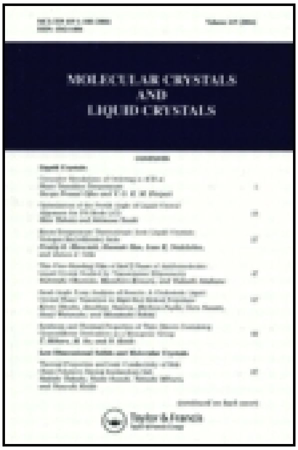

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Diffusion of Long Chain *n*-Alkylammonium Cations in Layer Compounds $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$

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Evidence for long range, anisotropic diffusion of the long chain *n*-alkylammonium cations in layer compounds $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ is presented. Annealing mechanical mixtures of such compounds with M = Mn, Zn; n = 12, 18 results in the formation of mixed crystals of composition $(n\text{-}C_{12}H_{25}NH_3)_{2x_{12}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{12}}MCl_4$ in which bilayers of *n*-alkylammonium groups with differing chain lengths, positionally and conformationally disordered, alternate with crystalline metal halide layers (modification β').

When the ionic layers are polymeric (M = Mn), solid solutions are obtained on cooling from modification β' in which the polymethylenic chains of the alkylammonium groups, while maintaining positional disorder, are partly cocrystallized in spite of the high difference in chain length (modification α'). Demixing into the pure components, on the other hand, is observed on cooling for nonmacroanionic systems (M = Zn).

Possible structural models of the mixed compounds in modifications α', β' are described, and the stability of such modifications relative to the unmixed components evaluated on the basis of a simple thermodynamical treatment.

INTRODUCTION

Salts of the type $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ (henceforth C*nM*) with n = 10, 11 . . ., 18 crystallize in layer structures of the kind shown in Figure 1 for M = Mn, Cu; in Figure 2 for M = Zn, Co.[1-4]

Bidimensional macroanions of composition MCl_4^{2-} made up of corner sharing MCl_6 octahedra, or planes of isolated MCl_4 tetrahedra are sandwiched between double layers of *n*-alkylammonium cations.

Two main crystalline modifications are known for these compounds. At low temperature, the alkyl chains are close-packed in the planar zig-zag conformation (modification α). At higher temperatures (300–400 K) they

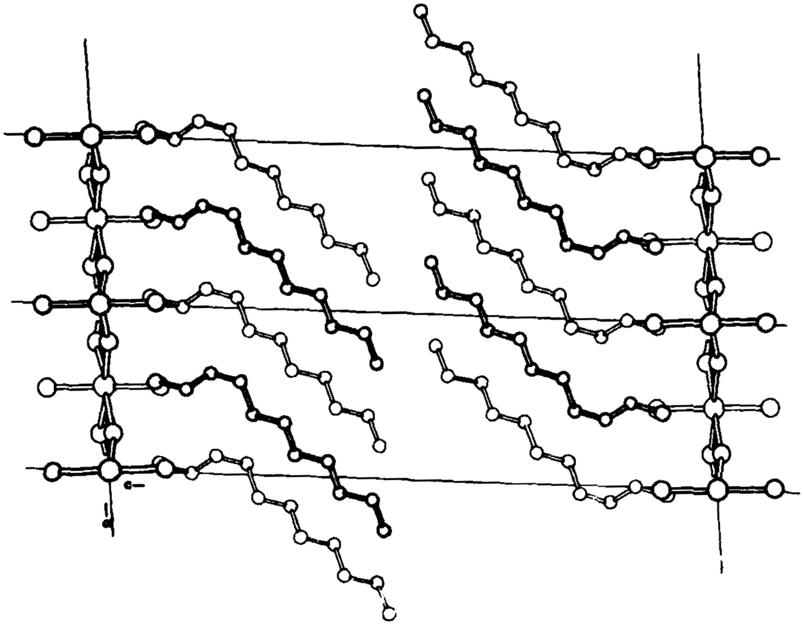


FIGURE 1 The structure of C10Mn at room temperature.[1]

melt to a liquid-like state (modification β) having some analogies with the well-known 'fluid' state of the lipid bilayer membranes.[5-8]

In spite of multiple hydrogen bonding with the metal halide lattice, the cations in modification β have translational freedom. This is a limiting case of anisotropic diffusion in the solid state, the mobility of the alkylammonium cations necessarily being strictly bidimensional.[9-11]

Mixed crystals of composition $(n\text{-}C_mH_{2m+1}NH_3)_{2x_m}(n\text{-}C_nH_{2n+1}NH_3)_{2-2x_m}MCl_4$ (short notation $(Cm)_x(Cn)_{1-x}M$, x = mole fraction of CmM) can be ob-

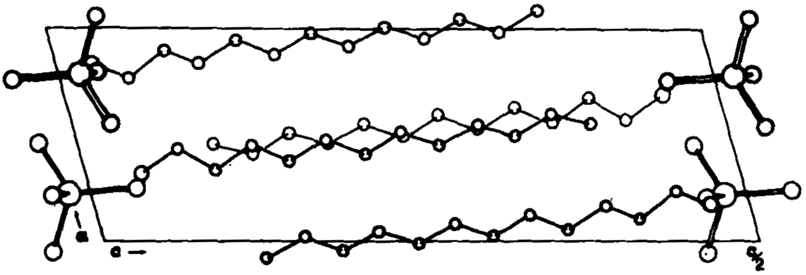


FIGURE 2 The structure of C12Zn at room temperature.[3]

tained by long range intermixing of *n*-alkylammonium cations with differing chain lengths.[9–12] As recently observed for *n*-paraffines in the hexagonal modification,[13,14] the migrating species are able to cover distances on a macroscopic scale, and to 'jump' between neighboring crystals.

