Phase Transitions in the Alkali C_1—*n.* C_4 Alkanoates

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(Z. Naturforsch. **30 a**, 1447—1454 [1975]; received August 6, 1975)

The enthalpies and entropies of fusion and of solid state transitions in Li formate and acetate; Li, Na, K, Rb, Cs propionates; Li, Rb, Cs *n.* butyrates were determined by differential scanning calorimetry. Supplementary information was provided through conductance measurements on solids. The collected data, together with those from previous papers, allowed to give a picture of the thermal behaviour of the alkali C_1—*n.* C_4 alkanoates.

Heat capacity data on solid and molten Na formate, acetate and propionate were also determined.

1. Introduction

In recent years a number of investigators have focused their attention on salts with organic anions, the physico-chemical properties of which look interesting from both the point of view of fundamental research and of possible technical applications.

However, the thermochemical information is so far largely incomplete; data on the number of polymorphs by different authors are often poorly agreeing and sometimes even conflicting; etc.

Concerning in particular the alkali $C_1-n.C_4$ alkanoate group, one of us and his associates had already referred on cryometric and/or calorimetric data taken on Na, K, Rb, Cs formates and acetates [1a–e], and more recently on the behaviour of Na and K *n.*butyrates, which show the peculiarity of forming smectic mesomorphic phases on melting [1f].

The present paper deals with a calorimetric investigation on the transition enthalpies and entropies of the ten remaining members of the group, i.e., Li formate and acetate; Li, Na, K, Rb, Cs propionates; and Li, Rb, Cs *n.*butyrates. Supplementary calorimetric data are also given for Na and K acetates, which have been previously submitted to cryometric investigation only, and for Rb formate and K *n.*butyrate. For a number of salts auxiliary information about solid state transitions (sstr's) was obtained by conductometric measurements.

On the basis of the collected results it is now possible to give a reasonably reliable and complete picture of the phase relations in the alkali formates, propionates and *n.*butyrates, whereas some uncertainties still remain in the case of the acetates, for reasons to be discussed below.

Finally, the molar heat capacities above room temperature of the Na salts in the solid and molten state are reported.

2. Experimental

2.1. *Materials*

As a rule, the salts were prepared by adding to an aqueous solution or suspension (deionized water employed) of the alkali carbonates a slight excess of the proper acid. The solids recovered by either evaporation under reduced pressure in a Rotavapor device or lyophilization were subsequently purified by recrystallization and/or fractional precipitation, and finally dried under vacuum at a suitable temperature. A few commercial products were also employed. Details on the material sources and handling are summarized in Appendix 1.

For a given salt, no significant differences could be observed in the transition temperatures and enthalpies of samples coming from different sources and/or subjected to a different handling.

2.2. *Apparatus and procedure*

A Perkin-Elmer differential scanning calorimeter Mod. DSC-2 was employed to measure the phase transition temperatures and enthalpies, and the heat capacities. Details on the procedure adopted were already given in Ref. [1f]. For each salt 3 to 11 samples were DSC analyzed in the range from ~110 K up to the melt region, using sealed Al containers.

It is known that some alkali alkanoates may undergo premelting phenomena. As an example, the microcalorimetric analysis (carried out by means of a Tian-Calvet microcalorimeter at the extremely

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Table 1. Alkali formates.

Salt	tr	T_{tr}/K	ΔH_{tr} / kcal mole^{-1}	ΔS_{tr} / cal mole^{-1} K^{-1}	Method	Ref.
HCOOLi	F	546	3.8_7	7.0_9	DSC-2	this work
	sstr A	496 ± 2	0.43	0.8_7		
HCOONa	F	$530._7$	4.0_5		cryom.	1 c
			4.1_0	7.7_2	DSC-1B	1 d
	sstr A	50_2	0.2_8	0.5_6		
HCOOK	F	$441._9$	2.8_4		cryom.	1 c
			2.8_1	6.3_6	DSC-1B	1 d
	sstr A	418	0.1_9	0.4_5		
HCOORb	F	443	2.8_4	6.4_1	DSC-1B	1 e
	sstr A	$368._1$	0.06	0.1_6	DSC-2	this work
HCOOCs	F	539	1.6_2	3.0_1	DSC-1B	1 e
	sstr A	312	1.0_8	3.4_6		

low heating rate of 0.86 K per hour) allowed Berchiesi and Laffitte [2] to split the fusion peak of K formate into two components, thus proving that in this case premelting occurs about 2 K below the melting temperature.

By DSC analysis on the same salt, however, Braghetti et al. [1d] could not distinguish the two components, although obtaining a $(\Delta H)_{total}$ value close to the sum $[(\Delta H)_{premelting} + (\Delta H)_{melting}]$ from Reference [2].

In the present work no attempt was made to single out any premelting contribution from the tabulated (total) melting enthalpies.

A Wayne-Kerr autobalance precision bridge Mod. B 331 Mk II (frequency: 1592 Hz; conductance range: $10^{-10} \div 10^{-2}$ Ohm^{-1}) in connection with a Gould Brush 500 XY plotter was used to continuously record the conductance of solid samples (in the form of pellets compressed between Ag electrodes) as a function of temperature.

3. Results and Discussion

In the following, details on the thermal behaviour of the investigated salts are given: the pertinent literature data are also reported for comparison.

The results coming from the present work and from Ref. [1] are summarized in Tables 1 – 4, where the phase transition temperatures (T_{tr}/K), enthalpies (ΔH_{tr}/kcal mole^{-1}) and entropies (ΔS_{tr}/cal mole^{-1} K^{-1}) concerning clearing (Cl, occurring at T_{Cl}) fusion (F, occurring at T_F) at T_A, T_B, ...) are tabulated. The number of the tabulated significant figures depends in each case on the degree of reproducibility in the pertinent set of experimental data, an example of the way followed is given in Appendix 2.

