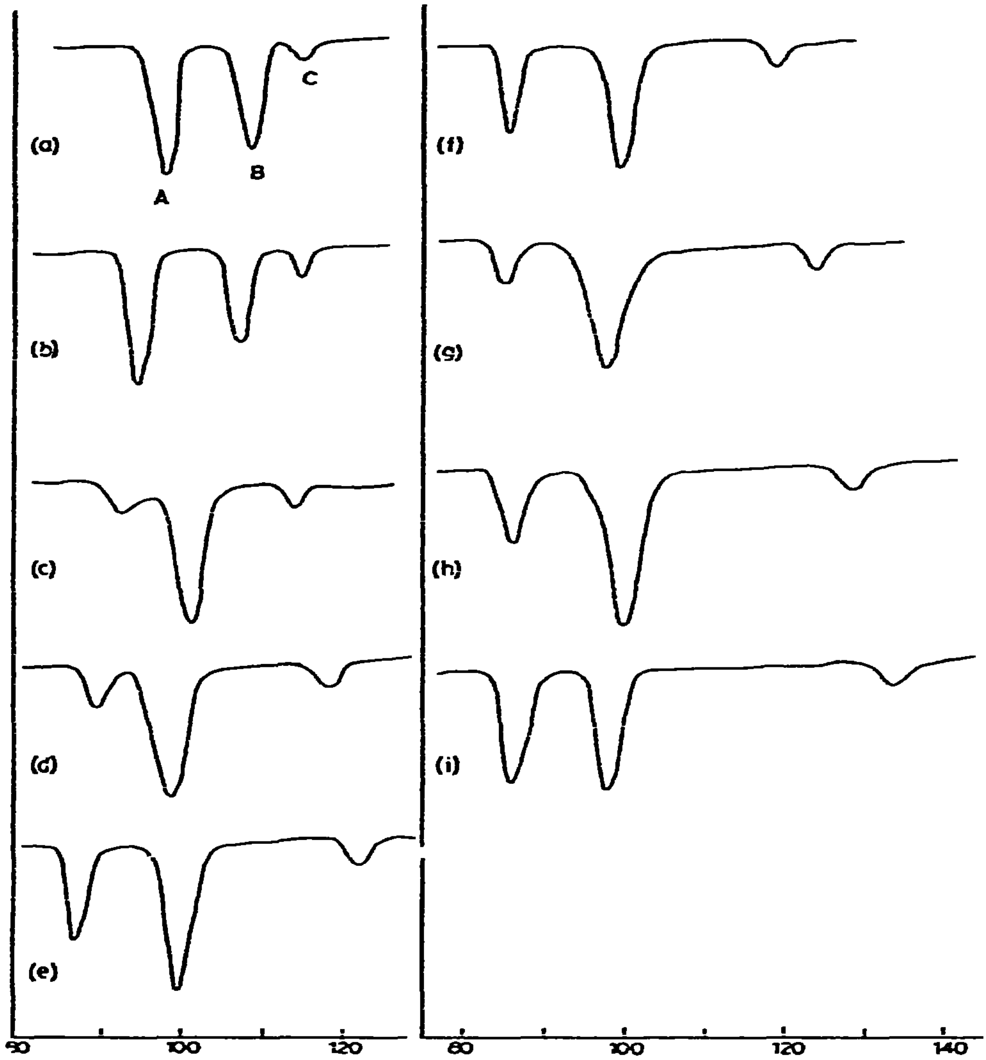

Fig. 1. DTA curves for $Pb(CH_3(CH_2)_{10}CO_2)_2/Pb(CH_3CO_2)_2$ mixtures. (a) Pure $Pb(CH_3(CH_2)_{10}CO_2)_2$. (b) $X_{Pb(CH_3CO_2)_2} = 0.011$. (c) $X_{Pb(CH_3CO_2)_2} = 0.049$. (d) $X_{Pb(CH_3CO_2)_2} = 0.101$. (e) $X_{Pb(CH_3CO_2)_2} = 0.150$. (f) $X_{Pb(CH_3CO_2)_2} = 0.202$. (g) $X_{Pb(CH_3CO_2)_2} = 0.248$. (h) $X_{Pb(CH_3CO_2)_2} = 0.301$. (i) $X_{Pb(CH_3CO_2)_2} = 0.353$. Scan speed, 1 K min^{-1}. Ordinate; ΔT. Abscissa; temperature (°C).

present in the mixture as the major contribution to the entropy change is the disordering of the hydrocarbon chain.