Interestingly, mixed crystals $(Cm)_x(Cn)_{1-x}M$ $(0 \leqslant x \leqslant 1)$ have been described for $|n - m|$ values up to $|n - m| = 6$,[12] whereas binary mixtures of *n*-hydrocarbon molecules with $|n - m| > 2$ usually are not able to cocrystallize except in very narrow compositional ranges.[15,16]

We report in this paper the results of a calorimetric and X-ray diffractometric characterization of mixed compounds $(C12)_x(C18)_{1-x}M$ with M = Mn, Zn. The structural organization of such compounds is described and some relationships between structure and properties are outlined. The thermodynamical stability of the mixed crystals relative to their pure components is also evaluated on the basis of a simple model, which agrees well with the experimental data.

EXPERIMENTAL SECTION

The salts C12*M*, C18*M* (*M* = Mn, Zn) were synthesized according to Ref. 17.

Mechanical mixtures of composition $(C12)_x(C18)_{1-x}M$ were prepared by suspending in a nonsolvent (diethyl ether) stoichiometric amounts of the pure components, finely ground (average crystallite dimension 10 μ), magnetically stirring the suspensions for 10 min, filtering and drying in vacuo.

The mechanical mixtures, sealed under vacuum (10^{-2} torr) in Pyrex glass tubes, were annealed at a temperature (400 K ±2K) at which both the pure components are in modification β.

The properties of the resulting materials, checked every 6 h by DSC and X-ray diffraction, were found to be fully reproducible (and different from those of the starting mechanical mixtures) after 24 h of annealing.

The DSC curves were registered with a PERKIN-ELMER DSC-2 calorimeter, between 300 K and 400 K, in nitrogen flow, at the scanning rate of 10 K/min. A sample of pure Indium ($\Delta h_m = 28.4$ Jg^{-1}) was used as a standard for the enthalpic measurements.

Variable-temperature X-ray photographs were taken with a flat camera at a fixed distance from the samples. Ni filtered Cukα radiation was used. The samples, sealed in Lindemann capillaries, were placed in an electrically heated oven (temperature control ±1 K). Powder spectra at room temperature were also taken by reflection for several compounds with a PHILIPS diffractometer with proportional counter.

For the mixed compounds $(C12)_{0.5}(C18)_{0.5}M$, the kinetics of the diffusion process was followed by DSC (see Results).

RESULTS

(a) Differential scanning calorimetry

For the salts C*n*M, the solid-solid transition modification $\alpha \rightarrow$ modification β appears in the DSC traces as a single, sharp peak when M = Zn; as two or more peaks, sometimes unresolved, when M = Mn.[17]

As do the pure components, all the mixed compounds prepared in this work undergo a solid-solid high enthalpy phase transition between a modification α', stable at low temperature, and a modification β', stable at higher temperatures.

The heating curves for the mixtures show a single endothermic peak, usually broad and often made up of two or more unresolved maxima. On cooling, the transition has a larger hysteresis than have the pure salts and, for M = Zn, spreads in some cases over 30–40 K.

Transition temperatures and enthalpies as measured from the DSC curves for the mixed compounds and their pure components are in Table I. The temperatures refer to the peak maxima; for a peak with two or more unresolved maxima, the temperatures are reported as T1, T2, . . .; for those transitions which on cooling are spread over 30–40 K, the two limiting temperatures are reported as T1 ÷ T2. 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 heating scans.

The enthalpic values of Table I are mean values of several measurements on independent samples. The standard deviation was of the order of 6%. On the other hand, slight differences in the purity of the commercial amines used in the syntheses, in the preparation of the mechanical mixtures, and in the annealing process are able to produce large variations in the transition enthalpies.[18]

The DSC curves of the mixed compounds differ from those of the original mechanical mixtures before annealing (Figure 3). The kinetics of diffusion of the alkyl ammonium cations can be followed through the changes in the DSC curves with variable annealing time.[14] For the systems $(C12)_{0.5}(C18)_{0.5}M$ (M = Mn, Zn), the weight fraction of mixed compound formed at an annealing time, t was evaluated by the ratio $\Delta H(t)/\Delta H(24\ \mathrm{h})$

TABLE I

Solid-solid transition temperatures and enthalpies as measured from the DSC curves for mixed compounds $(C12)_x$ $(C18)_{1-x}M$ (M = Mn, Zn).

