

THERMAL BEHAVIOUR OF MIXED LONG-CHAIN ALKYLAMMONIUM TETRACHLOROZINCATES

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ABSTRACT

Mixed crystals of composition $(n\text{-C}_m\text{H}_{2m+1}\text{NH}_3)_{2x_m}(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_{2-2x_m}\text{ZnCl}_4$ ($m = 12; n = 14, 16, 18$) are formed upon annealing mechanical mixtures of layer compounds $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$, through solid state diffusion of the n -alkylammonium cations. From a common high temperature monophasic modification, in which the polymethylenic chains are conformationally molten, different modifications are obtained on cooling [depending on the $(n - m)$ value] in which chain crystallinity is developed. The structure of such modifications is speculated on the grounds of DSC and preliminary X-ray diffractometric and IR data, and compared with that of similar previously characterized systems.

INTRODUCTION

Compounds of the type $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$ (short notation C_nM), with $\text{M} = \text{Mn}, \text{Cu}, \text{Hg}, \text{Zn}, \text{Co}$, crystallize in layer structures in which planar metal halide arrays are sandwiched between bilayers of n -alkylammonium cations [1–8] (Figs. 1 and 2). Two main crystalline modifications are known. In modification α , stable at low temperatures, the alkylammonium groups are close-packed in the planar zig-zag conformation; in modification β , stable at higher temperatures, they are in a liquid-like state analogous in some respects to the “fluid” state of the lipid bilayer membranes [8,9].

As part of a continuing study on the salts C_nM we investigated the thermal behavior and some relationships between structure and properties of mixed long-chain alkylammonium tetrachlorometallates $(n\text{-C}_m\text{H}_{2m+1}\text{NH}_3)_{2x_m}(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_{2-2x_m}\text{MCl}_4$ [henceforth $(\text{C}_m)_x(\text{C}_n)_{1-x}\text{M}$, $x \equiv$ mole fraction of C_mM] with $\text{M} = \text{Mn}$, $m, n \geq 10$, $m \neq n$ [10–12]. We showed that heating mechanical mixtures of two salts C_mMn , C_nMn of composition $(\text{C}_m)_x(\text{C}_n)_{1-x}\text{Mn}$ results in the formation of solid solutions in which the cations of different length are randomly arranged on the surface of planar macroanions of composition MnCl_4^{2-} , built up of corner-sharing MnCl_6 octahedra (Fig. 1). Mixing is achieved through long range bidimensional diffusion of the n -alkylammonium cations in modifica-

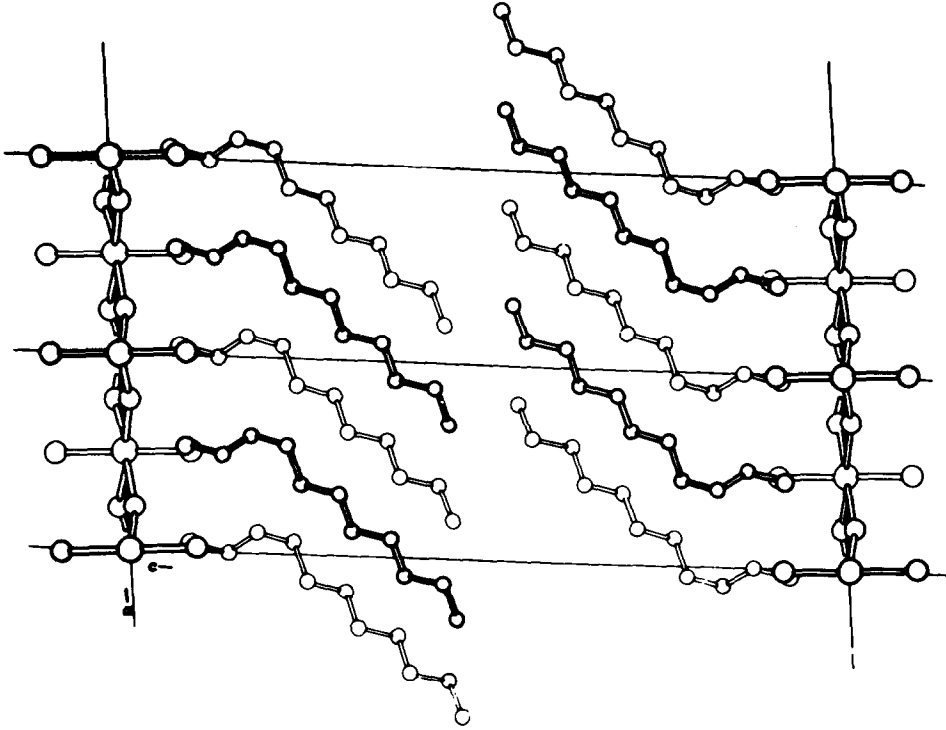


Fig. 1. The structure of C10Mn at room temperature [6].

tion β , in spite of multiple hydrogen bonding of the $-\text{NH}_3$ end groups with the metal halide lattice.

