

THE THERMAL BEHAVIOUR AND SPECTRAL PROPERTIES OF SOME LONG CHAIN COPPER(II) CARBOXYLATES

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ABSTRACT

Results are presented on the temperatures, enthalpies, and entropies of the phase transitions of the even chain length copper(II) carboxylates from decanoate to octadecanoate. The dodecanoate, tetradecanoate and hexadecanoate melt directly from crystal to isotropic liquid. However, with the decanoate and octadecanoate, an intermediate phase is observed between solid and isotropic liquid. Tentative assignments are made on the intermediate phases. Electronic and infrared spectra are reported for the solid copper(II) carboxylates. In both cases, the spectra provide clear evidence for there being at least two copper ions in the head-group region of each copper carboxylate system.

INTRODUCTION

Earlier papers from this laboratory have reported the phase transitions of the even chain length carboxylates of lead(II), zinc(II), cadmium(II), mercury(II) and manganese(II), either alone [1–4], or in binary mixtures [5]. In addition, studies have been made on the thermal behaviour of lead(II) and zinc(II) salts of some unsaturated fatty acids [6]. In the case of the carboxylates of lead(II) [1], cadmium(II) [2], manganese(II) [4] and certain mercury(II) soaps [3], one or more mesophases is observed between the solid and liquid phases. In contrast, whilst the zinc carboxylates show solid–solid phase transformations, they do not form liquid crystal phases [2]. For the lead(II) *n*-alkanoates, a comparison has been reported between the thermal behaviour of the odd and even carbon chain length derivatives. The phase transitions are similar in the two cases, although the enthalpies of the phase transitions do show odd-even variations [7]. The lead(II) and zinc(II) salts of certain unsaturated fatty acids do not form mesophases, but melt directly from solid to the isotropic liquid [6].

To try to understand the subtle factors which favour the formation of mesophases in these systems, it is necessary to obtain structural information on the various phases. Luzatti, Spegt, and co-workers have applied X-ray diffraction to the study of the phases formed on heating the long chain carboxylates of magnesium, calcium,

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zinc, strontium, cadmium and barium [8–10], and have shown a variety of possible lamellar, disc-like, and rod-like structures. However, it is likely in some cases, notably with the cadmium carboxylates [2], that they were looking at the basic salts rather than the true carboxylates.

It would be valuable to study a suitable bivalent metal carboxylate which is readily amenable to spectral studies in order to obtain information on the interactions occurring in the region of the metal ions. For this reason, we have studied the behaviour of the long chain carboxylates of copper(II), a system possessing a convenient electronic spectrum in the visible and near ultraviolet region.

EXPERIMENTAL

Materials

The soaps were prepared by metathesis in alcohol solution. The potassium salts of the acids were first prepared by dissolving the soaps in hot ethanol, and then adding the stoichiometric volume of potassium ethoxide solution. The potassium ethoxide solution was prepared by dissolving cleaned potassium metal in ethanol. The stoichiometric quantity of copper sulphate was dissolved in the minimum amount of water, and this was added slowly, with stirring, to the hot ethanolic solution of the potassium carboxylate. The resultant coloured precipitate was filtered off, washed with distilled water and ethanol, and recrystallised several times from hot benzene or toluene. All of the copper carboxylates were obtained as blue-green powders. In certain cases, an off-white powder co-precipitated with the coloured copper soaps. This was probably the basic carboxylate. It was readily removed from the copper carboxylate, as it was insoluble in hot benzene. Copper analyses were generally performed by EDTA titration using murexide indicator, as described in the literature [11,12]. In the case of copper octadecanoate, the end-point of the titration was

TABLE I

Melting points and elemental analyses of copper(II) carboxylates

Carbon chain length	M p (K)	Lit. m p (K)	C (%)		H (%)		Cu (%)	
			Theory	Found	Theory	Found	Theory	Found
10	379–381		59.16	59.14	9.43	10.38	15.64	15.39
12	385–386	384–386 ^a	62.38	62.45	10.03	10.70	13.74	13.18
14	389		64.89	64.77	10.50	11.48	12.25	11.44
16	387–388	393 ^a 388–393 ^b	66.92	66.92	10.88	11.67	11.06	10.37
18	383–385	398 ^a 384 ^c	68.58	68.43	11.19	11.21	10.07	9.89

^a Ref 25, ^b Ref 26, ^c Ref 13

difficult to determine, possibly as a result of complexing of the indicator with carboxylate ions. In this case, copper was determined by ashing. Elemental analyses and melting points of the copper carboxylates are presented in Table 1. The melting points of the copper dodecanoate and hexadecanoate were in reasonable agreement with literature values. The melting point for copper octadecanoate agrees well with the value reported by Lawrence for this compound [13].