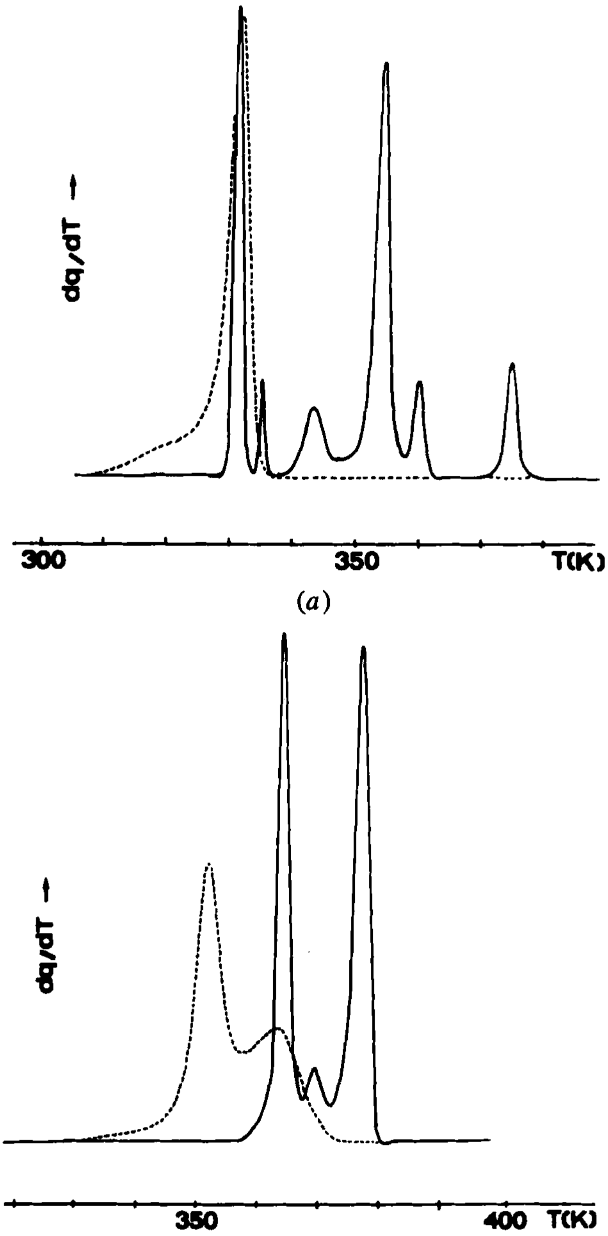
M	*x*	T(K) heating	T(K) cooling	ΔH(kJ mol^{-1})
Mn	0	354, 360, 375	345, 347, 370	80
	0.1	353, 360(s)†	340	74
	0.2	332(s), 354	312(s), 339	68
	0.3	324(s), 333, 353	312, 335	51
	0.4	324(s), 332, 346	315, 328(s)	52
	0.5	332	315	48
	0.6	324(s), 333	315	45
	0.7	328, 336	313	41
	0.8	327, 335	303, 312	33
	0.9	n.d.	n.d.	n.d.
	1	332	326	41
Zn	0	379	365	115
	0.1	378	355, 364(s)	95
	0.2	355, 373	352	84
	0.3	355, 371	332(s), 349	80
	0.4	353, 366	332, 344	75
	0.5	353, 364	320 ÷ 350	70
	0.6	354, 365	310 ÷ 357	66
	0.7	356, 366	310 ÷ 358	61
	0.8	355, 366	310 ÷ 359	60
	0.9	355, 365	350, 358	62
	1	367	355	58

†(s) ≡ shoulder

between the enthalpy of the $\alpha' \rightarrow \beta'$ transition in the curves of materials annealed for the time t, $\Delta H(t)$ and that of the mixed compounds subjected to the whole annealing process, $\Delta H(24\ \mathrm{h})$. The ratio $\Delta H(t)/\Delta H(24\ \mathrm{h})$ is diagrammed against t in Figure 4. The curve for M = Zn is not complete, owing to the difficulties in measuring $\Delta H(t)$ at short t's, due to partial overlapping with the peaks of the pure components.

(b) X-ray diffraction

The structure of the inorganic layers in modification α of C*n*Mn and C*n*Zn is almost invariant with the number *n* of chain C atoms, as shown in the X-ray diffraction patterns by the substantial coincidence of the reflections which can be indexed as (*h*kO) based on single crystal structural determinations performed for several terms of the two series.[1-3] The 'long



(*a*)

(*b*)

FIGURE 3 DSC heating curves of $(C12)_{0.5}(C18)_{0.5}Mn$ (a) and $(C12)_{0.5}(C18)_{0.5}Zn$ (b): solid line, mechanical mixture; dashed line, mixed compound.

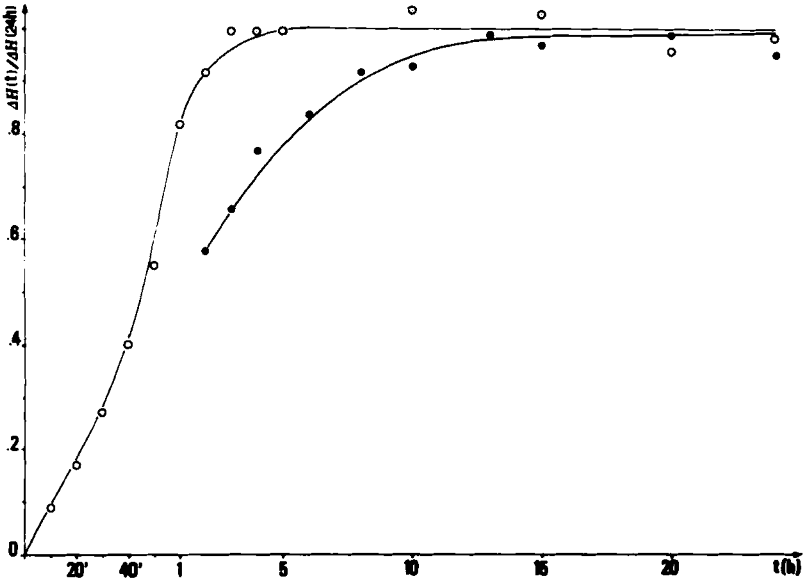


FIGURE 4 The ratio $\Delta H(t)/\Delta H(24\ \mathrm{h})$ (see text) vs. annealing time, t for $(\mathrm{C12})_{0.5}(\mathrm{C18})_{0.5}\mathrm{Mn}$ (○) and $(\mathrm{C12})_{0.5}(\mathrm{C18})_{0.5}\mathrm{Zn}$ (●).

spacing' between adjacent layers, on the other hand, increases linearly with increasing n (Table II and Ref. 4).

