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

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The investigation on phase relationships and pertinent heat effects in branched alkali alkanoates was extended to lithium, sodium and potassium 2,2-dimethylpropanoates, 2-ethylbutanoates and 3,3-dimethylbutanoates. The results allow to discuss some aspects of the thermal behaviour of these salts, among which only the potassium ones can still exist as mesomorphic liquids.

1. Introduction

With the papers of the present series it was aimed at studying the effect of branching on the thermal behaviour of alkali alkanoates. Note I [1] dealt with lithium, sodium and potassium *iso*butyrates, *iso*valerates and *iso*caproates: the investigation is now extended to the remaining optically inactive pentanoates and hexanoates, though with the exception of the 2,2-dimethylbutanoates, the parent acid of which was not at disposal in the required degree of purity.

To our knowledge no previous information is reported in the literature for what concerns either the phase relationships or the pertinent heat effects in the salt group here taken into account, i.e., Li, Na and K 2,2-dimethylpropanoates, 2-ethylbutanoates and 3,3-dimethylbutanoates (hereafter briefly indicated as Me**DMP**, Me**EB** and Me**DMB**, respectively, Me being the alkali metal).

2. Experimental

Fluka 2,2-dimehtylpropanoic (trimethylacetic, puriss.), 2-ethylbutanoic (diethylacetic, purum $\geqq 98\%$), 3,3-dimethylbutanoic (*tert*-butylacetic, purum $\geqq 98\%$) acids, Fluka puriss. Li_2CO_3, and Merck suprapur Na_2CO_3 and K_2CO_3 were used to prepare the salts according to Ref. [1]. Final purification was obtained either through recrystallization (from ethanol: Li**DMP**, Na**DMP** and Na**DMB**; from 2-propanol: Li**DMB**, K**DMP**, K**DMB**) or through fractional precipitation (by addition of 2-propanol to a methanolic solution: Li**EB**; of ethyl ether to an ethanolic solution: Na**EB**, K**EB**).

As for apparatus and procedure see Ref. [2].

The occurrence or absence of a mesomorphic liquid phase was also checked for each salt by visual observation [1].

3. Results and discussion

3.1. It can be preliminary noted that once more (see Ref. [1]) the purified materials were not always present in a fully crystalline form, so that the DSC traces recorded during the first heating runs might not be suitable for transition temperatures detection and/or ΔH evaluation.

The measured clearing (Cl), fusion (F) and solid state transition (sstr) temperatures (T_{tr}/K) and enthalpies (ΔH_{tr}/kcal mole^{-1}) are reported in Table 1.

Table 1. Phase transitions in Li, Na and K 2,2-dimethylpropanoates (**DMP**), 2-ethylbutanoates (**EB**) and 3,3-dimethylbutanoates (**DMB**).

anion	cation	tr	T_{tr}/K	ΔH_{tr}/kcal mole^{-1}
DMP	Li	sstr	502.6 ± 0.7	0.45 ± 0.03
		sstr	446 ± 2	1.42 ± 0.07
	Na	F	683.7 ± 0.7	2.13 ± 0.05
		sstr	630.6 ± 0.7	2.37 ± 0.05
	K	Cl	613.5 ± 0.8	0.75 ± 0.06
		F	612.6 ± 1.0	2.73 ± 0.05*
		sstr	598.5 ± 0.9	(0.1)
EB	Li	F	655.5 ± 0.1	4.06 ± 0.08
		sstr	591.6 ± 0.2	0.24 ± 0.01
	Na	F	651 ± 3	1.5 ± 0.2
		sstr	436 ± 3	0.83 ± 0.03
		sstr	419.4 ± 0.3	0.55 ± 0.04
	K	Cl	541.5 ± 0.8	0.40 ± 0.03
		F	424.3 ± 0.2	1.47 ± 0.02
DMB	Li	F	603.3 ± 0.9	2.07 ± 0.05
		sstr	536.8 ± 0.9	0.50 ± 0.02
		sstr	508.1 ± 0.5	1.94 ± 0.03
	Na	F	652 ± 3	3.91 ± 0.06
	K	Cl	654 ± 2	0.81 ± 0.04
		F	572.1 ± 0.9	1.04 ± 0.05
		sstr	517 ± 2	1.15 ± 0.02

* $\Delta H_{Cl} + \Delta H_F$: for explanation see text and Figure 1.

The Li**DMP** T_F value could not be given, inasmuch as this salt exhibits a sharp tendency to sublimation above $T \sim 570$ K: however, samples sealed under vacuum in Pyrex tubes, when submitted to rapid heating in the Polaroid equipped oven, allowed to observe the isotropic liquid formation in the neighbourhood of 650 K.