As for the pure components, two polymorphic crystalline modifications have been observed: a low temperature form (modification α'), in which the hydrocarbon chains of the alkylammonium groups are partially crystallized in the planar zig-zag conformation; and a high temperature one (modification β') obtained from the former through a high-entropy reversible solid-solid phase transition in which the alkyl chains have a highly disordered conformation [10-12].

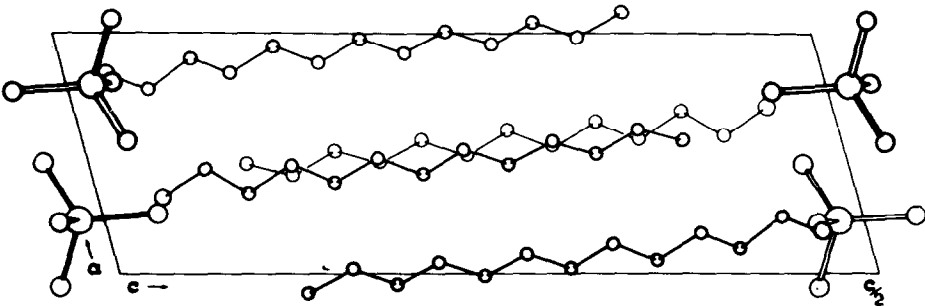


Fig. 2. The structure of C12Zn at room temperature [7].

In order to understand the influence, if any, of the metal halide lattice on the diffusional properties of the alkylammonium cations, we have extended our investigation to non-macroanionic systems of composition $(Cm)_x(Cn)_{1-x}Zn$, with $m = 12, n = 14, 16, 18$, in which the inorganic layers are planar arrays of unassociated $ZnCl_4^{2-}$ tetrahedra (Fig. 2).

EXPERIMENTAL

The synthesis of the pure long-chain alkylammonium tetrachlorozincates, $CnZn$, has been reported elsewhere [4,5].

Binary mechanical mixtures of the finely ground pure salts (average crystallite dimension $10 \mu m$), thoroughly mixed in the appropriate composition, were packed in aluminum pans and annealed at 400 K in a flow of nitrogen with a Perkin-Elmer DSC-2 differential scanning calorimeter. The properties of the resulting materials were checked every 6 h after the beginning of the thermal treatment; complete reproducibility was observed after 24 h of heating. In the following, when the properties of the annealed materials are compared with those of the pure salts, both are intended to have been subjected to the whole thermal treatment.

DSC curves were registered between 270 and 420 K in a flow of nitrogen at the scanning rate of $10 K min^{-1}$. The temperature scale was calibrated with pure reference compounds. Transition enthalpies were obtained using a sample of pure indium as reference standard ($\Delta h_m = 28.4 J g^{-1}$).

Each sample as recovered from the aluminum pan (6–10 mg) was also

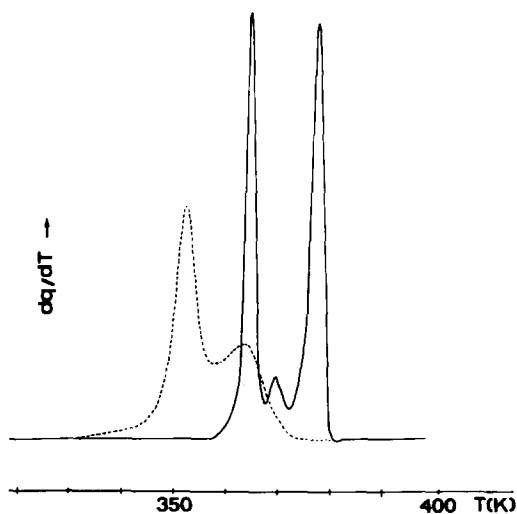


Fig. 3. DSC heating curves of $(C12)_{0.5}(C18)_{0.5}Zn$. (—) Mechanical mixture; (----) annealed compound.

characterized by X-ray diffractometric and IR techniques. Variable temperature X-ray photographs were taken with a flat camera at a fixed distance from the samples (2–3 mg) sealed in Lindemann capillaries (Ni-filtered $\text{CuK}\alpha$ radiation; temperature control ± 1 K). IR spectra were registered with a Perkin-Elmer 684 spectrometer, the powdered samples (4–7 mg) pressed in KBr pellets. Mixed materials of chosen compositions were also prepared by co-fusion of the pure components (5 min–5 h at 450 K), and their properties compared with those of compounds obtained by annealing in the solid state.

