On the Thermal Behaviour of the $n.C_{13}$— $n.C_{20}$ Potassium Alkanoates

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A DSC study, supplemented by X-ray diffraction measurements, was carried out on potassium soaps from n.tridecanoate to n.eicosanoate in the range between room temperature and the isotropic liquid region. The present results are combined with earlier ones for the shorter homologues down to methanoate to draw a rather comprehensive picture of the phase relationships concerned. The significant features shown for a number of transition series by plots ΔS *vs* the number of carbon atoms, as well as the dimorphism exhibited by tridecanoate at room temperature are also discussed.

1. Introduction

The results of differential scanning calorimetry (DSC) performed on the lithium *n*.alkanoates from tridecanoate to eicosanoate were discussed recently [1]. The purpose of the present paper is to contribute to a better understanding of the complicated phase relationships in the corresponding potassium homologues, which are still very little known. The literature information so far available is restricted to *n*.tetradecanoate, *n*.hexadecanoate and *n*.octadecanoate. Moreover, disagreements exist among data of different authors, possibly due to the fact that: (i) samples coming from the same batch may behave differently if their "thermal history" is different, and (ii) the actual possibility of detecting a given phase transition may be affected by the experimental technique adopted. DSC, in spite of some limitations, was expected to offer a rather convenient way for obtaining a general picture of the thermal behaviour of potassium soaps; this in particular if, on one hand, an unbroken (and sufficiently extended) succession of odd and even homologues was taken into account, and, on the other hand, samples submitted to uniform handling before measurement were employed.

2. Experimental

A Perkin-Elmer Mod. DSC-2 differential scanning calorimeter was employed to determine the phase transition temperatures and the pertinent enthalpy changes: for details on the procedure see [2].

The salts (hereafter indicated for the sake of brevity as $KC_{13}, \ldots, KC_{20}$) were prepared by reacting C. Erba "RP – ACS" K_2CO_3 with a moderate excess of the proper Fluka acid (tridecanoic, *purum*, $\cong 98\%$; tetradecanoic, *puriss*, 99.5; pentadecanoic, *puriss*, $\geqq 99$; hexadecanoic, *puriss*, >99; heptadecanoic, *puriss*, >99; octadecanoic, *puriss*, 99.5; nonadecanoic, *puriss*, >99.5; eicosanoic, *puriss*, >99) dissolved in methanol. After refluxing for 2 – 3 hours, the clear solution was evaporated to dryness under reduced pressure in a Rotavapor device. Preliminary assays led to choose as a suitable purification procedure the sequence of the following steps: (i) refluxing of the raw (powdered) material with dry acetone to remove most of the unreacted acid; (ii) recrystallizing from either *iso*propanol ($KC_{13} - KC_{18}$) or methanol (KC_{19}, KC_{20}); (iii) dissolving in methanol (solution saturated at room temperature) and slowly precipitating by dropwise addition of ethyl ether; (iv) further recrystallizing from the proper solvent. After each step a sample was submitted to DSC analysis to check the purification progress *.

Drying was accomplished under vacuum in a Büchi device Mod. TO-50. During the final crystal-

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* A reliable empirical criterion consisted in observing the features of the recorded traces in the region pertinent to clearing. As an example, in the case of KC_{16} the small clearing peak was hardly perceivable both in the raw material and after step (i); became detectable after step (ii) at 640—641 K, although with a low h/w ratio (h, w: peak height and width, respectively); could be neatly recorded after step (iii) at 643—644 K, and did not change any more after step (iv).

By the way, it can be noted that the cryometric constant for KC_{16} clearing amounts to 835 Km^{-1}: remarkable depressions of the clearing temperature would thus be caused by the presence of even very small percentages of (not miscible) foreign particles.

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lization and dehydration process (and for reasons discussed below) care was taken not to exceed 60 and 80 °C in the case of the even and odd homologues, respectively.

The calorimetric analysis was supplemented with a few X-ray diffraction measurements performed on powdered samples using a home-made polythermal attachment [3] connected with a standard Norelco diffractometer ($\mathrm{Cu}-\mathrm{K}_{\bar{\alpha}}$ radiation: $\lambda = 1.5418$ Å; 40 KV; 20 mA). Several high order lines being available in each case, the long spacings ($d = 1/c^*$) pertinent to the ionic layers could be evaluated with a programme minimizing the sum of the squared differences between the experimental and calculated Q values ($Q = 4 \sin^2 \vartheta/\lambda^2$). Allowance was made for the specimen-transparency aberration by inserting in the least-squares procedure a proper correction term [4].

