

INVESTIGATION OF THE THERMAL BEHAVIOUR OF FATTY ACID SODIUM SALTS

J. RÓTH, T. MEISEL, K. SEYBOLD and Z. HALMOS

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

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The thermal and thermo-electrical behaviour and properties, as well as the type structure and appearance of the liquid crystalline phases of the sodium salts of saturated, non-branching fatty acids were investigated. The measurements were carried out with a derivatograph, a DTA apparatus and a simultaneous DTA-electrical conductivity meter.

Relationships were found between the different thermal and electrical properties and the chain-length of the compounds.

The thermal and electrical behaviour and properties of the sodium salts of the saturated, non-branching fatty acids, acetic, propionic, *n*-butyric, valeric, capronic, caprylic, lauric and myristic acids were investigated.

Vorlander [1] was the first to demonstrate the liquid crystalline behaviour of these materials and the thermal properties of these compounds were investigated first by Vold [2, 3], who determined the temperatures of the polymorphic transitions and phase changes, and the transition heats, with a simple DTA device. He found that relatively small transition heats are associated with the mesophase – isotropic liquid transitions which occur at higher temperatures, but relatively large transition heats with the solid – mesophase transitions which occur at lower temperatures. According to his explanation there is a rearrangement of the fatty acid chain during the solid – mesophase transition (it “melts”), and of the polar head during the mesophase – isotropic liquid transition.

Duruz and Ubbelohde [4, 7] carried out electrical conductivity measurements together with DTA investigations to study the structure of the mesophase. They found that in the homologous series even sodium propionate has a liquid crystalline phase, extending through a narrow temperature range [4]. This is in contrast with the opinion generally accepted in the literature [2, 3, 5, 6], that the existence of the liquid crystalline phase in the homologous series of the fatty acid sodium salts can be observed only from the member having four carbon atoms. Their theory on the development and structure of the mesophase (which is based on the volume ratio of the cation and the anion) is in contrast with Vold's explanation [2, 3]. According to this, when the sample is heated the cation-lattice “melts” first in the solid – mesophase transition, and further heat transfer leads to the second step “melting” of the anion-lattice, that is of the whole sample, in the mesophase – isotropic liquid transition.

DTA and DSC methods have been quite widely used for the investigation of these compounds [5, 6], but differences and contradictions can be found in the results as regards the structure and appearance of the liquid crystalline state in the homologous series.

Experimental

The sodium salts of acetic, propionic, *n*-butyric, valeric, capronic, caprylic, lauric and myristic acids were prepared by the generally accepted method [7]: the anhydrous acid was dissolved in ethanol and boiled with the stoichiometric amount of sodium carbonate. Recrystallization was carried out from an ethanol-ether mixture. The sodium contents of the products were determined by the sulphate-ash-method. The results indicated the compounds to be the neutral sodium salts.

Methods for the investigation of the molten or liquid crystalline state

In order to investigate the general thermal behaviour of the fatty acid sodium salts and to determine the circumstances under which these salts can be studied without any thermal decomposition, we carried out measurements under different experimental conditions (heating rate, atmosphere, sample size, etc.) with the MOM Derivatograph [8].

To determine the transition heats and entropies quantitatively, we carried out measurements with a Mettler TA 2000 apparatus. The DTA curves of each salt were recorded during several heating and cooling cycles. We determined the transition temperatures by using the peak maximum temperatures of the DTA curve and the correction factor of the apparatus; and the heats of transitions by planimetry of the areas under the peaks and measuring indium standards.

Though valuable quantitative information can be gained for the different polymorphic transitions and phase changes with the DTA method it yields no detailed information directly about the phases themselves. In the case of compounds having liquid crystalline phases, an additional problem arises; namely by using this method alone it is difficult to determine exactly which DTA peaks belong to the solid - solid polymorphic transitions and which ones to the phase changes, that is to the melting points or to the solid - mesomorph, mesomorph - isotropic liquid transitions.

In order to overcome these problems, we made visual observations with a hot stage microscope in polarized light and also carried out measurements with a simultaneous DTA-electrical conductivity meter constructed by one of us [9].