3.1. Formates

HCOOLi. The following data were available from literature: T_F: 546 [3]; T_{sstr}: 505, 388, 360 [4]. The present DSC thermograms confirmed the literature melting temperature, but provided evidence for one sstr only (hereafter indicated as sstr A), which occurs not far from the highest among the three Sokolov's sstr's [4].

When heated for the first time, samples in the form of powder exhibited sstr temperatures some degrees higher than those in the form of compressed pellets, though the concerned heat effects were strictly similar. After fusion, however, should any sample recrystallize and rest at room temperature for a sufficient time (days or even weeks, owing to the strong hysteresis always offered by the solid to undergo – on cooling – the sstr), on re-heating sstr temperatures close to those taken on the powder might be obtained *. It is anyway to be noted that Li formate in the molten state exhibits an unusual tendency to undercooling and seems inclined to form glasses, either by abruptedly cooling to the liquid N_2 temperature or sometimes even spontaneously.

In fact, among alkali carboxylates glass formation was previously observed, e.g., by Bartholomew [5], who reported for Li acetate a thermogram showing (at the temperature T_{glass}) a small endothermic effect he attributed to a glass transition, followed by a large exothermic one he attributed to crystallization of the salt. A very similar trend (allowing to average a T_{glass} value of 354 ± 2 K) is

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* For this reason, in computing the T_A values reported in Table 1, data taken on unmelted pellets were discarded.

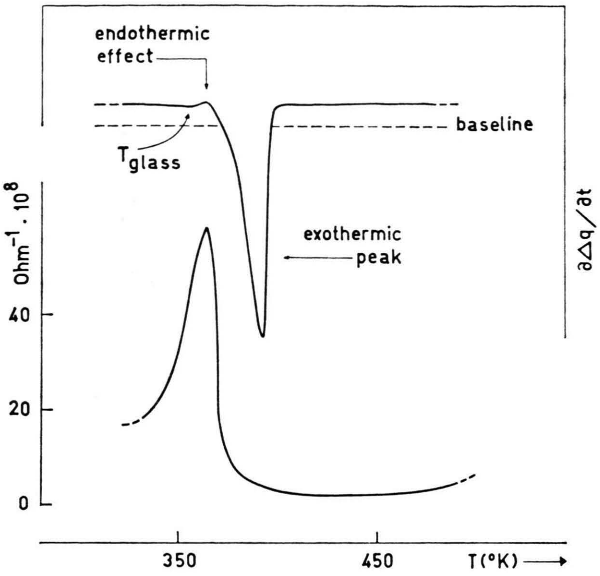

Fig. 1. Comparison between a DSC and a conductance curve for Li formate in the glass transition range (the temperature correspondence is limited by the fact that the temperature control in the furnace used for conductance measurements was less accurate than the DSC temperature control).

now apparent in the DSC curves taken on re-heating some either quenched or unquenched previously melted Li formate samples: an example of these curves is given in the upper part of Figure 1. By the way, it may be interesting to remark that the above phenomena occur within a temperature range roughly corresponding to that of Sokolov's second and third sstr's.

Conductance measurements were made both in the above temperature region (on pellets built up with the melted and quenched product) and in the region of sstr A (on pellets built up with the normal product).

Concerning the former case, a typical G/Ohm^{-1} vs. T plot is shown in the lower part of Figure 1.

Concerning the latter case, the recorded conductance curves exhibited a discontinuity in correspondence with the temperature (somewhat lower, as expected, than T_A as the samples were in the form of compressed pellets) at which the sstr occurred.

HCOORb. The previous investigation[1e] did not put into evidence any sstr. Since from the comparison with the remaining formates the existence of at least one ssrt might be expected, this salt was subjected to reinvestigation, which allowed to detect a sstr at 368 K, involving a very small heat effect.

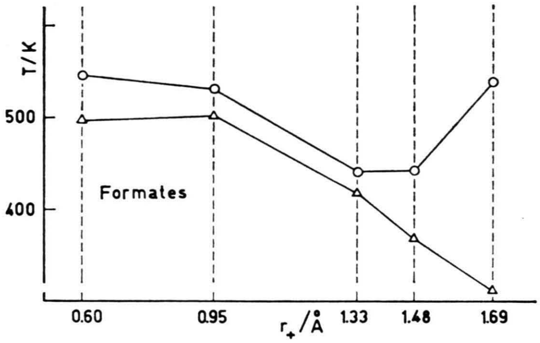

Fig. 2. Fusion (circles) and sstr (triangles) temperatures of alkali formates as a function of cationic radius (the lines connecting points of the same kind were drawn for better visualization).

The thermal data concerning the formate group are summarized in Table 1. The fusion and sstr temperatures are also drawn, as a function of the cationic radius ($r_{Li^+} = 0.60$, $r_{Na^+} = 0.95$, $r_{K^+} = 1.33$, $r_{Rb^+} = 1.48$, $r_{Cs^+} = 1.69$ Å[6]), in Figure 2.

3.2. *Acetates*

CH_3COOLi. The samples submitted to DSC analysis melted at 557 K, while literature T_F's range between 545 and 564 K[3] and gave no evidence for any sstr, contrary to the results by Diogenov[7] who reported a transition occurring at 530 to 536 K.

DSC traces taken on Li acetate glass at the heating rate of $5-10\ \text{K min}^{-1}$ exhibited a glass transition temperature of 401 ± 2 K, in satisfactory agreement with the value 394 K given by Bartholomew[5].

CH_3COONa. The cryometric meaturements by one of us[1b] led to $T_F = 601.3 \pm 0.2$ K (to be compared with literature data ranging from 592 to 610 K[3]) and to $\Delta H_F = 4.4 \pm 0.1\ \text{kcal mole}^{-1}$. The latter figure is confirmed both in a subsequent paper by Potemin et al.[8], who obtained by means of a derivatograph $\Delta H_F = 4.2 \pm 0.6\ \text{kcal mole}^{-1}$, and in the present calorimetric investigation (see Table 2).

