

Phase Transitions in Caesium $n.C_5 - n.C_{12}$ Alkanoates

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(Z. Naturforsch. **32a**, 285–288 [1977]; received January 19, 1977)

DSC analysis was performed on caesium $n.C_5 - n.C_{12}$ alkanoates between 330 and about 700 K. The temperatures of clearing and/or melting, and of solid state transitions were evaluated together with the associated heat effects. The occurrence of metastable melting was also put into evidence for the higher terms of the series.

1. Introduction

In a recent paper¹ the phase transitions in the alkali $C_1 - n.C_4$ alkanoates were reported. As part of an investigation now in progress on higher terms, the present work deals with the thermochemical behaviour of the caesium salts up to n .dodecanoate, a group of compounds for which the heat effects associated with phase transitions of any kind are still completely unknown, while the clearing and/or melting temperatures were given only for the C_5 , C_6 , C_7 ² and C_{12} ^{3, 4} terms.

2. Experimental

2.1 – Merck extrapure Cs_2CO_3 and Fluka puriss. n .pentanoic (>99.5 mole %), n .hexanoic (≥ 99), n .heptanoic (≥ 99), n .octanoic (≥ 99.5), n .nonanoic (>99), n .decanoic (≥ 99), n .hendecanoic (>99.5), n .dodecanoic (>99.5) acids were employed as starting materials. The solutions obtained by adding the proper acid to Cs_2CO_3 dissolved in anhydrous methanol were heated to boiling for a few minutes. The solvent was then removed by gentle heating under vacuum, and the solid residues (in some cases after having been washed with dry ether) were dissolved in 2-propanol and finally recovered by either precipitation through addition of 1,4-dioxane ($C_5 - C_7$ terms) or recrystallization at ice temperature.

As deliquescence strongly affects Cs alkanoates special attention was paid to protect samples from moisture contamination.

2.2 – Solid state transition (sstr), fusion (F) and clearing (Cl) temperatures (T/K) and heat

effects ($\Delta H/kcal\ mole^{-1}$) were measured by means of a Perkin Elmer Mod. DSC-2 differential scanning calorimeter (for details on procedure see Ref.s^{1, 5}). Visual observation at the heating stage polarizing microscope was also employed to obtain additional information.

3. Results and Discussion

3.1 – Let us first consider the solid-liquid transitions. Concerning the lower terms here taken into account Michels and Ubbelohde² already pointed out that solid Cs n .pentanoate directly melts into an isotropic liquid, whereas two steps (fusion and clearing) are involved in the case of n .hexanoate and n .heptanoate, the intermediate phase being a mesomorphic one. Such a phase was also visually observed in the highest term (Cs n .dodecanoate) by Baum et al.⁴, which qualitatively confirmed previous X-ray data by Gallot and Skoulios³, although the transition temperatures found by the former Authors were remarkably higher than those given by the latter.

In the present investigation, on one hand $C_5 - C_7$ samples when scanned for the first time gave DSC traces substantially confirming Michels and Ubbelohde's results, though the temperatures now detected are somewhat higher; on the other hand, a behaviour analogous to that of n .hexanoate and n .heptanoate could be put into evidence with the $C_8 - C_{12}$ terms only on samples preliminarily heated up to about 700 K (i.e., a temperature region where each salt exists as a stable isotropic melt), cooled down to room temperature and re-scanned**. The T and ΔH values thus obtained are summarized in Table 1.

* On sabbatical leave from Soreq Nuclear Center, Yavne, Israel. A grant from the Italian National Research Council (Rome) is gratefully acknowledged.

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** The features of the first heating curves will be discussed in the following section.



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Table 1. Clearing and fusion in caesium n . alkanoates. The quantities tabulated in this Table and in Table 2 are given with a number of significant figures depending on the reproducibility in each set of experimental results.

