On the Thermal Behaviour of Long-Chain Lithium and Sodium n.Alkanoates

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The phase relationships in Li and Na n.alkanoates from octanoate to dodecanoate were investigated by means of DSC analysis. Clearing (when present), fusion, and solid state transition (when possible) temperatures and enthalpies were measured. The collected results are discussed in comparison with literature data, mostly obtained by different techniques.

1. Introduction

An X-ray diffraction study carried out on the even Li soaps between LiC_{10} ** and LiC_{18} allowed Gallot and Skoulios [1] to identify: (i) in each of them two crystalline lamellar (CL) structures, and moreover (ii) in the homologues where $n_{\mathrm{C}} \geqq 12$, ribbon (R) structures ("waxy" phases) stable between the crystalline solid and the isotropic liquid field. The dilatometric investigation by Skoda [2] on the $\mathrm{LiC}_{14}-\mathrm{LiC}_{18}$ series and the microscopic observations by Baum et al. [3] on the even $\mathrm{LiC}_{12}-\mathrm{LiC}_{18}$ homologues substantially confirmed such views. So far, however, no data on any pertinent heat effect are known and, moreover, no information on phase transitions in odd homologues such as LiC_9 and LiC_{11} is available.

The phase relationships in Na soaps, remarkably more complicated than in the Li ones, were submitted to extensive investigation, among others, by Vold et al. [4] (dilatometric, "hot wire", microscopic and visual observations on even homologues between NaC_6 and NaC_{22}), Skoulios and Luzzati [5] (X-ray diffraction study on even homologues between NaC_{12} and NaC_{18}), Pacor and Spier [6] (DTA and DSC measurements on the series $\mathrm{NaC}_{10}-\mathrm{NaC}_{19}$), Baum et al. [3] (heating stage polarizing microscopy on several even and odd homologues). The agreement among different sets of data is not always satisfactory and once more the thermal information remains incomplete, e. g., for what concerns the transition from mesomorphic to isotropic liquid.

Two recent papers by our group dealt with the behaviour of long-chain Cs [7] and K [8] n. alkanoates: the present one aims at giving a contribution to the knowledge of the $\mathrm{LiC}_8-\mathrm{LiC}_{12}$ and $\mathrm{NaC}_8-\mathrm{NaC}_{12}$ series.

2. Experimental

C. Erba metallic Na, and Fluka puriss. $\mathrm{Li_2CO_3}$ ($\geqq 99.5$ mole%) and n. octanoic ($\geqq 99.5$), n. nonanoic (>99), n. decanoic ($\geqq 99$), n. hendecanoic (>99.5), n. dodecanoic (>99.5) acids were employed as starting materials. Li alkanoates were prepared by dissolving $\mathrm{Li_2CO_3}$ in a large excess of the corresponding acid at a proper temperature. When no more $\mathrm{CO_2}$ escaped the product was repeatedly washed with acetone; LiC_{12} was also re-crystallized from anhydrous ethanol. Na alkanoates were obtained in the way previously described [8] for K salts and purified by re-crystallization from suitable mixtures of anhydrous ethanol and 2-propanol.

A Perkin-Elmer differential scanning calorimeter Mod. DSC-2 was employed to measure the transition temperatures (T_{tr}/K) and enthalpies (ΔH_{tr}/kcal mole^{-1}), following a procedure the details of which were given elsewhere [9].

3. Results and Discussion

3.1 — The thermal behaviour of the $\mathrm{LiC}_8-\mathrm{LiC}_{12}$ series is summarized in Table 1. DSC analysis: (i) confirmed the results by Gallot and Skoulios [1] on LiC_{10}, LiC_{12}, and by Baum et al. [3] on the latter homologue, and (ii) allowed to state the phase relationships (so far unknown) in LiC_8, LiC_9, LiC_{11}.

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** For the sake of simplicity, the n. alkanoate in which the number of C atoms is $n_{\mathrm{C}}=x$ is here briefly indicated as MC_x, M being the proper alkali metal.

