On the Thermal Behaviour of Long-chain Rubidium *n.* Alkanoates

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Differential scanning calorimetry allowed to state the main phase relationships in Rb *n.* alkanoates from octanoate to dodecanoate, and to measure the pertinent heat effects. Before becoming (on heating) a clear melt each homologue can exist as a mesomorphic liquid over a 130–140 K wide interval. The collected results are compared with those previously obtained for the corresponding Li, Na, K and Cs salts.

1. Introduction

The phase relationships and thermal properties of long-chain Rb *n.* alkanoates for which the number of C atoms is $n_C \geqq 8$ are so far largely unknown: RbC_{12} ** and a few higher even homologues were submitted to observation at the heating-stage polarizing microscope by Baum et al. [1] and/or to roentgenographic investigation by Gallot and Skoulios [2], whereas a complete gap of information exists both for the odd homologues and for RbC_8, RbC_{10}.

Recent papers of this series dealt with differential scanning calorimetry on long-chain Cs [3], K [4], Li, and Na [5] *n.* alkanoates: in the present one the calorimetric analysis is extended to the RbC_8-RbC_{12} family.

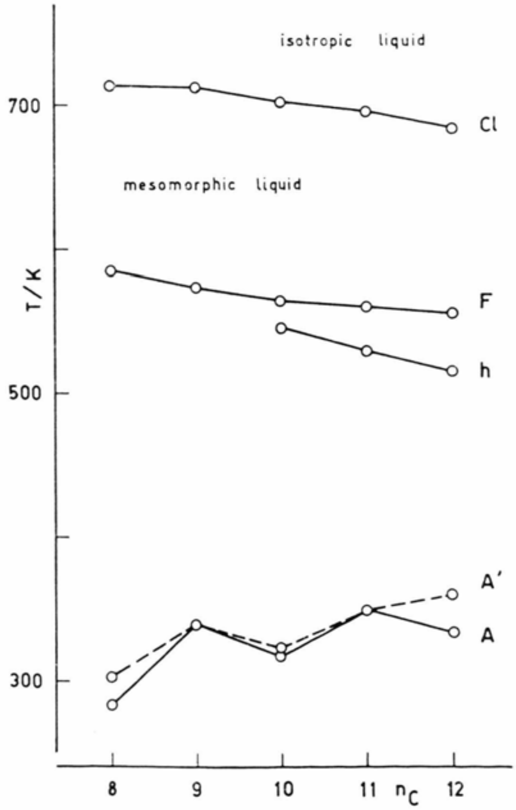

Fig. 1. Phase transition temperatures in the RbC_8-RbC_{12} salt family.

2. Experimental

Atomergic Chemetals Rb_2CO_3 (99.9 mole %), and Fluka *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. The salts were prepared by adding to Rb_2CO_3 dissolved in methanol a slight excess of the proper acid in methanol solution. After no more CO_2 escaped, the solvent was evaporated under vacuum and the product, after several washings with ether, was finally re-crystallized from 2-propanol.

Details on the experimental procedure were given elsewhere [6].

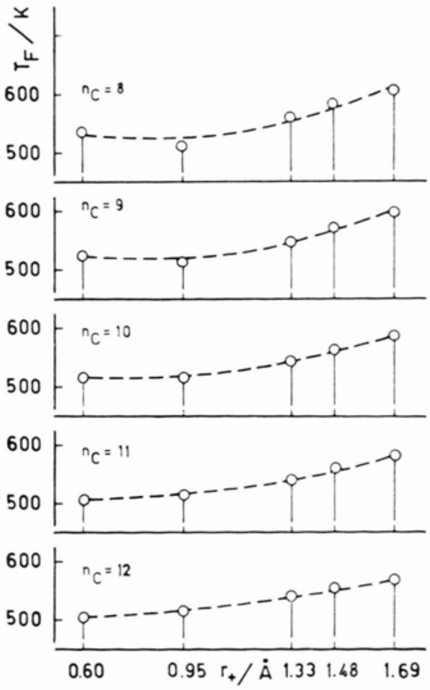

Fig. 2. T_F vs r_+ plots for the alkali *n.* $C_8-n.$ C_{12} alkanoates; T_F/K values from Refs. 3 (Cs salts), 4 (K salts), 5 (Li and Na salts), and from Table 1; r_+/Å values from Ref. 7 (r_{Li^+}: 0.60; r_{Na^+}: 0.95; r_{K^+}: 1.33; r_{Rb^+}: 1.48; r_{Cs^+}: 1.69).