3. Results and Discussion

3.1. The DSC traces recorded during the first heating runs were characterized by at least 5 (in the case of KC_{13}) and up to 10 (in the case of KC_{20}) endothermic peaks for each homologue in the range between room temperature and the isotropic liquid region. Following the order of decreasing temperature, one found: (i) the clearing (Cl) peak; (ii) the fusion (F) peak; (iii) a group of peaks (in the number of 1 in $\mathrm{KC}_{13}-\mathrm{KC}_{15}$, 3 in KC_{16}, and 4 in the remaining homologues), reasonably to be correlated with transitions either between two plastic phases or from a crystalline to a plastic phase, denoted with a_i and A, respectively, the latter being for each homologue that occurring at the lowest temperature and involving the largest ΔH value**; (iv) a second group of peaks (from 2 in KC_{13} to 4 in KC_{20}), reasonably to be correlated with intercrystalline transitions and hereafter denoted by the letters B (that involving the largest ΔH value), $\mathrm{b_i}$ (occurring at $T > T_\mathrm{B}$), and b′ (occurring at $T < T_\mathrm{B}$). During subsequent heatings the features of the traces remained unchanged above ≅ 490 K; i. e., for what concerns transitions $\mathrm{a_i}$, F and Cl, whereas they could undergo a number of modifications in the lower temperature region. In particular, during the second heating run, peaks A looked much less sharp and occurred at temperatures more or less considerably lower than in the first run; peaks $\mathrm{b_i}$ were reproducible only if T_A had not been exceeded during the first run; and peaks B (and *b′*) underwent complicated transformations (discussed separately, see § 3.4).

The actual behaviour of the A, $\mathrm{a_i}$ and F peaks in the case of KC_{18} is shown in Figure 1.

The phase transition temperatures observed in the $\mathrm{KC}_{13}-\mathrm{KC}_{20}$ homologues are reported in Table 1 together with the enthalpy changes pertinent to clearing, fusion, and transitions B, b_1 and b_2. In the Table the figures concerning B and A are averages of data taken only during first heating runs, while those concerning all other transitions come from two or more subsequent runs (at least four samples of each salt having been submitted to DSC analysis).

The reliability of the ΔH's can be considered as satisfactory (in terms of both reproducibility and self-consistency) for clearing, fusion and transitions B, b_1 and b_2, whereas considerations of various kinds caused the values obtained for the other transitions to be looked at less confidently. In particular, getting correct ΔH values from the small peaks $\mathrm{a_i}$ was not always possible because here unavoidable uncertainties in drawing baselines heavily affected (in percent) the determination of their areas. Moreover, sharpness progressively decreased

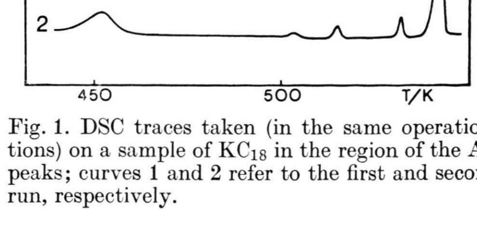


Fig. 1. DSC traces taken (in the same operational conditions) on a sample of KC_{18} in the region of the A, $\mathrm{a_i}$ and F peaks; curves 1 and 2 refer to the first and second heating run, respectively.

** In this connection, it may be noted that some information on the correlations between the DSC peaks and the nature of the phases involved in the corresponding transitions is often offered by the features (sharp or diffuse shape, degree of reversibility, amount of absorbed heat, etc.) of the peaks themselves: in particular, it was here possible *inter alia* to assume that each transition of the A series occurred between a crystalline and a non-crystalline (plastic) phase, a conclusion which, in the case of KC_{14}, KC_{16} and KC_{18}, agrees with the views of both Gallot and Skoulios [5] and Baum, Demus and Sackmann [6].

Table 1. Phase transition temperatures and enthalpies of potassium *n.* alkanoates from KC_{13} to KC_{20}.

Salt	tr	T_{tr}	ΔH_{tr}
		K	kcal mol^{-1}
KC_{13}	Cl	670.8 ± 0.6	0.37 ± 0.02
	F	542.1 ± 1.1	2.73 ± 0.05
	A	483.1 ± 1.1	—
	b_1	421.5 ± 0.3	0.8 ± 0.1
	B	363.1 ± 0.4	4.28 ± 0.03
KC_{14}	Cl	661.7 ± 0.8	0.33 ± 0.02
	F	540.3 ± 1.1	2.81 ± 0.06
	A	483.4 ± 0.6	—
	b_1	416.4 ± 0.6	0.6 ± 0.1
	b_2	407.5 ± 0.5	0.3 ± 0.1
	B	337.2 ± 1.1	3.77 ± 0.04
KC_{15}	Cl	652.9 ± 0.2	0.32 ± 0.02
	F	540.6 ± 0.5	2.68 ± 0.05
	A	471.1 ± 0.4	—
	b_1	427.3 ± 0.3	0.7 ± 0.1
	b_2	417.9 ± 0.3	0.4 ± 0.1
	B	367.2 ± 0.3	4.75 ± 0.03
KC_{16}	Cl	643.3 ± 0.6	0.29 ± 0.01
	F	539.0 ± 1.0	2.97 ± 0.02[a]
	a_1	[b]	—
	a_2	524.0 ± 0.4	—
	a_3	511.5 ± 0.4	—
	A	468.8 ± 0.6	—
	b_1	423.3 ± 0.3	0.7 ± 0.1
	b_2	406.7 ± 0.5	0.4 ± 0.1
	B	341.8 ± 0.5	4.07 ± 0.06
KC_{17}	Cl	635.1 ± 0.4	0.26 ± 0.02
	F	540.2 ± 0.6	2.92 ± 0.03[c]
	a_1	536.1 ± 0.9	—
	a_2	519.2 ± 0.7	—
	a_3	507.6 ± 0.9	—
	A	462.2 ± 1.5	—
	b_1	430.9 ± 0.7	0.8 ± 0.1
	b_2	415.4 ± 0.7	0.4 ± 0.1
	B	371.0 ± 0.8	5.3 ± 0.1
KC_{18}	Cl	627.1 ± 0.7	0.25 ± 0.01
	F	542.5 ± 1.1	2.83 ± 0.02
	a_1	532.5 ± 0.7	—
	a_2	515.6 ± 0.8	—
	a_3	504.1 ± 0.9	—
	A	464.1 ± 1.5	—
	b_1	425.8 ± 0.6	0.9 ± 0.1
	b_2	405.8 ± 0.3	0.4 ± 0.1
	B	349.1 ± 0.9	4.65 ± 0.03
KC_{19}	Cl	618.2 ± 0.8	0.24 ± 0.01
	F	540.8 ± 1.1	2.71 ± 0.05
	a_1	527.6 ± 0.9	—
	a_2	509.5 ± 0.8	—
	a_3	496.5 ± 0.1	—
	A	449.6 ± 1.8	—
	b_1	432.8 ± 0.9	0.8 ± 0.2
	b_2	414.0 ± 0.6	0.5 ± 0.1
	B	374.7 ± 0.7	5.73 ± 0.06
KC_{20}	Cl	613.1 ± 1.1	0.22 ± 0.01
	F	544.5 ± 1.0	2.84 ± 0.08
	a_1	526.2 ± 0.6	—
	a_2	508.7 ± 0.7	—
	a_3	495.0 ± 1.3	—
	A	456.5 ± 0.7	—
	b_1	426.5 ± 0.6	1.2 ± 0.1
	b_2	406.3 ± 0.6	0.4 ± 0.1
	B	354.0 ± 0.7	[d]
	b′	347.3 ± 0.5	—

