The Liquid Crystal Region in Cesium Soaps

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The temperatures and enthalpy changes pertinent to the fusion and clearing processes in the linear cesium alkanoates from tridecanoate to eicosanoate were measured by differential scanning calorimetry. The present information along with data previously taken on the lower homologs allows one to draw the boundaries of the region where cesium soaps can exist in the liquid crystal state.

1. Introduction

Previous DSC work in this laboratory [1, 2] dealt with phase relationships in cesium linear alkanoates up to dodecanoate. In particular, it was shown that starting with hexanoate the stepwise melting process – a peculiarity of so many alkali soaps – leads to the formation of a liquid crystalline phase before the isotropic liquid state is reached.

During the last four decades, DTA supplemented with microscopic observation [3], photometry [4], X-ray diffraction [5], and hot-stage polarizing microscopy [6], were employed by a number of investigators in order to identify the upper (T_{Cl}; Cl = clearing) and lower (T_F; F = fusion) limits of the temperature intervals where even homologs with $n_C \geqq 12$ (n_C = number of carbon atoms) can exist as stable mesomorphic liquids. The results, however, have been far from satisfactory, inasmuch as differences of tens of degrees do occur both in the T_{Cl} and T_F values reported by different authors for a given homolog. As an example, the data available for cesium dodecanoate (which is the highest homolog investigated so far in this laboratory, and also the lowest one considered in the above quoted papers by other authors) are summarized in Figure 1.

This situation suggested to extend DSC investigation (which has proved to be a proper thermoanalytical tool for solving such problems) to odd and even homologs from tridecanoate through eicosanoate (hereafter briefly indicated as CsC_{13}, ..., CsC_{20}, respectively) in order (i) to get from a homogeneous set of data a reasonably trustworthy picture of the liquid crystal region in long-chain cesium soaps, and (ii) to obtain information (at present completely missing) also on the molar enthalpy and entropy increments involved in the clearing and fusion processes.

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2. Experimental and Results

2.1. The soaps were prepared by reacting 99.95% Atomergic Chemetals Cs_2CO_3 with a slight excess of the proper Fluka acid (certified purity: C_{13}, ≅ 98%;

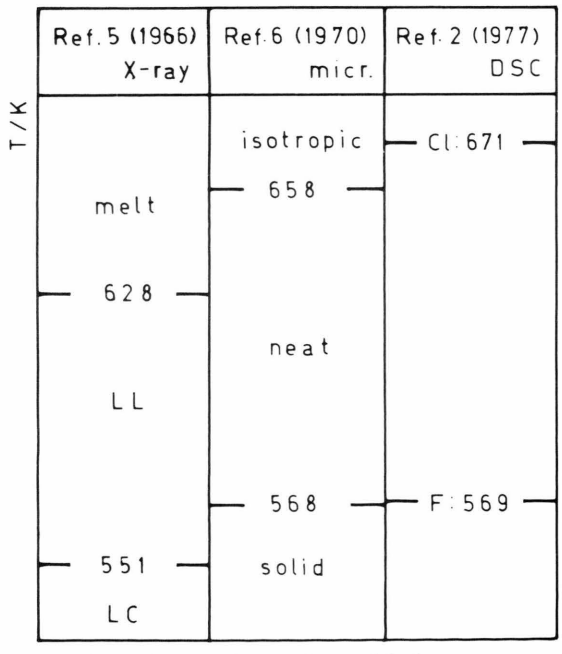

Fig. 1. Comparison of the clearing and fusion temperatures as detected by different authors for cesium dodecanoate. Phase designations according to the original papers (in particular, LL: "structure lamellaire labile"; LC: "structure lamellaire cristalline").

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C_{15}, C_{16}, C_{17}, C_{20}, ≧99; C_{14}, C_{18}, C_{19}, ≧99.5), both dissolved in anhydrous methanol. After refluxing for a few hours, the solvent was removed in a Rotavapor device under a reduced pressure. The solids recovered were washed with ethyl ether, then purified through (repeated, when necessary) fractional precipitation (with ethyl ether) from a methanolic solution, and/or crystallization from 2-propanol. After each step of the purification process, a sample of the soap concerned was submitted to DSC analysis. Purity was evaluated mainly on the basis of the clearing temperature and of the shape of the clearing peaks recorded, the occurrence of progressively higher T_{Cl} values, and of progressively higher ratios between peak height and width having been assumed to indicate increasing purity.

Four to six samples of each pure soap were scanned (at a rate of 10 K min^{-1}) with a Perkin-Elmer Mod. DSC-2 calorimeter supplied with a SAZ (Scanning Auto Zero) device. Due to the possible occurrence of metastable low melting forms [2], each sample was first heated up to clearing, then frozen down to 500 K, and eventually re-scanned between the latter temperature and the isotropic liquid region. For T_F and ΔH_F evaluation, only traces recorded during the second heating run were used, which – *inter alia* – exhibited sharper fusion peaks allowing one to draw more reliable base-lines. As an example, the results obtained for CsC_{18} are detailed in Table 1 and Figure 2.