Physical measurements

DTA measurements were made on a Mettler TA 2000 system at a heating rate of 1 K min^{-1} . Measurements were made on at least four samples for each compound studied. Details of the procedure have been given elsewhere [1]. Optical observations were made on a hot-stage polarising microscope.

Electronic spectra were run at room temperature on both single-beam and double-beam instruments using thin, microcrystalline samples of the copper carboxylates. Each sample was first melted on a microscope slide. A second slide was placed on top, and air bubbles removed from the resultant film by slight manual pressure. The samples were allowed to cool before spectra were run. The copper carboxylates appeared to pass through a plastic stage, as observed by Lawrence [13], before finally becoming microcrystalline. Molar absorptivities were estimated from the absorbance and thickness of each sample using densities [14] of related divalent soaps. Samples were typically of the order of $30 \mu\text{m}$ thick. Problems associated with the determination of the absorption spectra of such microcrystalline samples are described in detail elsewhere [15]. Infrared spectra were determined of the copper carboxylates as nujol mulls. In all cases, they showed the absence of absorptions attributable to free acid, water or hydroxyl groups.

RESULTS

Quantitative DTA

The even chain length carboxylates, C_{10} to C_{18} , of copper(II) were studied by quantitative DTA over the temperature range from room temperature to 410 K. It has previously been reported that copper(II) decanoate does not start to decompose until 483 K [11]. Copper(II) decanoate showed two, well-resolved peaks, while copper(II) octadecanoate showed two overlapping peaks. The DTA curves for the decanoate and octadecanoate are shown in Fig. 1. With the other carboxylates, only a single peak was observed. Studies using a hot stage microscope showed that the copper(II) dodecanoate, tetradecanoate and hexadecanoate melted directly from solid to isotropic liquid. The intermediate phase in the case of the copper(II) octadecanoate existed only over a limited temperature range. However, studies on a hot stage microscope did suggest that this phase was mechanically deformable, although visual observation under a polariser did not help in distinguishing the type of phase.

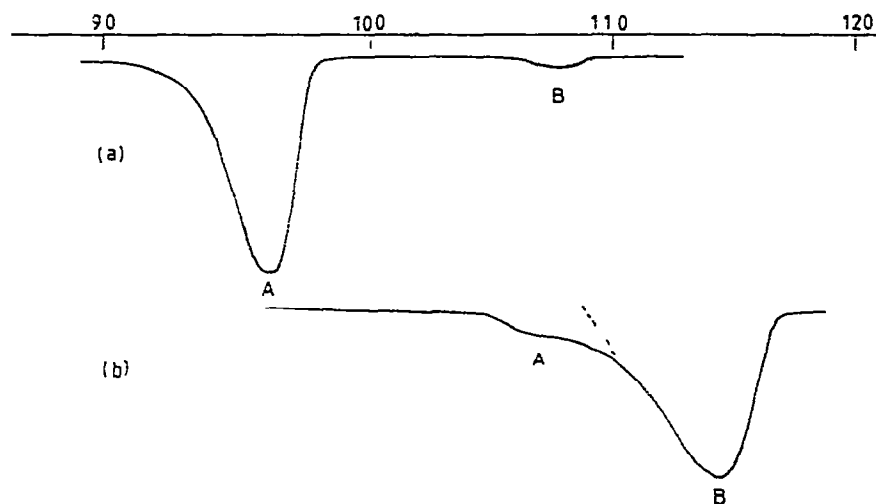


Fig 1 DTA curves giving. A. solid \rightarrow phase I transition. B. phase I \rightarrow liquid transition (a), copper(II) decanoate, (b) copper(II) octadecanoate Scan speed 1 K min^{-1} Abscissa ($^{\circ}\text{C}$)

When freshly prepared samples of copper(II) decanoate were studied by quantitative DTA, two peaks were observed, as shown in Fig. 1(a). However, if the sample was allowed to cool, and was then reheated, only a single peak was found corresponding to a transition from solid to isotropic liquid. In an attempt to identify the intermediate phase observed with fresh copper(II) decanoate, a sample was heated and observed under a microscope. At about 370 K, the colour of the decanoate darkened, and a new, mechanically deformable phase formed. It was not possible to further identify this new phase, as it was too dark to observe under a polariser. The sample did not show a clear transition to an isotropic liquid, but had melted by 382 K.