DISCUSSION

The most striking feature of the results is that addition of lead acetate to lead dodecanoate does not affect the phase sequence observed for pure lead dodecanoate i.e. crystal → *G* (smectic) → V_2 (cubic isomorphous) → liquid. This result is to be contrasted with the behaviour of the lead dodecanoate/lead oxide system. It has already been shown that addition of the slightest amount of lead oxide to lead dodecanoate causes the disappearance of the V_2 phase and that the *G* phase breaks

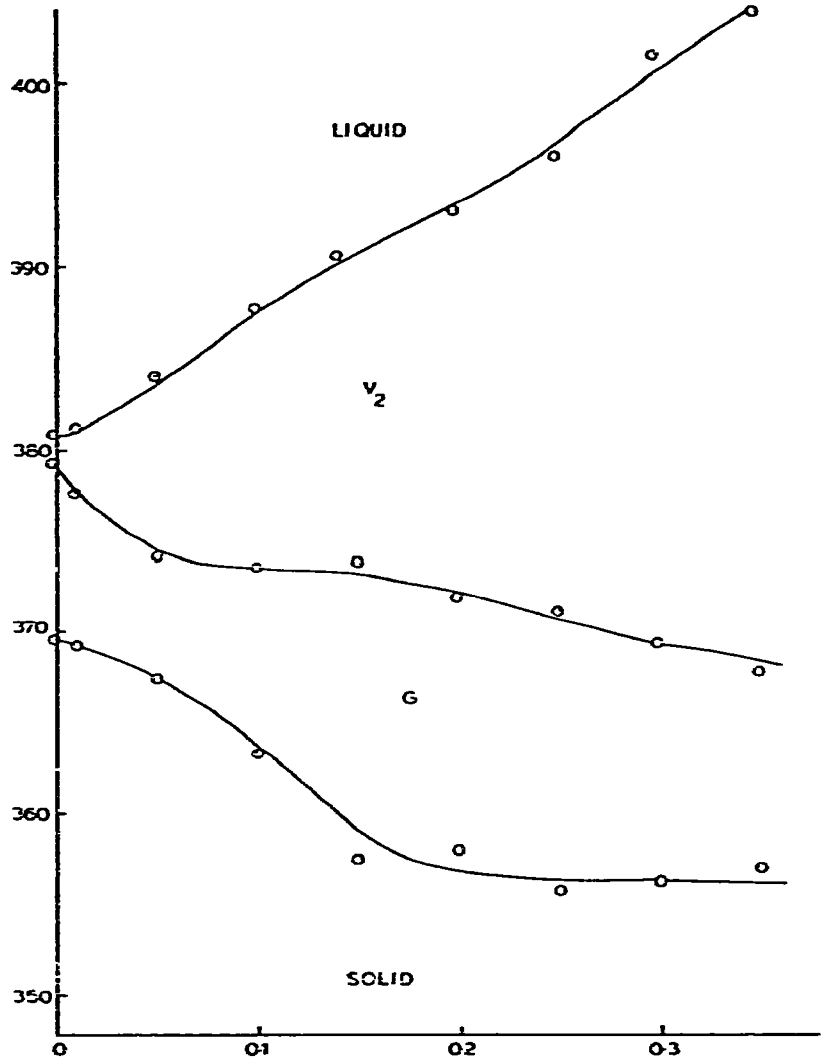

Fig. 2. Phase diagram for $Pb(CH_3(CH_2)_{10}CO_2)_2/Pb(CH_3CO_2)_2$ system. Ordinate: temperature (K). Abscissa: $X_{Pb(CH_3CO_2)_2}$.

down into three structurally different G phases. Also at high lead oxide concentration, cylindrical structures appeared at the high temperature region[2]. These results have been explained in terms of the R theory.

