On the Thermal Behaviour of the $n.C_{13}$-$n.C_{20}$ Rubidium Soaps

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The odd and even long-chain rubidium soaps from tridecanoate to eicosanoate were submitted to DSC analysis in the range between room temperature and the isotropic liquid region. The information thus obtained, together with that already collected for shorter homologues, made it possible, *inter alia*, to outline the boundaries of the mesomorphic liquid region in the whole C_5–C_{20} series. Comparison is also made with the previously investigated thermal behaviour of potassium *n*.alkanoates.

1. Introduction

Information about the phase relationships in the rubidium *n*.alkanoates with $n_C > 12$ (n_C: number of carbon atoms) is limited so far to an X-ray investigation by Gallot and Skoulios [1] on the even homologues up to $n_C = 22$, a hot stage microscopic study by Baum, Demus and Sackmann [2] on tetra-, hexa- and octadecanoate, and a few more data obtained by other authors [3–6] with different techniques on either hexa- or octadecanoate. On the whole, the above works show that the room temperature crystalline form of each homologue turns to an isotropic liquid through a multiplicity of phase transitions, and that a region exists — immediately below the isotropic liquid — where a mesomorphic liquid crystalline phase is stable. It is, however, to be noted that agreement is far from complete both for the total number of phases and for the extension of their fields of existence. Further, among the pertinent heat effects only those associated in rubidium hexadecanoate with fusion and with two lower transitions are available [3].

In the present paper, which aims at improving the knowledge of the thermal behaviour of long-chain rubidium soaps (including odd homologues, for which information, as seen, is at present practically nil), a detailed DSC investigation on the series from tridecanoate to eicosanoate (formulas are hereafter abbreviated as $RbC_{13}, \ldots, RbC_{20}$) is reported in prosecution of that recently carried out on the corresponding lithium [7] and potassium [8] salts.

2. Experimental

The rubidium salts were prepared, analogously to the lithium and potassium homologues, by adding a slight excess of the proper Fluka acid (of purity ranging between 98 and 99.5%, as specified in Ref. [8]) to a methanolic suspension of Atomergic Chemetals (99.95%) Rb_2CO_3. As a standard purification procedure, the solid residue recovered after removal of the solvent was first washed with ethyl ether, then twice dissolved in methanol and precipitated by the addition of ethyl ether, and finally recrystallized from 2-propanol. The purification advancement could be conveniently followed (see Ref. [8]) by observing after each step the features of the clearing peak. Final recrystallization and drying were performed never exceeding 340 K, and due care was taken to avoid moisture contamination.

The thermal data were obtained by means of a Perkin-Elmer Mod. DSC-2 differential scanning calorimeter, fitted with a Scanning Autozero device, which allows one to obtain automatically almost ideal (straight, flat) baselines. The calibration of the temperature scale and of the integrated power records was achieved through the melting parameters of high purity gallium, indium, tin, lead and zinc.

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3. Results and Discussion

3.1. In the case of the RbC_{13}—RbC_{20} homologues DSC analysis allowed us to distinguish (going from room temperature up): (i) a crystalline region whose upper limit, marked by the occurrence of the transition hereafter denoted as A, ranges between 492 and 448 K when n_C increases from 13 to 20*; (ii) an "intermediate" region whose upper limit is the fusion temperature, T_F/K, and actually keeps approximately constant at 550 ÷ 540 K: within this region there exist three series of minor transitions, denoted as a_1 (starting with RbC_{19}), a_2 and a_3 (both starting with RbC_{13}); (iii) the region of the mesomorphic liquid whose upper limit is the clearing temperature, T_{Cl}/K, and actually decreases smoothly from 676 (for RbC_{13}) to 619 (for RbC_{20}); (iv) the isotropic liquid region.

The general behaviour described above looks in several respects similar to that already discussed [8] for the corresponding potassium soaps.

3.2. Concerning the crystalline region, and in particular the portion of it between ≃330 and 430 K, let us discuss first in some detail the case of a sample of RbC_{20}, for which the traces reported in the upper section of Fig. 1 were recorded in four subsequent runs.

