On the Thermal Behaviour of Long-chain Potassium *n*.alkanoates

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Differential scanning calorimetry was performed between 110 K and the isotropic melt region on potassium *n*.alkanoates from octanoate to dodecanoate. Clearing, melting and (crystalline) solid state transition temperatures and heat effects were measured. In the higher homologues the occurrence of phases (likely "waxy") intermediate between crystalline solid and mesomorphic liquid could also be argued. The phase relationships are discussed in comparison with some roentgenographic and microscopic results of previous authors.

1. Introduction

The phase relationships in the even K *n*.alkanoates for which $8 \leqq n_C \leqq 18$ (n_C: number of C atoms) had been investigated: (i) from room temperature up to the isotropic melt region by Gallot and Skoulios [1] (X-ray diffraction patterns); (ii) between ~450 and ~670 K by Baum et al. [2] (visual observation at the heating stage polarizing microscope). The latter took also into account KC_9 **.

Both agreed on the fact that each salt could exist as a mesomorphic liquid ("neat" phase [2] of a "labile lamellar" structure [1]) in a temperature region the lower limit of which ranged between ~560 K in the case of KC_8 and ~540 K in the case of KC_{18}. Far diverging values were however attributed to the upper limits.

Moreover, at $T < 540$ K Gallot and Skoulios [1] identified: (i) in KC_8, KC_{10} two different, and in KC_{12}, KC_{14}, KC_{16}, KC_{18} three different "crystalline lamellar" (CL) phases; (ii) in KC_{14} several "disc", and in KC_{16}, KC_{18} several "ribbon" structures.

Anyway, the mentioned discrepancies, the poor information on phase relationships in odd homologues, and the absence of thermal data on any of the above transitions suggested as worthy a calorimetric re-investigation of this salt family. The present paper deals with the $KC_8 - KC_{12}$ series.

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** For the sake of simplicity, potassium *n*.octanoate, *n*. nonanoate, . . . , are here briefly indicated as KC_8, KC_9, . . . , respectively.

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2. Experimental

C. Erba RPE metallic potassium, and Fluka puriss. *n*.octanoic ($\geqq$ 99.5 mole %), *n*.nonanoic (>99), *n*.decanoic ($\geqq$ 99), *n*.hendecanoic (>99.5), *n*.dodecanoic (>99.5) acids were used as starting materials.

The alkanoates were prepared by reaction of finely divided K under toluene with the proper acid in toluene solution. When no more H_2 escaped, some anhydrous ethanol was added to dispose of any rest of unreacted metal. After filtration, the salts were repeatedly washed with acetone and finally re-crystallized from 2-propanol.

The transition (tr) temperatures (T_{tr}/K) and enthalpies (ΔH_{tr}/kcal mole^{-1}) were measured by means of a Perkin Elmer Mod. DSC-2 differential scanning calorimeter (for details on procedure see Ref. [3]). Sealed Al containers were employed.

3. Results and Discussion

3.1. Let us first consider the field of existence of the "neat" phase (see Table 1 and Figure 1).

Table 1. Clearing and fusion.

salt	tr	this work [a] T_{tr}/K	ΔH_{tr}/kcal mole^{-1}	Ref. 1 [b] T_{tr}/K	Ref. 2 [c] T_{tr}/K
KC_8	Cl	712 ± 2	0.63 ± 0.02	652	>673
	F	560.6 ± 0.8	4.38 ± 0.05	551	564
KC_9	Cl	707.4 ± 0.8	0.59 ± 0.03	–	>673
	F	549.1 ± 0.8	3.54 ± 0.10	–	555
KC_{10}	Cl	696	0.50 ± 0.02	649	>673
	F	544	2.91 ± 0.06	547	550
KC_{11}	Cl	691.4 ± 0.8	0.44 ± 0.01	–	–
	F	541 ± 2	2.87 ± 0.04	–	–
KC_{12}	Cl	679.2 ± 0.5	0.44 ± 0.01	647	668
	F	540.8 ± 0.5	2.83 ± 0.06	545	546