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Figure 1 shows that the fusion temperature (T_F/K, here assumed as the lower limit of the liquid field independently of the phase which at T_F is in equilibrium with the liquid one in a given soap) progressively decreases as n_C increases, whereas the temperature (T_A/K), at which the solid state transition A from a $(CL)_1$ to a $(CL)_2$ phase occurs, exhibits a marked alternating character, being higher in each odd homologue than in its even neighbours. Such an alternation is also apparent in the ΔS_A's (see Figure 2).

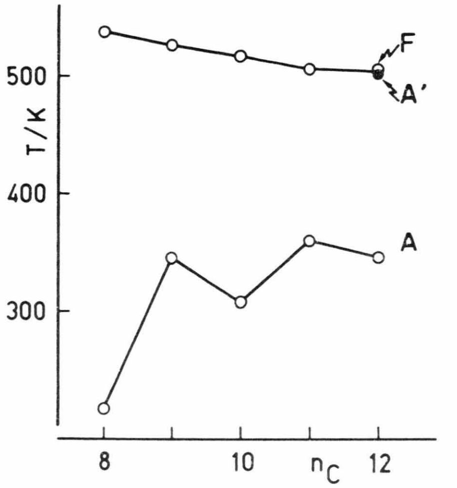

Fig. 1. Transition temperatures in the LiC_8-LiC_{12} series.

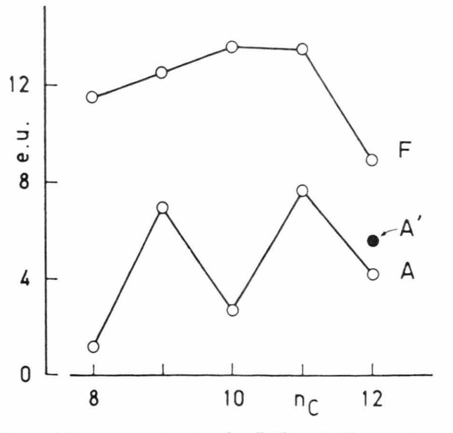

Fig. 2. Transition entropies in the LiC_8-LiC_{12} series

At $T/K > 500$ a single sharp peak corresponding to fusion was recorded for the LiC_8-LiC_{11} homologues, whereas in the same temperature region twin largely overlapping peaks were observed during the first heating run of LiC_{12} samples (see curve 1 in Figure 3). Such a DSC trace was consistent with the existence of a $(CL)_2-R$ [1] (or "fest-waxy" [3]) transition (indicated as A' in Table 1 and Figs. 1, 2) a few degrees below the LiC_{12} melting point. Concerning the pertinent heat effects, a $\Delta H_{tot} = \Delta H_{A'} + \Delta H_F$ value was easily drawn from the area, a_1, of the twin peaks, whereas ΔH_F could be evaluated as follows. During the cooling run of a previously melted sample a sharp exothermic peak occurred at $500 > T/K > 490$ of area $a_1' \sim 0.6\, a_1$ (see curve 1' in Fig. 3), reasonably to be attributed to freezing ("isotrop flüssig-waxy" transition [3]), while a second (unsharp) heat emission, pertinent to the "waxy-fest" transition, was observed only at a temperature some tens of degrees lower. Now, should cooling be stopped, e. g., at 480 K and the sample immediately re-heated, a single peak was recorded of an area, a_2, strictly close to a_1' and used for the ΔH_F calculation (see curve 2 in Figure 3). The $\Delta H_{A'}$ value reported in Table 1 was obtained as the difference between ΔH_{tot} and ΔH_F.

