

# ON THE CRYSTAL-TO-MESOPHASE PHASE TRANSITION IN COPPER(II) SALTS OF EVEN-CHAIN FATTY ACIDS

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## Abstract

The phase transition from the solid state to the liquid crystal state was investigated for the copper(II) salts of the fatty acids with 10, 12, 14, 16 or 18 carbon atoms in the chain, by measuring the temperature dependence of the conductance and capacitance of a cell containing the material under investigation. The temperatures deduced from these dependences agree reasonably with those found by DSC measurements and with those to be found in the literature. Differences in dielectric behaviour between the samples are qualitatively discussed.

**Keywords:** conductance and capacitance measurements, copper carboxylates, phase transition temperature

## Introduction

Some of the long-chain fatty acid salts of copper(II) [1-3] or other bivalent metal ions [4-6] have recently elicited interest in consequence of their behaviour as thermotropic liquid crystals. Copper(II) salts of fatty acids have a columnar mesophase structure, already characterized by optical microscopy, X-ray diffraction and differential scanning calorimetry: this phase has been described as corresponding to the stacking of the binuclear polar cores (containing the carboxylate groups) surrounded by aliphatic chains in a disordered state and laterally assembled in a two-dimensional hexagonal lattice [7]. Nevertheless, the

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properties of many such metal complexes are not completely known and characterized.

Since the phase transition in liquid crystals can be accurately detected by changes in the dielectric constant at the corresponding temperatures [8], we attempted to determine the transition from the crystalline phase to the liquid crystal phase for the copper(II) salts of the fatty acids with 10, 12, 14, 16 or 18 carbon atoms in the chain, by measuring the temperature dependence of the capacitance and conductance of a cell containing the material under investigation. The transition temperatures obtained in such a manner are in agreement with those determined by DSC and with those reported earlier in the literature.

## Experimental

The copper(II) salts  $\text{Cu}_2[\text{CH}_3(\text{CH}_2)_{n-2}\text{COO}]_4$  with  $n=10, 12, 14, 16$  or  $18$  were prepared as previously described [9]; their purities were checked by elemental analysis. Both elemental analysis and IR spectroscopy indicated that these salts were anhydrous. In the following, the samples are abbreviated as  $\text{CuC}_n$ , where  $n$  signifies the number of carbon atoms in the corresponding fatty acid.

DSC measurements were performed to check the transition temperature from the crystalline to the liquid crystal state under dry nitrogen by using a DSC-7 Perkin Elmer apparatus.

Test cells for dielectric measurements were parallel-plate capacitors thermostated with a resolution of  $\pm 0.05$  K; they consisted of two glass plates covered with ITO transparent electrodes. We chose these electrodes instead of gold ones to allow observation of the continuity of the layer under investigation. The electrode area was totally covered by the filled liquid crystal. The thermal equilibrium of the samples was monitored by two thermocouples mounted close to the test cell.

To avoid the thermal degradation of the copper salt during the cell filling, we proceeded in the following way: one of the glass plates covered by material in the crystalline phase was heated on a stage up to  $120^\circ\text{C}$ . The upper glass plate was then set above in such a manner that the material was placed between the transparent electrodes. When the solid phase was transformed into a highly viscous mass, i.e. the liquid crystal phase, the top glass plate was pressed uniformly to obtain a continuous layer; the layer thickness was between 50 and  $10\ \mu\text{m}$ . Finally, the glass plates were sealed with epoxy resin.

Measurements of the capacitance  $C$  and of the conductance  $G$  were carried out with a Universal Bridge B224 (Wayne Kerr) working at a frequency  $\nu=1592$  Hz, during both the heating and the cooling of the sample cell. The voltage applied by the bridge was 2.3 V. The heating rate was  $1^\circ\text{C}\ \text{min}^{-1}$  between 25 and  $80^\circ\text{C}$ , and  $0.2^\circ\text{C}\ \text{min}^{-1}$  at higher temperatures. The cooling-down to room temperature was performed at a rate of  $0.2^\circ\text{C}\ \text{min}^{-1}$ . This rather low rate, besides

maintaining the cell temperature constant for at least 5 min, ensured the attainment of equilibrium before the measurement was made.