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

According to the recorded DSC traces, the clearing temperature (T_{Cl}/K, at which the mesomorphic liquid changes into isotropic) progressively decreases from ~712 to ~679 K as n_C increases from 8 to 12: the figures given in Ref. 1 are therefore to be considered by ~60 to ~30 K too low, whereas the

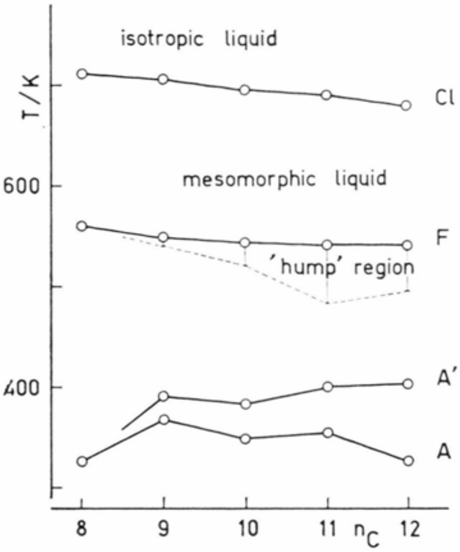

Fig. 1. Phase transition temperatures in the KC_8-KC_{12} series.

qualitative remark by Baum et al. [2] that T_{Cl} exceeds 673 K when $8 \leqq n_C \leqq 10$ remains valid.

A satisfactory convergency exists on the contrary between present and previous results on fusion temperatures (T_F/K, intended here as the lower limits of the "neat" fields independently of the nature of the phase in equilibrium – at T_F – with the "neat" one in each alkanoate).

It is anyway to be said that DSC analysis allowed to record a unique peak only in the case of KC_8, whereas in the higher homologues the peaks to be attributed to fusion were always preceeded by one or more "humps". Figure 2 shows a few examples of the latter, the nature of which may be tentatively explained as follows.

On one hand the already mentioned Gallot and Skoulios' ribbon or disc structures ("waxy" phases in the terminology by Baum et al.) were detected between T_F and (T_F-102), (T_F-85), (T_F-75) in KC_{18}, KC_{16}, KC_{14}, respectively, i.e., within temperature ranges becoming increasingly narrow as n_C decreases. On the other hand in the even homologues we took into account, "humps" were recorded between T_F and (T_F-46), (T_F-23) in KC_{12}, KC_{10}, respectively, and were absent in KC_8. Now, should the above ΔT's be plotted *vs* n_C (see Fig. 3) the

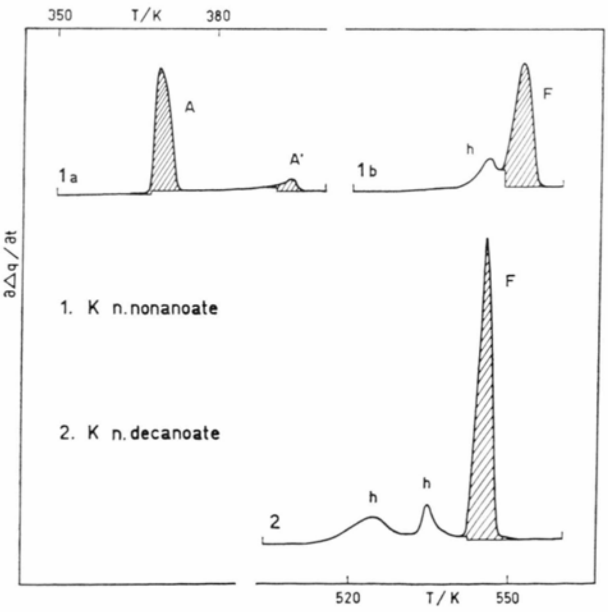

Fig. 2. DSC traces taken (in the same operational conditions) on a KC_9 and a KC_{10} sample. Curve 1 a: sstr's A and A' in KC_9; curve 1 b: "hump" (h) and fusion peak in KC_9; curve 2: "humps" and fusion peak in KC_{10}. Hatched areas taken into account for ΔH_{tr} calculations.

