On the Thermal Behaviour of the $n \cdot C_{13}$–$n \cdot C_{20}$ Lithium Soaps

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The phase transition temperatures and enthalpies were determined by differential scanning calorimetry between room temperature and the isotropic liquid region for the lithium n.alkanoates from tridecanoate to eicosanoate. The number and nature of the phases involved were discussed in comparison with the literature data available for some of the homologues concerned. For different kinds of transitions, the significant features of the plots ΔS vs. number of carbon atoms were put into evidence.

1. Introduction

In each n-alkanoate family characterized by the same alkali cation the transformation of a crystalline solid into a conventional isotropic liquid occurs directly only when low n_C values (n_C: number of carbon atoms) are concerned, whereas more than one step is usually required in the case of higher homologues.

As an example, cesium, rubidium, potassium and sodium n-alkanoates, starting from $n_C = 6, 5, 4$ and 4 respectively, give rise when heated to anisotropic "liquid crystals" before becoming "clear" melts. The stepwise melting process may also involve additional "plastic" phases which are stable at temperatures intermediate between those pertinent to the crystalline solid and the liquid crystals region.

Concerning lithium n-alkanoates both DSC analysis performed in our laboratory ($n_C = 1-4$, Ref. [1]; $n_C = 5-7$, Ref. [2]; $n_C = 8-12$, Ref. [3]) and literature data based on a variety of techniques (for an updated review, see Ref. [4]) substantially agree on the fact that conventional melting occurs up to $n_C = 11$. Starting from n-dodecanoate more complicate melting mechanisms are apparently to be taken into account although a clear picture cannot be drawn from the information at disposal inasmuch as the data available so far (see § 3.2) almost exclusively concern a few even homologues and, moreover, are somewhat conflicting about the number and nature of the phases involved. Consequently it seemed of some usefulness extending the DSC analysis to the lithium n-alkanoates from tridecanoate to eicosanoate (hereafter indicated, for the sake of brevity, simply as $LiC_{13}, \ldots, LiC_{20}$).

2. Experimental

The salts were prepared by refluxing for 2 – 3 hours a suspension of lithium carbonate in the methanol solution of the proper acid (present in a moderate excess). After hot-filtering, the solvent was removed under reduced pressure in a Rotavapor device and the solid residue was first washed with ethyl ether and then recrystallized (repeatedly when required) from methanol.

The chemicals employed were Fluka Li_2CO_3 (reagent for microscopy; stated purity $\geqq 99.5\%$), tridecanoic acid (*purum*, $\cong 98$), tetradecanoic acid (*puriss*, 99.5), pentadecanoic acid (*puriss*, $\geqq 99$), hexadecanoic acid (*puriss*, >99), heptadecanoic acid (*puriss*, >99), octadecanoic acid (*puriss*, 99.5), nonadecanoic acid (*puriss*, >99.5) and eicosanoic acid (*puriss*, >99).

The phase transition temperatures and enthalpies were determined by means of a Perkin-Elmer Mod. DSC-2 differential scanning calorimeter, following the procedure described elsewhere [5].

3. Results and Discussion

3.1. The DSC traces recorded on heating (between room temperature and the melt region) were characterized for each homologue with three endothermic peaks, hereafter denoted, in order of increasing temperature, as B, A and F.

Provided that heating did not reach T_A, transition B behaved as fully reversible (supercooling within few degrees; temperature and peak area