Temperatures, heats and entropies of phase changes, together with standard deviations are presented in Table 2. With the octadecanoate, as the two peaks overlapped and graphical separation was necessary, the errors for each transition were quite large. However, the total heat change was accurate to $\pm 2\%$. A similar problem has been noted in analysis of overlapping peaks with certain lead(II) carboxylates [1]. Values for the total enthalpy and entropy change for the decanoate and octadecanoate in passing from crystalline solid to isotropic liquid are also given in Table 2. Plots of total enthalpy or entropy change for the solid \rightarrow isotropic liquid transition against carbon chain length were linear for the compounds C_{12} to C_{18} . Copper decanoate did not fit these graphs. However, it was observed that the enthalpy or entropy for the solid \rightarrow phase I transition in this case did fit the graphs. It is not immediately obvious why this should be so, but the result does suggest that phase I must have a structure fairly similar to the isotropic liquid. The graph for the entropy change against carbon chain length is shown in Fig. 2. Least squares analysis of the data, including the results for the solid \rightarrow phase I transition in the case of the decanoate, gave slopes of $4.21 \pm 0.27 \text{ kJ mole}^{-1} (\text{C atom})^{-1}$, and $10.3 \pm 0.7 \text{ J K}^{-1} (\text{C atom})^{-1}$ for the enthalpy and entropy plots, respectively.

TABLE 2

Thermodynamic data for phase changes in copper(II) carboxylates

Carbon chain length	T (K)	ΔH (kJ mole ⁻¹)	ΔS (J K ⁻¹ mole ⁻¹)
<i>Solid—phase 1</i>			
10	368.8	33.0 ± 1.9	89.4 ± 5.1
18	386.7	16.2 ± 3.5	42.0 ± 9.0
<i>Phase 1—liquid</i>			
10	380.7	18.8 ± 0.9	49.4 ± 2.4
18	389.0	50.6 ± 3.2	130.1 ± 8.4
<i>Solid—liquid</i>			
12	385.3	39.0 ± 1.6	103.2 ± 4.0
14	389.1	50.2 ± 0.7	129.1 ± 1.8
16	386.7	55.6 ± 1.6	143.8 ± 4.2
<i>Total change for solid—liquid</i>			
10		51.8 ± 2.8	138.8 ± 7.5
18		66.8 ± 6.7	172.1 ± 17.4

Electronic and infrared spectra

Electronic absorption spectra were run between 300 and 1000 nm of thin, microcrystalline samples of each of the copper carboxylates at room temperature. In all cases, the spectra were similar, consisting of a medium intensity absorption (molar absorptivity $40 \pm 20 \text{ m}^2 \text{ mole}^{-1}$) around 680 nm, a slightly weaker shoulder near 370 nm, and an intense absorption with a maximum at wavelengths shorter than 300 nm. A typical spectrum is shown in Fig. 3(a), and spectral data for all of the carboxylates are summarised in Table 3. Assignment of these bands can readily be made by comparison with the electronic spectra of other copper(II) carboxylates [16–20]. The 680 nm absorption is assigned to the $d-d$ transition of the copper(II) ion, while the intense absorption at wavelengths shorter than 300 nm is attributed to a charge-transfer transition from the carboxylate grouping to copper(II) [19]. The most interesting part of the spectrum from a structural point of view is the shoulder observed near 370 nm. This absorption is similar to that observed in dimeric copper acetate systems [18], and is assigned to a transition involving two metal ions, either by direct copper(II)–copper(II) interaction [18], or by interaction involving bridging carboxylate ions [20]. For this to occur, the copper ions must be very close to each other. To confirm this assignment to an internuclear transition, the spectra of concentrated and dilute solutions of copper(II) decanoate in benzene at about 40°C were run [Fig. 3(b)]. This shoulder at 370 nm is observed to be present in concentrated solutions, but to disappear on dilution. It is known from ebullioscopic measurements of copper(II) dodecanoate and octadecanoate in benzene [16] that micellar aggregates containing 6–8 monomers are present in concentrated solutions,