RESULTS AND DISCUSSION

The DSC curves of the annealed materials differ from those of the original mechanical mixtures before annealing (Fig. 3). The overall thermal behavior is similar to that found for the mixed compounds $(\text{Cm})_x(\text{Cn})_{1-x}\text{Mn}$ [10–12].

The heating curves (Fig. 4) show a single endotherm, usually broad and

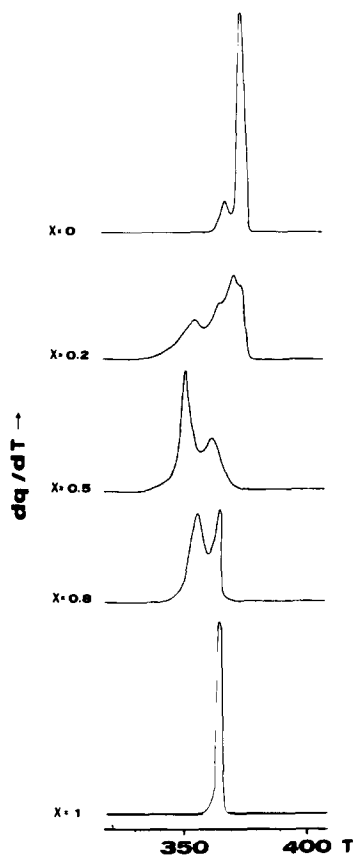


Fig. 4. DSC heating curves of $(\text{C12})_x(\text{C18})_{1-x}\text{Zn}$ for $x = 0, 0.2, 0.5, 0.8, 1$.

TABLE 1

Solid-solid transition temperatures and enthalpies as obtained from DSC scans

x	T (K) heating	T (K) cooling	ΔH (kJ mole ⁻¹) heating
<i>(A) (Cl2)_x(Cl4)_{1-x} Zn</i>			
0	372	361	76
0.1	370	354	75
0.2	350,361	341	61
0.3	350,363	344	59
0.4	351	360-320	62
0.5	345,348(s)	333	49
0.6	350	332,324	45
0.7	350	357-315	49
0.8	350,358	357-315	49
0.9	362	348	55
1	367	355	58
<i>(B) (Cl2)_x(Cl6)_{1-x} Zn</i>			
0	376	366	88
0.1	374	351	69
0.2	348(s),369	346	68
0.3	349,366	344,329(s)	71
0.4	350,362	350-320	57
0.5	350,358(s)	340-315	50
0.6	350	321	52
0.7	352	319	48
0.8	350	350-315	51
0.9	n.d.	n.d.	n.d.
1	367	355	58
<i>(C) (Cl2)_x(Cl8)_{1-x} Zn</i>			
0	379	365	115
0.1	378	364(s),355	95
0.2	355,373	352	84
0.3	355,371	349,332(s)	80
0.4	353,366	344,332	75
0.5	353,364	350-320	70
0.6	354,365	357-310	66
0.7	356,366	358-310	61
0.8	355,366	359-310	60
0.9	355,365	358,350	62
1	367	355	58

(s) = Shoulder.

often made up of two or more unresolved maxima, associated to a solid-solid phase change between a low temperature stable modification and a higher temperature stable modification, designated α' , β' , respectively, in analogy with the Mn salts. Single, sharp peaks are found, on the contrary, in the