[a] this figure includes the heat effect pertinent to transition a_1.

[b] the occurrence of a transition a_1 at a temperature close to T_F is proved by the existence of an inflection at the foot of the large fusion peak and by the fact that the value 2.97 kcal mol^{-1} tabulated for the enthalpy of fusion leads to an anomalously high entropy value (see the upper section of Fig. 5).

[c] this figure includes the heat effect pertinent to transition a_1; in the DSC trace the small peak corresponding to the latter is widely overlapping with the large one corresponding to fusion.

[d] partial overlapping of the (not far different in area) peaks B and b′ makes in this case difficult the accurate ΔH evaluation; the overall heat effect, however, can be taken roughly as amounting to $4 \div 5$ kcal mol^{-1}.

following the sequence $a_1 \rightarrow a_2 \rightarrow \ldots$, and in some cases, e. g., for transition a_1 in KC_{16} and KC_{17} (see footnotes a and c of Table 1) overlapping with other peaks also occurred. Nevertheless, ΔH values of $0.2 \div 0.3$ and $0.1 \div 0.2$ kcal mol^{-1} can be suggested as reasonable for a_1, a_2 and for a_3, respectively.

Data on the B transition in KC_{13} are detailed in Table 2 to give an idea, at least in one case, of the reproducibility of the measurements.

The present T_{tr} data (summarized in Table 1) together with those reported in our previous papers [2, 7–9] allow one to draw a comprehensive picture, shown in Fig. 2, of the phase relationships (as detectable by DCS) in the $KC_1 - KC_{20}$ *n.*alkanoates. For better visualization, solid or dashed lines were employed to connect series of points pertinent to transitions thought to be of the same type.

The above mentioned picture looks as remarkably more complicated than that recently drawn [1] for the corresponding lithium salts, due to the occurrence of: (i) a mesomorphic liquid region (absent when lithium is the cation) from KC_4 up; (ii) a

Table 2. DSC data for transition B in KC_{13}.

Sample	Sample weight	T_{tr}	ΔH_{tr}
	g	K	kcal mol^{-1}
1	0.002159	362.4	4.313
2	0.002314	362.9	4.279
3	0.003358	363.4	4.266
4	0.003416	363.4	4.328
5	0.003923	363.6	4.212
6	0.004080	362.8	4.267

Mean values: $T_{tr} = 363.1 \pm 0.4$ K; $\Delta H_{tr} = 4.278 \pm 0.029$ kcal mol^{-1} (reported in Table 1 as4.28 $\pm$ 0.03 kcal mol^{-1}). Scan speed: 10 K min^{-1}.