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Also worthy of comment is the behaviour of the K analogue (**KDMP**). Slightly above 600 K, DSC traces taken on heating showed a large peak, the shape of which indicated the occurrence close to each other of two distinct endothermic effects (Fig. 1, curve 1), which could be subsequently singled out, taking advantage of the different magnitude in their undercooling (Fig. 1, curve 4). Attribution of the lower- and higher-temperature effect to fusion and clearing, respectively, was supported by the good evidence of a mesomorphic liquid phase (although in a very narrow range) offered by visual observation (through crossed Polaroids) of a sample, when slowly cooled after having been heated up to the isotropic liquid region.

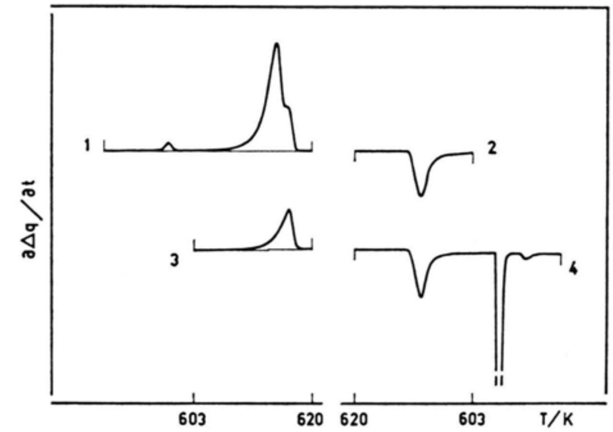

Fig. 1. DSC traces taken in the same operational conditions on a given **KDMP** sample. Curve 1: heating run showing the sstr and the (F + Cl) peaks; curve 2: cooling run stopped at 603 K, showing the transition from isotropic to mesomorphic liquid; curve 3: heating run from 603 up to 620 K, proving the reproducibility of the latter transition; curve 4: cooling run down to 590 K, showing the separation, due to different undercooling magnitude, of the isotropic-to-mesomorphic-liquid and of the mesomorphic-liquid-to-solid transitions.

3.2. The role played by the branching position with respect to the thermal behaviour of the salts studied can be put into evidence by the following remarks.

(i) In branched Na and K pentanoates and hexanoates, when the branching position is changed according to the sequence 3 → 2, or 4 → 3 → 2, respectively, the width of the mesomorphic liquid field ($\Delta T = T_{\mathrm{Cl}} - T_{\mathrm{F}}$) is progressively reduced and even effaced, as shown in Table 2.

Table 2. Width of the mesomorphic liquid field for different branching positions in Na and K branched pentanoates and hexanoates.

n_{C}[a]	anion	cation	branching position	ΔT/K
5	**MB**[b]	Na	3	97.5[d]
	DMP	Na	2	—
	MB[b]	K	3	148[d]
	DMP	K	2	0.9
6	**MP**[c]	Na	4	92[d]
	EB	Na	3	—
	DMB	Na	2	—
	MP[c]	K	4	197[d]
	EB	K	3	117.2
	DMB	K	2	81.9

[a] number of carbon atoms.
[b] **MB**: 3-methylbutanoate.
[c] **MP**: 4-methylpentanoate.
[d] From Ref. [1].

(ii) Concerning the branched hexanoates a more immediate evidence of the influence exerted by the branching position on the isotropic-liquid-formation temperature (T_{i}/K)* can be gained if differential rather than absolute temperatures are considered. As an example, when the T_{i}'s detected for the Na salts are chosen as references, plotting these

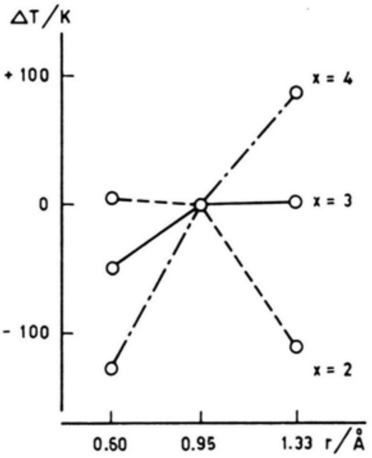

Fig. 2. Plots of ΔT vs. r in branched alkali hexanoates (r: cationic radius; $\Delta T = T_{x,\mathrm{Me}} - T_{x,\mathrm{Na}}$; $T_{x,\mathrm{Me}}$ and $T_{x,\mathrm{Na}}$: T_{i}'s of the Me and Na analogues, branched in position $2 \leq x \leq 4$, respectively; Me: Li, Na, K).

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* Irrespective of the fact that for different salts this might be a T_{Cl} or a T_{F} value.

temperature differences for the various branching positions vs. the cationic radius shows the trends reported in Figure 2.

Acknowledgements

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[1] P. Ferloni, M. Sanesi, P. L. Tonelli, and P. Franzosini, Z. Naturforsch., in press.

[2] P. Ferloni and P. Franzosini, Gazz. Chim. Ital. **105**, 391 (1975).