Salt	tr	T_{tr} K	ΔH_{tr} kcal mole ⁻¹	Previous T_{tr} data
CsC ₅ H ₉ O ₂	F	655.5 ± 0.9	3.97 ± 0.07	640 ²
CsC ₆ H ₁₁ O ₂	Cl	672	1.11 ± 0.04	668 ²
	F	632	2.6 ± 0.2	624 ²
CsC ₇ H ₁₃ O ₂	Cl	694 ± 2	1.14 ± 0.04	682 ²
	F	618.4 ± 0.7	2.45 ± 0.03	613 ²
CsC ₈ H ₁₅ O ₂	Cl	698.0 ± 0.8	0.96 ± 0.04	—
	F	607.7 ± 0.3	2.60 ± 0.07	—
CsC ₉ H ₁₇ O ₂	Cl	697.8 ± 0.7	0.86 ± 0.06	—
	F	598.6 ± 0.4	2.54 ± 0.08	—
CsC ₁₀ H ₁₉ O ₂	Cl	688 ± 2	0.72 ± 0.03	—
	F	586.9 ± 0.6	2.4 ± 0.1	—
CsC ₁₁ H ₂₁ O ₂	Cl	681	0.57 ± 0.08	—
	F	582.4 ± 0.5	2.62 ± 0.09	—
CsC ₁₂ H ₂₃ O ₂	Cl	671	0.48 ± 0.03	628 ³ ; 658 ⁴
	F	569	2.91 ± 0.06	551 ³ ; 568 ⁴

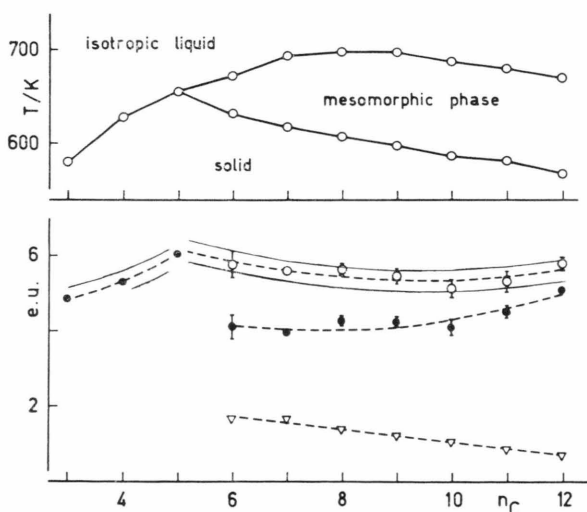


Fig. 1. Thermal data for clearing and/or fusion in Cs n . alkanoates as a function of carbon atom number. Upper part: transition temperatures. Lower part: ΔS_{Cl} (triangles); ΔS_F (filled circles); $\Delta S_{Cl} + \Delta S_F$ (empty circles; the thin solid lines correspond to $\pm 5\%$ of the sum).

The general trend of these transition temperatures (including also the previous data¹ on Cs propionate and n .butyrate) is drawn in the upper part of Fig. 1 as a function of the carbon atom number, n_C . The lower part of the same figure, where the pertinent entropy changes are given, shows that: (i) the ΔS_{Cl} 's for the C₆–C₁₂ terms almost linearly decrease with increasing chain length; (ii) a break occurs on passing from C₅ to C₆ between the steadily increas-

ing ΔS_F 's of the lower terms and those of the higher ones; (iii) should for the latter the total entropy change involved in the transition from solid to isotropic liquid be considered, the $\Delta S_F + \Delta S_{Cl}$ values fall on a boat shaped curve which on the left points to the maximum ΔS value belonging to n .pentanoate.

Referring now to the solid state, DSC traces obtained either in whatever heating run of the C₅–C₇ terms or in runs subsequent to the above specified preliminary heating of the higher terms allowed to detect in each salt the occurrence of a sstr (denoted in Table 2 as sstr A) within the temperature range 360–390 K. In the upper part of Fig. 2 the T_{sstr} 's

Salt	T_{tr} K	ΔH_{tr} kcal mole ⁻¹
CsC ₅ H ₉ O ₂	369.4 ± 0.6	0.78 ± 0.01
CsC ₆ H ₁₁ O ₂	385.2 ± 0.4	0.45 ± 0.02
CsC ₇ H ₁₃ O ₂	383.3 ± 0.5	0.41 ± 0.01
CsC ₈ H ₁₅ O ₂	373.4 ± 0.3	0.38 ± 0.01
CsC ₉ H ₁₇ O ₂	374.5 ± 0.2	0.37 ± 0.02
CsC ₁₀ H ₁₉ O ₂	373.9 ± 0.2	0.42 ± 0.01
CsC ₁₁ H ₂₁ O ₂	378.1 ± 0.2	0.43 ± 0.02
CsC ₁₂ H ₂₃ O ₂	377.1 ± 0.4	0.42 ± 0.03

Table 2. Solid state transition A in caesium n . alkanoates.