Widely diverging opinions, on the contrary, have been expressed by previous investigators on the solid polymorphs, as four sstr's (at 511 – 513, 403. 391 and 331 K) were found by Sokolov[4], and only one both by Bergman and Evdokimova[9] and by Diogenov et al.[7, 10a, 10b], though at largely differing temperatures (527 and 583 – 596 K, respectively).

Table 2. Alkali acetates.

Salt	tr	T_{tr} / K	ΔH_{tr} / kcal mole^{-1}	ΔS_{tr} / cal mole^{-1} K^{-1}	Method	Ref.
CH_3COOLi	F	557 ± 2	2.8_4	5.1	DSC-2	this work
CH_3COONa	F	$601._3$	4.4		cryom.	1 c
			4.2_9	7.1_3	DSC-2	this work
	sstr A	527 ± 15	(0.0_4)	(0.0_8)		
	sstr B	465 ± 3	(0.1_0)	(0.2)		
	sstr C	414 ± 10	(0.0_7)	(0.1_7)		
CH_3COOK	F	$578._7$	3.6_3		cryom.	1 d
			3.6_4	6.2_9	DSC-2	this work
	sstr A	$422._2$	0.1_0	0.2_4		
CH_3COORb	F	514	2.6_4	5.1_4	DSC-1B	1 e
	sstr A	498	0.5_2	1.0_4		
CH_3COOCs	F	463	2.8_8	6.2_2	DSC-1B	1 e

Above room temperature we were able to detect (on heating) endothermic effects in three different regions, although only approximate T_{tr} and ΔH_{tr} values (reported in brackets in Table 2) could be drawn from the unsharp peaks of the DSC traces. On subsequent cooling the expected exothermic peaks were never observed, which proves a remarkable hysteresis. Only with samples let rest days (or even weeks) at room temperature, re-heating might allow to put again into evidence the endothermic peaks, sometimes at temperatures and with areas more or less changed in respect to those of the first heating run.

In the region below room temperature and down to 110 K, no evidence was obtained for other sstr's, though this cannot allow to conclude for the nonexistence of sstr's in this range, on account of the mentioned hysteresis. For the sake of completeness it is anyway to be said that Strelkov[11] observed a peak at 21 K in the $C_P(T)$ curve.

CH_3COOK. Literature T_F data range between 565 and 584 K[3], while the cryometric measurements by one of us[1a] gave $T_F = 578.7 \pm 0.3$ K. The corresponding ΔH_F amounted to 3.63 ± 0.07 kcal mole^{-1}: this figure is now confirmed as thermograms taken on three different samples gave a value of 3635 ± 12 cal mole^{-1}. It is therefore surprising the value (5.4 ± 0.6 kcal mole^{-1}) found by Potemin et al.[8].

Once more, poor agreement exists about sstr's, which should be: two (at 428 and 331 K, visual polythermal analysis) according to Sokolov[4], only one (at 565 – 569 K, same technique) in Diogenov's opinion[10a, 12], three (at about 503, 433 and 353 K) from the dilatometric measurements by Hazlewood et al.[13]. More recently, by X-ray diffraction analysis Hatibarua and Parry[14] stated that K acetate exists in an orthorombic structure from the melting point to 428 K, in a monoclinic form from 428 to ~ 348 K and in another monoclinic form with different cell volume from ~ 348 K to room temperature.

Our thermograms provided sure evidence for only one sstr at 422 K, i.e., sufficiently close to the temperatures of the first Sokolov's, the second Hazlewood's and the first Hatibarua's transition, whereas in the range 320 – 350 K the DSC traces exhibited small endothermic deflections, probably related to the monoclinic-monoclinic transition. As no quantitative data could be drawn in the latter case, the sstr at 422 K only is tabulated.

The thermal data coming from the present investigation and from Ref.[1] and concerning the acetate group are summarized in Table 2.

The phase relations in the solid state, however, represent a matter still open to discussion. In particular, results coming from different authors and obtained by different techniques apparently con-

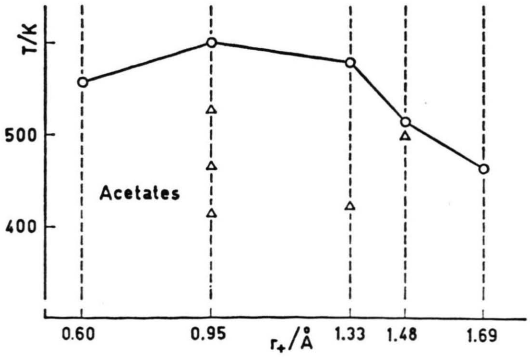

Fig. 3. Fusion (circles) and sstr (triangles) temperatures of alkali acetates as a function of cationic radius.

verge to indicate the occurrence of sstr's in the regions 510 – 540, 390 – 420 K for the Na salt, and in the regions 420 – 440, 320 – 350 K for the K salt. This information can therefore be regarded as reasonably reliable, whereas the other above mentioned sstr's, for which only data from unique sources are available so far, need further experimental support.

A picture of Table 2 T_{tr} data is given in Figure 3.