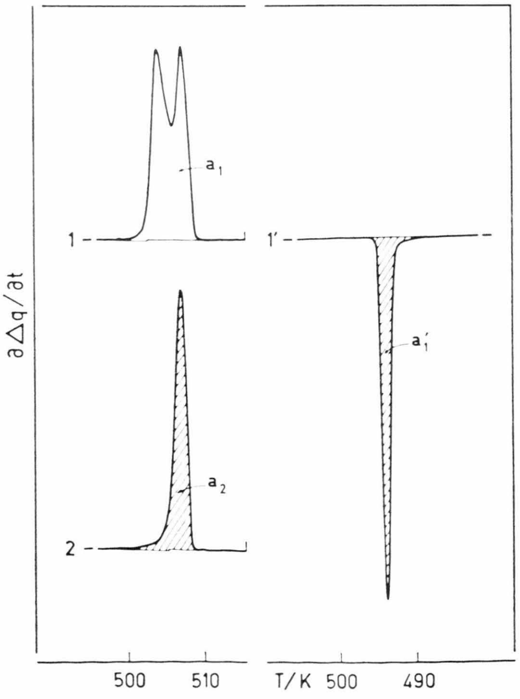

Fig. 3. DSC traces taken in the same operational conditions on heating (curves 1, 2) or cooling (curve 1') a LiC_{12} sample: for explanation see text.

Table 1. Phase transitions in Li n.alkanoates ($8 \leq n_C \leq 12$).

salt	this work [a]			Ref. [1b]		Ref. [3c]	
	tr	T_{tr}/K	ΔH_{tr}/kcal mole^{-1}	tr	T_{tr}/K	tr	T_{tr}/K
LiC_8	A	217.5 ± 0.8	0.26 ± 0.01	—	—	—	—
	F	539.2 ± 0.3	6.17 ± 0.06	—	—	—	—
LiC_9	A	346.2 ± 0.1	2.41 ± 0.02	—	—	—	—
	F	526.1 ± 0.3	6.61 ± 0.07	—	—	—	—
LiC_{10}	A	308.5 ± 0.3	0.83 ± 0.01	$(CL)_1-(CL)_2$	312	—	—
	F	517.8 ± 0.5	7.05 ± 0.06	$(CL)_2$-isotropic liquid	511	—	—
LiC_{11}	A	360.3 ± 0.1	2.76 ± 0.05	—	—	—	—
	F	507.2 ± 0.3	6.85 ± 0.13	—	—	—	—
LiC_{12}	A	345.8 ± 0.6	1.45 ± 0.05	$(CL)_1-(CL)_2$	340	—	—
	A′	503	2.8 ± 0.3	$(CL)_2$-R	502	fest-waxy	500
	F	506	4.51 ± 0.07	R-isotropic liquid	512	waxy-isotrop flüssig	510

[a] DSC.
[b] X-ray diffraction patterns.
[c] Heating stage polarizing microscope.

A large inertia was also exhibited by all salts in undergoing transition A when cooled after having been melted: therefore the ΔH_A's were evaluated only from DSC traces taken on unmelted samples.

3.2 – The main peculiarities of the considered Na soaps are: (i) the ability to exist as mesomorphic liquids ("neat" phases) between an upper temperature limit (clearing temperature, T_{Cl}/K) which decreases from ~ 635 to ~ 600 as n_C increases from 8 to 12, and a lower limit (T_F/K ~ 515 *) practically independent of chain length (see Fig. 4), and (ii) the occurrence between T_F/K and room temperature of phase transitions in an unusually large number, increasing with chain length.

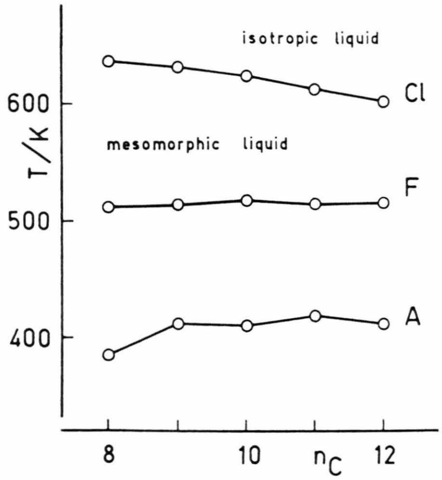

Fig. 4. Main phase transitions in the NaC_8-NaC_{12} series.

The features of DSC traces recorded in subsequent heating, cooling and re-heating runs of a given sample generally allowed to assume as satisfactorily correct the thermal information on clearing and fusion, whereas peak unsharpness and/or overlapping, thermal inertia and poor reproducibility for a number of transitions reduced (often exceedingly) data trustworthiness at $T/K < 515$.

As for the "neat" fields, a sufficient agreement exists between the temperature limits found by us and those reported in Ref. [3] (see Table 2).