With this apparatus we recorded the DTA and electrical conductivity curves simultaneously as a function of temperature with an X-Y-Y' recorder. This technique not only permits measurement of the two characteristic properties (DTA,

electrical conductivity) simultaneously in one sample, during one heating or cooling cycle, under the same experimental conditions but is also a suitable tool to determine which DTA peak corresponds to which transition, with the help of the electrical conductivity jumps occurring in parallel.

Results and discussion

Investigations by means of the derivatograph

The measurements were carried out under the following experimental conditions: heating rates : 3 and 5°/min; sample size: 100 mg; atmosphere: air or nitrogen; inert material: Al_2O_3 , heated up to 1300°.

As an example of the general thermal behaviour of fatty acid sodium salts, the case of sodium myristate can be seen in Fig. 1.

Comparison of the measurements in air and nitrogen atmospheres shows that in the former case (dotted line) there is a small exothermic peak on the DTA curve around 180°, accompanied by a weight loss of about 1 per cent (TG curve), and a large one at 280°, with a weight-loss of 7 per cent; in nitrogen there is no

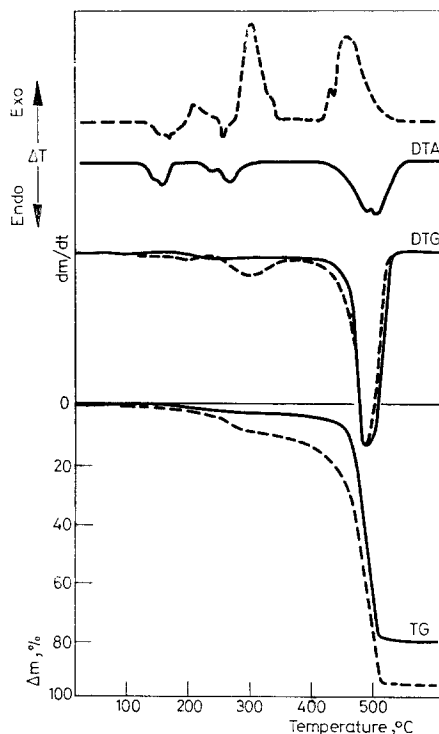


Fig. 1. Thermal curves of sodium myristate

Table 1
Decomposition temperatures of Na salts

	In air, °C	In N ₂ , °C
Formate	330	350
Acetate	360	400
Propionate	350	380
Butyrate	350	370
Capronate	300	365
Caprylate	260	360
Laurate	220	320
Myristate	190	410

exothermic peak, nor any significant weight loss until the decomposition of about 80 per cent at 480°.

A similar increased thermal stability in nitrogen could be observed for all the other sodium salts (Table 1). Accordingly the results of derivatography suggested that in order to ensure heat-stable molten or liquid-crystalline phases the application of an inert atmosphere is necessary.