3.3. Propionates

C_2H_5COOLi. The pertinent literature data are: T_F: 602, 600[3]; T_{sstr}: 538[4]. An interesting peculiarity of this salt seems to have escaped the attention of previous investigators, i.e., the existence of two melting points, of which the stable one, $T_{F'}$, is some degrees higher than literature T_F's, whereas the metastable one, $T_{F''}$, is some twenty degrees lower. As an impressive example the thermal behaviour of a particular sample is shown in Fig. 4, where the portions covering the melting and freezing region of five thermograms taken in the same operational conditions are reported. Curve 1 was recorded on heating starting from room temperature: the sample, after having undergone sstr A (discussed below) at T_A, melted at $T_{F'}$. Curve 2 was taken on cooling: the melt solidified at T_f (a temperature only approximately reproducible in subsequent runs, but always higher than T_A), and cooling was stopped at $T' > T_A$ ($T' = 550$ K). Reheating starting from T' (curve 3) led to fusion at $T_{F''}$. On the next run (curve 4) the sample was cooled down to $T'' < T_A$ ($T'' = 400$ K). After having let the sample rest 100 min at this temperature (since Li propionate exhibits a not negligible hysteresis to sstr on cooling), re-heating led again to the sstr at T_A and then to fusion at $T_{F'}$ (curve 5). Agreement existed on one hand between the areas of peaks F', and on the other hand among the (remarkably larger) areas of peaks f and F'', the latter coincidence proving metastable solid formation from the melt.

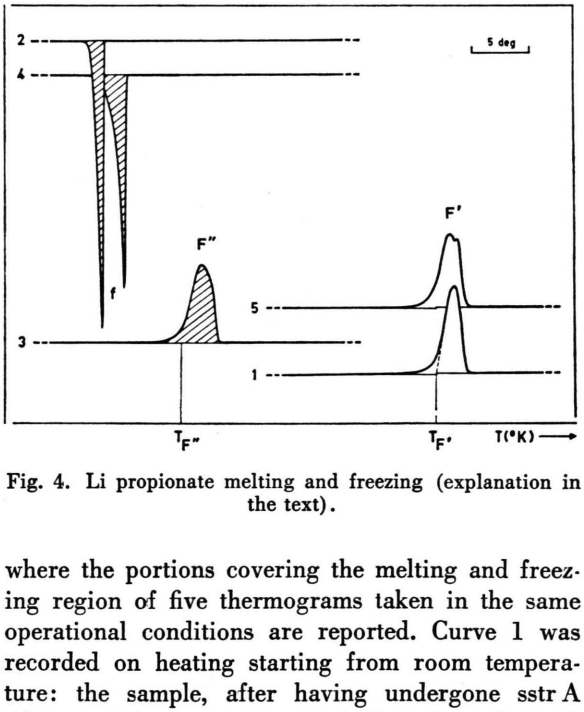

Fig. 4. Li propionate melting and freezing (explanation in the text).

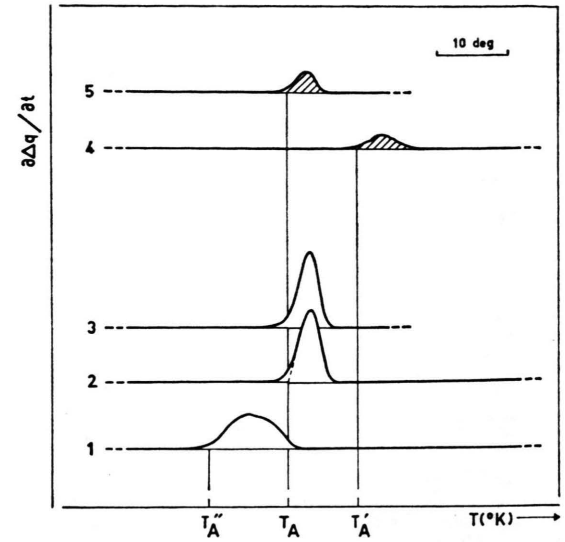

Fig. 5. Li propionate sstr A. The five thermograms were taken on heating at the same sensitivity range, scan speed and chart speed: 1, 2, 3 on a 17.70_3 mg compressed sample (1, starting from room temperature; 2, after fusion, cooling down to 400 K and resting 100 min at this temperature; 3, after re-fusion, cooling down to room temperature and resting overnight); 4, 5 on a 4.64_9 mg powder sample (4, starting from room temperature; 5, after fusion, cooling down to 400 K and resting at this temperature). The convergence of T'_A and T''_A to T_A is apparent; moreover, a satisfactory agreement exists among the peak areas of the thermograms 1, 2, 3, on one hand, and of the thermograms 4, 5, on the other hand. At no definite exothermic peaks could be recorded on cooling the samples down to 400 K at the usual scan speed of 5 – 10 K min^{-1}, no cooling curves are reported.

Sokolov's observation of a unique sstr (at 538 K) appears to be confirmed by DSC analysis carried out down to 110 K. A remarkable difference (even larger than in the case of Li formate) was observed between the sstr temperature $T_A{}'$ of the powder and $T_A{}''$ of the compressed pellets. All samples, however, exhibited satisfactorily agreeing sstr temperatures, T_A (intermediate between $T_A{}'$ and $T_A{}''$, see Fig. 5),

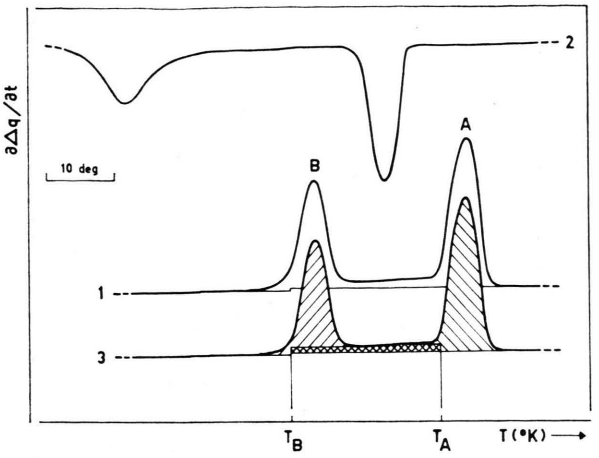

Fig. 6. Na propionate sstr's A and B. The three thermograms were taken on the same sample in the same operational conditions: 1, on heating; 2, on cooling; 3, on reheating after 40 min rest at 430 K. The heat effects corresponding to the sum of the shaded + cross-hatched areas, and to each of the shaded areas are given in Table 3.

when re-heated after having been melted, cooled down and let rest at a suitable low temperature *.