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** The *n.* alkanoate with $n_C = x$ is here briefly indicated as MC_x, M being the proper alkali metal.

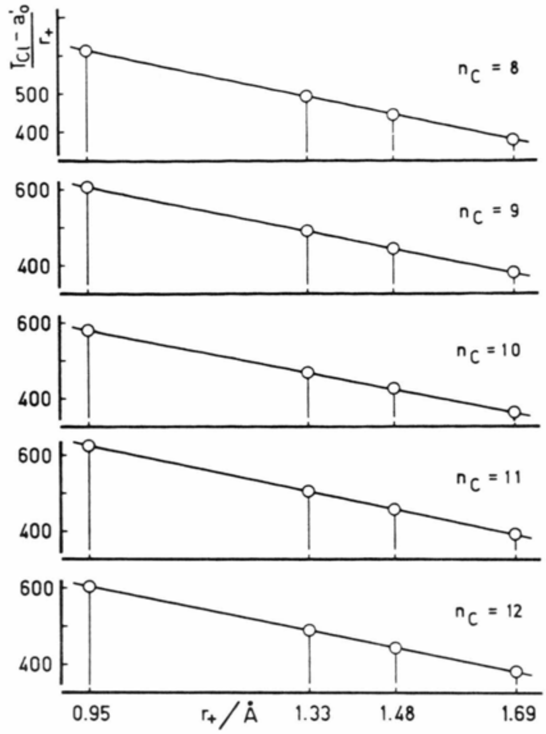

Fig. 3. T_{Cl} dependence on r_+ for the Na, K, Rb and Cs $n.\ C_8-n.\ C_{12}$ alkanoates: T_{Cl}/K values from Refs. 3, 4, 5 and from Table 1; $a_0'=51.48$, 53.81, 71.76, 17.14, 25.88 for $n_C=8$, 9, 10, 11, 12, respectively.

Table 1. Transition temperatures and heat effects (the number of significant figures depends in each case on the reproducibility of the pertinent experimental data. Figures in brackets merely indicate the order of magnitude).

salt	tr	T_{tr}/K	ΔH_{tr}/kcal mole^{-1}
RbC_8	Cl	713 ± 2	0.88 ± 0.05
	F	585 ± 3	2.72 ± 0.08
	A′	303.3	(2.0)
	A	283.5 ± 0.4	(0.6)
RbC_9	Cl	712 ± 2	0.84 ± 0.07
	F	572.8 ± 0.7	2.46 ± 0.03
	A	339	(4.0)
RbC_{10}	Cl	701.9 ± 0.4	0.64 ± 0.07
	F	564 ± 3	2.42 ± 0.08
	h	545 ± 2	0.6
	A′	323	(3.8)
	A	318	
RbC_{11}	Cl	695 ± 3	0.61 ± 0.03
	F	560 ± 3	2.48 ± 0.08
	h	529.1 ± 0.2	0.7
	A	349.1	(5.1)
RbC_{12}	Cl	683 ± 3 *	0.48
	F	555 **	2.15 ± 0.05
	h	515.3 ± 0.5	0.9
	A′	360 ± 2	(0.5)
	A	334	(4.4)

* Ref. 1: ~673; ** Ref. 1: 573; according to Ref. 1 "Die Substanzen sind stark zersetzlich".