The retention of the layer structure [(OOl) reflections at low angles, Table III] and the liquid-like character of the n-alkylammonium cations (diffuse halo centered around $\lambda/2 \sin \theta = 4.5$ Å) can be inferred from the patterns of modification β.[5]

With only one exception (see further), the X-ray photographs of the mixed compounds in modification β' (Figures 5, 6) are analogous to those of the pure components in modification β. They are consistent with a structure in which conformationally molten hydrocarbon regions alternate with thin crystalline ionic layers. The long spacings for some representative compounds are given in Table III.

The photographs of modification α' (Figures 7, 8), are somewhat more complex. On one hand, they give evidence that the structure of the inorganic regions is the same as is found in modification α of the pure components (coincidence of the (hkO) reflections). On the other hand, the low angle region shows a unique series of (OOl) reflections for each compound for M = Mn only (the corresponding long spacings are in Table IV), whereas it cannot be reduced to a single periodicity for M = Zn.

The powder spectra in reflection show better resolution. A single long spacing for each compound, intermediate between those of the pure compo-

TABLE II

Selected Bragg distances, d(hkl) for compounds C12M, C18M (M = Mn, Zn) in modification α.

M	n	(hkl)	d(hkl) (Å)
Mn	12	110	5.1
		200	3.64
		220	2.54
		001	30.1
		002	15.0
		003	10.0
	18	110	5.1
		200	3.61
		220	2.56
		002	20.1
		003	13.4
Zn	12	120	4.2
		200	3.70
		210	3.44
		002	21.4
		004	10.7
		006	7.1
	18	120	4.2
		200	3.67
		210	3.41
		004	14.4
		006	9.6

TABLE III

Long spacings, c of some representative mixed compounds $(C12)_x(C18)_{1-x}M$ (M = Mn, Zn) in modification β′ and of their pure components in modification β (T = 400 K).

M	*x*	c (Å)†
Mn	0	45.5
	0.2	42.2
	0.5	39.7
	0.8	33.9, 38.2
	1	33.4
Zn	0	35.3
	0.2	35.3
	0.5	30.3
	0.8	27.6
	1	25.8

†Long spacings calculated from (003)

nents in modification α, is found for *M* = Mn (Figure 9 and Table IV); two series of (00l) reflections, coincident with those of the pure components in modification α and whose relative intensity is not far from the ratio of their mole fractions, are observed for *M* = Zn (Figure 9 and Table V).

The mixed compound $(C12)_{0.8}(C18)_{0.2}Mn$ is an exception in that a double periodicity on the (00l)'s is found both for modification α′ and modification β′ (Tables III, IV). The two long spacings in modification α′ coincide with those of the pure components in modification α.

DISCUSSION

Mechanical mixtures of salts C*nM* (*M* = Mn, Zn) in modification β change, by lateral diffusion of the *n*-alkylammonium cations, into mixed compounds whose X-ray diffraction patterns at higher temperatures (modification β′) suggest, with only one known exception, that they are solid solutions in which the alkylammonium groups of different length in a

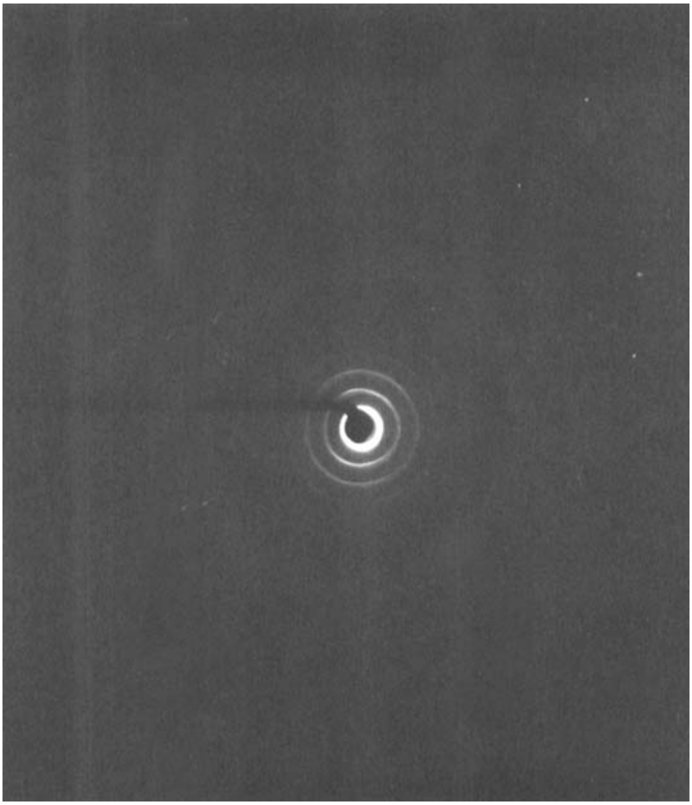


FIGURE 5 X-ray photograph of $(C12)_{0.5}(C18)_{0.5}Mn$ in modification β' (T = 400 K).

TABLE IV

Long spacings, c of mixed compounds $(C12)_x(C18)_{1-x}Mn$ in modification α' (T = 300 K).

x	c (Å)[†]	x	c (Å)[†]
0	40.1	0.6	34.7
0.1	40.4	0.7	34.7
0.2	40.4	0.8	30.8, 35.3
0.3	40.1	0.9	n.d.
0.4	38.8	1	30.0
0.5	35.8		

[†] Long spacings calculated from (003)

TABLE V

Long spacings, c of some representative mixed compounds $(C12)_x(C18)_{1-x}Zn$ in modification α' (T = 300 K).

x	c (Å)[†]
0	28.8
0.2	21.5, 29.2
0.5	21.5, 29.2
0.8	21.5, 29.2
1	21.3

[†] Long spacing calculated from (004)