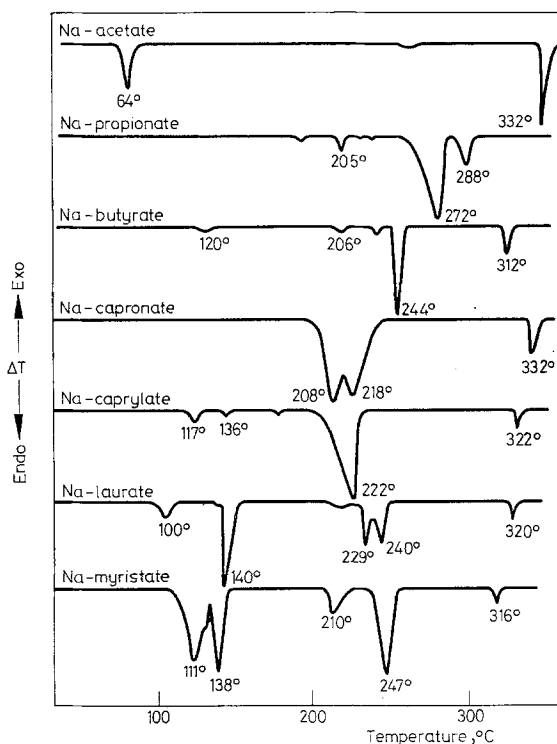


Fig. 2. DTA curves of sodium salts

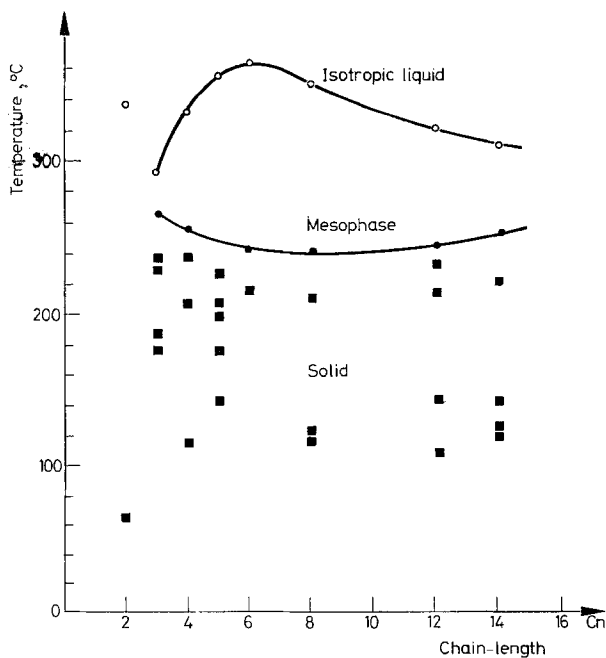


Fig. 3. Transition temperatures of sodium salts

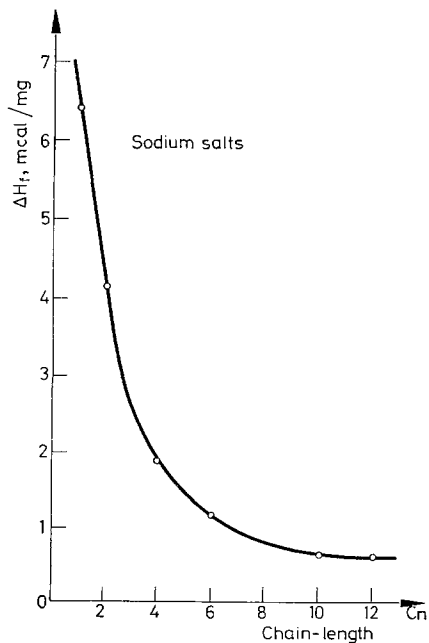


Fig. 4. Transition heats of mesophase-isotropic liquid transitions

Quantitative DTA measurements

Measurements with the Mettler TA 2000 apparatus were carried out in closed-sample-holders, with sample weights of about 5–10 mg and 5°/min heating and cooling rates. The accuracy was about 2–3%.

The DTA curves of the salts as a function of temperature can be seen in Fig. 2, and the transition temperatures as a function of the carbon number of the fatty acid-anion in Fig. 3. The smooth curves represent the temperatures of the solid

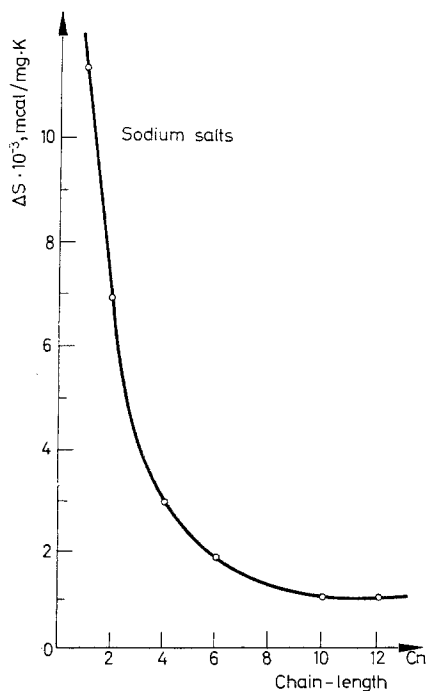


Fig. 5. Transition entropies of the mesophase isotropic liquid transitions

– mesophase and mesophase – isotropic liquid transitions, respectively. The transition temperatures observed under a hot-stage microscope showed similar tendencies. These tendencies correspond well to that which is the most general type in the case of homologous series having smectic liquid crystalline phases [10].