Trace 1 (heating stopped at ≃430 K) refers to the fresh sample (as obtained from a crystallization and drying procedure in the course of which — see § 2 — the temperature of 340 K was never exceeded) and is characterized by the occurrence of the large peak B_1, followed by a pair of partially overlapping smaller peaks b_2 and b_1.

In trace 2 (heating stopped again at ≃430 K) the large peak, now designated as B_2, occurred at a somewhat lower temperature and the transition involved a smaller amount of heat**, while b_2 and b_1 remained unchanged. Such a behaviour was obeyed also in the third (pushed up to clearing) and fourth (stopped once more at ≃430 K) runs, but for the fact that in the latter trace sharper peaks were recorded, reasonably due to the change of the sample geometry by the complete melting occurred in the third run.

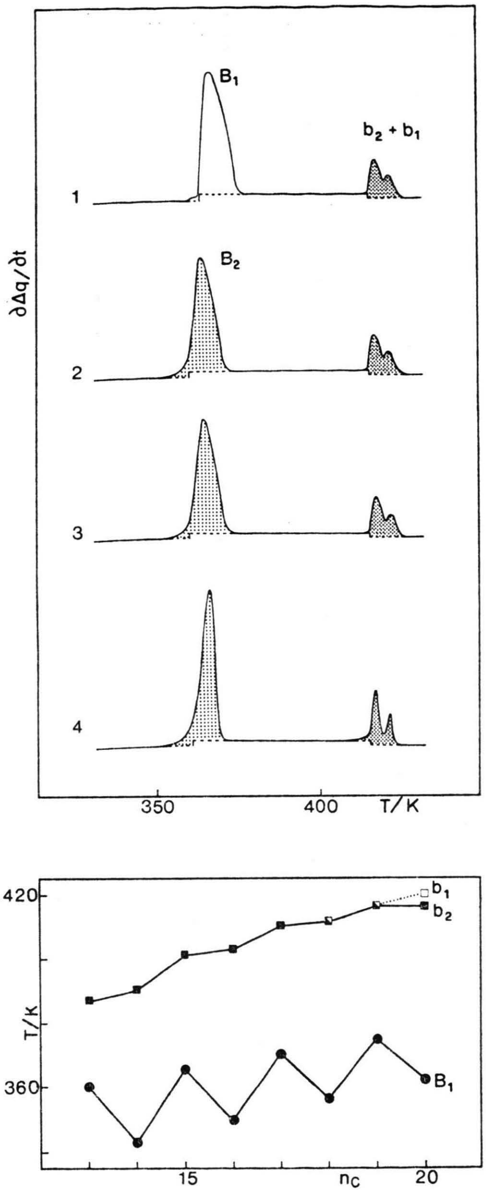

Fig. 1. *Upper section*: DSC traces taken (in the same operational conditions) on a sample of RbC_{20} over the B_i, b_i peaks; first, second and fourth heating runs stopped just after b_1; third run stopped after clearing.
Lower section: trends of the B_1, b_i transition temperatures *vs* n_C in the RbC_{13}—RbC_{20} *n*.alkanoates.

The above observations might suggest for RbC_{20} the possibility to exist (immediately below 360 K)

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* The assumption that the A's are transitions from a fully to a notfully crystalline state is justified by the features (diffuse shape — maintained also after previous heating up to clearing —, etc.) of the peaks themselves, and by considerations of analogy with the lithium and potassium series. For further discussion on this subject, see § 3.4.

** On an average (four samples examined):
$T_{B_1} = 362.4 \pm 0.1$ and $T_{B_2} = 360.0 \pm 0.5$ K;
$\Delta H_{B_1} = 7.95 \pm 0.05$ and $\Delta H_{B_2} = 6.68 \pm 0.06$ kcal mol^{-1}.

Table 1. Temperatures and enthalpies of some intercrystalline transitions in rubidium *n*.alkanoates from RbC_{13} to RbC_{20}.