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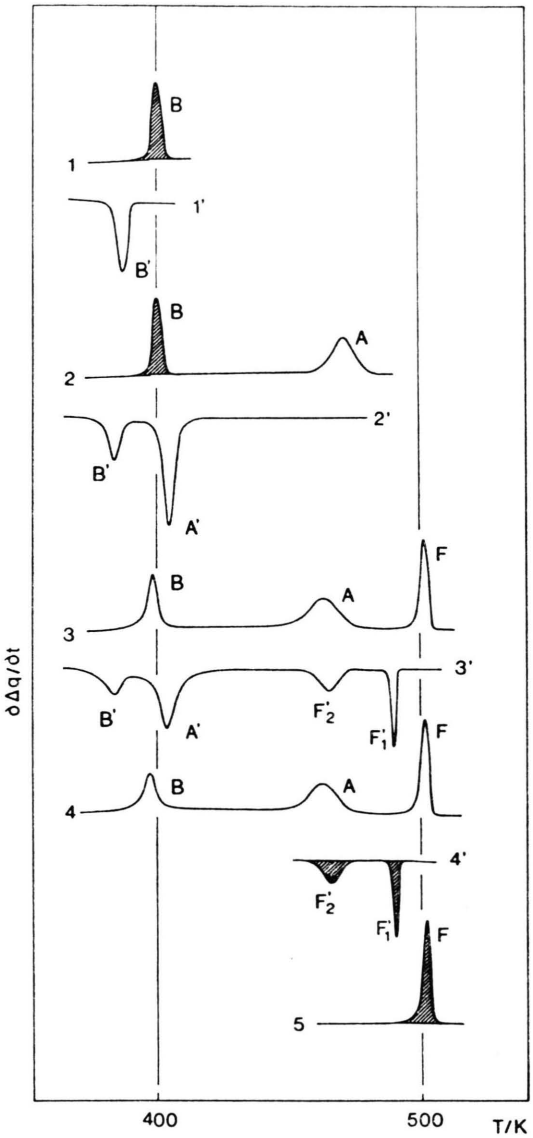

Fig. 1. Thermal behaviour of a LiC_{20} sample. The unprimed and primed DSC traces, which refer to heating and cooling respectively, were all taken in the same operational conditions (scan rate: 10 K min^{-1}). Trace 1: heating stopped at $T_B < T < T_A$; trace 2: heating stopped at $T_A < T < T_F$; trace 4': cooling stopped at $T_{A'} < T < T_F$. A strict coincidence exists between the hatched areas referring to B in traces 1 and 2, and between the hatched areas referring to $F_1' + F_2'$ ($F_1' \simeq F_2'$) and to F in traces 4' and 5. For further explanations see text.

coincident in subsequent heating runs). If on the contrary T_A was exceeded, so large a hysteresis took place that keeping the samples at room temperature even for weeks was not sufficient to let peak *B* reassume its original features.

Transition *A* gave rise to a peak for which supercooling was large and the reproducibility of both temperature and area was poor.

Finally, peculiar features were shown by peak *F*, which looked as single on heating while on cooling it was apparently splitted into two components: this means that the sample reached the liquid state through a pair of transitions occurring very close to each other and whose existence could be visualized only on cooling due to their different supercooling effect.

A picture of the above phenomena is given, as an example, in Fig. 1 for the case of the eicosanoate.

The figures summarized in Table 1 represent mean values of the data obtained in repeated heating scans of at least four samples of each salt. The following details, however, are to be pointed out. For peak *B* all heating runs not reaching T_A were employed for data evaluation. In the shorter homologues peaks *F* and *A* partially overlapped but luckily, owing to different supercooling, it was always possible to record *F* free from overlapping by reheating the sample first melted and then cooled to a temper-

Table 1. Phase transition temperatures and enthalpies of lithium *n*.alkanoates from LiC_{13} to LiC_{20}.

Salt	tr	T_{tr} / K	ΔH_{tr} / kcal mol^{-1}
LiC_{13}	*F*	505 ± 1	4.42 ± 0.05
	A	497.1 ± 0.7	—
	B	377.2 ± 0.1	3.48 ± 0.05
LiC_{14}	*F*	504.6 ± 0.6	4.44 ± 0.10
	A	489.4 ± 0.3	—
	B	366.8 ± 0.1	2.14 ± 0.06
LiC_{15}	*F*	502.3 ± 0.5	4.26 ± 0.10
	A	478.8 ± 0.1	—
	B	383.5 ± 0.1	3.90 ± 0.10
LiC_{16}	*F*	502.0 ± 0.7	4.47 ± 0.07
	A	480 ± 1	—
	B	381.3 ± 0.2	2.78 ± 0.04
LiC_{17}	*F*	502.6 ± 0.4	4.51 ± 0.04
	A	473 ± 1	—
	B	392.0 ± 0.3	4.37 ± 0.10
LiC_{18}	*F*	501.2 ± 0.2	4.49 ± 0.08
	A	464.6 ± 0.4	—
	B	390.4 ± 0.1	3.49 ± 0.08
LiC_{19}	*F*	500 ± 1	4.32 ± 0.06
	A	456 ± 1	—
	B	396.8 ± 0.6	4.78 ± 0.09
LiC_{20}	*F*	499.1 ± 0.4	4.48 ± 0.07
	A	462 ± 2	—
	B	397.2 ± 0.1	4.05 ± 0.02

