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THERMAL BEHAVIOUR OF THALLIUM(I) FATTY ACID SALTS, II

T. MEISEL, K. SEYBOLD and J. RÓTH

Institute for General and Analytical Chemistry,
Technical University of Budapest, Hungary

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The electrical conductivity (EC) changes of thallium(I) salts of fatty acids, which possess liquid crystalline phases, were investigated as a function of temperature. It was found that sharp EC jumps are associated with the phase transitions. The EC of the liquid crystalline phases depended not only on the temperature, the molecular weight and the geometry of the measuring cell, but also very sensitively on the heat treatment conditions which affect the relative magnitude of the EC in the mesophases.

Study of these dependences revealed a "memory effect". An explanation is given for this phenomenon.

We have already reported on the thermodynamic data of the polymorphic and phase changes and on the characteristics of the thermal decompositions of the thallium(I) salts of fatty acids [1]. From the homologue having five carbon atoms, these salts possess thermotropic liquid crystalline phases, which belong to the amphiphile smectic type [2–4]. As a continuation of this work we have thoroughly investigated the thermoelectrical properties of these compounds, paying special attention to the behaviours of their mesophases.

Experimental

The thallium(I) salts of saturated, open-chain, non-branching monocarboxylic acids (C_1 – C_9, C_{12}, C_{14}, C_{16}, and C_{18}) were produced, purified and analysed in the previously-described way [1].

Three different types of cells were applied for the measurement of electrical conductivity: a crucible type for the simultaneous DTA – TEC (differential thermoanalysis – thermal electrical conductivity) measurements, which was made of platinum [5, 6], a glass capillary type [5, 7, 8], and a micro-cell with gold electrodes evaporated onto glass slide surfaces.

Results

In complicated cases when several DTA peaks occur during heat-treatment, the previously-reported [5, 6] DTA – TEC measuring device is found to be a useful tool in evaluating the DTA peaks, because the sharp rises in the EC curve can be correlated only to the phase transitions, e.g. to the solid – mesophase, mesophase – isotropic liquid transitions.

As an example of the behaviour of salts having 1 to 4 carbon atoms, the DTA–TEC curves of thallium(I) propionate are shown in Fig. 1. The EC jump simply corresponds to the solid-isotropic liquid transition.

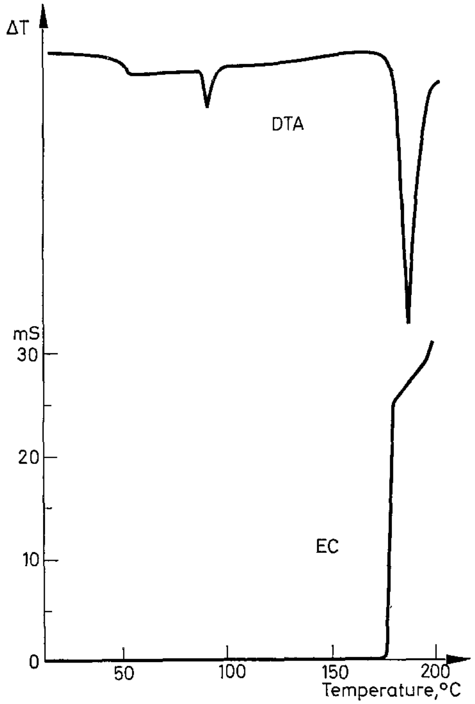


Fig. 1. DTA—TEC curves of thallium(I) propionate

The salts having 5 to 18 carbon atoms behave differently, as illustrated in Fig. 2 by the example of thallium(I) stearate. The EC curve exhibits two jumps here, on both heating and cooling, related to the solid-mesophase and mesophase–isotropic liquid transitions. The electrical conductivity of the mesophase in no case exceeds that of the isotropic liquid phase. We have observed a small-range and not-well-established dependence of the EC in the liquid crystalline phase on the cooling rate applied during the isotropic liquid — mesophase transition. However, this phenomenon can be studied more exactly with the capillary-type cell where this dependence is more pronounced and evaluable.