Salt	tr	T_{tr}	ΔH_{tr}	Salt	tr	T_{tr}	ΔH_{tr}
		K	kcal mol^{-1}			K	kcal mol^{-1}
RbC_{13}	b_2	386.8 ± 0.1	0.94 ± 0.02	RbC_{17}	b_2	410.2 ± 0.2	1.54 ± 0.01
	B_1	360.1 ± 0.2	6.07 ± 0.05		B_1	370.3 ± 0.4	7.98 ± 0.06
RbC_{14}	b_2	390.3 ± 0.3	0.99 ± 0.02	RbC_{18}	b_1	[a]	1.60 ± 0.03 [b]
	B_1	343.0 ± 0.2	5.42 ± 0.07		b_2	411.3 ± 0.3	
					B_1	356.4 ± 0.3	6.99 ± 0.02
RbC_{15}	b_2	401.2 ± 0.1	1.17 ± 0.03	RbC_{19}	b_1	[a]	1.80 ± 0.01 [b]
	B_1	365.7 ± 0.2	6.92 ± 0.09		b_2	416.3 ± 0.2	
					B_1	374.8 ± 0.2	9.04 ± 0.09
RbC_{16}	b_2	403.0 ± 0.1	1.28 ± 0.02	RbC_{20}	b_1	419.9 ± 0.4	1.86 ± 0.01 [b]
	B_1	349.7 ± 0.2	6.1 ± 0.2		b_2	415.9 ± 0.3	
					B_1	362.4 ± 0.1	7.95 ± 0.05

[a] The large overlapping of the b_1 and b_2 peaks in the DSC trace makes difficult the accurate evaluation of T_{b_1}.
[b] This figure includes the heat effects pertinent to both the b_1 and b_2 transitions.

in two different forms, although the stability relations between these forms and that below T_{b_2} still remain an open question. Such a situation is analogous to that of several long-chain potassium *n*.alkanoates [8].

The lower homologues down to tridecanoate substantially behave as RbC_{20}: a satisfactory reproducibility of the transition temperatures and heat effects, however, was in general obtained only for B_1 and b_i: this is why only thermal data pertinent to these transitions are reported in Table 1. It is further to be noted that the overlapping of b_2 and b_1 increases with decreasing n_C in such a way that from RbC_{17} down only single peaks, denoted as b_2 in Table 1, could be recorded with the routinary scanning rate of 10 K min^{-1}.

The odd-even alternating effect, very marked in the B_1 series and still perceivable with the b_i's, is shown in the lower section of Figure 1.

For the sake of completeness, it must be finally mentioned that for all the homologues concerned here only poorly reproducible traces could be recorded between room temperature and T_{B_1}, so that it was not possible to obtain quantitative data about the endothermic effects exhibited by some of them.

3.3. Turning now attention to regions (ii)—(iv), a group of traces relevant to a sample of RbC_{15} is shown in Fig. 2 as a convenient example of DSC records over the A, a_3, a_2, F and Cl transitions. On passing from RbC_{15} to longer homologues peaks a_3 and a_2 progressively decrease in magnitude till vanishing in correspondence with RbC_{19} and RbC_{20}, respectively, while on passing to shorter ones, peaks A and a_3 tend more and more to overlap. Partial overlapping also occurs for peaks a_1 and F in the case of RbC_{19}. Under such circumstances, and since in general for the A and a_i peaks the accuracy attainable in drawing base-lines was not fully satisfactory, the pertinent heat effects have not been tabulated.

The data collected at $T/K > 430$ on clearing, fusion and transitions A, a_i are reported in Table 2. A comprehensive picture of the phase relations in the same temperature range for the whole family of the rubidium *n*.alkanoates from methanoate to

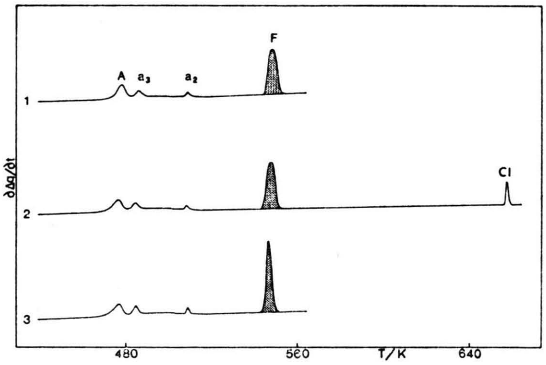

Fig. 2. DSC traces taken (in the same operational conditions) on a sample of RbC_{15} over the A, a_i, F and Cl peaks: the first and third heating runs were stopped just after fusion, the second one after clearing. A strict coincidence exists among the areas of the (shadowed) fusion peaks.