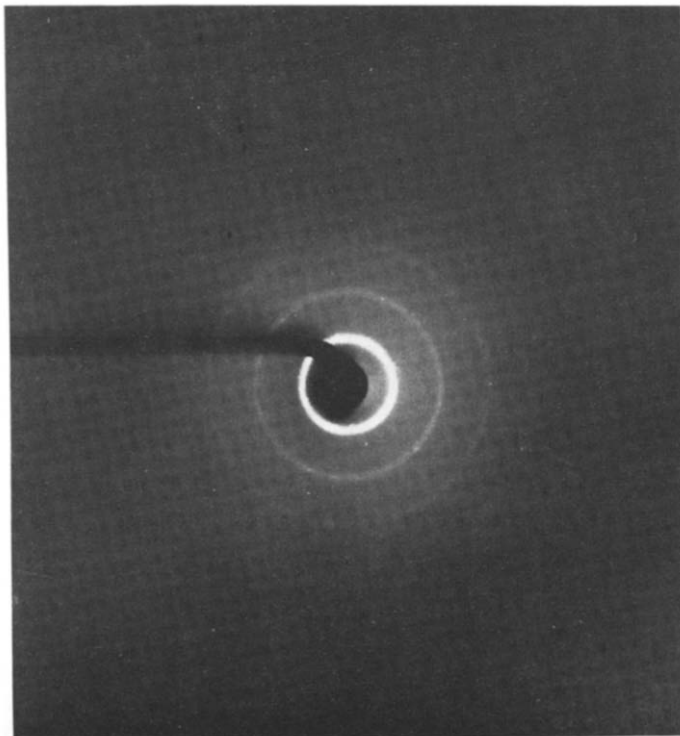


Fig. 5. X-Ray photograph of $(C12)_{0.5}(C18)_{0.5}Zn$ in modification β' ($T = 400$ K); magnification of the low angle region.

curves of the pure components. On cooling, the transition has a larger hysteresis than have the pure salts and spreads in some cases over 30–40 K.

Transition temperatures and enthalpies as measured from the DSC curves for the mixed materials and their pure components are given in Table 1. Temperatures refer to the peak maxima; for a peak with two or more unresolved maxima, the temperatures are reported as T_1, T_2, \dots ; for those transitions which on cooling are spread over 30–40 K, the two limiting temperatures are reported as T_1-T_2 . Heating enthalpies always refer to the overall endotherm.

The DSC curves are substantially reproducible; slight differences in the shape of the peaks are observed in some cases between the first and further scans. The enthalpic values of Table 1 are mean values of several measurements on independent samples. The standard deviation was of the order of 6%.

The formation of mixed compounds following annealing is indicated by the X-ray diffraction data.

The X-ray photographs (Fig. 5) show that modification β' is monophasic for all the mixed materials (unique 'long spacing' [9] for each compound), with conformationally disordered alkylammonium groups (halo centered at