For an illustration of typical behaviour in the capillary-type cell the example of thallium(I) stearate is presented again (Fig. 3). The following phenomena could be observed:

The magnitude of the electrical conductivity of an individual sample, in a capillary cell of given diameter, is determined only by the cooling rate applied during the previous isotropic liquid–mesophase transition. Even if the sample is cooled down to the solid phase it will follow the same EC curve in the next heating cycle as in the previous cooling one, just as if "remembering" it.

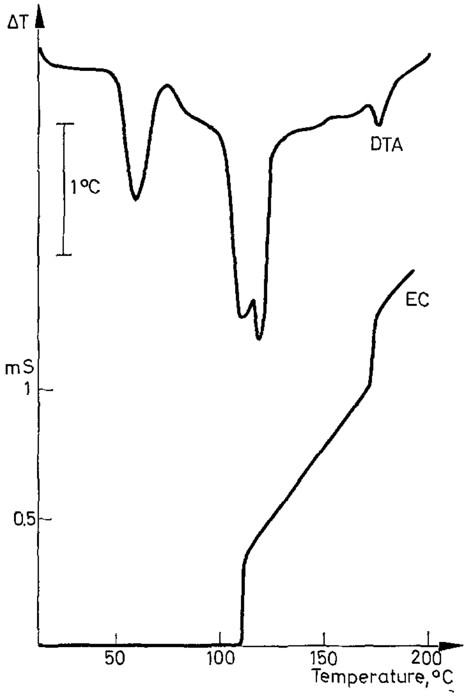


Fig. 2. DTA–TEC curves of thallium(I) stearate

On increase of the cooling rate, the EC curves of the mesophase shift to higher values, and when relatively high cooling rates are applied EC curves even higher than that of the isotropic liquid phase can be reached in the mesophase of salts possessing 14 to 18 carbon atoms.

The displacement of the EC curves in the mesophase against the cooling rate applied during the isotropic liquid-mesophase transition is reproducible; and if the sample is held isothermally for a longer time at any temperature in the liquid crystalline range the EC does not change.

If a shear force is applied along the wall surface of the capillary (at any temperature and EC level in the mesophase), a maximum value of EC is reached instantaneously. The curve (possessing the highest values) obtained in this way is also reproduced during the following heating period.

The same displacements of the EC curves are observed with the measuring conductivity meter switched off during the transition in question, which means that its electric field (A.C.) has no effect on the phenomenon.

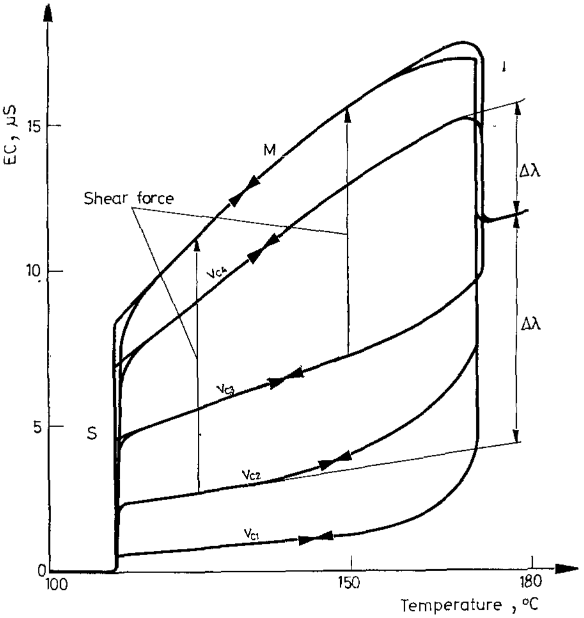


Fig. 3. TEC curves of thallium(I) stearate measured in a capillary-type cell; S — solid, M — mesophase, I — isotropic liquid; v_c — cooling rate, $\Delta\lambda$ — EC jumps; $v_{c4} > v_{c3} > v_{c2} > v_{c1}$