Table 2. Temperatures and enthalpies of phase transitions occurring above 430 K in rubidium *n*.alkanoates from RbC_{13} to RbC_{20}.

Salt	tr	T_{tr} / K	ΔH_{tr} / kcal mol^{-1}
RbC_{13}	Cl	675.7 ± 0.2	0.48 ± 0.02
	F	552 ± 1	2.23 ± 0.04
	a_2	508.7 ± 0.1	—
	a_3	497.4 ± 0.2	—
	A	491.9 ± 0.1	—
RbC_{14}	Cl	667.2 ± 0.1	0.40 ± 0.02
	F	550.8 ± 0.2	2.21 ± 0.01
	a_2	513.5 ± 0.3	—
	a_3	491.1 ± 0.3	—
	A	485.6 ± 0.3	—
RbC_{15}	Cl	658.2 ± 0.5	0.37 ± 0.02
	F	548 ± 1	2.16 ± 0.03
	a_2	508.9 ± 0.6	—
	a_3	485.0 ± 0.4	—
	A	475.2 ± 0.7	—
RbC_{16}	Cl	649.8 ± 0.4	0.33 ± 0.01
	F	542 ± 1	2.06 ± 0.02
	a_2	502.3 ± 0.3	—
	a_3	479.8 ± 0.9	—
	A	468 ± 2	—
RbC_{17}	Cl	642.2 ± 0.4	0.32 ± 0.01
	F	543.0 ± 0.8	2.07 ± 0.03
	a_2	497.6 ± 0.6	—
	a_3	477.9 ± 0.7	—
	A	462 ± 2	—
RbC_{18}	Cl	634.6 ± 0.4	0.30 ± 0.01
	F	541 ± 2	2.05 ± 0.07
	a_2	$\cong 493$	—
	a_3	$\cong 475$	—
	A	460 ± 2	—
RbC_{19}	Cl	626.9 ± 0.4	0.30 ± 0.01
	F	541.6 ± 0.4	2.09 ± 0.05[a]
	a_1	538.7 ± 0.2	
	a_2	$\cong 487$	—
	A	454 ± 2	—
RbC_{20}	Cl	619.1 ± 0.3	0.28 ± 0.02
	F	540.1 ± 0.3	1.76 ± 0.02
	a_1	520.6 ± 0.3	—
	A	448 ± 2	—

[a] This figure includes the heat effects pertinent to fusion and to transition a_1; in the DSC trace the small peak corresponding to the latter is widely overlapping with the large one corresponding to the former.

eicosanoate can be outlined as shown in Fig. 3 on the basis of Table 2 and of previous results on RbC_1—RbC_{12} [9—11].

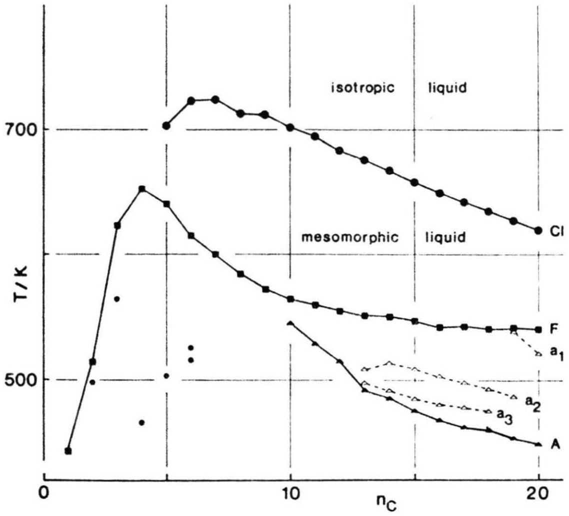

Fig. 3. Phase transition temperatures occurring above 430 K in the RbC_1—RbC_{20} *n*.alkanoates according to [9—11] and the present work. Open circles: intercrystalline transitions.