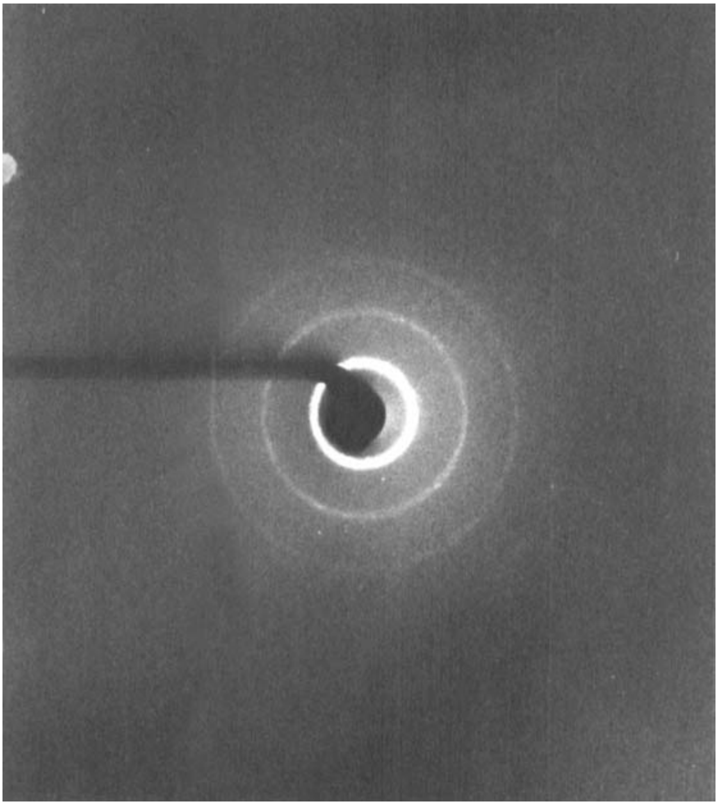


FIGURE 6 X-ray photograph of $(C12)_{0.5}(C18)_{0.5}Zn$ in modification β′ (T = 400 K); magnification of the low angle region.

conformationally molten state are randomly arranged on the surface of the metal halide lattice (Figure 10). The monophasic character of modification β′ is shown, in particular, by the uniqueness of the long spacing for each mixed compound, its value being not far from the weighted average between the long spacings of the pure components in modification β.

The polymethylenic chains crystallize on cooling (exothermal transition β′ → α′). IR evidence of chain crystallinity in modification α′ is given in Refs. 11 and 12. The data in Table I suggest that only partial crystallization occurs, the transition enthalpies being sensibly lower than the weighted averages between the β → α enthalpies for the pure components.

The structure of modification α′ is not the same in the two series of mixed compounds. The X-ray patterns when M = Zn reveal the demixed

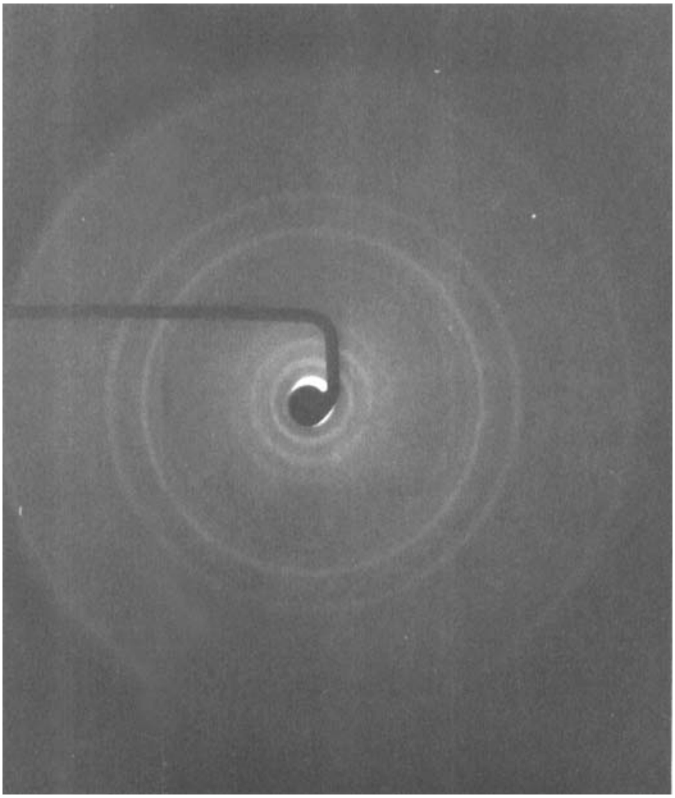


FIGURE 7 X-ray photograph of $(C12)_{0.5}(C18)_{0.5}Mn$ in modification α' (T = 300 K).

components in modification α. The nature of solid solution seems to be preserved, on the other hand, when M = Mn.

The thermodynamical stability of a solid solution $(Cm)_x(Cn)_{1-x}M$ relative to the unmixed components can be approximately evaluated on the basis of a simple structural model, for mole fractions around $x = 0.5$.