The transition enthalpies and entropies of the mesophase-isotropic liquid transitions decrease with increasing chain-length of the fatty acid anion (Figs 4, 5). The entropies of the solid-mesomorph transitions are about twice those of the mesophase – isotropic liquid transitions, which suggests that a definitely larger order-change occurs during the former one.

Simultaneous DTA-electrical conductivity measurements

The simultaneous DTA-electrical conductivity measurements were carried out under the following experimental conditions: heating rate: $10^{\circ}/\text{min}$; cooling rates: 0.5, 2, 5 and $10^{\circ}/\text{min}$; sample size: 10–20 mg; atmosphere: nitrogen.

The temperature was programmed by a "Programik" (Miki) temperature-programmer, the temperature difference signal was amplified by a Hewlett-Packard 419A.DC null voltmeter, and the electrical conductivity was measured with a Radelkisz OK 102/1 conductivity meter. The DTA and electrical conductivity curves were recorded as functions of temperature with a Bryans 26000A3 X-Y-Y' recorder.

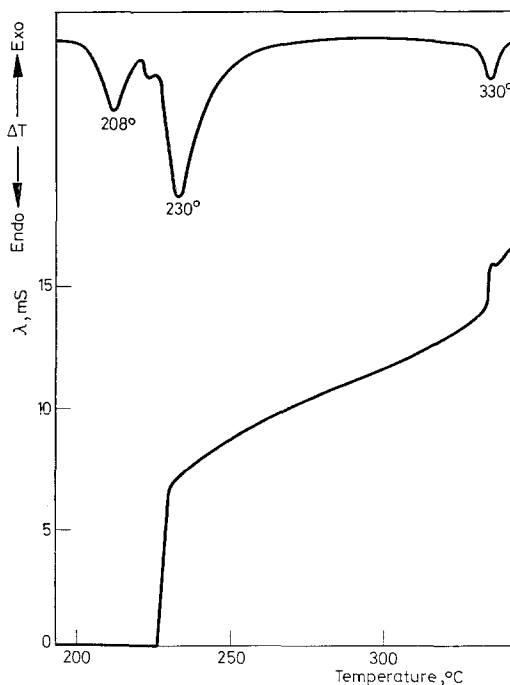


Fig. 6. Simultaneous electrical conductivity DTA of sodium capronate. Heating rate: $10^{\circ}/\text{min}$. Atmosphere: nitrogen

The measuring ranges were chosen so that the electrical conductivity jumps occurring during the phase-transitions could be recorded, but the electrical conductivity in the solid phase could not be measured with this sensitivity.

A typical record is shown in Fig. 6 on the example of sodium capronate.

The two sharp rises in the electrical conductivity curve, indicating two phase-changes, divide the investigated temperature range into three parts. The first is the range of the solid phase, extending up to the solid – mesophase transition,

where the first electrical conductivity jump is found. The second range is that of the mesophase, where the electrical conductivity increases continuously with increasing temperature. The third, above the second electrical conductivity rise,

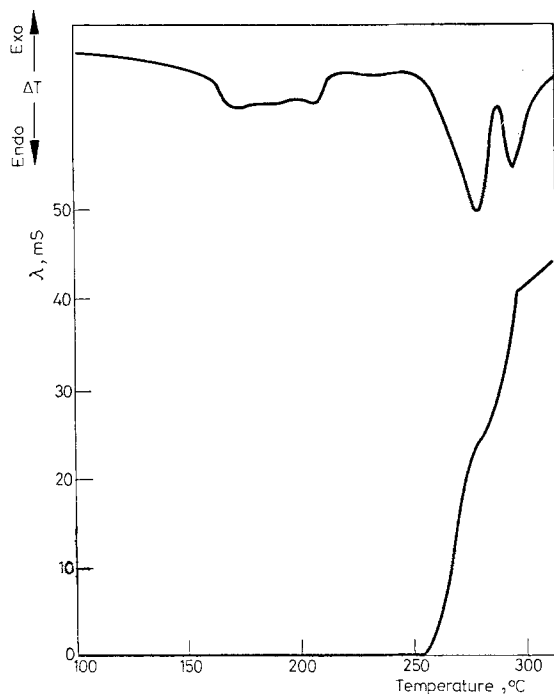


Fig. 7. Simultaneous DTA-electrical conductivity of sodium propionate. Heating rate: $10^{\circ}/\text{min}$, atmosphere: nitrogen

is that of the isotropic liquid range. These two electrical conductivity jumps occurred in parallel with the corresponding DTA peaks, at the same temperatures.

