

On the Thermal Behaviour of Some Alkali Branched Alkanoates. Note I

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Lithium, sodium and potassium *isobutyrate*, *isovalerate* and *isocaproate* were submitted to a differential scanning calorimetric investigation in the temperature range between 320 K and the isotropic melt region. The collected phase transition temperatures and heat effects are compared to those of the corresponding linear isomers. In particular the occurrence of mesomorphic liquids and the width of their existence fields is discussed.

1. Introduction

Many thermodynamic data on the alkali linear alkanoates for which $1 \leq n_C \leq 12$ (n_C = number of carbon atoms) have recently been obtained by DSC analysis [1]. Although for solid state transitions (sstr) several gaps do still remain due to hysteresis and/or other causes, this information is thought to offer a satisfactory degree of completeness and trustworthiness at least for what concerns clearing (Cl) and fusion (F) temperatures (T/K) and enthalpies ($\Delta H/kcal\ mole^{-1}$).

For a given n_C value, branching is of course expected to affect heavily the mode of packing of the anionic chains and consequently the melting mechanism. As an example, the mesomorphic liquid phase, whose field of existence covers 76 K [1a] in the linear sodium butyrate, is completely missing in the branched isomer [2].

Data on such branching effects were so far only occasionally reported in the literature, whereas the increasing interest presently devoted to salts with organic anions fully justifies a more systematic study: this paper aims at investigating the thermal behaviour of Li, Na and K *isobutyrate*, *isovalerate* and *isocaproate* (hereafter indicated as $MC_{x,i}$, where M = Li, Na, K and $x = 4, 5, 6$).

2. Experimental

Fluka 2-methylpropanoic (*isobutyric*; puriss. p. a. $\geq 99\%$), 3-methylbutanoic (*isovaleric*; puriss. ~ 99), 4-methylpentanoic (*isocaproic*; purum ~ 99) acids, Fluka puriss. Li_2CO_3 , and Merck suprapur Na_2CO_3 and K_2CO_3 were employed as starting materials. The *isosalts* were recovered from the reaction methanol solution by removing the solvent under reduced pressure in a Rotavapor device, then washed with either ethyl ether or acetone and furtherly purified as follows. The lithium salts, dissolved either in ethanol ($LiC_{4,i}$) or methanol, were fractionally precipitated by addition of 2-propanol. The sodium and potassium salts were (repeatedly, if necessary) recrystallized from either ethanol ($NaC_{6,i}$), or 2-propanol, or both ($KC_{6,i}$).

For details on the calorimetric apparatus and procedure see Reference [1].

$MC_{4,i}$ and $MC_{5,i}$ samples (sealed under vacuum in Pyrex tubes) were also visually observed in a Polaroid equipped oven, in order to check in each case the presence (or absence) of a mesomorphic liquid phase.

3. Results and Discussion

3.1. The phase transition temperatures and enthalpies taken on the investigated *isoalkanoates* are summarized in Table 1 where, as usual [1], the given number of significant figures depends on the degree of reproducibility obtained in each case.

It may be noted that preparing satisfactorily moisture-free samples was more difficult with the *isosalts* than with the linear ones, owing to increased hygroscopicity.

Moreover, it frequently occurred that the purification procedure did not succeed in giving completely crystalline specimens, and consequently the first heating DSC traces could exhibit endo- or exothermic pen deflections (poorly reproducible in different samples from the same salt batch) due to glass transition or crystallization phenomena, respectively. In these cases it was preferred to employ for calculations only traces recorded after a preliminary heating up to the melt region. In the same cases, owing to the fact (i) that the first heating trace was not to be taken into account, and (ii) that hysteresis might prevent the crystalline solid coming from a melt to undergo all the pertinent

sstr's, it cannot be excluded that some incompleteness might affect Table 1 for what concerns transitions in the solid state.

The scanty information offered by the literature is limited to the few T_{tr} 's and ΔH_{tr} 's mentioned later on.

3.2. As for sodium isobutyrate, which looked as fully crystalline, the following can be pointed out. First heating traces recorded on hand-compressed pellets systematically gave melting points higher (by up to 10 degrees) than the tabulated one, averaged from some twenty single values obtained either in any subsequent run of the same samples or in the first heating of not compressed ones (526.9 ± 0.7 K). This figure, though lower than Sokolov's [3] and Sokolov and Pochtakova's [4] data (533–535 K, visual polythermal method), is coincident with that of Duruz et al. [2] (527 K, DTA): complete agreement with the latter authors also exists about the fact that isomerization effaces any mesomorphic liquid phase in NaC_4 . In the solid state, DSC analysis did not allow to put into evidence any phase transition, whereas three (at 493, 364 and 340 K) and two (at 493 and 468 K) sstr's are reported by Sokolov [5] and by Duruz et al. [2], respectively. Should, however, a sample be exposed (by drilling a fine bore in the Al container lid) to atmospheric moisture for 2–3 hours, the next heating trace exhibited at $320 \leq T \leq 450$ K endothermic pen deflections, completely disappearing in subsequent runs, among which the sharpest one occurred at 337 K, i.e., close to the lowest "sstr" by Sokolov: this may therefore allow to consider the latter as a transition of a possible hydrated form of the salt, although the problem still remains open concerning the occurrence of sstr's at $T > 450$ K. Samples coming from two independently prepared and purified salt batches gave identical results.

