

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

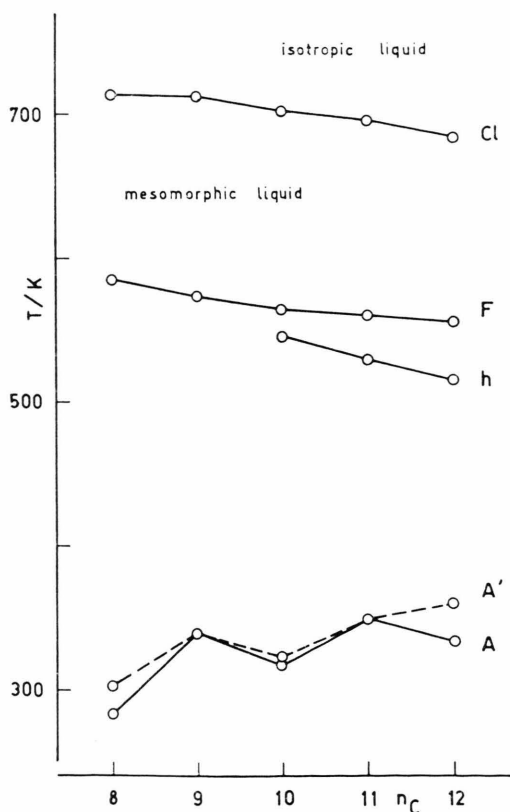


Fig. 1. Phase transition temperatures in the RbC₈–RbC₁₂ salt family.

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

of C atoms is $n_C \geq 8$ are so far largely unknown: RbC₁₂** 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 Skoulios², whereas a complete gap of information exists both for the odd homologues and for RbC₈, RbC₁₀.

Recent papers of this series dealt with differential scanning calorimetry on long-chain Cs³, K⁴, Li, and Na⁵ *n*. alkanoates: in the present one the calorimetric analysis is extended to the RbC₈–RbC₁₂ family.

2. Experimental

Atomergic Chemetals Rb₂CO₃ (99.9 mole %), and Fluka *n*. octanoic (≥ 99.5), *n*. nonanoic (>99), *n*. decanoic (≥ 99), *n*. hendecanoic (>99.5), *n*. dodecanoic (>99.5) acids were employed as starting materials. The salts were prepared by adding to Rb₂CO₃ dissolved in methanol a slight excess of the proper acid in methanol solution. After no more CO₂ 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 elsewhere⁶.

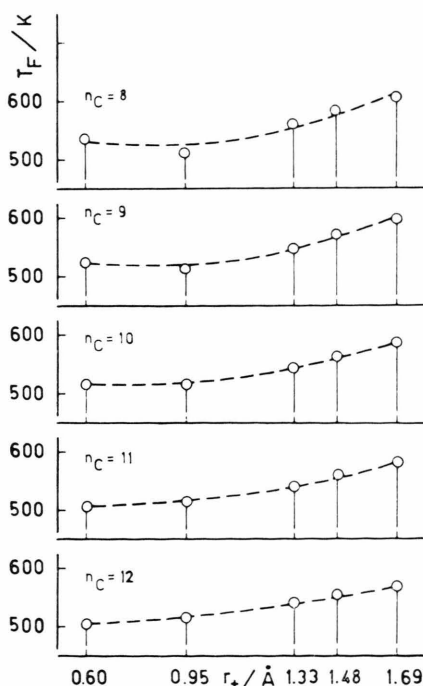


Fig. 2. T_F vs r_+ plots for the alkali *n*. C₈–*n*. C₁₂ alkanoates; T_F /K values from Refs. 3 (Cs salts), 4 (K salts), 5 (Li and Na salts), and from Table 1; r_+ /Å values from Ref. 7 (r_{Li^+} : 0.60; r_{Na^+} : 0.95; r_{K^+} : 1.33; r_{Rb^+} : 1.48; r_{Cs^+} : 1.69).