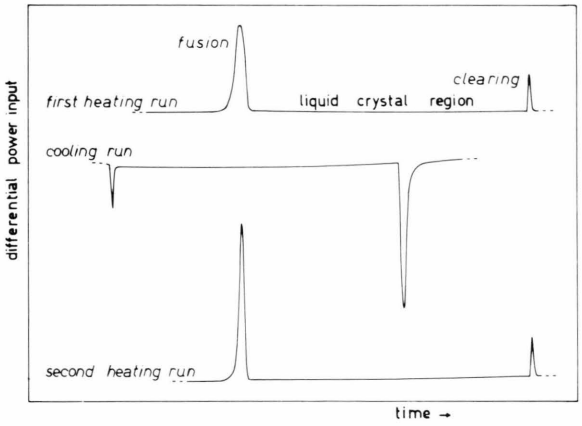

Fig. 2. DSC traces recorded over the fusion and clearing region for the CsC_{18} sample No. 2 of Table 1.

Table 2. Fusion and clearing data of linear C_{13}–C_{20} cesium alkanoates.

Salt	tr[a]	T_{tr} K	ΔH_{tr} kcal mol^{-1}
CsC_{13}	F	564.7 ± 0.4	2.65 ± 0.11
	Cl	666.8 ± 0.6	0.51 ± 0.03
CsC_{14}	F	560.6 ± 1.4	2.72 ± 0.05
	Cl	659.4 ± 0.8	0.45 ± 0.01
CsC_{15}	F	555.2 ± 0.2	2.54 ± 0.06
	Cl	650.9 ± 0.3	0.42 ± 0.02
CsC_{16}	F	550.2 ± 0.4	2.42 ± 0.09
	Cl	642.5 ± 0.2	0.35 ± 0.01
CsC_{17}	F	547.5 ± 0.8	2.43 ± 0.02
	Cl	634.9 ± 0.3	0.34 ± 0.01
CsC_{18}	F	546.1 ± 0.1	2.34 ± 0.05
	Cl	628.5 ± 0.1	0.34 ± 0.01
CsC_{19}	F	543.1 ± 0.4	2.34 ± 0.03
	Cl	621.0 ± 0.4	0.34 ± 0.05
CsC_{20}	F	540.1 ± 0.5	2.30 ± 0.08
	Cl	612.9 ± 0.2	0.27 ± 0.03

[a] tr = transition.

2.2. The clearing and fusion temperatures and molar enthalpy changes of CsC_{13}-CsC_{20} are summarized in Table 2. Both the T_{Cl} and T_F values, as well as the corresponding ΔS's decrease smoothly with increasing n_C. Least-squares fitting gave the

Table 1. DSC data taken on different samples of cesium octadecanoate.

Sample	Sample mass mg	T_F K	ΔH_F kcal mol^{-1}	T_{Cl} K	ΔH_{Cl} kcal mol^{-1}
1	3.68	546.0	2.28	628.6	0.36
2	3.58	546.0	2.33	628.5	0.32
3	3.65	546.1	2.39	628.7	0.35
4	3.68	546.3	2.28	628.6	0.34
5	2.15	546.0	2.40	628.4	0.32
6	3.20	545.9	2.37	628.3	0.35
	Mean values:	546.1 ± 0.1	2.34 ± 0.05	628.5 ± 0.1	0.34 ± 0.01