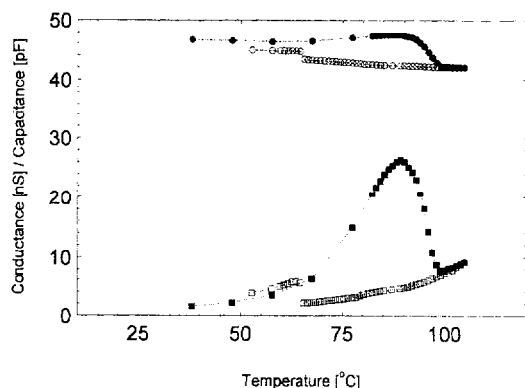
In the following, we use the values obtained for the cell capacitance and conductance without converting them to the components of the complex dielectric permittivity of the material [10] because cell calibration was not possible under the given filling conditions.

## Results

Observations proved to be difficult due to rather high transition temperature, the high viscosity in the liquid crystal state and the thermal decomposition of the material at temperatures lower than the clearing point.

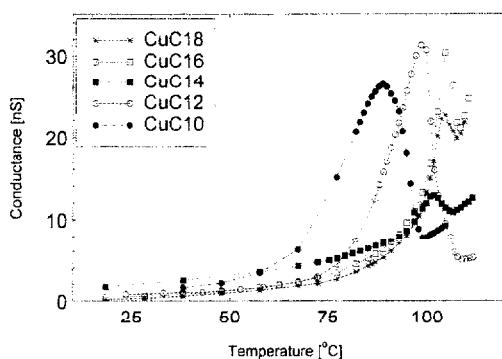
Phase transitions above 115°C have been indicated in the literature [1] for copper salts of fatty acids containing more than 12 carbon atoms. However, we did not find any sudden change in the capacitance and/or conductance values corresponding to transition temperatures higher than 115°C, e.g. up to 125°C for CuC12, or up to 130°C for CuC14. Therefore, we limited the studied temperature range to 115°C.

Figure 1 presents the dielectric response of the CuC10 sample as a function of temperature, during both the heating and the cooling process. The data reveal a well-developed peak in the conductance curves. An expected hysteresis of tens of degrees is observed due to undercooling effects: the same shift to lower temperature as that observed for the cooling curves of conductance measurements occurs in the corresponding cooling capacitance curves. The conductance increases towards high temperatures, whereas the capacitance curves are rather constant; this increase might correspond to *dc* conduction. The shape of the dielectric response of CuC10 is typical of the samples studied.



**Fig. 1** Dielectric response of the cell filled with CuC10 as a function of temperature; capacitance (circles) and conductance (squares). Filled symbols were obtained during heating, and empty symbols during cooling. Lines are merely guides for the eye

We presume that our measurements yielded average values instead of values for perpendicular or parallel orientation relative to the molecular axis of the liquid crystal, because we used unoriented samples. However, some flow alignment of the layer [11] might be inferred for the procedure of cell filling.



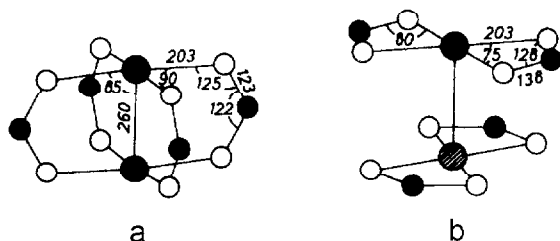
**Fig. 2** Variation with temperature of sample conductance during the heating process. Lines are merely guides for the eye

Conductance curves during heating are collected in Fig. 2 for all the samples under investigation. Although these differ considerably in the high-temperature region, they are similar as concerns the shape of the peak. The differences stem mainly from the peak position and width. It may be observed that the peak position is shifted towards higher temperatures with increase in the carbon chain length, as expected for the transition temperature from other types of measurements. As concerns the peak width, it seems to be larger for the samples with fewer carbon atoms in the chain.

The changes observed around the transition point in the capacitance *vs.* temperature curves in this study are similar to those found for the related *1-n* alkoxybenzoic acids [12] when such changes were related with the changes in the association of the molecular dipoles. In our case, we cannot assume large changes in the dipole moments at the phase transitions. It is known that copper salts of fatty acids exhibit units with a tetrakis(carboxylate)dimetal structure [13, 14]: whenever possible, two of the carboxylate chains adopt a *gauche* conformation near the metal centre to facilitate the crystal packing. Moreover, such units may be aggregated, to complete hexacoordination around the copper. These binuclear units with bridging bidentate coordination (Fig. 3a) have nearly compensated dipole moments. In this case, it is well known that antiparallel dipolar association leads to a considerable reduction of the parallel component of the permittivity, unless the contribution of the electronic polarizability is increased.