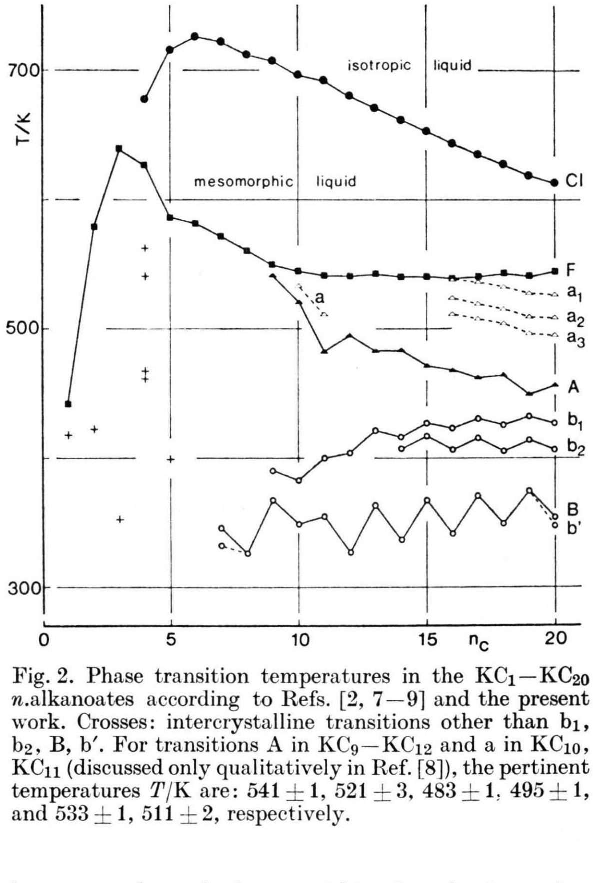


Fig. 2. Phase transition temperatures in the KC_1-KC_{20} *n*.alkanoates according to Refs. [2, 7–9] and the present work. Crosses: intercrystalline transitions other than b_1, b_2, B, b'. For transitions A in KC_9-KC_{12} and a in KC_{10}, KC_{11} (discussed only qualitatively in Ref. [8]), the pertinent temperatures T/K are: 541 ± 1, 521 ± 3, 483 ± 1, 495 ± 1, and 533 ± 1, 511 ± 2, respectively.

larger number of phases within the plastic region (which, moreover, starts from $n_C = 12$ with lithium, but from $n_C = 9$ with potassium; n_C = number of carbon atoms); (iii) several (instead of one) intercrystalline transition series (B, b_1, b_2).

3.2. Previous literature gives information restricted to the three even homologues KC_{14}, KC_{16} and KC_{18}, whose phase transitions were studied by several authors through a multiplicity of experimental techniques. The pertinent temperatures, coming from a number of selected papers, are given diagrammatically (and in comparison with the present results) in the three sections of Figure 3, Ref. [10–20].

The most detailed description of the sequence of phases occurring in these salts from room temperature up was reported by Gallot and Skoulios [5] who, from their polythermal X-ray patterns analysis, concluded that, after a succession of crystalline phases (LC structures) and before reaching the state of anisotropic liquid crystal (LL structure), the tetradecanoate goes through four plastic phases characterized by disc (D) structures, whereas the hexadecanoate and octadecanoate go respectively through four and five plastic phases characterized by ribbon (BO) structures.

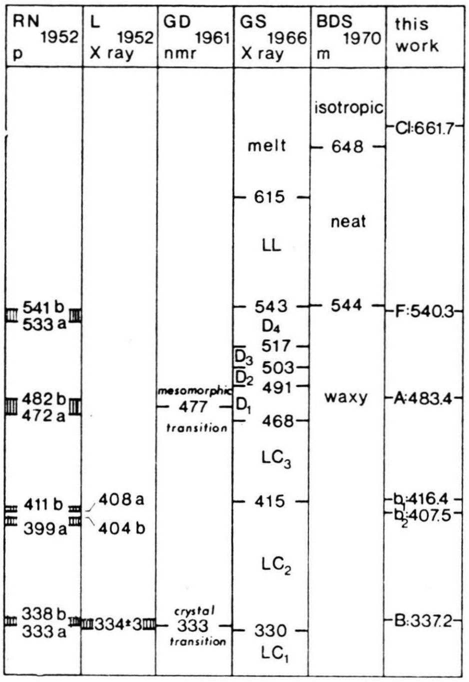
Concerning the ΔH's, the only data so far available are those measured some 35 years ago by Vold and Vold [13] for the transitions they found on (previously dried at 105 °C) KC_{16} at 532, 447, 425, 404 and 333 K, i. e., respectively 2500, 1500, 1000, 900 and 4900 cal mol^{-1}.

3.3. For a given potassium *n*.alkanoate characterized by $n_C \geqq 4$, the upper and lower temperature limits of the mesomorphic liquid field are indicated in the present paper as the clearing and fusion point of the salt, respectively, although other authors may prefer different nomenclatures.

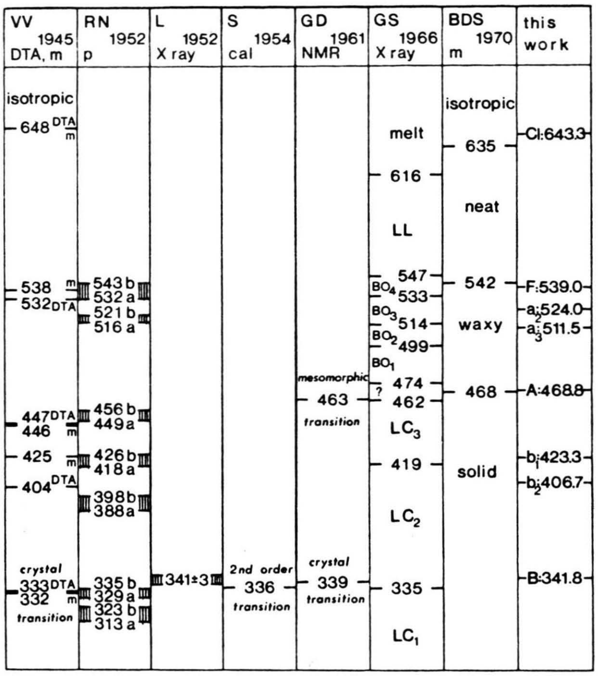
The differences $\Delta T = T_{Cl} - T_F$ are plotted vs. n_C in the upper section of Figure 4. The width of the mesomorphic liquid region increases from some 50 K up to more than 150 K on passing from KC_4 to KC_9, then smoothly decreases reaching about 70 K for KC_{20}: such figures look as noticeably larger than most of those given by previous investigators. The entropy changes pertinent to clearing decrease monotonously with increasing n_C, as shown in the lower section of Figure 4.