C_2H_5COONa. Most literature[3] fusion temperatures are in sufficient agreement with one another and with the present results. For the solid state on the contrary, while Sokolov[4] reported four sstr's at 560, 490, 468 and 350 K, respectively, Duruz et al.[15] pointed out the existence of two sstr's only, at temperatures (498 ± 1, 465 ± 1 K) approximately corresponding to the second and third Sokolov's transitions: the present results are in substantial agreement with the British authors'.

On cooling, the hysteresis to sstr is significantly reduced in comparison to the Li salt: although the appearance of the exothermic peaks (in particular of the lower temperature one) was somewhat delayed, a brief rest at a suitable temperature was sufficient to allow both peaks to reassume on subsequent heating the original positions (with respect to the temperature scale) and areas.

Owing to the proximity of peaks A and B, some difficulty arose in singling out the component areas: as in a previous case[1f] the "transition group" was considered as a whole (shaded + cross hatched areas in Fig. 6) and a mean sstr temperature was employed to evaluate the pertinent enthalpy and entropy.

The provisional ΔH_F value ($2.1\ \mathrm{kcal\ mole^{-1}}$) available from literature[16] seems somewhat low.

C_2H_5COOK. The presently found melting temperature strictly agrees with the two highest literature values[3]. As for the solid state, DSC analysis in the range from T_F down to 110 K showed the existence of two sstr's, A and B, occurring at some fifty degrees above and some forty degrees below room temperature, respectively. The thermograms proved that the hysteresis is now reduced to a small extent. Sokolov[4] pointed out the existence of sstr's at 603 and 341 K: the latter may be compared with sstr A, whereas the former could not be confirmed.

C_2H_5COORb. The present T_F is 5 K higher than the only value in literature (618 K[17]). No mention, on the contrary, was previously made of the two

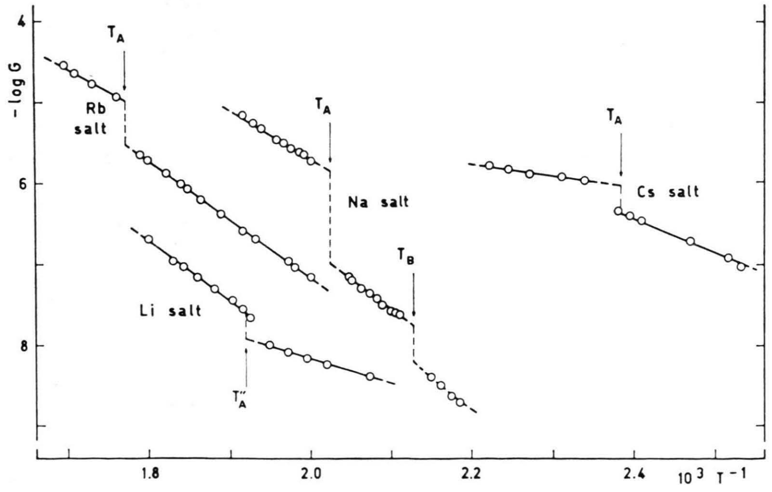

Fig. 7. Conductometric sstr detection in Li, Na, Rb and Cs propionates. The abscissas corresponding to the transition temperatures obtained by DSC are shown by the arrows; in the case of C_2H_5COOLi the comparison is obviously made with the temperature T''_A of Fig. 5, since in both cases samples compressed at roughly 1 ton cm^{-2} were employed.

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* For the sake of completeness it should be also mentioned that some 50 K above T_A a slight (endothermic) pen deflection could be clearly observed with powder samples, and less clearly with compressed or previously melted ones.

Table 3. Alkali propionates.

Salt	tr	T_{tr} / K	ΔH_{tr} / kcal mole^{-1}	ΔS_{tr} / cal mole^{-1} K^{-1}	Method	Ref.
C_2H_5COOLi	F	$606._8$	3.7_9	6.2_5	DSC-2	this work
	F (m)	$584._6$	4.2_6	7.2_9		
	sstr A	533 ± 2	0.8_0	1.5_0		
C_2H_5COONa	F	$562._4$	3.2_0	5.6_9	DSC-2	this work
	sstr A	494 } 482 *	1.7_6 *	3.6_5		
	sstr B	$470._2$				
C_2H_5COOK	F	$638._3$	4.8_1	7.5_4	DSC-2	this work
	sstr A	$352._5$	0.41	1.1_6		
	sstr B	258 ± 2	0.0_8	0.3		
C_2H_5COORb	F	$623._1$	3.4_8	5.5_8	DSC-2	this work
	sstr A	$564._3$	0.71	1.2_6		
	sstr B	317 ± 2	0.3_6	1.1		
C_2H_5COOCs	F	580	2.8_0	4.8_3	DSC-2	this work
	sstr A	419 ± 2	0.46	1.1_0		
	sstr B	$314._2$	0.32	1.0_2		

* For explanation see text; heat effects corresponding to shaded areas A and B in Fig. 6: 0.9_2 and 0.6_3 kcal mole^{-1}, respectively.

sstr's now put into evidence, about which it can be also said that hysteresis has vanished.

C_2H_5COOCs. In this case too the existence of sstr's was proved for the first time, and the melting temperature was found to be remarkably higher than the only literature datum (568 K[17]).

The sstr number and position in the propionate group were checked, whenever possible *, by the independent method of conductometry. Discrete points read off the significant portions of the recorded G vs. T curves are plotted as $\log G$ vs. T^{-1} in Figure 7.