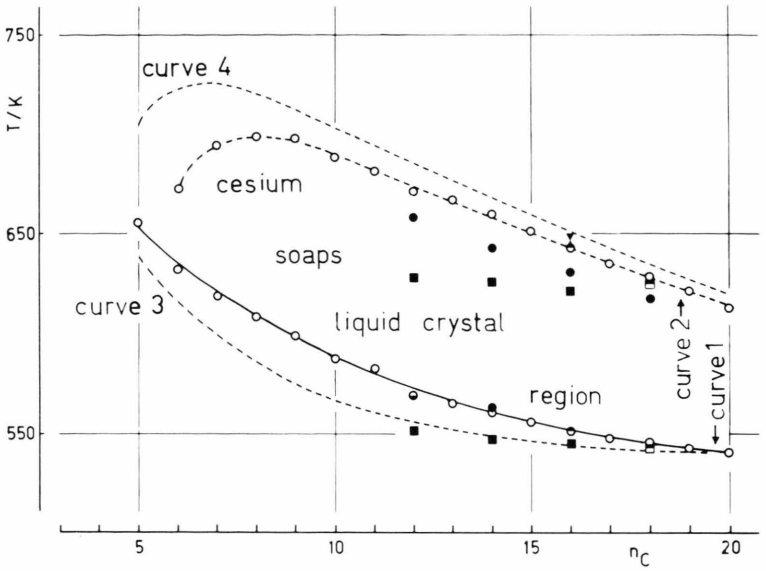

Fig. 3. Circles: [2] (CsC_5-CsC_{12}) and this work ($CsC_{13}-CsC_{20}$); triangle (microscopy) and inverted triangle (DTA): [3] (CsC_{16}); empty squares: [4] (CsC_{18}); filled squares: [5] (CsC_{12}, CsC_{14}, CsC_{16}, CsC_{18}); filled circles: [6] (CsC_{12}, CsC_{14}, CsC_{16}, CsC_{18}). Curve 1 ($T_F/K = 768.54 - 29.565\,n_C + 1.373\,n_C^2 - 2.33\cdot10^{-2}\,n_C^3$; $\sigma=2$): fusion of CsC_5-CsC_{20} from [2] and this work; curve 2 (hand-drawn): clearing of CsC_6-CsC_{20} from [2] and this work; curves 3 and 4: fusion and clearing, respectively of RbC_5-RbC_{20} according to [7, 8].

following 2nd order equations:

$$T_{Cl}/K = 786.95 - 10.24\,n_C + 7.80\cdot10^{-2}\,n_C^2;$$
$$\sigma = [\sum \Delta^2/(n-1)]^{1/2} = 0.5,$$
$$T_F/K = 679.20 - 12.27\,n_C + 2.67\cdot10^{-1}\,n_C^2;$$
$$\sigma = 0.8,$$
$$\Delta S_{Cl}/\text{cal K}^{-1}\,\text{mol}^{-1} = 2.269 - 0.168\,n_C + 3.93\cdot10^{-3}\,n_C{}^2; \quad \sigma = 0.03,$$
$$\Delta S_F/\text{cal K}^{-1}\,\text{mol}^{-1} = 7.444 - 0.286\,n_C + 6.31\cdot10^{-3}\,n_C^2; \quad \sigma = 0.09.$$

The data from Table 2 and those from [1, 2] allow one to outline the boundaries of the liquid crystal region in the series of the linear cesium soaps from CsC_6 (which is the lowest homolog exhibiting a mesomorphic liquid phase) to CsC_{20}, as shown in Fig. 3, where the T_F for CsC_5 [2] and the T_{Cl}'s and T_F's from the literature are also reported. In addition, the boundaries of the liquid crystal region in rubidium soaps (from RbC_5 up, as detected in this laboratory [7, 8]) are drawn for comparison.

Concerning cesium soaps, poor reliability seems to be attached in particular to the Cl temperatures given in [5, 6]. A fair agreement with the present results does occur only for the T_{Cl} value detected microscopically by Vold and Vold [3]. The overall trustworthiness and self-consistency of our DSC findings are supported: (i) by the similarity of the

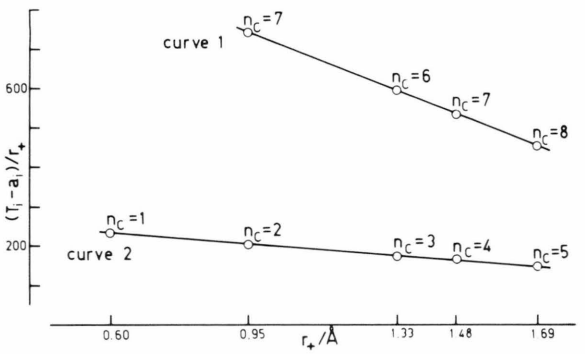

Fig. 4. Parabolic dependence of $(T_{Cl})_{max}$ and $(T_F)_{max}$ on the cationic radii. Curve 1: $T_i = (T_{Cl})_{max}$, $a_i = -63.164$; curve 2: $T_i = (T_F)_{max}$, $a_i = 406.94$. The cationic radii (r_+/Å = 0.60, 0.95, 1.33, 1.48, 1.69 for Li^+, Na^+, K^+, Rb^+, Cs^+, respectively) from [9]. In the different alkali linear alkanoate series the homologs exhibiting the highest T_F values are LiC_1, NaC_2, KC_3, RbC_4, and CsC_5, respectively; those exhibiting the highest T_{Cl} values are NaC_7, KC_6, RbC_7, and CsC_8, respectively (no liquid crystal forms in the Li series). The T_{max} values are those produced in this laboratory [10].

T_{Cl} and T_F trends for the Rb [7, 8] and Cs linear alkanoate series, and (ii) by the regularities (see Fig. 4) observed for the Cl and F temperatures [$(T_{Cl})_{max}$ and $(T_F)_{max}$, respectively] of those homologs which, in each of the five alkali linear alkanoate series, exhibit the highest T_{Cl} and/or T_F values.

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