No calorimetric evidence was obtained of the peculiarities ("two phases ... present, in stable equilibrium" at 618 ÷ 626 K, and "a small, but very definite and reproducible change" of light transmission at about 583 K) observed photometrically by Benton, Howe and Puddington [16] for KC_{18} in the mesomorphic liquid state. Slight endothermic effects, however, could be observed in several DSC traces recorded on samples of KC_{17}, KC_{18}, KC_{19} and KC_{20}, respectively at about 551, 561, 563 and

K tetradecanoate



K hexadecanoate



K octadecanoate

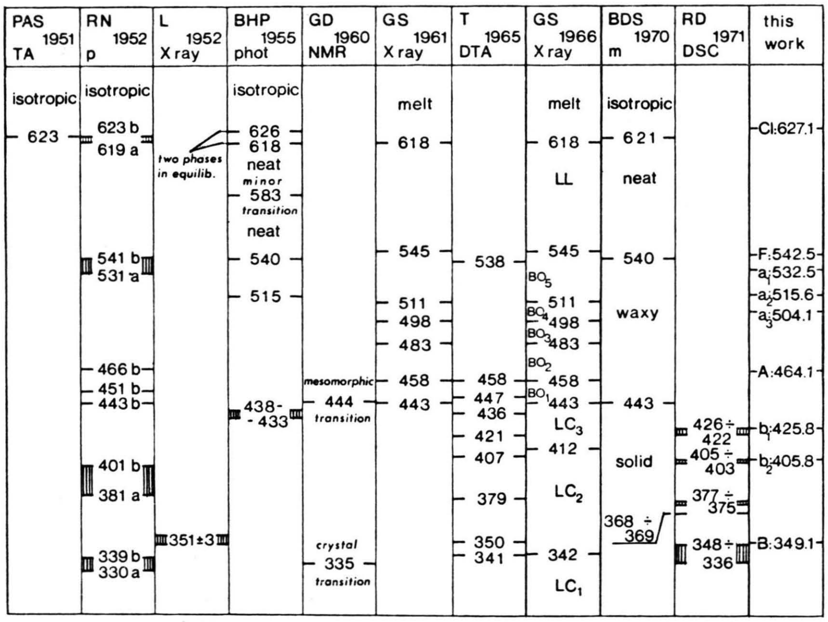


Fig. 3. Comparison of phase transition temperatures as detected by different authors with several techniques in potassium tetradecanoate (3, a), hexadecanoate (3, b) and octadecanoate (3, c).
Authors: RN, Ravich and Nechitaylo [10]; L, Lomer [11]; GD 1961, Grant and Dunell [12]; GS 1966, Gallot and Skoulios [5]; BDS, Baum, Demus and Sackmann [6]; VV, Vold and Vold [13]; S, Shmidt [14]; PAS, Penther, Abrams and Stross [15]; BHP, Benton, Howe and Puddington [16]; GD 1960, Grant and Dunell [17]; GS 1961, Gallot and Skoulios [18]; T, Trzebowski [19]; RD, Ripmeester and Dunell [20]. RN, L, GD, S, T and RD did not extend the observations up to the clear melt.

Techniques: p, Kurnakov pyrometry; m, microscopic observation; cal, calorimetry; TA, thermal analysis; phot, photometry.
Phase designations (according to the original papers): LL, "structure lamellaire labile"; D, "structure à disques"; LC, "structure lamellaire cristalline"; BO, "structure à rubans bidimensionnelle oblique".
Concerning RN, the temperature marked with (a) and (b) were taken in correspondence with the peak starts and maxima, respectively. Concerning VV, in some cases the transition temperatures detected could be somewhat different according to the technique employed; the transition at 404 K was observed only by DTA.
RN data on KC_{16} were taken on samples previously dried at 105° C; samples dried at room temperature over $CaCl_2$ differed just in that they exhibited below 350 K only one transition at 330 (a) – 341 (b) K.
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 KC_{18} (further details in the text).