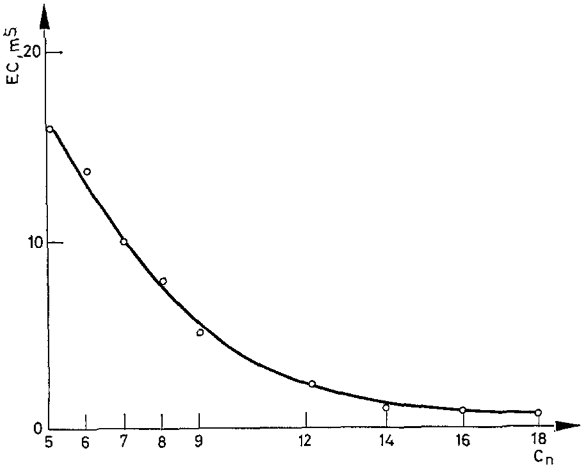


Fig. 4. Electrical conductivity of the isotropic liquid phases against the chain-length of the fatty acid anion

When a cell with greater diameter (0.5 → 1.0 mm) is used, the tendencies observed remain the same, apart from the fact that the cell constant increases.

The electrical conductivity values of the isotropic liquid phases of each salt, measured 5° above the mesophase – isotropic liquid transition, are plotted against the chain-length of the fatty acid anion in Fig. 4, where a well-defined tendency can be observed.

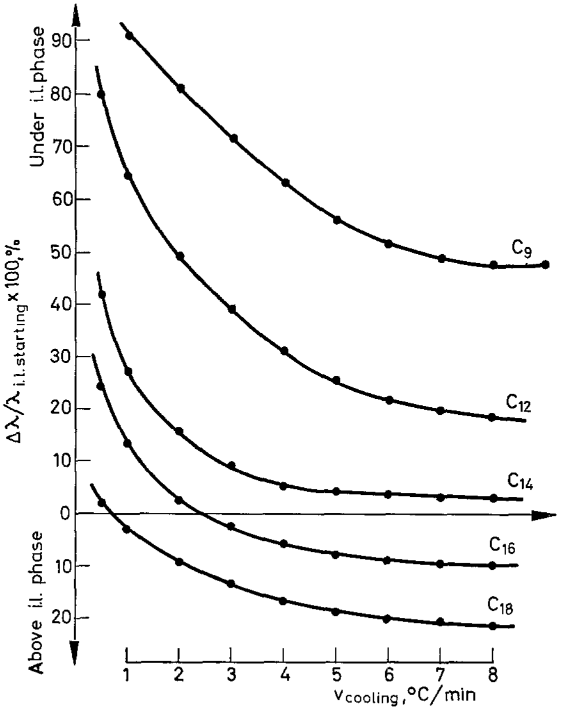


Fig. 5. Relative EC jumps as a function of the chain-length

Figure 5 shows the dependence of the electrical conductivity jumps ($\Delta\lambda$) occurring at the isotropic liquid – mesophase transitions (as a percentage of the starting EC value of the isotropic liquid phase) for each salt as a function of the cooling rate. The X axis represents the EC level of the isotropic liquid range.

Conclusions

The salts dissociate more or less in their melts depending on the temperature, and practically only the rather small thallium ions take part in the conduction and show macroscopically different mobilities in differently-ordered textures. The development of these textures is a result of the orientation effects of the geometry and material of the measuring cell and of the rate of cooling applied during the transition from the statistically-disordered isotropic liquid phase to the liquid crystalline phase showing semi-order.

The shear force most probably orientates the smectic planes parallel with the cell wall. This is the most favorable texture for electric conduction in the direction of the electrodes, because the thallium ions move towards the electrodes in the channels formed between the planes.

