Melting Behavior of Hydrocarbon Chain Molecules with Ionic End:Groups: Primary n-Alkylammonium Halides

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Stepwise melting behavior for a series of primary long chain **n**-alkylammonium chlorides was pointed out. A plastic phase, a smectic mesophase and a "clear" liquid possibly unisotropic were observed. The same trend seems to be common to other hydrocarbon molecules with ionic end-groups, including alkali metal **n**-alkanoates.

Hydrocarbon chain molecules with ionic end-groups have been widely investigated. The association of these amphiphilic molecules to aggregates of variable shape and size in aqueous solution has been the subject of a number of recent reviews [1–3]. Less attention has been paid to the structure of the pure systems. Systematic data are available for the anhydrous soaps only. Early calorimetric reports [4, 5] and variable temperature X-ray diffraction studies on the long chain Na **n**-alkanoates [6, 7] revealed a complex polymorphism in the solid state and the existence of smectic mesophases with wide stability ranges. Ubbelohde et al. [8–10] reported on the smectic phases of a few homologs with 3 to 5 chain C atoms and stressed the unusual properties of these mesogens with totally flexible molecules lacking any obvious geometrical anisotropy.

Although the relevance of such ionic organic melts has been recognized from both the theoretical and technological points of view, alkali metal **n**-alkanoates and a few strictly related derivatives are the only saturated aliphatic compounds for which non lyotropic liquid crystalline states have been reported [11].

In a recent paper [12], we have shown that the compound **n**-$C_{15}H_{31}NH_3Cl$ can exist as a smectic mesophase (liquid crystal), whose stability range covers about 40 K and whose structure is similar to that of the "neat" phase of the anhydrous soaps. We have also shown that the liquid crystalline state is reached from a double-layered plastic crystalline form (form I) in which the alkyl chains of the **n**-pentadecylammonium groups are in a liquid-like state. This compound thus undergoes a three-step melting mechanism: the conformational disordering of the hydrocarbon moieties is followed by the "bidimensional" fusion of the ionic residues, and finally by the clearing of the resulting mesomorphic liquid. This behavior is common to all the long chain primary **n**-alkylammonium chlorides and bromides.

We report here the results of a calorimetric investigation on chlorides with 6 to 18 C atoms *. In Table 1 the melting parameters (as obtained from DSC heating traces recorded between 320 K and 600 K) are listed. The three transitions involved in the melting mechanism are denoted with "cm", "f" and "cl". For the compounds with less than 9 C atoms, form I is the stable polymorph above 320 K [13].

The dependence of the clearing temperatures, and of the fusion and clearing entropies on the chain length is shown in Figs. 1, 2 for the **n**-alkylammonium chlorides and for a few series of alkali metal **n**-alkanoates. The data for the **n**-alkanoates are from Refs. [14–19].

The data of Table 1 and the inspection of Figs. 1, 2 allow the following remarks to be made for all the compounds considered:

a) No simple dependence of the entropy of fusion, $\Delta S(f)$, on the chain length is seen. Further, the order of magnitude is the same for the $\Delta S(f)$'s and the melting entropies of AB type salts without conformationally flexible bonds [20];

* Data on the shorter homologs are not reliable due to sublimation.

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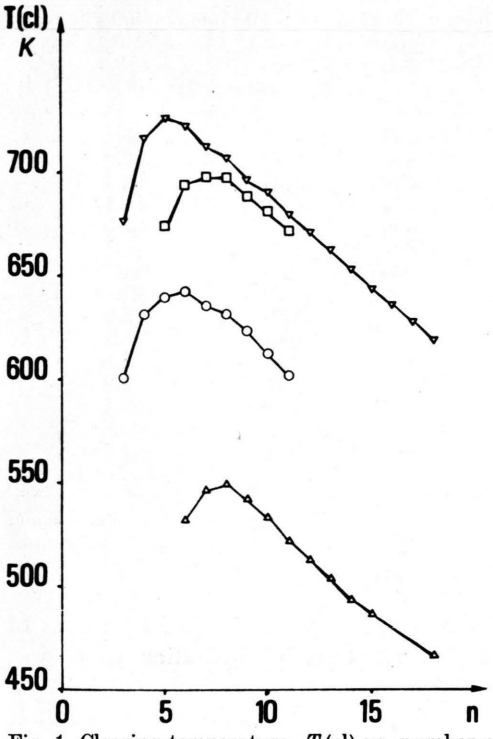

Fig. 1. Clearing temperature, T(cl) vs. number of chain C atoms, n, for long chain primary n-alkylammonium chlorides (△) and for Na(○), K(▽), and Cs(□) n-alkanoates [14—19].

b) the clearing temperatures, T(cl), when plotted vs. the chain length show a flat maximum at 5 – 8 chain C atoms;

c) the clearing entropies, ΔS(cl), decrease monotonically with increasing chain length.

The overall melting behavior thus appears to be only slightly affected by the nature of the ionic end-group.

The key to such a behavior is to be found in the tendency of the ionic "heads" towards segregation in layers, in order to reduce the unfavourable interactions with the aliphatic chains whose dielectric constant is low.