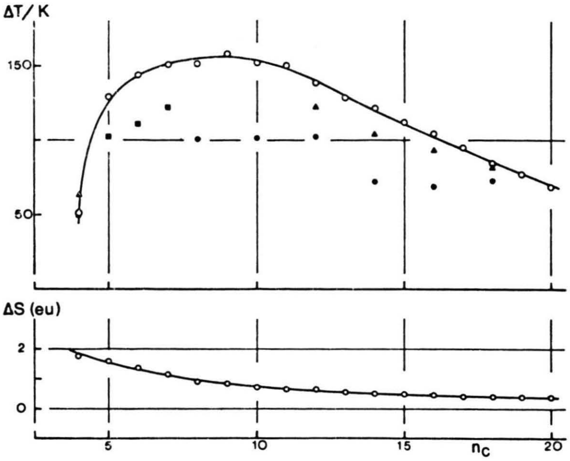


Fig. 4. Upper section: $\Delta T = T_{Cl} - T_F$ *vs* n_C for KC_4—KC_{20} (empty circles: present work and Refs. [7—9]; filled circles: Gallot and Skoulios [5]; triangles: Baum, Demus and Sackmann [6]; squares: Michels and Ubbelohde [21]).
Lower section: entropy of clearing *vs* n_C for KC_4—KC_{20} (present work and Refs. [7—9]).

569 K (i. e., at 11 ÷ 24 K above the corresponding fusion points), but elucidating their significance requires further investigation.

Concerning fusion, a characteristic feature is that T_F keeps approximately constant (at 540 – 550 K) for $n_C \geqq 9$. An analogous behaviour was already observed [1] in the lithium *n*.alkanoates although for $n_C \geqq 12$: in both salt families, however, such T_F stabilization starts from the first homologue exhibiting a transition of the A type, i. e., in concomitance with the occurrence of at least one plastic phase. Also significant is the plot (shown in the upper section of Fig. 5) of ΔS_F vs. n_C, where three branches may be easily distinguished. Breaks occur on passing from propanoate to *n*.butanoate (i. e., with the arising of a mesomorphic liquid phase) and from *n*.octanoate to *n*.nonanoate (i. e., with the arising of a plastic phase): along branch III a stabilization of ΔS_F (analogous to that of T_F) also occurs.

The trends of the T_A's and T_F's indicate that, in the stepwise fusion process, increasing the number of carbon atoms from $n_C = 9$ up causes the paraffinic chains to melt at progressively decreasing T values, although not affecting the temperature of fusion of the polar end groups.

In the range between T_F and T_A the present results prove in each of the $KC_{16} - KC_{20}$ homologues the existence of three minor transitions of the a_i type. Since, however, the pertinent heat effects tend to become almost vanishingly small with increasing i, the possibility that other transitions of the same type (apparently bound to some of the BO structures detected by Gallot and Skoulios [5] in hexadecanoate and octadecanoate) may occur between T_{a3} and T_A (see Fig. 2, and Gallot and Skoulios' results in Figs. 3 b and 3 c), although escaping DSC analysis, is to be taken into account. Evidence could not be obtained (too small heat effects too?) for minor transitions either in KC_{14} or in its odd neighbours, in spite of the fact that in the case of tetradecanoate Gallot and Skoulios could single out a variety of D structures. On the other hand, in KC_{10} and KC_{12} the above authors were not able to detect between the crystalline solid and the mesomorphic liquid any intermediate phase, whose existence on the contrary was apparent from the DSC traces discussed in Ref. [8] and looks as consistent both with the general picture of Fig. 2 and with the ΔS_F trend shown in the upper section of Figure 5.

In the range between T_A and room temperature, the DSC traces pointed to the occurrence of two, three and four transitions respectively for $KC_9 - KC_{13}$ (b_1, B), for $KC_{14} - KC_{19}$ (b_1, b_2, B) and for KC_{20} (b_1, b_2, B, b′). Each of the series B,

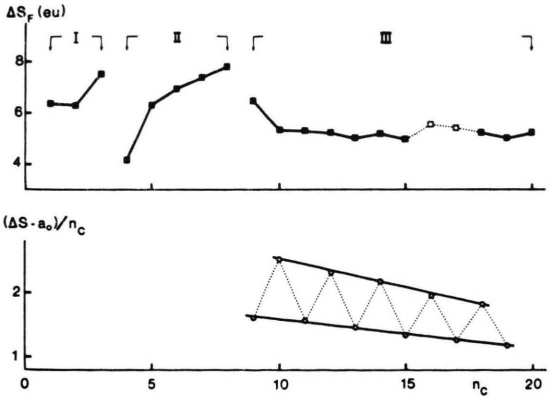


Fig. 5. Upper section: entropy of fusion *vs* n_C for KC_1—KC_3 (branch I), KC_4—KC_8 (branch II, where for KC_5 the heat effect taken into account includes the contribution of the close-to-fusion phenomenon described in Ref. [9]) and KC_9—KC_{20} (branch III, where the empty squares referring to KC_{16} and KC_{17} include the contribution due to the corresponding transition of type a_1: see footnotes b and c of Table 1).
Lower section: parabolic dependence of ΔS_B on n_C for the odd homologues from KC_9 to KC_{19} ($a_0 = -7.2108$) and for the even homologues from KC_{10} to KC_{18} ($a_0 = -19.6614$); this plot concerns all homologues pertinent to branch III of the upper section of the figure, but for KC_{20} (see text, § 3.4).

b_1 and b_2 exhibits a pronounced odd-even alternating effect, and the self-consistency of the results is proved, e. g., by the ΔS_B vs. n_C plot shown in the lower section of Figure 5.