ature low enough to cause solidification but not transition *A*. On the contrary, the attempt to obtain in an analogous way separation of the components of *F* was unsuccessful: even in a favourable case such as that shown in Fig. 1 (*), no stable baseline was obtainable when cooling the melt was stopped just after the appearance of F_1'. This is why only data referring to *F* as a whole are tabulated. Moreover, the poor reproducibility in the areas of peak *A* with different samples of the same salt, even when overlapping with *F* was absent, and of temperature and area in subsequent scans of the same sample, advised to tabulate only T_A values taken in the first heating runs, although it may be added that the corresponding heat effects amounted roughly to 4 ± 1 kcal mol^{-1} for all members of the series.

3.2. As far as we know, only the dilatometric investigation by Skoda [6] on $LiC_{14}, \ldots, LiC_{18}$ covers an unbroken succession of even and odd homologues. In each member of the series he found "three distinct transition regions: at about 110 °C (...), at about 200 °C (...) and at about 230 °C" (the latter into the molten state), but unfortunately he reported his results only in graphical and not in numerical form.

Further literature information is restricted to the even homologues LiC_{14}, LiC_{16} and LiC_{18}: the relevant phase transition temperatures drawn from the most significant papers are schematically shown in Fig. 2, for which the following details are worthy to be pointed out.

In a work devoted to the polythermal X-ray investigation of the even lithium soaps from LiC_{10} to LiC_{18} Gallot and Skoulios [7] found for the three homologues concerned here: (i) two "lamellar crystalline" structures, LC_1 and LC_2, in which both the polar end groups and the (extended) hydrocarbon chains are arranged in an ordered state; (ii) two ribbon-like structures, BR_1 and BR_2 (BR: "bidimensional rectangular"), in which only the polar end groups are still in a fully ordered state. These BR structures, therefore, ought to belong to the "waxy" and not to the "neat" type (in the soapboilers' language), the latter being characterized by a "lamellar labile" structure, as recognized by the same authors, e. g., in several alkali alkanoates with Na, K, Rb, Cs as the cation [4]).

Observations at the hot-stage polarizing microscope led also Baum, Demus, and Sackmann [8] to identify in LiC_{14}, LiC_{16} and LiC_{18} only waxy phases in the temperature region intermediate between the crystalline solid and the isotropic liquid, i. e., their conclusions were parallel to those by Gallot and Skoulios but for the fact that in lithium tetradecanoate a single waxy phase was identified.

Vold and coworkers, who repeatedly investigated lithium hexadecanoate and octadecanoate, recognized: (i) for LiC_{16}, three forms of which form III was formerly (1943, 1945) indicated as "resembling the waxy forms of sodium soaps" [9] but subsequently (1976) claimed to be a liquid crystalline mesophase **; (ii) for LiC_{18}, two crystalline and one waxy phase.

Finally Cox and McGlynn [15] from their DTA investigation on octadecanoate came to the conclusion that, among the three peaks they could record on heating, the one occurring at the highest temperature ought to conceal two different phase changes: actually on subsequent cooling it "was resolved by different amount of supercooling into two peaks". The involved phase changes "occurred probably at 225 °C (498 K) or slightly higher and (...) at 229 °C (502 K)", and in this interval supplementary visual observations showed that "the soap softened to a jelly-like, brightly birefringent, liquid-crystalline phase".

3.3. The features of the heating and cooling DSC traces, described in § 3.1, suggest that each of the $LiC_{13}, \ldots, LiC_{20}$ salts can exist from room temperature up in five different phases, although the phase immediately preceding the isotropic liquid occurs in a very narrow interval. This means that the picture outlined by Cox and McGlynn for LiC_{18} is just a single case out of a much more generalized type of behaviour.

Concerning the nature of the phases, the full reversibility of transition B and the poor reversibility of transition A support the idea (agreeing

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* The extent of separation between peaks F_1' and F_2' in cooling runs progressively decreases with decreasing n_C, so that in the three shorter homologues partial overlapping still occurred.

** Vold, Funakoshi and Vold [11], *inter alia*, from X-ray patterns supplementing their DSC analysis inferred "for the phase existing just below the melting point" a structure different from that given by Gallot and Skoulios.