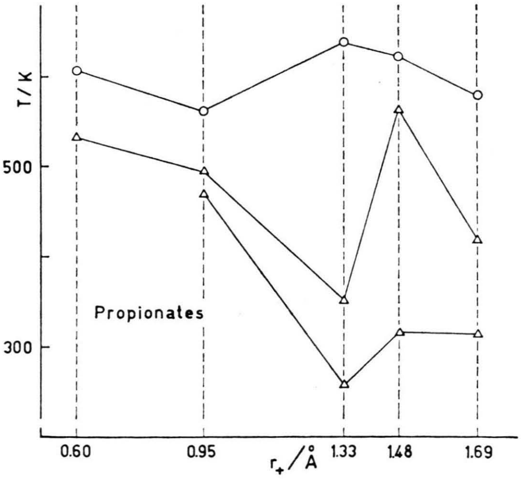

Fig. 8. Fusion (circles) and sstr (triangles) temperatures of alkali propionates as a function of the cationic radius.

The DSC data are summarized in Table 3 and Figure 8.

3.4. *n.Butyrates*

$n.C_3H_7COOLi$. The DSC analysis confirmed Michels and Ubbelohde's[17] statement that (differently from what happens in Na and K *n*.butyrates) no mesomorphic phase exists. On the contrary, the present thermograms (taken from 110 K) did not allow to put into evidence any sstr, in spite of previous Sokolov's results[4].

$n.C_3H_7COOK$. About the low temperature two-peak transition group E – F the qualitative information given in Ref.[1f] was completed after an improved calibration of the calorimeter in the pertinent range. In order to evaluate the corresponding heat effect the transition group was treated as a whole for the same reasons as in the case of Na propionate.

$n.C_3H_7COORb$ and $n.C_3H_7COOCs$. The here detected T_F values are 9 and 12 K, respectively, higher than reported in literature[17], while no mention was previously made of the existing sstr's.

The conductometric measurements performed (at $T > 380$ K) on solid Li, Rb and Cs *n*.butyrates confirmed the DSC data, i.e., the existence of a sstr in this range only for the Rb salt.

The thermal data collected here and in Ref.[1] are summarized in Table 4 and Figure 9. In the sequence Cs → Rb → K *n*.butyrates and increasing

* As, for instrumental reasons, measurements could start from about 380 K, sstr A of the K salt and sstr's B of the K, Rb and Cs salts necessarily escaped this check.

Table 4. Alkali *n.* butyrates.

salt	tr	$\frac{T_{tr}}{K}$	$\frac{\Delta H_{tr}}{\text{kcal mole}^{-1}}$	$\frac{\Delta S_{tr}}{\text{cal mole}^{-1}\,\text{K}^{-1}}$	Method	Ref.
n.C_3H_7COOLi	F	$591._7$	4.9_7	8.4_0	DSC-2	this work
n.C_3H_7COONa	Cl	$600._4$	0.53	0.8_8	DSC-2	1 f
	F	$524._5$	2.4_9	4.7_5		
	sstr A	$508._4$	0.4_4	0.8_7		
	sstr B	$498._5$	0.18	0.3_6		
	sstr C	$489._8$	0.13	0.2_7		
	sstr D	$450._4$	0.41	0.9_1		
n.C_3H_7COOK	Cl	$677._3$	1.1_9	1.7_6	DSC-2	1 f
	F	$626._1$	2.5_9	4.1_4		
	sstr A	$562._2$ } 552 *	1.0_6 *	1.9_2		
	sstr B	541				
	sstr C	$467._2$ } $464._3$ *	0.2_8 *	0.6_0		
	sstr D	$461._4$				
	sstr E	123 ± 2 } 133 *	0.1_6 *	$1._2$	DSC-2	this work
	sstr F	143 ± 2				
n.C_3H_7COORb	F	652	3.7_6	5.7_7	DSC-2	this work
	sstr A	$466._0$	0.5_6	1.2_0		
	sstr B	346 ± 2	0.24	0.6_9		
	sstr C	191	0.5_7	3.0		
n.C_3H_7COOCs	F	628 ± 2	3.3	5.3	DSC-2	this work
	sstr A	$343._9$	0.3_5	1.0		
	sstr B	263 ± 3	0.3	$1._1$		

* For explanation see text and Ref. [1f].

complexity in the phase relations is apparent; inspection of Fig. 9 might also suggest the existence of sstr's in the Na salt below 110 K.

As a final remark, it may be noted that the trend of the fusion temperatures of the highest melting formate (HCOOLi), acetate (CH_3COONa), propionate (C_2H_5COOK) and *n.*butyrate (*n.*C_3H_7COORb) is formally described (see Fig. 10) by the parabolic equation

$$T_F = 469.68 + 86.75\, n_C - 10.28\, n_C^2 \qquad (1)$$

where n_C = number of carbon atoms in the anion.

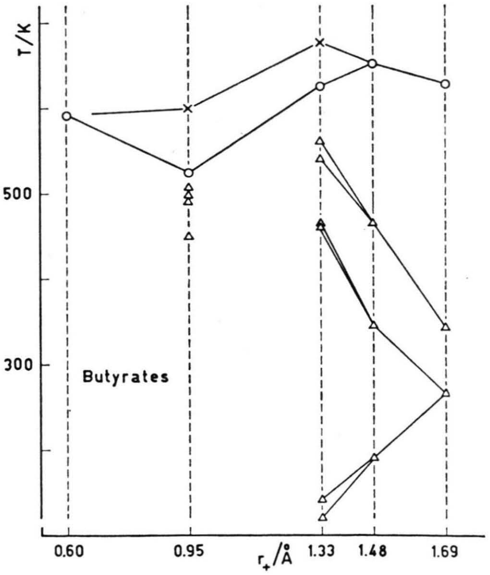

Fig. 9. Transition temperatures of alkali *n.* butyrates as a function of cationic radius (crosses: clearing; circles: fusion; triangles: sstr's). As regards the lines among sstr temperatures in K, Rb and Cs salts, see text.