3.4. It is now to be stressed that the regions below $\cong 380$ K and below $\cong 360$ K are those where, respectively in the case of the odd and even homologues, a different preliminary handling may lead to significant differences in the thermal behaviour of the potassium soaps, in particular during the first heating run.

It seems worthy to report first in some detail the findings of a few previous investigators on this particular subject.

On one hand, Shmidt [14] observed (calorimetrically) that KC_{16} showed below 360 K one transition when freshly recrystallized from ethanol, and two transitions when previously heated for a long time at 60 – 80 °C; he considered the two-transition form as the stable one. To conclusions substantially agreeing with those by Shmidt came (i) Ravich and Nechitaylo [10] who detected for the same salts one transition (at 330 – 341 K, see caption of Fig. 3) in samples dried over $CaCl_2$ and two transitions (at 313 – 323 and 329 – 335 K, see Fig. 3 b) in samples dried at 105 °C; (ii) Trzebowski [19] and Ripmeester and Dunell [20] who detected for KC_{18} one transition (at 345 K) on samples they respectively dried in air and under vacuum at room temperature, and two transitions (at 341, 350 K and at 340, 348 K) on samples they respectively dried at 150 and at 110 – 120 °C *.

On the other hand, only one transition was found by Vold and Vold [13] on KC_{16} dried at 105 °C and by Gallot and Skoulios [5, 22] on their even homologues dried at 110 °C under vacuum over $CaCl_2$.

In the present attempt to contribute to solve, at least in part, this conflicting situation, besides having adopted a crystallization and drying procedure (see § 2) such as to assure as far as possible for all of the $KC_{13}-KC_{20}$ salts a homogeneous "initial state" (although likely corresponding to that defined for KC_{16} as metastable by Shmidt [14]), it was gone somewhat deeper into the thermal behaviour of KC_{13}. The latter salt was chosen owing to the fact that only in its case the DSC traces recorded during the first run and those recorded after heating up to $T_{b1} < T < T_A$ offered sharp peaks well apart from each other, whereas in the case of the higher homologues most of the peaks detected after heating up to the said T values could either be complicated by the presence of shoulders, or fall at temperatures too close to those at which transitions occurred during the first run, or suffer other troubles, all these circumstances making rather puzzling the identification (at least through DSC) of the different phases possibly present.

When a sample of KC_{13} was submitted to subsequent heating runs ending at progressively increasing temperatures (see the left-hand section of Fig. 6, where temperatures ranging between 370 and 430 K are taken into account), one observed the gradual disappearance of the peak occurring in the trace recorded on the fresh salt (peak B; on an average: $T_B = 363.1 \pm 0.4$ K and $\Delta H_B = 4.28 \pm 0.03$ kcal mol^{-1}; see Table 1) and concomitantly the arising of a new peak (peak B′; on an average: $T_{B'} = 352.9 \pm 0.3$ K and $\Delta H_{B'} = 3.55 \pm 0.12$ kcal mol^{-1}).

A progressive conversion of B into B′ could also be obtained by repeatedly keeping a sample at a convenient temperature (e. g., 380 K; see the right-hand section of Fig. 6) for increasing times, whereas a single heating to $T_{b1} < T < T_A$ was sufficient to cause complete conversion. Contrary to B, peak B′ was proved (through a series of heating and cooling cycles) to be easily reversible.

The above observations apparently point to the existence at room temperature of two KC_{13} forms **, the characterization of which was obtained through X-ray powder diffractometry. This gave for the fresh (form I) and "converted" (form II) salt the patterns shown in Sects. a and b of Fig. 7, respectively. Diffraction patterns taken at $T_{b1} < T < T_A$ and subsequently (on the same sample) at $T_{B'} < T < T_{b1}$ (see Fig. 7) then enabled to characterize the form existing immediately above T_{b1} (form IV),

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* Ripmeester and Dunell [20] found again a single transition on previously melted KC_{18}, although at a temperature (336 K) lower than in the case of the samples simply dried under vacuum at room temperature; parallel observations were carried out by Grant and Dunell [12] on KC_{14}, KC_{16} and KC_{18}.

Discussing the behaviour of previously melted samples, however, goes beyond the scope of the present work.

** Previous DSC results [8] seem not to support the occurrence of an analogous behaviour in the case of shorter soaps: the results by Lomer [11], who studied the even homologues from KC_4 to KC_{18}, lead to the same conclusion, but for dodecanoate.