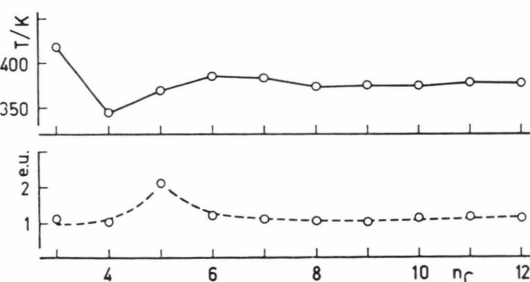


Fig. 2. Transition temperatures (upper part) and entropies (lower part) for sstr A in Cs n . alkanoates as a function of the carbon atom number.

are plotted *vs* n_C , along with those of the C₃ and C₄ terms. The corresponding ΔS 's (among which the maximum value belongs to the C₅ term) are given in the lower part.

Cs n .pentanoate looks as peculiar, not only for exhibiting the maximum ΔS values shown in Figs. 1 and 2, but also for being in the Cs series the last term directly melting into an isotropic liquid and in the whole alkali n .alkanoate group the highest melting one.

As for the problem of deliquescence and the effect of moisture on the features of DSC traces, a number

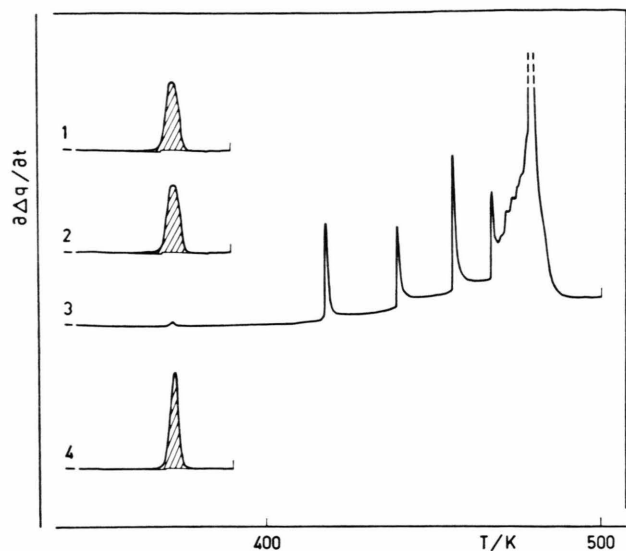


Fig. 3. DSC traces taken in the same operational conditions on the same Cs n . pentanoate sample in the absence (curves 1, 2 and 4) and in the presence (curve 3) of moisture: for explanation see text.

of heating curves outlined in Fig. 3 and taken on a sample of n .pentanoate (the most hygroscopic of our salts) seem worthy of comment. Two subsequent heating runs on the sample tightly sealed in an Al container are shown by curves 1 and 2. The peaks represent sstr A , the reproducibility of which is proved by agreement (better than 1%) of the shaded areas. A fine bore was then drilled in the container lid and the sample exposed to atmospheric moisture until reaching a weight increase corresponding to somewhat less than 1 mole water per mole salt. The next heating trace (curve 3) shows only a small pen deflection at T_A followed by a series of sharp peaks between ~ 410 and ~ 470 K, and finally by a large endothermic effect between ~ 470 and ~ 490 K, reasonably to be referred to water removal. The physical change caused by the water absorbed had left only a small fraction of salt able to undergo sstr A . After heating up to 500 K, the sample weight went back to the original value and the next run (curve 4) again exhibited at T_A a peak of area strictly coincident with those in curves 1 and 2. Similar experiments on higher terms, together with some additional information obtained by NMR, allowed to confidently assume that the adopted preparation and purification procedure always yielded solvent and moisture free products.