A part of the corresponding heat effects may be compared with previous data on NaC_{10}, NaC_{11}, NaC_{12}, unfortunately reported only in a graphic form by Pacor and Spier. The order of magnitude attributed by these Authors to ΔH_{Cl} and ΔH_F (0.2 and 2 kcal mole^{-1}, respectively) is confirmed by the present DSC traces, from which, however, the suggested alternating character can be argued neither for ΔH_{Cl}, ΔH_F nor for ΔS_{Cl}, ΔS_F. The trend of the latter quantities is shown as a function of n_C in the upper section of Figure 5.

Traces recorded on a given NaC_{10} sample and reported in Fig. 6 give an idea of the difficulties offered by experimental results obtained at $T/K < 515$ to a correct interpretation. Baum et al. [3], Vold et al. [4], and Pacor and Spier [6] agree on the existence in NaC_{10} of a transition ("fest-waxy" [3],

* Such a lower limit is in the following considered as the fusion temperature, independently of the phase in equilibrium —at T_F — with the "neat" one in each soap.

Table 2. Phase transitions in Na n. alkanoates ($8 \leqq n_C \leqq 12$).

salt	this work [a]			Ref. [4b]		Ref. [5c]		Ref. [3d]	
	tr	$\frac{T_{tr}}{K}$	$\frac{\Delta H_{tr}}{\text{kcal mole}^{-1}}$	tr	$\frac{T_{tr}}{K}$	tr	$\frac{T_{tr}}{K}$	tr	$\frac{T_{tr}}{K}$
NaC_8	A	385	(1.5)	?	387	—	—	—	—
	F	512	2.02 ± 0.03	?	516	—	—	superwaxy-neat	516
	Cl	635.5 ± 0.6	0.32 ± 0.01	neat soap-liquid	620	—	—	neat-isotrop flüssig	633
NaC_9	A	412 ± 3	(2.4)	—	—	—	—	—	—
	F	514 ± 2	2.02 ± 0.03	—	—	—	—	superwaxy-neat	516
	Cl	630.6 ± 0.8	0.31 ± 0.01	—	—	—	—	neat-isotrop flüssig	628
NaC_{10}	A	410 ± 2	(2.0)	?	412	—	—	fest-waxy	413
	F	516.8 ± 0.6	2.00 ± 0.04	?	520	—	—	superwaxy-neat	518
	Cl	622.7 ± 0.6	0.28 ± 0.01	neat soap-liquid	616	—	—	neat-isotrop flüssig	621
NaC_{11}	A	417.9 ± 0.7	(2.5)	—	—	—	—	—	—
	F	513.6 ± 0.9	1.87 ± 0.04	—	—	—	—	—	—
	Cl	611.8 ± 0.8	0.26 ± 0.01	—	—	—	—	—	—
NaC_{12}	A	411 ± 2	(1.9)	subwaxy-waxy	414	subwaxy-waxy	415	fest-waxy	414
	F	515 ± 2	1.72 ± 0.08	subneat soap-neat soap	528	subneat-neat	525	subneat-neat	519
	Cl	600.7 ± 0.8	0.21 ± 0.01	subneat soap-neat soap	609	neat-liquid	598	neat-isotrop flüssig	602

[a] DSC. [b] Dilatometric, "hot wire" and visual observations.
[c] X-ray diffraction patterns. [d] Heating stage polarizing microscope.

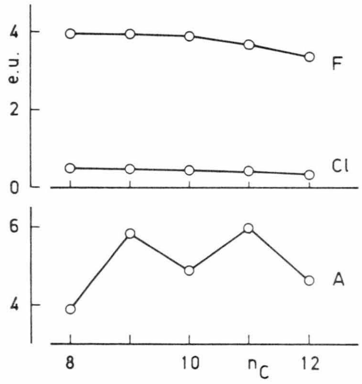

Fig. 5. Transition entropies in the $NaC_8 - NaC_{12}$ series.