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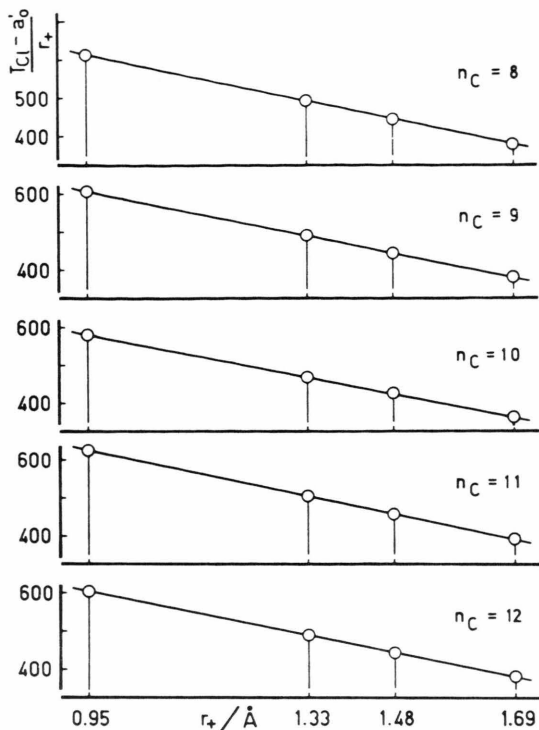


Fig. 3. T_{Cl} dependence on r_+ for the Na, K, Rb and Cs n . C_8 – n . C_{12} alkanates: T_{Cl}/K values from Refs. 3, 4, 5 and from Table 1; $a'_0 = 51.48, 53.81, 71.76, 17.14, 25.88$ for $n_C = 8, 9, 10, 11, 12$, respectively.

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	$\Delta H_{tr}/kcal\ mole^{-1}$
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 RbC₈ and RbC₁₂ but partially overlapping for RbC₁₀: 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-

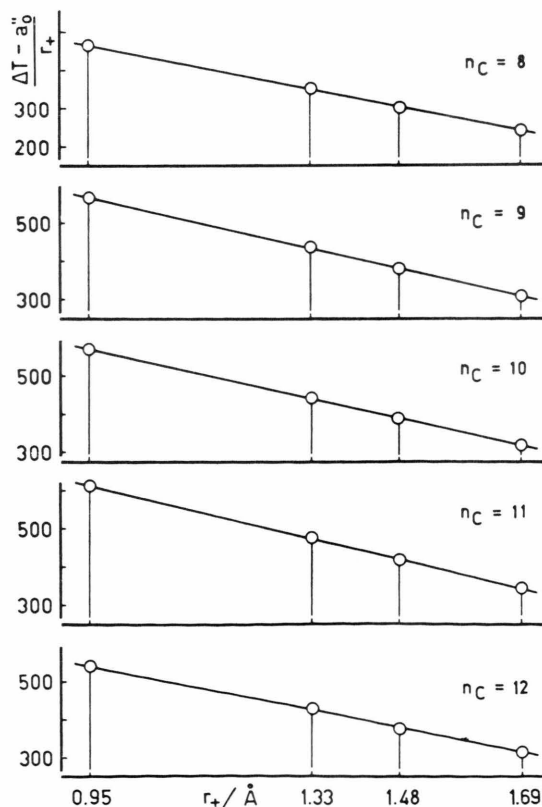


Fig. 4. ΔT dependence on r_+ for the Na, K, Rb and Cs n . C_8 – n . C_{12} alkanates; $\Delta T/K$ values from Refs. 3, 4, 5, and from Table 1 data; $a''_0 = -318.95, -423.92, -437.04, -482.89, -427.62$ for $n_C = 8, 9, 10, 11, 12$, respectively.

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 salts⁴.

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 $8 \leq n_C \leq 12$.

(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 ($r_+/\text{\AA}$) are formally described by parabolic equations (see Figures 3, 4).

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⁴ P. Ferloni, G. Spinolo, M. Zangen, and P. Franzosini, *Z. Naturforsch.* **32a**, 329 [1977].

⁵ P. Ferloni, M. Zangen, and P. Franzosini, *Z. Naturforsch.*, in press.

⁶ P. Ferloni and P. Franzosini, *Gazz. Chim. Ital.* **105**, 391 [1975].

⁷ G. J. Janz, *Molten Salts Handbook*, Academic Press, New York 1967.