All the other sodium salts (from the member having three carbon atoms) behaved similarly and exhibited two electrical conductivity jumps at the temperatures of the "last two" DTA peaks. As can be seen in Fig. 7, the existence of the liquid crystalline phase in the case of sodium propionate could be proved by this simultaneous method.

As illustrated in Fig. 8, the values of the electrical conductivity jumps at the solid - mesophase transitions decrease with increasing chain-length of the fatty acid anion.

Though the electrical conductivity of the fatty acid thallium salts at the mesophase - isotropic liquid transition showed some "memory effect" as a function of the cooling rate in a capillary type of cell, [11] in our case, using a crucible type of cell, no such effect could be observed.

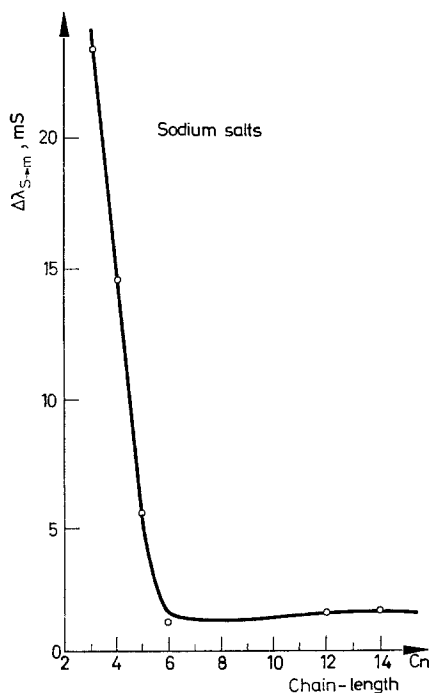


Fig. 8. Electrical conductivity jumps at the solid - mesophase transition

Conclusions

The results presented here verify that thermal analysis can be efficiently used for the investigation of compounds having complicated polymorphism, phase-changes and liquid crystalline states; in particular the simultaneous DTA-electrical conductivity technique, especially if supplemented with visual observations with the help of a hot-stage microscope is expected to be a powerful and suitable method for obtaining reliable information.

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RÉSUMÉ — On a étudié le comportement et les propriétés thermiques et thermoélectriques, ainsi que le type, la structure et l'aspect des phases cristallines liquides de sels de sodium d'acides gras saturés, non ramifiés.

Des corrélations entre les diverses propriétés thermiques et électriques et la longueur de la chaîne des composés étudiés ont été trouvées.

ZUSAMMENFASSUNG — Das thermische und thermo-elektrische Verhalten bzw. die Eigenschaften, sowie Typ, Struktur und Erscheinung der flüssigen kristallinen Phasen der Natriumsalze gesättigter unverzweigter Fettsäuren wurden untersucht. Die Messungen wurden mit Hilfe eines Derivatographen, einer DTA-Apparatur und einer simultanen DTA-Leitfähigkeitsmeß-Anordnung durchgeführt.

Zusammenhänge wurden zwischen den verschiedenen thermischen und elektrischen Eigenschaften und der Kettenlänge der Verbindungen gefunden.

Резюме — Исследовано термическое и термо-электрическое поведение, а также такие свойства, как тип, структура и появление жидко-кристаллических фаз натриевых солей неразветвленных жирных кислот. Измерения были выполнены с помощью Дериватографа, аппаратуры DTA и прибора для одновременного измерения DTA-электрической проводимости. Найдена взаимосвязь между различными термическими и электрическими свойствами и длиной цепи этих соединений.