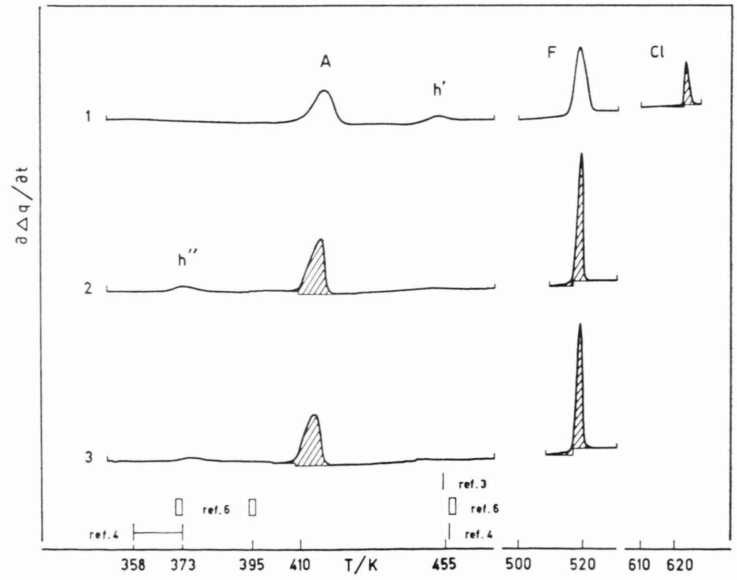

Fig. 6. DSC traces taken on a NaC_{10} sample (operational conditions: scan speed $10\,K\,min^{-1}$; chart speed $20\,mm\,min^{-1}$; sensitivity range $10\,mcal\,sec^{-1}$, but for the Cl peak for which range 5 was employed). For comparison, a few transition temperatures by previous Authors are also shown: for explanation see text. Reference [6] data could be read on the published plot only approximately, and therefore were not reported in Table 2. The hatched areas were employed for the ΔH calculations.

"subwaxy-waxy" [6]) at $T/K \sim 410$ which ought to be: (i) followed by a further one ("waxy-superwaxy" [3]) at $T/K \sim 455$, and (ii) preceeded either by no one, or by one (at 358 – 373 K), or by two (at ~372 and ~395 K, the latter from a "curd" to a "subwaxy" phase) more transitions according to Refs. 3, 4 and 6, respectively. In Figure 6 curve 1 refers to heating of the fresh sample up to the isotropic melt region, whereas curves 2 and 3 were recorded 3 days and 70 days later up to the "neat" field. At $T/\mathrm{K} < 515$: (i) the peak expected at ~ 410 K (peak A in Fig. 6) was always present and satisfactorily reproducible, though only the two latter (and sharper) traces were used to evaluate ΔH_A; (ii) in the region of the "waxy-superwaxy" transition curve 1 (fresh sample) exhibited a hump (h′) which became hardly detectable in the other curves; (iii) in the temperature region about 370 K a hump (h″) was on the contrary apparent only in curves 2 and 3 (previously melted sample); (iiii) no clear evidence for a definite heat absorption was ever obtained in correspondence with Pacor and Spier's "curd-subwaxy" transition. As a consequence, we preferred to restrict data tabulation at $T/\mathrm{K} < 515$ to transition A: moreover, the ΔH_A value was reported in brackets (see Table 2) inasmuch as superposition with a possibly existing "curd-subwaxy" transition cannot be excluded at all.

A transition (characterized by a heat effect larger than any other at $T/\mathrm{K} < 515$, and again indicated as A) occurs in each of the remaining Na soaps here considered, though it seems, e. g., to have escaped the microscopic observations by Baum et al.[3] on $\mathrm{NaC_8}$, $\mathrm{NaC_9}$.

An alternating character, similar to that put into evidence in Li soaps for the $(\mathrm{CL})_1 - (\mathrm{CL})_2$ phase change, is apparent in the T_A and, more markedly, in the ΔS_A values (see Fig. 4 and the lower section of Fig. 5, respectively). Moreover, the features of the A transition, and in particular its large heat effect, point to the correctness of the idea expressed by Pacor and Spier[6] that in a long-chain Na n. alkanoate the passage from a tri- to a bi-dimensional network ought to occur at T_A and not at any lower temperature.

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