The upper section of Fig. 4, where the differences $\Delta T = T_{Cl}$-T_F are plotted vs n_C, shows that both in the rubidium and potassium series the largest extension of the mesomorphic liquid region is reached (with ΔT values not far from each other) around $n_C = 9$, even if the concerned phase begins

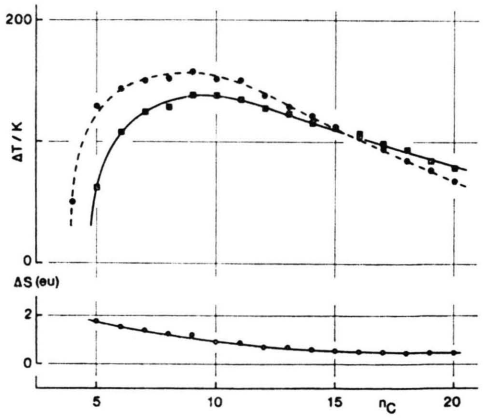

Fig. 4. *Upper section*: $\Delta T = T_{Cl} - T_F$ *vs* n_C for RbC_5-RbC_{20} (squares; this work and [10, 11]) and for KC_4-KC_{20} (circles; [8]).
Lower section: entropy of clearing *vs* n_C for RbC_5-RbC_{20} (this work and [10, 11]).