3.2 — First heating above 330 K of C₈–C₁₂ samples gave DSC traces which on one hand always showed a more or less sharp peak at about 430 K, associated with a large heat effect (ranging between ~ 2.5 kcal mole⁻¹ for n .octanoate and ~ 5.6 kcal mole⁻¹ for n .dodecanoate), and on the other hand exhibited neither sstr A nor the fusion and clearing phenomena described in Section 3.1. Moreover, when a sample was submitted to cycles in each of which the first step consisted in keeping the salt for a given time at a temperature (T'/K) not far above 430 K*, the second in cooling to 330 K, and the third in re-heating up to T' , in subsequent heating runs a significant decrease of the peak area (along with a small lowering of the corresponding temperature) was always observed. This area decrease looked as dependent both on the difference $T'-430$ and, for a given T' , on the stay time at this temperature. As an example, referring to a sample of n .dodecanoate submitted to cycling between 330 and 540 K, in the upper part of Fig. 4 the percent

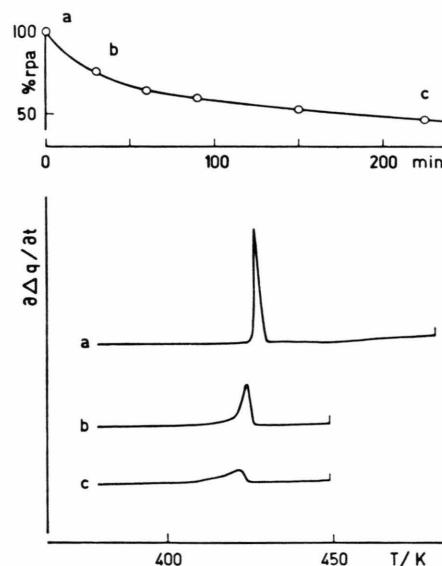


Fig. 4. Metastable fusion of a sample of Cs n . dodecanoate in subsequent heating runs (for explanation see text; the DSC traces were recorded in the same operational conditions). Upper part: percent residual peak area (% rpa) vs stay time at 540 K (in minutes; heating and cooling times neglected). Lower part: DSC traces corresponding to points a, b and c of the upper curve (peak area in trace a=100).

* Should on the contrary the temperature be raised up to ~ 700 K, in the next cooling run three exothermic peaks are recorded which correspond to the phase transitions discussed in Section 3.1.

residual peak area (as recorded in each cycle) is plotted *vs* the stay time at the higher temperature. Among the pertinent DSC traces a few significant ones are also given in the lower part of the same figure.

At the heating stage polarizing microscope it was observed for each C_8 – C_{12} salt that at ~ 430 K the crystalline solid collapsed into an optically isotropic liquid, in the bulk of which new localized anisotropic structures began slowly to appear at somewhat higher temperatures.

As a tentative explanation of the above experimental evidence, the recorded peaks might be attributed to fusion of metastable polymorphs obtained through the adopted preparation process. A recent investigation⁶ on barium *n*.butyrate showed that this alkanoate undergoes a metastable melting followed by immediate recrystallization into a stable phase, which in turn re-melts some seventy degrees higher. The present caesium C_8 – C_{12} *n*.alkanoates

might behave in a similar way though with an important difference: i.e., crystals of the stable solid phase seem to form and grow so slowly that the associated heat emission cannot be expected to give origin to any definite exothermic peak in the DSC traces.

3.3 – Below 330 and down to 110 K sstr's are exhibited both by stable and metastable solids, which however so often were affected by hysteresis to undergo such transitions that no satisfactorily reproducible data could be obtained. Anyway it could be stated that: (i) each term of the series exhibits at least one sstr in the region 220–320 K, and (ii) samples not preliminarily heated up to 700 K of the C_8 – C_{12} terms, undergo a metastable sstr at temperatures ranging from ~ 311 K for *n*.octanoate to ~ 328 K for *n*.dodecanoate.

Acknowledgements – Thanks are due to Mr. C. Bardoni for his help in performing DSC analysis.

¹ P. Ferloni, M. Sanesi, and P. Franzosini, *Z. Naturforsch.* **30 a**, 1447 [1975].

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³ B. Gallot and A. Skoulios, *Kolloid-Z., Z. Polymere* **213**, 143 [1966].

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⁵ P. Ferloni and P. Franzosini, *Gazz. Chim. Ital.* **105**, 391 [1975].

⁶ P. Ferloni, M. Sanesi, and P. Franzosini, *Z. Naturforsch.* **31 a**, 679 [1976].