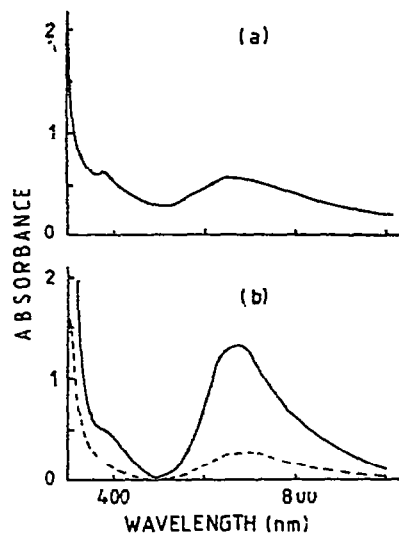
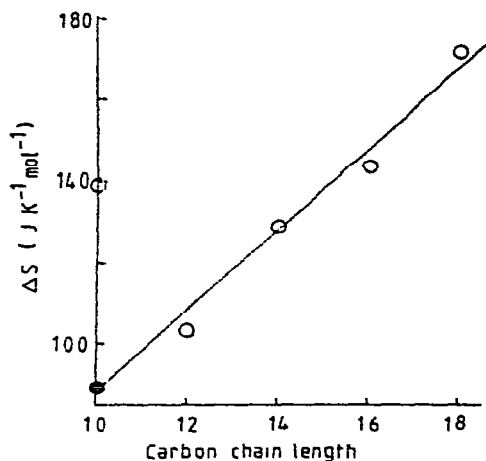


Fig 2 Plots of entropy of (○) solid→liquid, and (●) solid→phase I, transitions against carbon chain length for copper(II) carboxylates

Fig 3 Electronic absorption spectra of copper(II) decanoate: (a), as a thin microcrystalline film; (b), in benzene solution at ca. 40°C. solid line, 0.04 mole dm⁻³ solution, 2 mm cells. dashed line, 3 × 10⁻³ mole dm⁻³ solution, 10 mm cells

TABLE 3

Electronic absorption spectral data for copper(II) carboxylates as thin films at room temperature

Carbon chain length	Absorption maximum (nm)	Intensity (relative to long wavelength absorption)
10	690 ± 20	1
	386 ± 10 (sh)	0.85
	<300	>0.9
12	664 ± 20	1
	368 ± 20 (sh)	0.89
	<300	>1.1
14	686 ± 10	1
	368 ± 10 (sh)	0.89
	<300	>1.1
16	671 ± 20	1
	367 ± 10 (sh)	0.90
	<300	>1.3
18	668 ± 10	1
	367 ± 10 (sh)	0.81
	304 ± 5 (sh)	1.37
	<290	>1.7

TABLE 4

Infrared absorption spectral data for copper(II) carboxylates (as Nujol mulls)

Carbon chain length	Absorption (cm^{-1})			
	$\bar{\nu}_{\text{asCO}_2^-}$	$\bar{\nu}_{\text{sCO}_2^-}$	δ (OCO)	other bands
10	1588	1410	720	1505, 1315
12	1587	1405	720	1555, 1318
14	1587	1405	720	1510, 1315
16	1590	1410	720	1540, 1315
18	1586	1420, 1405	720	1505, 1315

whilst with more dilute solutions only monomeric copper(II) carboxylate species are expected to be present. Thus, the spectra of the solid copper(II) soaps seem to give clear evidence for the phase having more than one metal ion in close proximity in the carboxylate head-group region. The idea is supported by the magnetic properties of long chain copper(II) carboxylates [17] which show clear evidence of copper-copper interactions, leading to subnormal magnetic moments.

Further information on the structures of the carboxylate group region of these systems was obtained from studies of the carboxylate stretch vibrations in the infrared spectra of these compounds (Table 4). Assignment of fundamental vibrations was based on results on the infrared spectra of other metal carboxylates [21]. All of the copper(II) soaps showed sharp asymmetric ($\bar{\nu}_{\text{asCO}_2^-}$) and symmetric ($\bar{\nu}_{\text{sCO}_2^-}$) carboxylate group stretch absorptions around 1590 cm^{-1} and 1410 cm^{-1} respectively, in addition to carboxylate bending vibrations at 720 cm^{-1} , and various other bands. For copper(II) decanoate, the infrared spectrum was similar to that described previously [11]. The position and sharpness of the carboxylate asymmetric stretch vibration provides clear evidence for a carboxylate group of each fatty acid bridging between two copper(II) ions [21]. Similar behaviour is observed in the spectra of various other copper(II) carboxylate dimers. Thus, both infrared and electronic absorption spectra give clear evidence for the solid phase of the long chain copper(II) carboxylates having a polar region in which more than one metal ion is present, with the metal ions being joined together by carboxylate bridges.