The structure assumed for modification β', with the alkylammonium groups disordered both positionally and conformationally, has been sketched in Figure 10. The crystallization of the polymethylenic chains, if the positional disorder is to be preserved, should lead to a structure not far from that schematically shown in Figure 11: for a mixed compound $(Cm)_x(Cn)_{1-x}M$ ($m < n$), the 'common' chain segments (m C atoms) are close-packed in the planar zig-zag conformation; the terminal segments of the longer chains

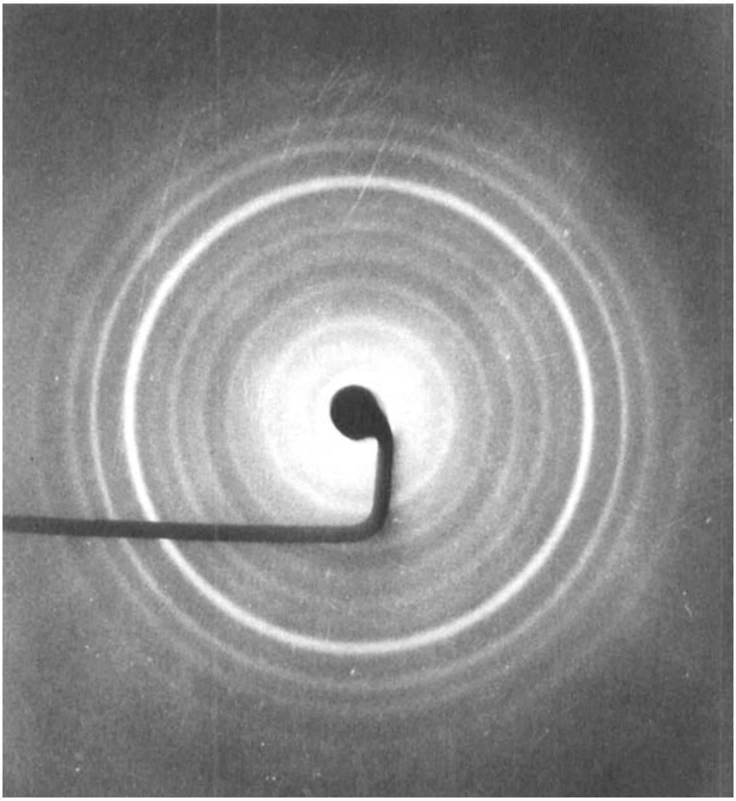


FIGURE 8 X-ray photograph of $(C12)_{0.5}(C18)_{0.5}Zn$ in modification α' (T = 300 K).

[$(n - m)$ C atoms], not able to crystallize, form a conformationally molten region between adjacent layers.

Let us now consider the following ideal thermodynamical cycle:

$$\begin{tikzcd} \text{Mechanical mixture } (\beta) \arrow[r, "\Delta G_2"] & \text{Solid solution } (\beta') \arrow[d, "\Delta G_3"] \\ \text{Mechanical mixture } (\alpha) \arrow[u, "\Delta G_1"] & \text{Solid solution } (\alpha') \arrow[l, "\Delta G_4"'] \end{tikzcd}$$

The stability of a solid solution in modification α' relative to a mechanical mixture of its components in modification α is measured by the term ΔG_4.

In the case of ideal mixing of the alkylammonium cations, at equilibrium it can be set:

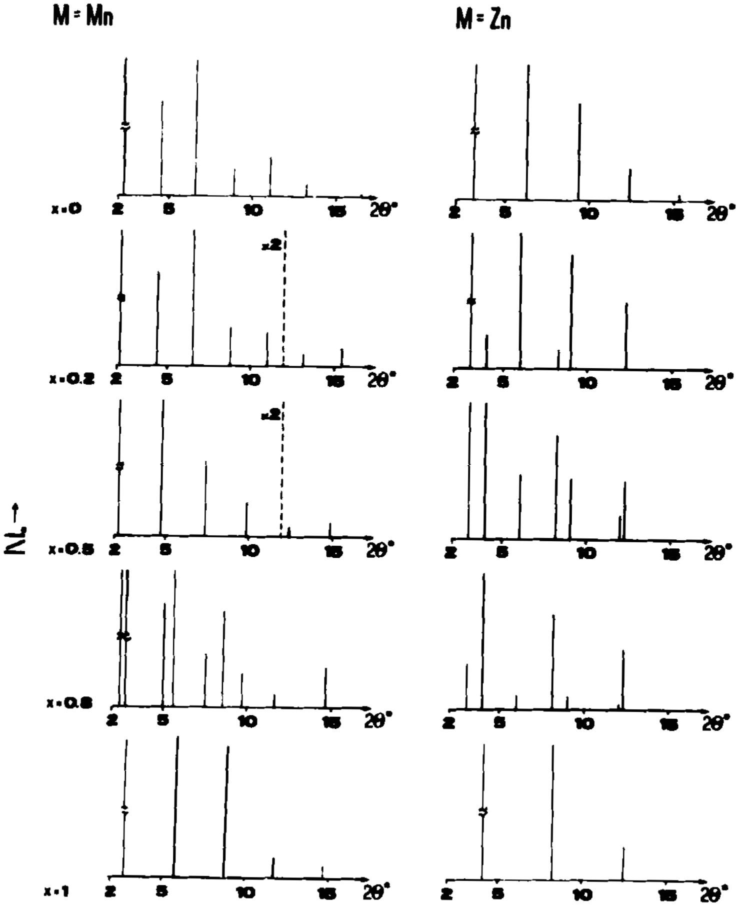


FIGURE 9 Low angle region of the X-ray diffraction patterns in reflection for some representative compounds $(C12)_x(C18)_{1-x}M$ (M = Mn, Zn) in modification α' (T = 300 K).