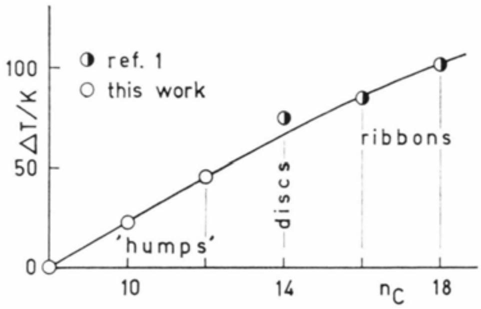

Fig. 3. Width of the "intermediate phases" region in even K *n*.alkanoates: for explanation see text.

Table 2. Solid state transitions.

salt	this work [a] tr	T_{tr}/K	ΔH_{tr}/kcal mole^{-1}	Ref. 1 [b] tr	T_{tr}/K
KC_8	A	326.6 ± 0.1	2.26 ± 0.05	$(CL)_1-(CL)_2$	331
KC_9	A	367.5 ± 0.5	2.69 ± 0.02	–	–
	A'	390.5 ± 0.4	0.32 ± 0.03	–	–
KC_{10}	A	348.7 ± 0.5	1.96 ± 0.02	$(CL)_1-(CL)_2$	350
	A'	382.9 ± 0.6	0.24 ± 0.01	–	–
KC_{11}	A	355.0 ± 0.6	3.56 ± 0.06	–	–
	A'	400 ± 2	0.66 ± 0.05	–	–
KC_{12}	A	327.2 ± 0.4	2.79 ± 0.03	$(CL)_1-(CL)_2$	328
	A'	404 ± 2	0.72 ± 0.06	$(CL)_2-(CL)_3$	408

[a] DSC

[b] X-ray diffraction patterns.

trend of the curve suggests that "waxy" phases intermediate between mesomorphic liquid and crystalline solid may exist (though having escaped to previous investigations) also in potassium *n*.alkanoates where $n_C < 14$, and vanish only when $n_C = 8$.

3.2. Coming to the crystalline solid field, DSC traces proved in each member of the $KC_8 - KC_{12}$ series the occurrence at $320 < T_{tr} < 370$ of a solid state transition (sstr A, see Table 2) involving a heat effect at least as large as 2 kcal $mole^{-1}$. This transition too appears to be unique in KC_8 only, whereas in each of the higher homologues it is accompanied by a sstr A′, which occurs at $380 < T_{tr} < 410$ and involves a remarkably smaller heat effect (0.7 kcal $mole^{-1}$, or less). An example of such twinning is shown in Figure 2.

As for the even homologues where $8 \leqq n_C \leqq 12$ sstr's from $(CL)_1$ to $(CL)_2$ phases were already observed [1] at temperatures satisfactorily agreeing with the present T_A's. Evidence for a further transition from a $(CL)_2$ to a $(CL)_3$ phase could however be obtained by Gallot and Skoulios only in KC_{12}: DSC analysis has now improved the picture showing the occurrence of a second sstr also in the three lower homologues KC_{11}, KC_{10}, KC_9.

3.3. Samples of $KC_8 - KC_{12}$ were scanned down to 110 K, but none was found to undergo any other sstr in this temperature region.

[1] B. Gallot and A. Skoulios, Kolloid-Z., Z. Polymere, **210,** 143 [1966].

[2] E. Baum, D. Demus, and H. Sackmann, Wiss. Z. Univ. Halle **XIX** '70, 37.

[3] P. Ferloni and P. Franzosini, Gazz. Chim. Ital. **105,** 391 [1975].