DISCUSSION

Electronic and infrared absorption spectral studies clearly demonstrate that the solid phase in the copper(II) soap system has copper ions in the polar region linked together *via* carboxylate bridges. Probably, the structures are of lamellar type, as suggested by X-ray diffraction studies of solid phases of other divalent metal soaps [9]. All of the copper(II) soaps show formation of an isotropic liquid phase in the temperature range 380–390 K. The values of ΔS_{total} for transformation from solid to isotropic liquid are significantly smaller than those of the lead, mercury, and zinc

soaps, but are comparable with those of cadmium and manganese soaps [1–4]. Values for the hexadecanoates of copper, manganese, cadmium, zinc, lead and mercury are 143.8, 108.2, 122, 229, 268 and 281.5 J K⁻¹ mole⁻¹, respectively. This probably indicates that the isotropic liquid phases of the copper carboxylates, like those of the cadmium and manganese soaps, are more ordered than those of the lead, zinc or mercury soaps. As with the cadmium and manganese soaps [2,4] it is probable that copper carboxylates consist of long cylindrical micelles, rather than the spherical micelles proposed for the other soaps in the liquid phase [1–3]. As can be seen from Fig. 2, the entropy for the solid–liquid phase transformation (or the solid–phase I transition for the copper decanoate) is a reasonably linear function of carbon chain length, increasing with an increase in chain length. As with other divalent metal soaps [1–4], this strongly suggests that the major step in the melting process involves disordering of the hydrocarbon chains.

With copper(II) decanoate and octadecanoate, an intermediate phase is observed between the solid and isotropic liquid phases. Identification of this phase is difficult in the absence of further data. In both cases, the phases were deformable, indicating that they are true mesophases rather than new solid phases. Characterization under a polarizing microscope was not possible due to the strong light absorption by the soaps. However, the enthalpy change for the solid → phase I transition in the decanoate (33.0 kJ mole⁻¹) is very close to that for the solid → G phase transition for lead(II) decanoate (32.7 kJ mole⁻¹) [1], and it is tempting to suggest that the mesophase in the copper(II) decanoate is also of the lamellar G type [22]. With copper(II) octadecanoate, the enthalpy and entropy changes for forming this phase were considerably less than those observed with the decanoate mesophase, suggesting a different type of structure.

Studies of the phase changes occurring on heating long chain carboxylates of various divalent metal ions have shown the importance of the metal ion in determining the behaviour [1–7]. Thus, whilst lead(II) and cadmium(II) carboxylates form liquid crystalline mesophases, the zinc(II) soaps melt directly from solid to isotropic liquid [1,2]. The stability or instability of mesophases in amphiphilic systems depends on a balance between the electrostatic interactions occurring in the polar region, and hydrophobic interactions occurring in the hydrocarbon region of these systems [23]. The similarity of the ionic radii [24] of copper(II) (72 pm) and zinc(II) (74 pm) implies some similarity in the electrostatic interactions in the copper(II) and zinc(II) carboxylates. It is therefore not too surprising to observe that the copper(II) dodecanoate, tetradecanoate and hexadecanoate, like the zinc soaps, all melt directly from solid to isotropic liquid without any intermediate mesophases. In contrast, with larger cations such as lead(II) (radius 120 pm), electrostatic interactions may become more important, leading to formation of mesophases in their carboxylates [1]. With the copper(II) carboxylates, the electrostatic interactions are expected to become more important relative to hydrophobic interactions with a decrease in the size of the hydrocarbon grouping. Such an idea provides a ready explanation for the observation of a mesophase with the shortest chain length system studied, copper(II) decanoate. The presence of a mesophase in the copper(II) octadecanoate system, and

the proposed difference in structure of the liquid phases in the copper and zinc soaps strongly suggests that the size of the metal ion is not the only important factor. With transition metal soaps, such as those of copper and manganese, involvement of metal *d*-orbitals in bonding with the soap carboxylate group may also be expected to affect phase behaviour.

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