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 = 2[xm + (1 - x)n]\,\delta H - 2T[xm + (1 - x)n]\,\delta S \qquad (1)$$

$$\Delta G_2 = \Delta H_2 - T\Delta S_2 = -2RT[x \ln x + (1 - x)\ln(1 - x)] \qquad (2)$$

$$\Delta G_3 = \Delta H_3 - T\Delta S_3 = -2m\delta H + 2Tm\delta S \qquad (3)$$

$$\Delta G_4 = \Delta H_4 - T\Delta S_4 = -2x(n - m)\,\delta H + 2T\{x(n - m)\,\delta S - R[x \ln x + (1 - x)\ln(1 - x)]\} \qquad (4)$$

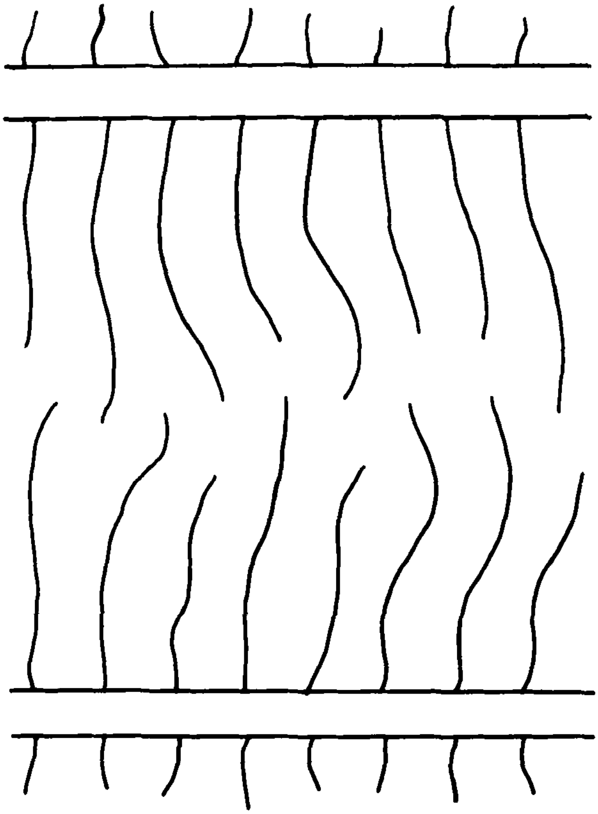


FIGURE 10 Schematic view of a possible structural model of solid solutions $(Cm)_x(Cn)_{1-x}M$ (M = Mn, Zn) in modification β' (x not far from 0.5).

In Eqs. 1–4, δH (δS) is the enthalpy (entropy) of solid-solid transition per mole of CH_2 groups. From experimental data for the salts CnM[19,20] δH can be taken as 3.0 kJ, δS as 0.9 R.

For $x = 0.5$, $T = 300$ K, the values of ΔG_4 for several $(n - m)$ values have been calculated, and listed in Table VI. According to the model, solid solutions in modification α' are thermodynamically stable for $(n - m) \leq 2$; for $(n - m) > 2$ demixing into the pure components in modification α is favored.

Also, it can be observed that it always is $\Delta G_2 < 0$: solid solutions in modification β' are more stable than the unmixed pure components in modification β. ΔG_2 is the driving force of the mixing process through lateral diffusion in the solid state.

Although the previous observations rely on a number of assumptions, and cannot be extrapolated to systems with mole fractions far from $x = 0.5$

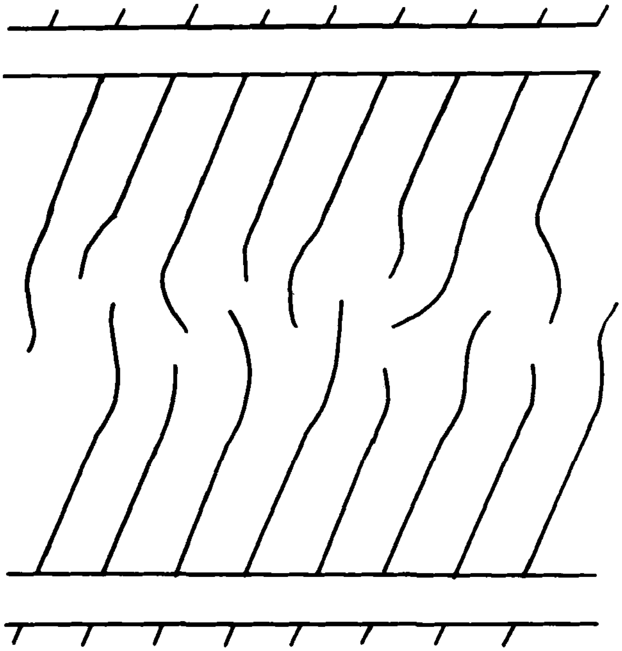


FIGURE 11 Schematic view of a possible structural model of solid solutions $(Cm)_x(Cn)_{1-x}M$ (M = Mn, Zn) in modification α' (x not far from 0.5).

(for which the structure of Figure 11 is not consistent), they agree well with the experimental results for mixed compounds $(Cm)_x(Cn)_{1-x}Zn$, for which the transition $\beta' \rightarrow \alpha'$ implies demixing into the pure components, but only for $(n - m) > 2$.[11] In addition, they are in line with the behavior of binary mixtures of *n*-alkanes.[15,16]

TABLE VI

Calculated values of ΔG_4 vs (n−m) (see text).

(n −m)	ΔG_4 (kJ mol^{-1})
1	+1.0
2	+0.3
3	−0.4
4	−1.1
5	−1.8
6	−2.5

It has to be explained, on the other hand, why demixing is not observed and mixed crystals in modification α' are obtained for $(C12)_x(C18)_{1-x}Mn$, for which $(n - m) = 6$, a substantial difference in chain length.

A trivial kinetic explanation based on the hypothesis of highly different mobilities of the alkylammonium cations in the two classes of mixed compounds with M = Mn, Zn seems to be inconsistent with the curves of Figure 4.

We have already observed that mixed compounds in modification β' have a unique long spacing, intermediate between those of the pure components in modification β. Demixing at the $\beta' \rightarrow \alpha'$ transition means that crystalline domains of the pure components in modification α with different long spacings are formed, this requiring the local fragmentation of the mixed crystals into initially small crystallites of the pure components.