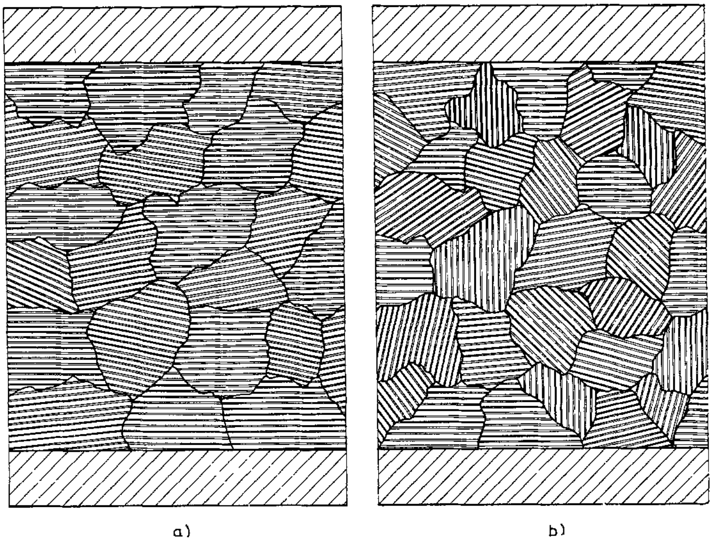


Fig. 6. Schematic arrangement of the domains in the capillary
a) after quick cooling, b) after slower cooling

A rather significant temperature gradient develops between the wall and the bulk of the capillary during quick cooling, so nucleation starts at the cooler cell wall, generating a nearly homogeneous structure with the planes parallel to the wall (Fig. 6/a).

On decrease of the cooling rate, the temperature gradient also decreases, and nucleation takes place more and more in the bulk too, and therefore the resultant directions of the domains developing from these centers become statistical; this arrangement is much less favorable for the transportation of electric charge (Fig. 6/b).

Once a structure is formed in this way it remains unchanged even during the transition to the solid phase; that is, the cooling rate applied during the isotropic liquid – mesophase transition also determines the structure of the solid phase, this phenomenon being the basis of the "memory effect".

The transition entropies (ΔS) and electrical conductivity jumps ($\Delta\lambda$) of the isotropic liquid – mesophase transition plotted against the cooling rate applied here for a given, but arbitrary member of the homologous series (Fig. 7) show that the transition entropies are independent of it while the EC jumps decrease quite rapidly. However, both parameters are characteristic for order-changes,

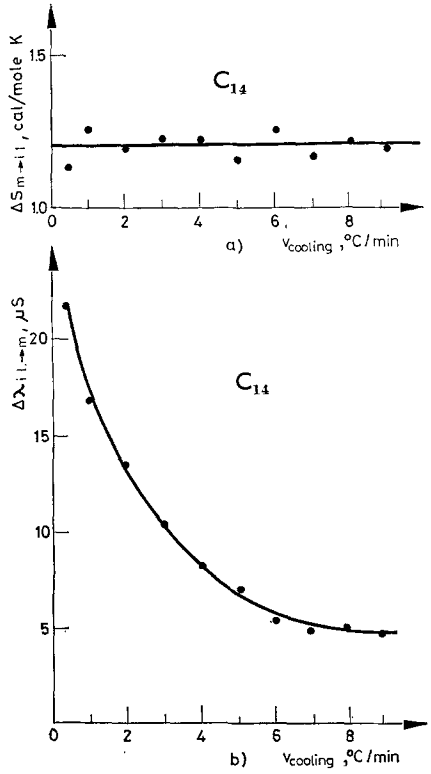
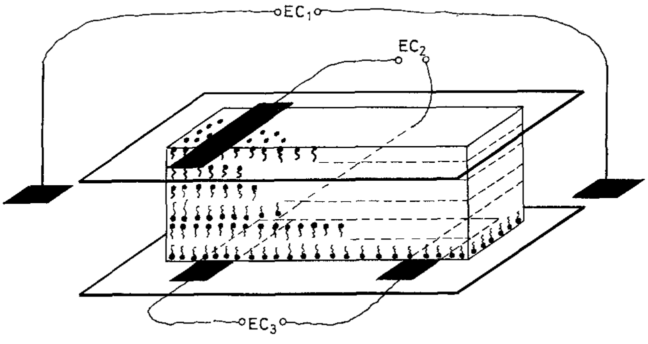