3. Results and Discussion

3.1. The investigated salt family is characterized (see Table 1 and Fig. 1) by the occurrence of: (i) mesomorphic (likely "neat"[1]) phases over wide T ranges, the upper (clearing temperature, T_{Cl}/K) and lower (fusion temperature, T_F/K) limits of which gradually decrease (from ~713 to ~683 K, and from ~585 to ~555 K, respectively) as n_C increases from 8 to 12; (ii) solid state transitions (sstr's) at $280 < T/K < 360$ involving heat effects often larger than the corresponding ΔH_F's.

In the sstr region, DSC traces exhibited peaks which were single (A, in Table 1) in the case of the odd homologues, and twinned (A, A′ in Table 1) in that of the even ones, the latter peaks well apart from each other for RbC_8 and RbC_{12} but partially overlapping for RbC_{10}: the pertinent ΔH values were less satisfactorily reproducible than the ΔH_{Cl}'s and ΔH_F's, and therefore tabulated in brackets.

More or less evident endothermic pen deflections (at least one for each salt) were recorded also at $T_F > T > T_A$ (or $T_{A'}$) but, owing to the poor re-

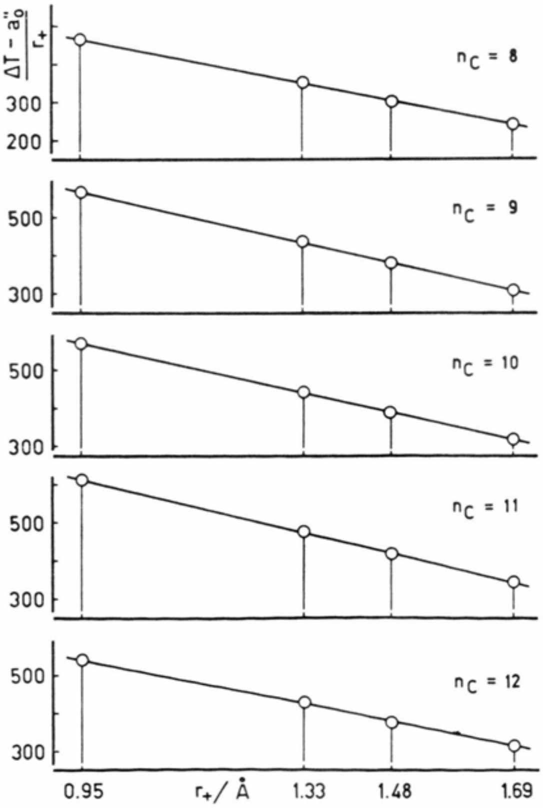

Fig. 4. ΔT dependence on r_+ for the Na, K, Rb and Cs $n.\ C_8-n.\ C_{12}$ alkanoates; ΔT/K values from Refs. 3, 4, 5, and from Table 1 data; $a_0''=-318.95$, -423.92, -437.04, -482.89, -427.62 for $n_C=8$, 9, 10, 11, 12, respectively.

producibility of a number of them, the related thermal information was judged as trustworthy only in the case of the "humps" (h, in Table 1) occurring at $20-40$ K below T_F in the three higher homologues. A similar "hump" region was already observed in the corresponding K salts[4].

3.2. Previous data from Refs.[3–5] together with the present ones allowed to put into evidence the following features in the behaviour of the alkali *n*. alkanoate series formed with different cations and a common anion for which $8 \leqq n_C \leqq 12$.

(i) In each series the Cs salt is the highest melting one (see Figure 2).

(ii) Going from Cs^+ to Li^+, the T_F's gradually decrease when $n_C = 12$ or 11, and pass through an increasingly marked minimum (in correspondence with the Na salt) when $n_C = 10$, 9, 8, respectively.

(iii) In each series the (crystalline or "waxy"[5]) Li salt directly melts into an isotropic liquid, whereas the other ones exhibit an intermediate "neat" phase in a temperature range the width ($\Delta T/K$) of which goes through a maximum in correspondence with the K salt.

(iv) For a given n_C the T_{Cl} and ΔT trends vs the cationic radius ($r_+/\text{Å}$) are formally described by parabolic equations (see Figures 3, 4).

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