Concerning $\text{NaC}_{5,t}$, the agreement of T_{Cl} and T_F (Table 1) with Ref. [2] (553 and 461 K) is satisfactory and somewhat worse with Refs. [3, 5] (535 and 451 K). As for the latter, it is still to be specified that, according to the Russian author's terminology, the higher temperature is referred to as a melting instead of a clearing point, and the lower one as a transition instead of a melting temperature. The existence of $\text{NaC}_{5,t}$ as a mesomorphic liquid over a temperature range of about 100 degrees is anyway concordantly proved by the

Table 1. Phase relationships in the Li, Na and K isobutyrate, isovalerate and isocaproate.

anion	cation	tr	T_{tr} K	ΔH_{tr} kcal mole ⁻¹	
$C_{4,t}$	Li	F	502.7 ± 0.9	2.06 ± 0.05	
		sstr	435.7 ± 0.6	1.76 ± 0.07	
	Na	F	526.9 ± 0.7	2.03 ± 0.06	
		K	Cl	625.6 ± 0.8	1.08 ± 0.02
			F	553.9 ± 0.5	2.10 ± 0.03
sstr		424 ± 3	1.95 ± 0.03		
$C_{5,t}$	Li	F	534 ± 2	2.8	
		sstr	365.4 ± 0.8	0.44 ± 0.03	
	Na	Cl	559	0.30 ± 0.02	
		F	461.5 ± 0.6	1.68 ± 0.03	
		K	Cl	679 ± 2	1.01 ± 0.02
F	531 ± 3		1.81 ± 0.05		
$C_{6,t}$	Li	F	500.0 ± 0.9	2.28 ± 0.06	
		Na	Cl	626 ± 2	0.38 ± 0.02
	F		534 ± 2	2.5 ± 0.2	
	K		Cl	713 ± 2	0.93 ± 0.04
		F	516 ± 2	2.3	

present and Duruz' investigations*, which also agree on the fact that the sstr at 425 K mentioned by Sokolov [5] is likely erratic.

Among the potassium isosalts, $\text{KC}_{4,t}$ and $\text{KC}_{5,t}$ were employed by Sokolov and coworkers in the study of several phase diagrams. In particular, for the isobutyrate the above authors reported: (i) "melting points" ranging from 629 to 638 K [4, 6, 7] and a "transition" at 621 K [5] (all of which likely to be compared with our clearing temperature); (ii) a second "transition" at 546 K [5] (which should actually correspond to our melting temperature); (iii) a third transition at 481 K which ought to be a true sstr, though hardly comparable with that detected through DSC analysis some 60 degrees below. A picture of the thermal behaviour of this salt is given in Figure 1.

Concerning the higher homologue, a "melting point" of 669 K (not far from our T_{Cl}) and two "transitions" at 618 and 327 K were reported by the Russian authors [7]. Since, according to the present results, the mesomorphic liquid field ranges from 679 down to 531 K and since the latter figure is confirmed by the trend of the thermomagnetic curves plotted by Duruz and Ubbelohde [8], Sokolov's higher transition appears to be erratic, whereas the lower one could not be revealed by DSC.

* Some discrepancies were found only in the magnitude of the heat effects involved in the clearing and melting processes.

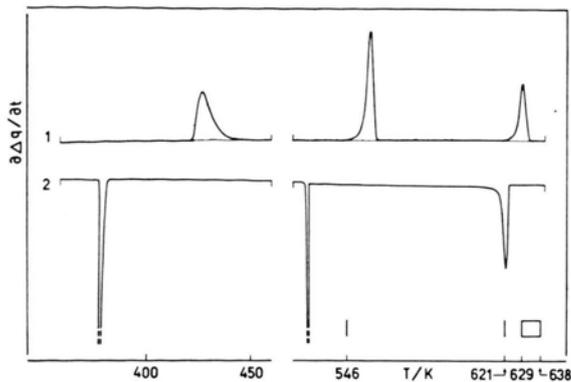


Fig. 1. DSC traces taken on heating (curve 1) and cooling (curve 2) a $\text{KC}_{4,i}$ sample in the same operational conditions, compared with Sokolov and coworkers data (for explanation, see text).

As for the other salts here taken into account no numerical data, so far as we know, are available in the literature.

3.3. The following remarks can finally be made about clearing and fusion in the different salt families here taken into account.

Each linear Na and K alkanolate for which $n_C \geq 4$ can exist as a mesomorphic liquid over a more or less wide temperature range [1]: in any corresponding isosalt the clearing temperature is always sharply pulled down although the field of existence

of the liquid crystals might result either reduced (and even effaced) as in the Na homologues, or enhanced as in the K ones (see the upper part of Figure 2). The entropy change is on the contrary only slightly affected and quite uniformly lessened (as shown in the lower part of the same Figure).

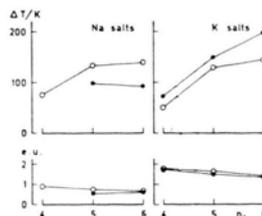


Fig. 2. $\Delta T = T_{C1} - T_F$ (upper section) and ΔS_{C1} (lower section), both plotted vs. n_C for C_4 – C_6 sodium and potassium linear and isoalkanoates (empty and filled circles, respectively).

The corresponding lithium salts exhibit no mesomorphic liquid phases.

With regard to fusion, all the linear butyrates, valerates and caproates exhibit a minimum T_F value when Na is taken as the cation. Among the branched homologues, however, such a behaviour is limited to isovalerates since branching abates the melting point in all cases but for the two even Na isosalts. The entropy change too does not show any uniformity in its trend, though without exception caused by branching to become smaller.

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