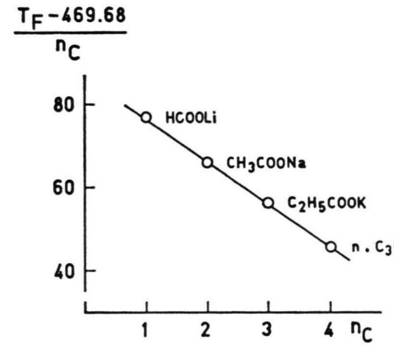

Fig. 10. T_F dependence of the highest melting salt in each alkanoate series on the number, n_C, of carbon atoms of the anion.

4. Heat Capacity Measurements

The quantitative determination of specific heat capacity by DSC, based upon the equation:

$$c_P(\text{sample}) = \frac{m(\text{sapphire})\, d(\text{sample})}{m(\text{sample})\, d(\text{sapphire})}\, c_P(\text{sapphire})$$

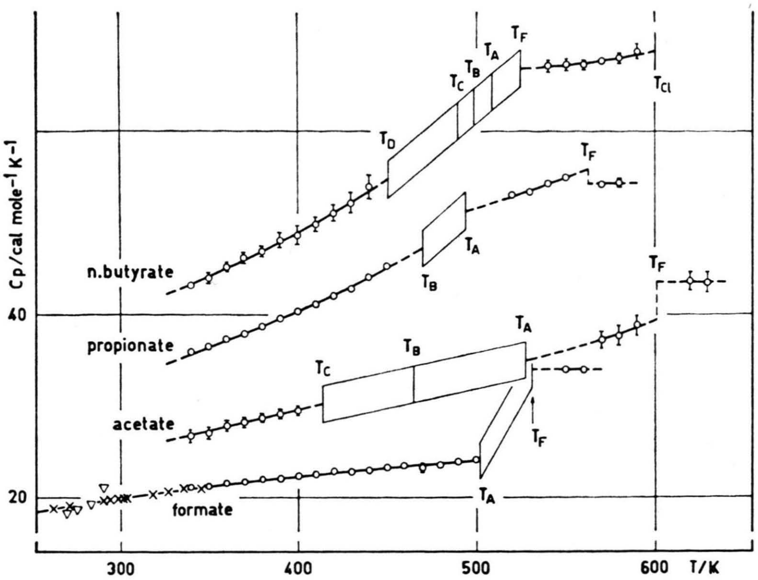

Fig. 11. Molar heat capacities of Na formate, acetate, propionate and *n.* butyrate. The uncertainty of each experimental point (when exceeding the diameter of circles) is indicated. Circles: present work and ref. [1f]; crosses: Westrum's data for the formate [20]; triangles: Strelkov's data for the acetate [11].

Table 5. Heat capacities of Na formate, acetate and propionate.

T/K	C_P/cal mole^{-1} K^{-1} formate	acetate	propionate
340	$21._{1}\pm 0._{3}$ (2)	$26._{7}\pm 0._{7}$ (4)	$35._{9}\pm 0._{2}$ (3)
350	$21._{2}\pm 0._{2}$ (3)	$27._{0}\pm 0._{7}$ (4)	$36._{5}\pm 0._{2}$ (3)
360	$21._{5}\pm 0._{1}$ (3)	$27._{8}\pm 0._{6}$ (4)	$37._{3}\pm 0._{2}$ (3)
370	$21._{7}\pm 0._{1}$ (5)	$28._{2}\pm 0._{5}$ (4)	$37._{9}\pm 0._{1}$ (3)
380	$21._{9}\pm 0._{3}$ (5)	$28._{7}\pm 0._{4}$ (5)	$38._{7}\pm 0._{2}$ (3)
390	$22._{0}\pm 0._{3}$ (5)	$29._{1}\pm 0._{5}$ (6)	$39._{6}\pm 0._{3}$ (3)
400	$22._{3}\pm 0._{3}$ (5)	$29._{5}\pm 0._{5}$ (6)	$40._{4}\pm 0._{3}$ (3)
410	$22._{5}\pm 0._{3}$ (5)	—	$41._{2}\pm 0._{3}$ (3)
420	$22._{8}\pm 0._{4}$ (5)	—	$42._{1}\pm 0._{3}$ (3)
430	$22._{7}\pm 0._{3}$ (4)	—	$42._{9}\pm 0._{3}$ (3)
440	$22._{9}\pm 0._{4}$ (4)	—	$44._{1}\pm 0._{3}$ (3)
450	$23._{2}\pm 0._{4}$ (4)	—	$45._{3}\pm 0._{3}$ (3)
460	$23._{4}\pm 0._{4}$ (4)	—	—
470	$23._{2}\pm 0._{5}$ (2)	—	—
480	$23._{5}\pm 0._{3}$ (3)	—	—
490	$23._{9}\pm 0._{1}$ (2)	—	—
500	$24._{1}\pm 0._{2}$ (2)	—	—
520	—	—	$53._{1}\pm 0._{2}$ (2)
530	—	—	$53._{4}\pm 0._{2}$ (5)
540	—	—	$54._{3}\pm 0._{1}$ (5)
550	$34._{0}\pm 0._{1}$ (3)	—	$55._{0}\pm 0._{1}$ (5)
560	$33._{9}\pm 0._{1}$ (3)	—	—
570	—	$37._{2}\pm 0._{9}$ (3)	$54._{2}\pm 0._{4}$ (5)
580	—	$37._{7}\pm 1._{1}$ (3)	$54._{4}\pm 0._{5}$ (5)
590	—	$38._{8}\pm 1._{1}$ (3)	—
620	—	$43._{6}\pm 1._{0}$ (3)	—
630	—	$43._{5}\pm 1._{1}$ (3)	—

In brackets the number of samples taken into account at each *T* is indicated.