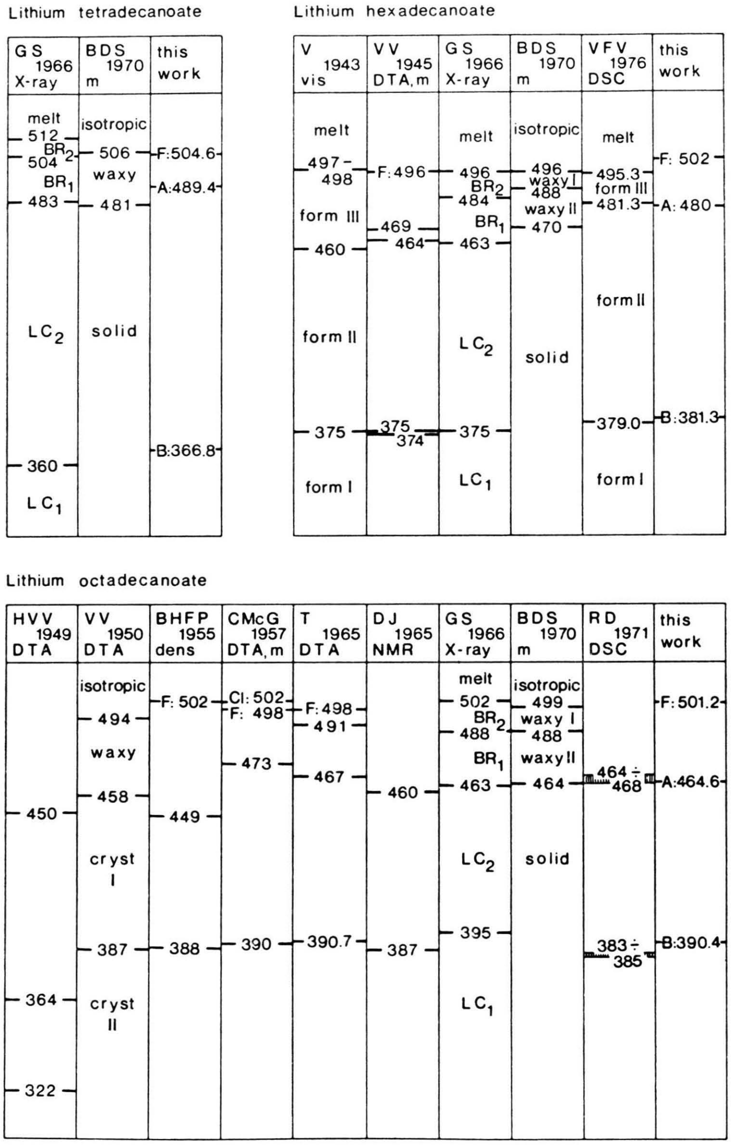

Fig. 2. Comparison of phase transition temperatures in K as detected by different authors with several techniques in lithium tetradecanoate, hexadecanoate, and octadecanoate. *Authors:* GS, Gallot and Skoulios [7]; BDS, Baum, Demus, and Sackmann [8]; V, Vold [9]; VV 1945, Vold and Vold [10] (the values 374, 464 and 375, 469 were taken respectively by DTA and m, the value 496 by both techniques); VFV, Vold, Funakoshi, and Vold [11]; HVV, Hattiangdi, Vold, and Vold [12]; VV 1950, Vold and Vold [13]; BHFP, Benton, Howe, Farnand, and Puddington [14]; CMcG, Cox and McGlynn [15]; T, Trzebowski [16]; DJ, Dunell and Janzen [17]; RD, Ripmeester and Dunell [18]. HVV, DJ and RD did not extend the observations up to fusion. *Techniques:* m, microscopic observation; vis, visual observation; dens, density measurements. *Phase designations* (according to the original papers): BR, "structure à rubans", bidimensional rectangular; LC, "structure lamellaire cristalline".

with the views by Gallot and Skoulios, by Baum, Demus, and Sackmann – but for the tetradecanoate – and by Cox and McGlynn) that: (i) equilibrium ought to exist at T_B between two crystalline phase and at T_A between one crystalline and one non-crystalline phase; (ii) since the total number of phases is five, including the isotropic melt, the phase immediately above T_A ought not to be a liquid crystalline one. The question, however, whether the phases and at T_A between one crystalline and one reported by Gallot and Skoulios and by Baum, Demus, and Sackmann) or a liquid crystalline one (as proposed by Cox and McGlynn) remains open, although by comparing the trend of the T_F values as a function of n_C in lithium alkanoates with those of both T_F and T_{Cl} (Cl: clearing) in the other alkali n-alkanoate families [4], one might be inclined to accept rather the first possibility.