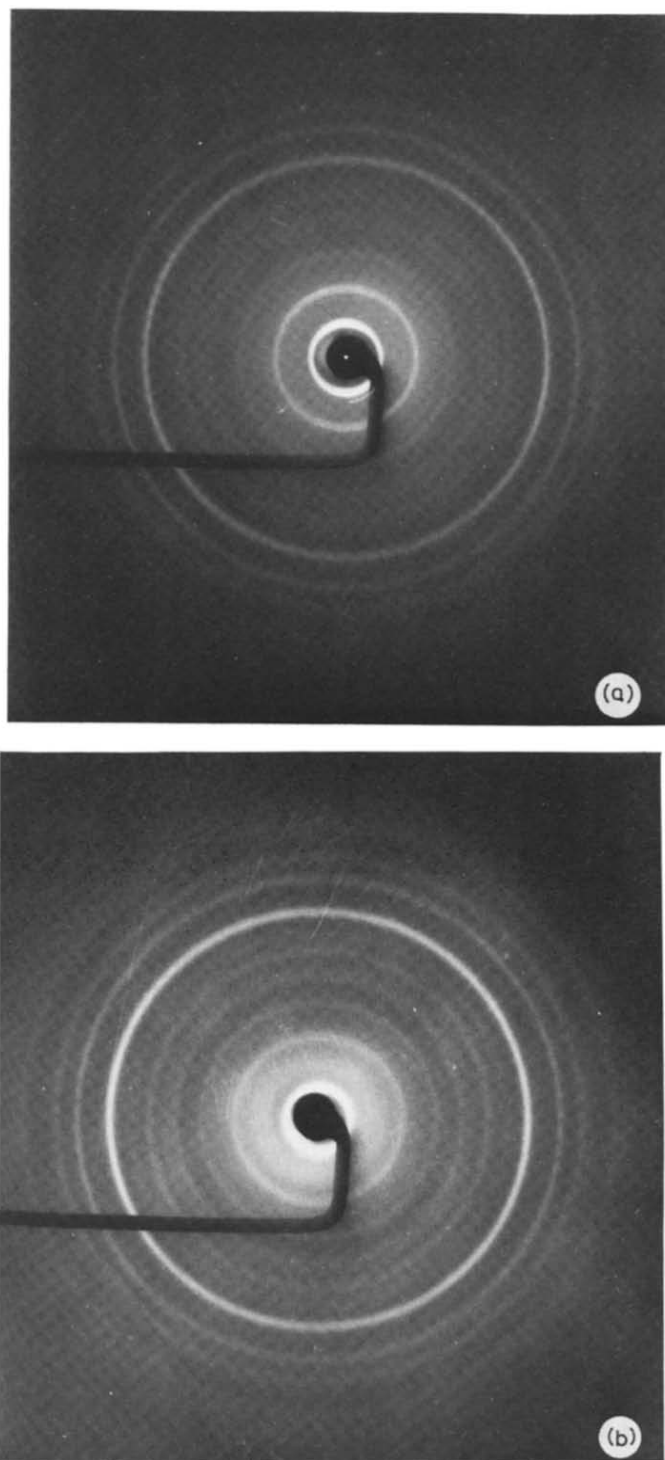


Fig. 6. X-Ray photographs of (a) $(\text{C12})_{0.5}(\text{C14})_{0.5}\text{Zn}$ and (b) $(\text{C12})_{0.5}(\text{C18})_{0.5}\text{Zn}$ in modification α' ($T = 300 \text{ K}$).

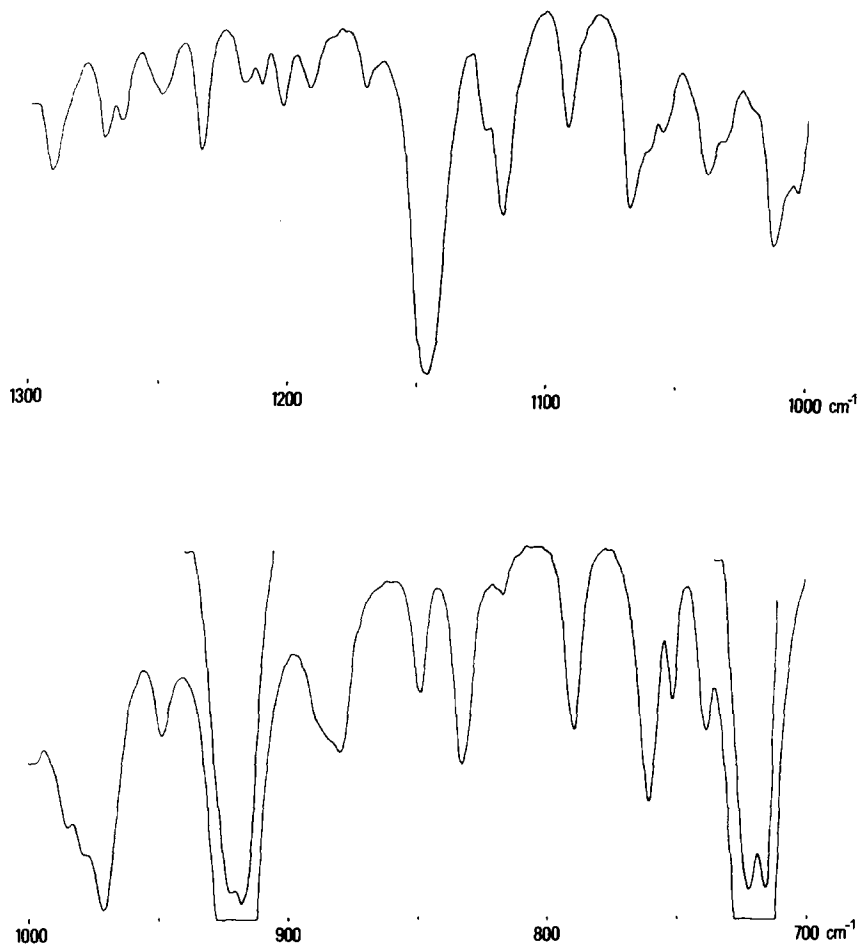


Fig. 7. 1300–650 cm^{-1} region of the IR spectrum of $(\text{C12})_{0.5}(\text{C18})_{0.5}\text{Zn}$ in modification α' ($T = 300 \text{ K}$).