(where: m = mass; d = "ordinate displacement"; synthetic sapphire being usually taken as the external standard) allowed us [1f] to reproduce the trustworthy data by Sokolov and Shmidt [18] on solid (between 350 and 450 K) and liquid (between 590 and 610 K) Na nitrate within 0.5 and 2%, respectively. The same technique was employed successfully, e.g., by Angell et al. in a number of cases [19].

This fact and the complete lack of information on the heat capacities of alkali alkanoates above room temperature suggested as worthy an extension of the investigation in this direction, in spite of some criticism on the use of DSC for c_P determination.

The results obtained for Na formate, acetate and propionate between 340 K and the melt region are summarized in Table 5 and shown in Fig. 11, together with Ref. [1f] data on the *n.*butyrate. The mean deviation did not exceed 3% in the case of the acetate and was remarkably lower in the other cases; the accuracy of the data can be reasonably expected to be within 2 – 3%, The "windows" in the figure indicate the temperature regions where reliable measurements could not be performed owing to the occurrence of phase transitions close to each other. It can also be pointed out that the difference $C_{P,\text{liquid}} - C_{P,\text{solid}}$ appears to be positive with Na acetate and slightly negative with Na propionate.

Adiabatic calorimetry data taken by Westrum et al. [20] on the formate and by Strelkov [11] on the acetate are also drawn for comparison. The satisfactory overlapping of the extreme portions of Westrum's and our curve is encouraging, whereas no sure explanation can be given of the fact that

Strelkov's acetate points intersect (at about 290 K) the formate curve.

Acknowledgements

The help of Dr. G. Chiodelli in performing the conductometric measurements is friendly acknowledged.

Table 6.

salt	starting materials	recovering procedure	further handling	product
HCOOLi	C1+A1	Ev	Cr aq. MeOH (50%)	1 a
HCOONa	P1	—	Fp from aq. MeOH (85%) with EtOH	2 a
HCOORb	C5+A1	Ev	Cr EtOH	3 a
CH_3COOLi	C1+A2	Ev	Fp from MeOH with iso.PrOH	4 a
CH_3COONa	P2	—	—	5 a
	P2	—	Fp from MeOH with dioxane	5 b
CH_3COOK	C4+A2	Ev	Cr EtOH	6 a
C_2H_5COOLi	C1+A3	Ly	Fp from MeOH with dioxane	7 a
	id.	Ev	id.	7 b
	id.	Ev	Cr MeOH	7 c
C_2H_5COONa	P3	—	Cr MeOH+EtOH (1:3)	8 a
	C2+A3	Ev	id.	8 b
C_2H_5COOK	C4+A3	Ly	Cr EtOH+iso. PrOH (1:2)	9 a
	id.	Ev	id.	9 b, 9 c
C_2H_5COORb	C5+A3	Ly	Fp from sec. BuOH with dioxane	10 a
C_2H_5COOCs	C6+A3	Ly	Fp from iso. PrOH with dioxane	11 a, 11 b
$n.C_3H_7COOLi$	C1+A4	Ly	Fp from MeOH with dioxane	12 a
$n.C_3H_7COORb$	C5+A4	Ev	Cr sec. BuOH	13 a
	C5+A5	Ly	Fp from sec. BuOH with dioxane	13 b
$n.C_3H_7COOCs$	C6+A4	Ev	Fp from iso. PrOH with dioxane	14 a
	C6+A5	Ly	id.	14 b
	C6+A4 (C6 suspended in MeOH)	Ev	id.	14 c

Ev = evaporation in Rotavapor; Ly = lyophilization; Cr = recrystallization from; Fp = fractional precipitation; aq. = aqueous. Anhydrous (unless otherwise stated) reagent grade solvents were used. Final drying was accomplished under vacuum at proper temperatures.

Appendix 1

As starting materials the following carbonates (C's), acids (A's) or commercial products (P's) were employed: Fluka "puriss" Li_2CO_3 (C1), Merck "Suprapur" Na_2CO_3 (C2), Fluka "puriss" (C3) and Merck "Suprapur" (C4) K_2CO_3, Atomergic Chemetals 99.9% Rb_2CO_3 (C5), Merck "reinst" Cs_2CO_3 (C6), Erba "RP" 85% HCOOH (A1), Merck "Suprapur" CH_3COOH (A2), Fluka "puriss" C_2H_5COOH (A3), Fluka "puriss" (A4) and Erba "standard for gas chromatography" (A5) $n.C_3H_7COOH$, Erba "RPE" HCOONa (P1), Merck "Suprapur" anhydrous CH_3COONa (P2), Erba "RP" C_2H_5COONa (P3).

For each product, details on the handling procedure are reported in Table 6.

Appendix 2

In Table 7 the DSC experimental results concerning fusion of *K* propionate are detailed for the different examined samples. Scan speeds of 5 or 10 K min^{-1} and different sensitivity ranges (as required by sample size) and chart speeds were employed.

Table 7.

product	sample	sample wt. / g	T_F/K	ΔH_F / kcal mole^{-1}
9 a	1 (powder)	0.004015	638.3	4.80
	2 (pellet)	0.019166	638.4	4.88
9 b	1 (powder)	0.002415	637.8	4.75
	2 (powder)	0.002903	637.8	4.78
	3 (powder)	0.005556	639.0	4.84
9 c	1 (powder)	0.001563	638.2	4.83

The mean values of the fusion temperature and enthalpy, i.e.,

$$T_F = 638.3 \pm 0.3\ \mathrm{K},$$

$$\Delta H_F = 4.81 \pm 0.04\ \mathrm{kcal\ mole^{-1}}$$

were reported in Table 3 as 638.$_3$ and 4.8$_1$, respectively.

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