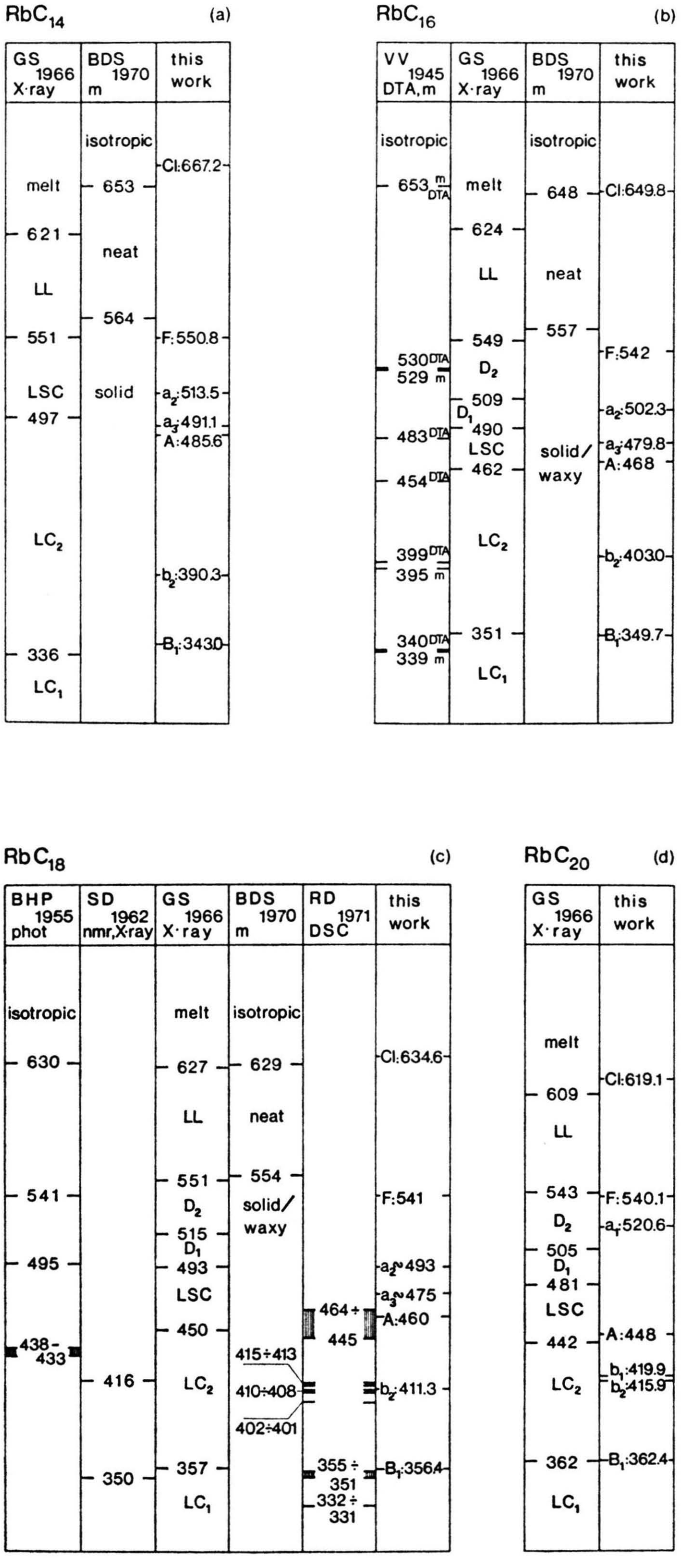

Fig. 5. Comparison of the phase transition temperatures as detected by different authors with several techniques in rubidium tetradecanoate (a), hexadecanoate (b), octadecanoate (c) and eicosanoate (d).
Authors: GS, Gallot and Skoulios [1]; BDS, Baum, Demus and Sackmann [2]; VV, Vold and Vold [3]; BHP, Benton, Howe and Puddington [4]; SD, Shaw and Dunell [5]; RD, Ripmeester and Dunell [6]. SD and RD did not extend their observations up to the clear melt.
Techniques: m, microscopic observation; phot, photometry.
Phase designations (according to the original papers): LL, "structure lamellaire labile"; LSC, "structure lamellaire semicristalline"; LC, "structure lamellaire cristalline"; D, "structure à disques".
Concerning VV, in some cases the transition temperatures detected for RbC_{16} could be somewhat different according to the technique employed; the transitions at 454 and 483 K were observed only by DTA.
To simplify the drawing, only pairs of figures corresponding to the lowest and highest temperatures detected for each transition on samples of different thermal history are here given in the case of RD data on RbC_{18} (for details see the original paper).

to occur respectively at $n_C = 5$ and $n_C = 4$. For what in particular regards clearing, when rubidium is the cation the pertinent entropy change decreases monotonously from $\simeq 1.8$ for the pentanoate to $\simeq 0.5$ cal mol^{-1} K^{-1} for the eicosanoate (see the lower section of Figure 4). An analogous behaviour was observed also for the potassium homologues, although for the latter moderately (on an average, some 20%) lower ΔS_{Cl} values were always found [8].

3.4. The results of the present work are schematically compared in Fig. 5 with the scanty information available in the literature.

Of a special relevance is the paper by Gallot and Skoulios [1]. Their X-ray patterns enabled them to give a rather extensive description — at least for the even homologues — of the sequence and nature of the phases, and points to the existence of four phase groups characterized respectively by crystalline lamellar (LC), semi-crystalline lamellar and disc (LSC and D), labile lamellar (LL), and isotropic liquid structures. This is consistent with the subdivision outlined in § 3.1. It is, however, to be noted that: (i) within the "intermediate" region there is poor agreement between DSC and Gallot and Skoulios' X-ray measurements on the number and location of the minor transitions, in particular in the case of RbC_{14}; (ii) within the crystalline region they distinguished only two structures, LC_1 and LC_2 (with transition temperatures not far from our T_{B_1}'s), so that the b_i transitions seem to have escaped their attention.

On the other hand: (i) Vold and Vold [3] obtained evidence, both by the hot-wire microscopic technique and by DTA, for an intercrystalline transition to occur in RbC_{16} at 395—399 K ($T_{b_2} = 403$ K; see Table 1); (ii) Shaw and Dunell [5], who studied the proton magnetic resonance absorption in solid RbC_{18}, could detect in this salt (through abrupt changes in line width and second moment) a transition at about 416 K ($T_{b_2} = 411$ K), and were able to confirm this result by X-ray measurements. Vold and Vold also gave the only ΔH_{tr} data existing till now for a long-chain rubidium soap, i.e., once more RbC_{16}: in particular, for fusion they found a value ($\Delta H_F = 2290$ cal mol^{-1}) lying not far away from the present one (2.06 kcal mol^{-1}; see Table 2).

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