$\lambda/2 \sin \theta \approx 4.5 \text{ \AA}$ [9]). The structure of modification α' is more controversial. The X-ray patterns of $(\text{C12})_x(\text{C14})_{1-x}\text{Zn}$ [Fig. 6(a)] are consistent with the retaining of the monophasic character; those of $(\text{C12})_x(\text{C16})_{1-x}\text{Zn}$, $(\text{C12})_x(\text{C18})_{1-x}\text{Zn}$ are quite complex [Fig. 6(b)] and appear to result from the superposition of the patterns of two or more differing phases. No evidence of chain conformational disorder is seen. Accordingly, the IR spectra of modification α' (Fig. 7) show chain crystallinity (splitting of the rocking fundamental at 720 cm^{-1} and the twisting absorption in the range $1200\text{--}1300 \text{ cm}^{-1}$ [9]). The mixed materials obtained by co-fusion, subjected to the same characterization, turned out to be undistinguishable from those with equal composition prepared by annealing in the solid state.

On the basis of the previous results, the mobility of the *n*-alkylammonium cations in modification β of the salts C_nM is confirmed and appears not to

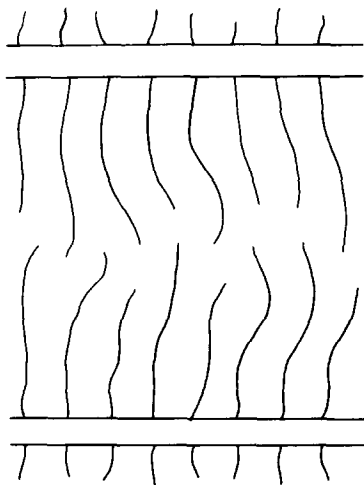


Fig. 8. Schematic view of a possible structural model of solid solutions $(Cm)_x(Cn)_{1-x}M$ ($M = Mn, Zn$) in modification β' .

be considerably affected by the structure of the metal halide lattice. As also found for the macroanionic homologues [10–12] and for other long-chain compounds—primarily *n*-alkanes [13,14]—the migrating species in $CnZn$ are able to cover macroscopic distances and to ‘jump’ between neighboring crystals. This results in the formation of mixed crystals in modification β' , whose structure, as suggested by the X-ray diffractometric data and by the identity with those obtained through co-fusion, could be that sketched in Fig. 8, the alkylammonium groups of differing lengths being disordered both positionally and conformationally.

On the other hand, the nature of the inorganic layers seems to play a major rôle in determining the behavior of the mixed compounds on going through the $\beta' \rightarrow \alpha'$ transition. The macroanionic systems $(Cm)_x(Cn)_{1-x}Mn$

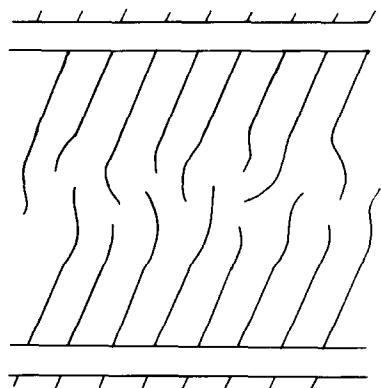


Fig. 9. Schematic view of a possible structural model of solid solutions $(Cm)_x(Cn)_{1-x}M$ ($M = Mn, Zn$) in modification α' .

crystallize as monophasic solid solutions, [whose possible structure could be that sketched in Fig. 9 (cf. ref. 12 for discussion)], irrespective of the $(n - m)$ value [10–12]. The same appears to be true for the non-macroanionic compounds $(Cm)_x(Cn)_{1-x}Zn$ when $(n - m) = 2$ only. For higher $(n - m)$ values indeed polyphasic materials are obtained.

Binary mixtures of molten n -alkanes C_mH_{2m+2} with $(n - m) > 2$ are known to give demixing into the components on crystallization but in narrow compositional ranges [15,16]. This could be the case for the compounds under study also, even though the X-ray characterization of the microsamples is not adequate to give conclusive evidence in this respect.

The DSC data are not inconsistent with this hypothesis. In fact, the $\alpha' \rightarrow \beta'$ transition enthalpies of $C(12)_x(C16)_{1-x}Zn$, $(C12)_x(C18)_{1-x}Zn$ are unusually high when compared with the corresponding values for the Mn homologues [10–12], as would be expected were the components allowed to crystallize separately in homodomains rather than as solid solutions. The fact that the DSC heating curves of these systems are not coincident with those of the original mechanical mixtures previous to annealing (Fig. 3) could be an indication that demixing is not complete.

An extensive diffractometric investigation on macrosamples of the same compounds is presently in progress, in order to achieve detailed information on the nature of modification α' , and to clarify the effect of the metal halide lattice on the behavior of the alkylammonium cations on crystallization.

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