A comprehensive picture of the phase relationships in the $LiC_1, \ldots, LiC_{20}$ series, as resulting from our present and previous papers [1–3], is given in Fig. 3, where the transition temperatures are plotted as a function of n_C and the most significant features are: (i) the stabilization (at $n_C > 11$)

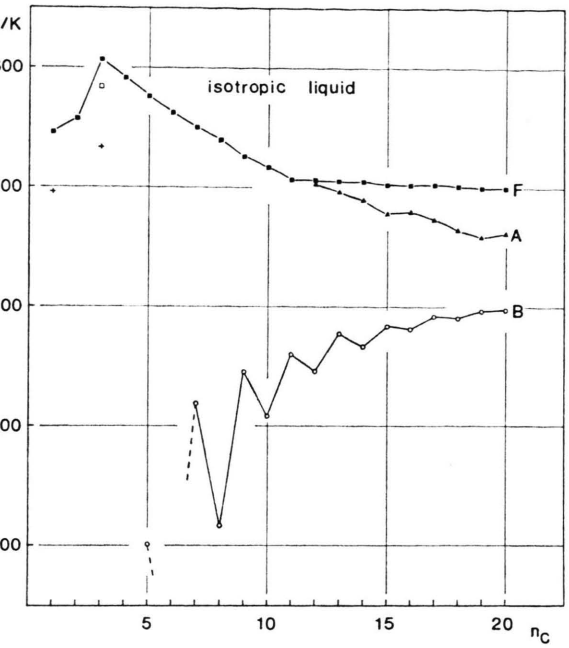

Fig. 3. Phase transition temperatures in the LiC_1, ..., LiC_{20} *n*. alkanoates according to Refs [1–3] and the present paper. Crosses: intercrystalline transitions other than B; empty square: metastable fusion of LiC_3. For further explanation see text.

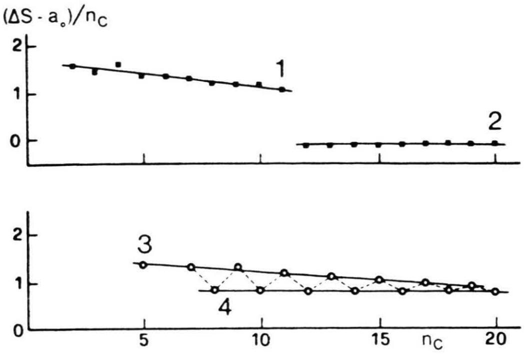

Fig. 4. Upper part: parabolic dependence of ΔS_F on n_C (curve 1: $a_0 = 1.67907$; curve 2: $a_0 = -0.19235$). Lower part: parabolic dependence of ΔS_B on n_C (curve 3, odd homologues: $a_0 = 1.56815$; curve 4, even homologues: $a_0 = 0.82404$).

of the lower temperature limit of the isotropic liquid field concomitantly to the arising of the crystalline-plastic transition *A*; (ii) the odd-even alternation apparent for the intercrystalline transition *B*.

On passing from $n_C = 11$ to $n_C = 12$ a break occurs also in the trend of the entropy change ΔS_F (Fig. 4, upper part), while the alternating effect is once more put into evidence by the different trends of the entropy change ΔS_B in the odd and even homologues (Fig. 4, lower part).

As a final remark it can be mentioned that no previous data on enthalpy changes were known except the few following. Vold and Vold [10] gave 5760, 3900 and 3400 cal mol^{-1} for the transitions of LiC_{16} at 496, 464 and 374 K (see Fig. 2), respectively; Vold, Funakoshi, and Vold [11], 5.60 and 5.09 kcal mol^{-1} for the transitions of the same salt at 495.3 and 379.0 K. Further, Hattiangdi, Vold, and Vold [12] reported 2860 and 3130 cal mol^{-1} for the transitions of LiC_{18} at 450 and 364 K, respectively. In the case of the former salt the above ΔH_{496}, $\Delta H_{495.3}$ and ΔH_{374}, $\Delta H_{379.0}$ look as too large when compared with the ΔH_F and ΔH_B data given in Table 1, whereas in the case of the latter salt ΔH_{364} seems somewhat too low with respect to Table 1 ΔH_B.

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