The segregation in layers of the ions is maintained at temperatures well above those corresponding to the onset of almost complete conformational disorder of the hydrocarbon "tails", which undergo with increasing temperature a number of rearrangements from the polyethylenic-like packing to a state strictly analogous to the well-known "fluid" state of lipid bilayer membranes [21]. The constraints on the chain conformation deriving from the fixed position of the end-groups and from excluded volume effects in this liquid-like state have been examined in detail by Monte Carlo simulation in our laboratory and described elsewhere [22].

Therefore fusion for these compounds mainly implies bidimensional disordering of the ionic layers (remark a)).

Remarks b), c) are somewhat more difficult to be rationalized without the aid of detailed structural information. Remark c), in particular could imply that the smectic mesophase is progressively less organized with increasing chain length, or alternatively that the clear liquid shows a residual anisotropy whose extent is greater the longer the aliphatic chains.

The relatively low fusion and clearing temperatures for the n-alkylammonium chlorides, when compared with those of the anhydrous soaps, should allow for the former a complete structural characterization of the mesophasic and of the clear melts.

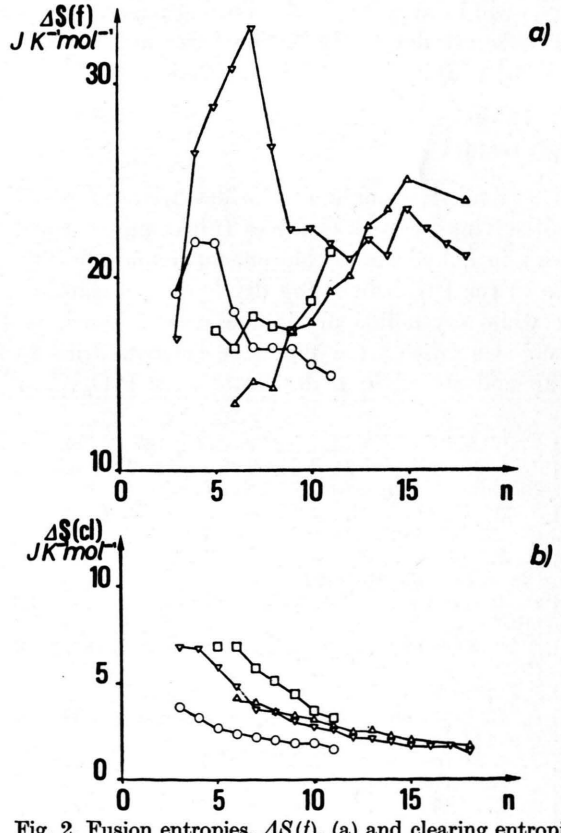

Fig. 2. Fusion entropies, $\Delta S(f)$, (a) and clearing entropies, ΔS(cl), (b) vs. number of chain C atoms, n, for long chain primary n-alkylammonium chlorides (△) and for Na(○), K(▽) and Cs(□) n-alkanoates [14—19].

Table 1. Melting parameters, as obtained from heating DSC scans, for long chain primary n-alkylammonium chlorides.

n	Transition	T(K)	ΔH kJ (KJ mol^{-1})	ΔS (JK^{-1} mol^{-1})	n	Transition	T(K)	ΔH kJ (KJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
6	f	494	6.56	13.4	12	cm	347	2.91	8.4
	cl	532	2.21	4.2		f	458	9.20	20.0
7	f	479	6.94	14.6		cl	512	1.21	2.4
	cl	546	2.21	4.0	13	cm	359	4.00	11.1
8	f	472	6.64	14.2		f	456	10.32	22.6
	cl	549	1.96	3.5		cl	503	1.25	2.5
					14	cm	365	4.32	11.8
9	cm	325	3.16	9.7		f	450	10.62	23.4
	f	471	8.11	17.1		cl	493	1.09	2.2
	cl	542	1.80	3.3	15	cm	374	5.67	15.2
10	cm	321	4.17	13.0		f	447	11.16	25.0
	f	466	8.23	17.6		cl	486	1.00*	2.0*
	cl	533	1.67	3.1	18	cm	386	7.86	20.4
11	cm	339	2.87	8.5		f	436	10.45	23.8
	f	461	8.86	19.2		cl	466	0.79	1.7
	cl	521	1.46	2.8					

* This value is sligthly different from that reported for the same compound prepared from absolute ethanol and conc. HCl(aq.) [12]. Although clearing transitions are known to be extremely sensitive to accidental impurities, we cannot give any definite explanation for this discrepancy, which has not been reproduced.

This investigation is presently in progress, and its results will be reported in a following paper.

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Experimental

The n-alkylammonium chlorides were prepared by dissolving the n-alkylamines (Fluka pure reagent grade) in anhydrous trichloromethane and allowing them to react with bubbling dry hydrogen chloride. The white crystalline precipitates were filtered, recrystallized twice from the same solvent, dried in vacuo and stored in a desiccator over P_2O_5. The purity of the compounds was checked by means of IR and NMR. No trace of hydration water was found.

The DSC curves were recorded between 320 K and 600 K with a Perkin-Elmer DSC-2 apparatus, in flowing N_2, at the scanning rate of 5 K min^{-1}. The temperature scale was calibrated with pure reference compounds. A sample of pure Indium ($\Delta H = 28.4$ J·g^{-1}) was used as a standard for the enthalpic measurements. The data of Table 1 are mean values of several measurements on independent samples. The standard deviation was of about 3%. Transition temperatures were always reproducible within ± 0.5 K.

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