When the temperature is raised, carbon chain conformational disorder occurs of necessity: consequently, an alteration in the coordination type associated with

mesophase formation takes place [9, 17]. The bridging bidentate coordination changes then to chelating bidentate coordination (Fig. 3b). A slight reorganization of the coordination shell, which retains the binuclear structure of the complex, has been found from the temperature behaviour of the magnetic susceptibility [18]. The bridging structure has a higher energy than the chelating structure. This difference seems to be larger [15–17] for the higher members of the studied series of molecules. Even though the latter structure results from a  $\pi/2$  rotation of some of the component parts with respect to the other parts, the dipole moments are also nearly compensated in the units of the chelating coordination structure. Thus, it is essentially the relative importance of the conformational disorder oriented with the alkyl chains in the two phases under analysis that determines their relative mean dipole moments, and this will certainly lead to merely a small difference between them.



**Fig. 3** Cooper(II) coordination structures ( $pm/degrees$ ) in a) crystalline state (parameters taken from XRD or EXAFS data [14–17]) and b) the columnar liquid crystals (parameters calculated by molecular mechanics [17])

Since it has been established spectroscopically that the two structure types coexist, their relative population depending upon the temperature [9, 17], and since the dielectric behaviour of the material must be deeply influenced by the dipole moments carried by each component of the mixture, the dielectric constant (varying like the capacitance  $C$ ) is expected to be appreciably dependent on the relative concentrations of the mixture components. However, at this stage of the investigations, we could still not attain a complete image of the equilibrium present in the liquid crystal phase, further examinations being necessary from this respect.

Instead, the increasing dependence of the conductance *vs.* temperature curves towards higher temperatures (Fig. 2) might indicate a modification of the conduction mechanism, a change in the sample thickness and/or the role played by the annealing.

The temperatures for the transition crystalline phase–liquid crystal  $K \rightarrow D$  and the reverse process were obtained from the dielectric behaviour by considering the onset temperature: from this point of view, our method is a method of thermodielectric analysis. The transition temperatures are compiled in Table 1, to-

gether with those already reported [1]. It is to be noted that the values of both the capacitance  $C$  and the conductance  $G$  are taken directly from measurements without any corrections.

**Table 1** Transition temperatures ( $^{\circ}\text{C}$ ) of copper(II) salts of fatty acids as determined by dielectric measurements or existing in the literature

Material	$G^*$		$C^{**}$		Optical microscopy	DSC
	heating	cooling	heating	cooling	heating	heating
CuC10	92	68	91	69	–	105 (Ref. [17])
CuC12	101	76	101	78	110 (Ref. [1])	107 (Ref. [1])
CuC14	105	82	102	82	119 (Ref. [1])	116 (Ref. [1])
CuC16	108	88	107	86	117 (Ref. [1])	116 (Ref. [1])
CuC18	108	90	107	88	116 (Ref. [1])	116 (Ref. [1])

\*  $G$  – conductance measurements

\*\*  $C$  – capacitance measurements

There are very small differences between the transition temperatures deduced from the two kinds of curves, conductance or capacitance vs. temperature. On the other hand, the transition temperatures in the literature are greater by 6–14 $^{\circ}\text{C}$  than the present results. Excluding systematic experimental errors between the different sets of measurements, the differences between the transition temperatures found by different groups might be related to the differences in purity of the materials and in the heating rates, as emphasized elsewhere [19].

## Conclusions

The temperature variation of the dielectric behaviour (as conductance and capacitance values) provides evidence of the temperatures for the transition crystalline phase–liquid crystal  $\text{K} \rightarrow \text{D}$  and for the reverse process, for the copper(II) salts of some even-membered long-chain fatty acids. The onset temperatures found in this manner agree satisfactorily with those afforded by methods specific for liquid crystal behaviour. From this point of view, measurement of the conductance and the capacitance as functions of temperature is a method of thermodielectric analysis.

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