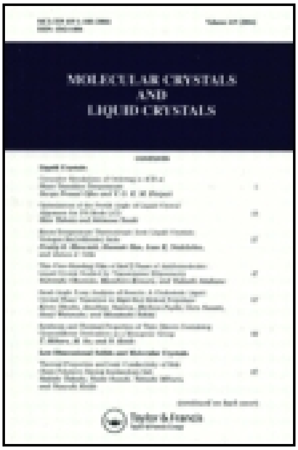

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On the Liquid Crystalline Behaviour of Bis(n-Penta-Decylammonium)Tetrabromozincat

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ON THE LIQUID CRYSTALLINE BEHAVIOUR OF BIS(n-PENTADECYLAMMONIUM)TETRABROMOZINCATE

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Apart from the liquid crystalline phases of a number of derivatives of long chain mono- and dicarboxylic acids, few evidences have been reported so far on the existence of (non lyotropic) mesophases of aliphatic compounds.[1]

In a recent paper[2] we have described the liquid crystalline behaviour of an aliphatic compound having a simple chemical constitution, n-pentadecylammonium chloride, which shows two mesophases the first of which is smectic and stable over a temperature range of more than 35°K.

On the other hand, more complex systems of the kind $(RNH_3)_2MX_4$, obtained through the reaction of a long chain n-alkylammonium halide with the halide of a divalent metal, have been extensively studied in recent years for their interesting polymorphism.,[3,4] since they give rise, between 270° and 370°K, to disordered layered solid phases in which the greatest part of the molar volume is occupied by the long alkyl chains, in a "liquid-like" state.[5,6]

Though, on one hand, an evident analogy exists between the structural organization of the hydrocarbon chains in these phases and that in a smectic mesophase (also in relation to systems of relevant biological interest such as, for instance, the lipid bilayer membranes),[6-8] on the other hand no true liquid crystalline phases have been described until now for such compounds.

We wish to report in this paper the results of an investigation of the thermal behaviour of the bis(*n*-pentadecylammonium)tetrabromozincate, since this compound gives rise, in addition to the previous disordered solid phases, to a true mesophase which is stable over a wide temperature range.

Table 1 lists transition temperatures, enthalpies and entropies for the compound under study, together with the values of the "long spacings" of all its stable polymorphs as deduced by a variable temperature x-ray diffraction investigation.

TABLE 1

T(K)	ΔH(kJ/mol)	ΔS(J/K mol)	c(Å)
Heating			
332	13.1	39.5	23.8
393	38.6	98.2	24.8
429[a]	8.2	19.1	28.2
			29.6
Cooling			
321	12.6	39.2	
388	38.4	99.0	
424	9.4	22.1	

[a] Melting

The two transitions at 332 and 393°K are solid-solid phase changes, in which the greatest amount of entropy increase may be attributed to the conformational disordering of the alkyl chains, which "melt" from an ordered all-trans state to a "liquid-like" one characterized by a conformational freedom comparable to that of the n-hydrocarbons in the melt.[5,6] The increase of the long spacing at the transition points can be explained on the ground of a variation in the packing of the hydrocarbon chains, from a double layer structure with intercalation of chains from adjacent layers to a double layer one with less or no intercalation, as evidenced for similar systems.[3]

The bis(n-pentadecylammonium)tetrabromozincate melts at 429°K giving a smectic mesophase whose diffraction pattern shows three reflection maxima which are successive orders corresponding to a long spacing of 29.6 Å. An x-ray photograph of this phase taken at 450°K is shown in Figure 1. This mesophase is no doubt the most similar to the high temperature phase of a lipid bilayer membrane among the disordered forms of compounds of the kind $(RNH_3)_2MX_4$ observed up to now.

According to the DSC curves and x-ray diffraction patterns, no isotropism is detectable at temperatures as high as 550°K. On one hand, this unusually wide stability range cannot be considered surprising for a system like the one under study, since the highly directional interactions which stabilize the layered structure of the mesophase--that is the cooperative optimization in the packing of the long hydrocarbon chains and of their polar heads--allow, at lower temperatures, even the existence of a stable crystalline phase in which, as already reported, the greatest fraction of the molar volume is in a "liquid-like" state.

On the other hand, the systematic occurrence of layered structures in nearly all the systems constituted

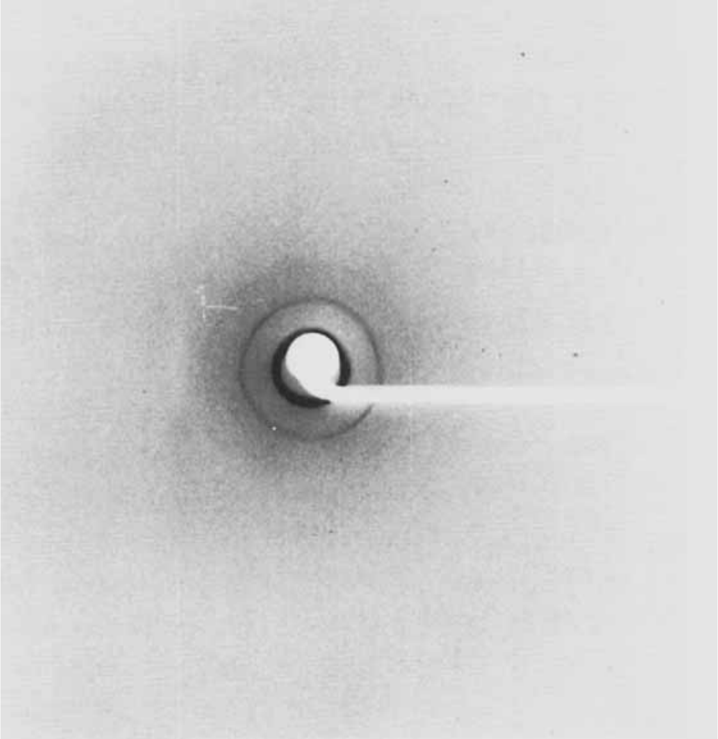

FIGURE 1

by long aliphatic chains in which one or both the molecular heads are polar[1-4,9,10] suggests that such interactions be present in a comparable amount in all the compounds of this kind, and possibly effective enough to allow the persistence of the layers even in the melt.

EXPERIMENTAL

$(\underline{n}\text{-}C_{15}H_{31}NH_3)_2ZnBr_4$ was prepared by dissolving n-pentadecylamine in glacial acetic acid, and adding concentrated HBr(aq) and then $ZnBr_2$ in stoichiometric amounts. After boiling for 5 minutes, the resulting solution was allowed to cool to room temperature, and the white precipitate filtered off, recrystallized twice from the same solvent and dried *in vacuo*. The purity of the produce was checked by elemental analysis, IR and NMR.

The DSC curves were registered between 270° and 550°K on a Perkin-Elmer DSC-2 apparatus, at the scanning rate of 10°K/min, in N_2 atmosphere.

Optical observations have been made with a Leitz polarizing microscope, equipped with a Mettler PF-5 microfurnace.

X-ray powder diffraction measurements were performed on a Philips PW-1011 diffractometer with proportional counter (Cu K_α radiation, Ni filter); variable temperature x-ray photographs were taken with a flat camera at a fixed distance from the samples.

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