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 ($\bar{C}$) become convex towards its lipophilic environment ($\bar{O}$) and those tending to make it become convex towards its polar environment ($\bar{W}$). Following Winsor's notation[3], the ratio, R, of these tendencies, can be expressed as

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

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

TABLE I

THERMODYNAMIC DATA FOR PHASE CHANGES IN THE LEAD DODECANOATE/LEAD ACETATE SYSTEM[a]

$X_{Pb(CH_3COO)_2}$	Crystal → G		G → V_2		V_2 → liquid		ΔH_{total}	ΔS_{total}
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS		
0	24.2	66.0	14.9	39.6	0.5	1.3	39.6	106.9
0.011	21.5	58.2	11.2	29.7	0.6	1.6	33.3	89.5
0.049	8.5	23.1	23.2	61.9	0.6	1.5	32.3	86.5
0.101	3.7	10.2	25.3	67.7	0.5	1.3	29.5	75.2
0.150	6.3	17.6	19.7	52.7	0.5	1.3	26.5	71.6
0.202	4.4	12.4	18.6	50.1	0.7	1.7	23.7	64.2
0.248	2.3	6.3	18.0	48.5	0.7	1.7	21.0	56.5
0.301	6.3	17.8	12.7	34.4	0.7	1.6	19.7	53.8
0.353	9.8	21.9	8.5	23.1	0.8	1.7	19.1	46.7

[a] ΔH values are expressed in KJ (mole of hydrocarbon chain)$^{-1}$ while ΔS values are expressed in JK^{-1} (mole of hydrocarbon chain)$^{-1}$. Errors in the values are within ±2%.

maintain the lamellar structure of the *G* phase, *R* must be unity in all directions within the lamellae. The effects of changes in composition and temperature on the ratio *R* and consequently on micellar shape may therefore be considered from their probable effects on $A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$.

Our results on the lead dodecanoate/lead acetate system can also be explained in terms of the *R* theory. When lead acetate is added to lead dodecanoate it is incorporated into the ionic portion of the amphiphiles. The repulsive and attractive forces within the ionic portion of the lamellae in the lead dodecanoate/lead acetate mixtures would not be significantly different from those in pure lead dodecanoate since the lead and acetate ions of lead acetate are in an environment of similar ions i.e. lead ions and the carboxylate head groups of the soap. This would be particularly true at low lead acetate concentration. Thus the intermolecular attractions responsible for $A_{\bar{C}\bar{W}}$ are not considerably altered on the addition of lead acetate. Similarly, the intermolecular attractions responsible for $A_{\bar{C}\bar{O}}$ are not significantly affected on addition of lead acetate since the lipophylic portion of the amphiphiles remains the same. The result is that the value of *R* remains essentially unity and the lamellar structure of the *G* phase in preserved.

In terms of the *R* theory the change from the *G* to V_2 phase is a result of increasing thermal disruption of the interaction of the alkanoic chains which finally results in the formation of quasi-spherical micelles.

Another notable feature of the results is the decrease in the total entropy change for the process crystal → liquid with increase in lead acetate concentration (Table I). This suggests either that the carbon chains in the crystal are more disordered or that they become more ordered in the liquid phase on addition of lead acetate. One way of testing increased freedom of the hydrocarbon chains in the crystal is to measure the