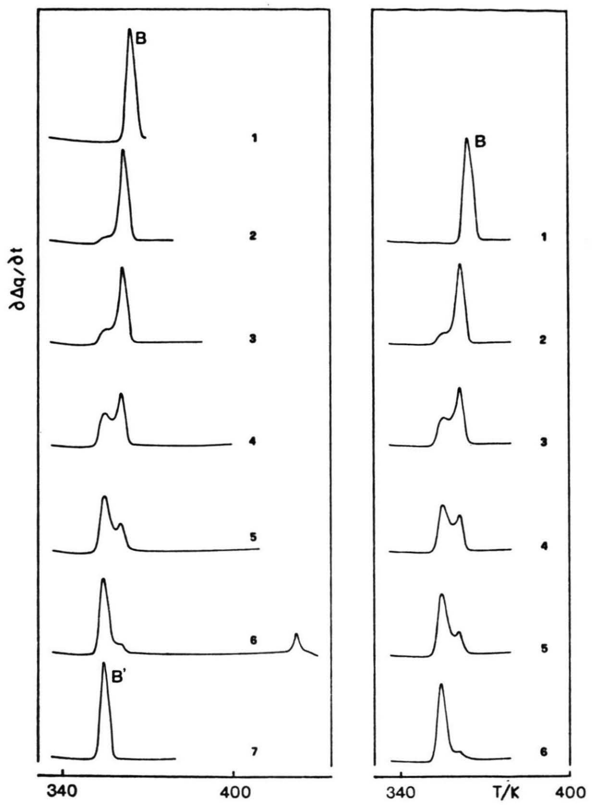

Fig. 6. DSC traces recorded on two different KC_{13} samples in subsequent heating runs as specified hereafter. Left-hand section: curve 1, fresh salt; curves 2–7, after heating during runs 1–6 up to 370, 380, 390, 400, 410 and 430 K, respectively. Right-hand section: curve 1, fresh salt; curves 2–6, after heating the sample at 380 K at the end of runs 1–5 for 0, 15, 30, 45, and 60 min, respectively. After each run the samples were quickly cooled down to 320 K; a heating rate of 5 K min^{-1} was always employed.

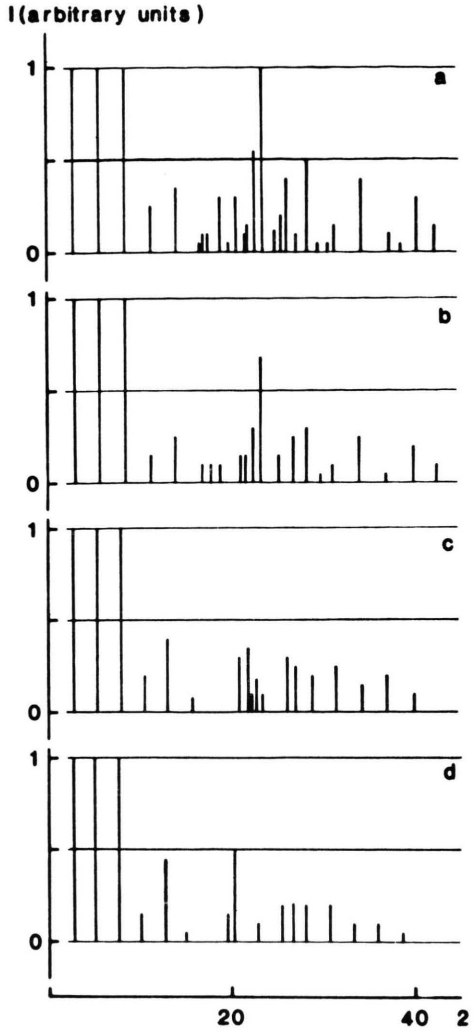

Fig. 7. X-ray powder diffraction patterns for KC_{13}: a, form I (at 290 K); b, form II (at 291 K); c, form III (at 372 K); d, form IV (at 439 K). Abscissae: 2ϑ angles; ordinates: peak intensities in arbitrary units. The most apparent differences among the above patterns occur at $15^0 < 2\vartheta < 30^0$.

and that (form III) pertinent to the "converted" salt and present between the latter temperature and $T_{B'}$.

When, however, a fresh sample was heated at $T_B < T < T_{b1}$ (e. g., 390 K) and kept at this temperature for a period of hours, more complicate patterns were recorded, whose features changed as a function of time and where the lines due to form III at last predominated.

A set of data relevant to forms I – IV (obtained from patterns taken at the specified temperatures) is given hereafter:

form:	T/K:	d/Å:
I	290.1 ± 0.1	31.326 ± 0.033
II	289.9 ± 0.1	31.594 ± 0.043
III	409.2 ± 0.5	34.041 ± 0.027
IV	429.4 ± 0.1	34.162 ± 0.020

In conclusion, the scheme

$$\mathrm{II} \overset{\text{trans.B}'}{\rightleftarrows} \mathrm{III} \overset{\text{trans.b}_1}{\rightleftarrows} \mathrm{IV}$$

may be reasonably adopted to correlate forms II, III, IV, whereas the stability relations of the latter with form I remain unfortunately not fully clear.

Concerning the B transitions, it is finally to be stressed as peculiar that the regular trends of the ΔS's, shown in the lower section of Fig. 5, were observed on salt samples as obtained by recrystallization from a lower alcohol, regardless of their possible (stable or metastable) state. Such regularities (i) involve all those homologues (from KC_9 up, except for KC_{20}, not considered owing to the complication arising from the splitting into B and b′) for which other characteristic features were already pointed out, i. e., the stabilization of T_F and the occurrence of at least one plastic phase and one transition of b_i type; (ii) do not extend to KC_8 and KC_7 (although their transitions at 327 and at 345 K, respectively, were also marked with B in Fig. 2), in which a different stepwise melting mechanism ought to be effective.

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