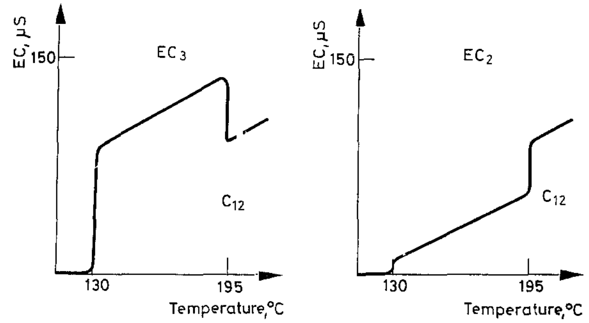
Fig. 7. Transition entropies and EC jumps of the isotropic liquid — mesophase transition as a function of the cooling rate for thallium(I) myristate

but ΔS is a scalar term and $\Delta\lambda$ is a vectorial one, and thus the different mesophase structures are thermodynamically equivalent: i.e. the molecules remain perpendicular to the smectic planes in all cases, and the different cooling rates change only the resultant orientation of the domains compared to the direction of the electrodes, so only the values of EC jumps are affected.

Measurements carried out with a micro-cell in two perpendicular directions also prove the above conclusions. The relative electrode arrangements are illustrated in Fig. 8/a. In the micro-cell the smectic planes are presumed to be homogeneously oriented in parallel with the glass surface, so the EC measurements carried out in this cell in two perpendicular directions represent the two extreme cases which can be achieved in the capillary cell (Fig. 8/b). This observation is in accordance with the fact that smectic liquid crystals possess negative dielectric anisotropy [9].



a)



b)

Fig. 8/a. Relative electrode arrangements: EC_1 — characteristic for the capillary cell, EC_2 — characteristic for the micro-cell with electrodes evaporated onto opposite glass surface — perpendicular to the smectic planes; EC_3 — characteristic for the micro-cell with electrodes evaporated onto the same glass surface — parallel with the smectic planes

Fig. 8/b. Electrical conductivity curves for thallium(I) laurate measured in a micro-cell with the EC_3 and EC_2 electrode arrangements

Consequently, the results of our investigations prove that a reproducible conductivity anisotropy can be developed with alteration of the circumstances of heat treatment in the liquid crystalline phases of fatty acid salts; and furthermore that the different EC values produced in this way in the mesophases can be stored in the solid phases for a longer time by cooling the samples down.

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Résumé — On a étudié les variations de la conductibilité électrique (EC) des sels de thallium(I) des acides gras possédant des phases cristallines liquides, en fonction de la température. On a établi que les variations brusques d'EC correspondent aux transitions de phases. L'EC des phases cristallines liquides dépend non seulement de la température, de la masse molaire et de la géométrie de la cellule de mesure, mais aussi, et d'une manière très sensible, des conditions du traitement thermique qui affectent l'amplitude relative de l'EC dans les mésophases.

Un « effet de mémoire » a été observé lors de l'étude de ces phénomènes, dont on donne une explication.

Zusammenfassung — Die Änderungen der elektrischen Leitfähigkeit (EC) von Fettsäure-Thalium(I)-Salzen mit flüssig-kristallinen Phasen wurden als Funktion der Temperatur untersucht. Es wurde festgestellt, daß den Phasenübergängen scharfe EC-Sprünge entsprechen. Die EC der flüssig-kristallinen Phase hängt nicht nur von der Temperatur, dem Molekulargewicht und der Geometrie der Meßzelle ab, sondern auch — in sehr empfindlicher Weise — Phasen bestimmen.

Die Untersuchung dieser Zusammenhänge führte zur Beobachtung eines »Memorieeffektes«. Eine Erklärung dieser Erscheinung wird gegeben.

Резюме — Были исследованы изменения электро проводности таллиевых (I) солей жирных кислот, находящихся в жидкокристаллических фазах, как функция температуры. Найдено, что резкие скачки электропроводности обусловлены фазовыми переходами. Электропроводность жидко-кристаллических фаз зависит не только от температуры, молекулярного веса и геометрии измерительной ячейки, а также от условий тепловой обработки, которые затрагивают относительные значения электропроводности в мезофазах. При изучении этих зависимостей наблюдали «эффект памяти». Дано объяснение этому явлению.