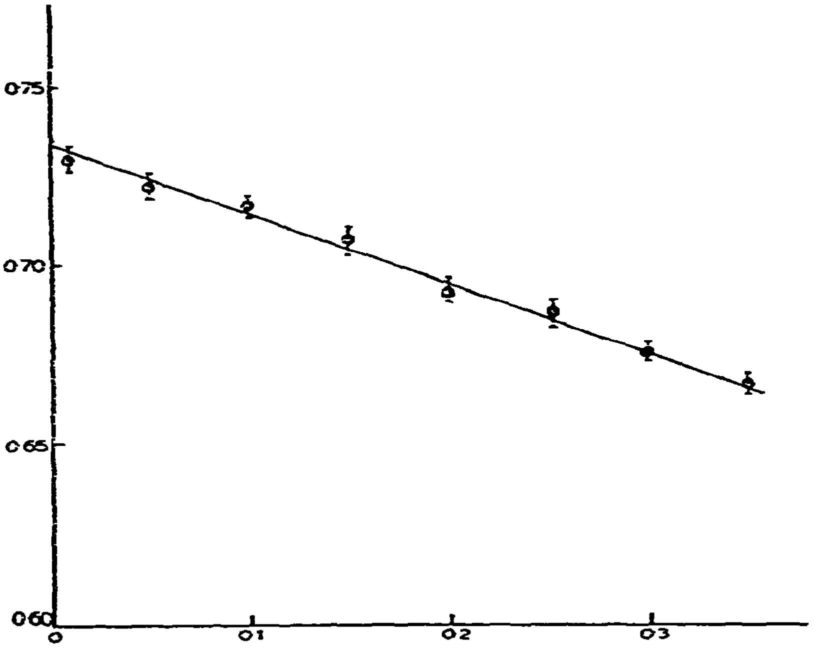

Fig. 3. Specific heats for solid $Pb(CH_3(CH_2)_{10}CO_2)_2/Pb(CH_3CO_2)_2$ mixtures. Φ..Φ, measured values at 323 K. Solid line; the prediction of simple additivity. Ordinate: C_P/KJ K^{-1} (mole of mixture)$^{-1}$. Abscissa: $X_{Pb(CH_3CO_2)_2}$.

specific heats of the samples. Fig. 3 shows a plot of specific heats of the solid mixtures at 323 K (per mole of mixture) as a function of mole fraction of lead acetate added. The solid line corresponds to the specific heats calculated on the basis of simple additivity. The two sets of specific heat values are almost exactly the same, which suggests that addition of lead acetate to lead dodecanoate does not bring about greater freedom of the hydrocarbon chains in the solid phase. It follows, therefore, that addition of lead acetate causes the hydrocarbon chains in the liquid phase to be more ordered.

The entropy change accompanying the $V_2 \rightarrow$ liquid phase change is between 1.3 and 1.7 J K^{-1} (mole of hydrocarbon chain)$^{-1}$ which is similar to the value of 1.5 J K^{-1} (mole of hydrocarbon chain)$^{-1}$ reported for pure lead dodecanoate[1]. It was suggested earlier[1] that, based on the molar entropies of fusion of some plastic crystals[7, 8] the value of 1.5 J K^{-1} (mole of hydrocarbon chain)$^{-1}$ for the entropy change in the $V_2 \rightarrow$ liquid phase transition, corresponds to a micellar unit of approximately 3 or 4 molecules in the V_2 as well as in the liquid phases. By the same argument, the values of between 1.3 and 1.7 J K^{-1} (mole of hydrocarbon chains)$^{-1}$ observed for the mixtures, suggests that the micellar unit in the liquid phase of the lead dodecanoate/lead acetate system consists also of approximately 3 or 4 molecules.

We therefore conclude that the addition of lead acetate to lead dodecanoate does not alter the phase sequence observed in the pure soap nor does it affect the state of aggregation of the soap in the liquid phase.

REFERENCES

1 S. O. Adeosun and S. J. Sime, *Thermochim. Acta*, 17 (1976) 351.
2 S. O. Adeosun, W. J. Sime and S. J. Sime, *Thermochim. Acta*, 19 (1977) 275.
3 P. A. Winsor, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974, Chap. 5.
4 M. E. Ekwunife, M. U. Nwachukwu, F. P. Rinehart and S. J. Sime, *J. Chem. Soc., Faraday Trans. I*, 71 (1974) 1432.
5 A. Saupe, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974, p. 38.
6 P. A. Winsor, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974, p. 224.
7 P. A. Winsor, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester 1974, p. 50.
8 A. R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford, 1965, p. 102.