Differently from the case of the compounds with M = Zn, in which the inorganic layers are made up of isolated anions, for M = Mn such a fragmentation would imply the rupture of substantially covalent bonds in the polymeric anions (Figures 1, 2). This could be the reason why mixed crystals are found even in modification α', irrespective of the $(n - m)$ value, the $\beta' \rightarrow \alpha'$ transition being somewhat similar to a glass transition.

An apparent contradiction could be noticed at this point from the exam of the calorimetric data of Table I for the compounds $(C12)_x(C18)_{1-x}Zn$, for which demixing at low temperature has been deduced, the DSC curves of such compounds being markedly different from those of mechanical mixtures with the same composition (Figure 3). An explanation can be found assuming incomplete demixing and/or the presence of disorder in the contact areas between neighboring crystallites. Therefore, for these compounds also the notation "mixed compounds in modification α'" rather than "mechanical mixtures in modification α" is to be used.

For mixed compounds $(Cm)_x(Cn)_{1-x}M$ with x far from 0.5, Figure 11 and Eqs. 1–4 obviously become inadequate. The observation of Kitaigorodsky[21] for binary mixtures of n-alkanes that the packing hindrance produced by low mole fractions of long chains in shorter ones is sensibly higher than that present in the reverse situation (Figure 12) seems to be confirmed for the systems under study also by the enthalpic data of Table I and by the behavior of the compound $(C12)_{0.8}(C18)_{0.2}Mn$. This compound is biphasic not only in modification α', but also in modification β', in which (cf. Results) two mixed phases are present, with compositions—deduced from the values of their long spacings—of the order of $x' \simeq 0.5$, $x'' \simeq 1$.

The latter observation is not at all surprising, the hydrocarbon regions of the mixed compounds in modification β' being comparable to binary mixtures of n-alkanes not in the isotropic liquid state, but in a hypothetical

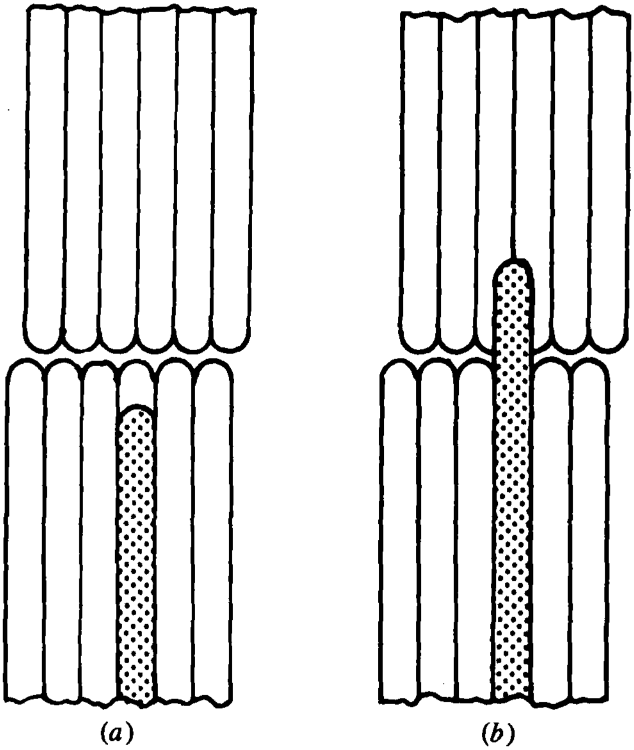

(a) (b)

FIGURE 12 Schematic view of the packing of crystalline *n*-alkanes of different chain length, showing that undistorted packing is feasible for low mole fractions of short chains in longer ones (a) and not for the reverse situation (b) (red. from Ref. 21).

smectic mesophase. In fact, excluded volume effects and the fixed position of the ammonium end groups on the inorganic layers force the disordered alkyl chains to run mainly perpendicular to the latter (for a detailed discussion cf. Ref. 22). The anisotropy of the liquid-like state is higher the smaller the cross-section, *A* available to each chain on the surface of the metal halide lattice, *A* being particularly reduced for M = Mn.[1,4] The observed partial immiscibility of the alkylammonium cations in modification β' of the compound $(C12)_{0.8}(C18)_{0.2}Mn$ is likely due to this anisotropy, the overall structural organization of the liquid-like state still resembling that sketched in Figure 12b.

As a final note, the mobility of the alkylammonium cations in modification β, β' of the salts C*nM* and of the mixed compounds $(Cm)_x(Cn)_{1-x}M$ (M = Mn, Zn) could originate from the observed motion of their ammonium end groups, which rotate adopting different hydrogen bonding schemes with the chlorine atoms in the metal halide lattice.[6,23] This seems to be suggested by the fact that no mixed compounds have been obtained by annealing mechanical mixtures of salts C*n*M in modification α, in which the rotation of the —NH_3 groups is said to be disallowed.[6,23]

The motion of the alkylammonium cations is reported to be slow relative to the time scale of EPR from measurements on spin labeled systems,[18] and the hypothesis has been made that diffusion occurs via lattice defects. If the process implies 'jumps' of the cations from an occupied lattice site to an adjacent vacancy, an activation energy of the order of 10^2 kJ/mol appears to be a sound estimate,[24] considering that the ammonium end groups are embedded in cavities on the surface of the metal halide lattice.[1,23] This would correspond to an Eyring frequency of the order of 10^4 s^{-1}, which is not inconsistent with the results of the EPR measurements[18] and with the kinetic curves of Figure 4.

CONCLUSIONS

The lateral diffusion of the *n*-alkylammonium cations in modification β of layer compounds C*n*M with M = Mn, Zn allows one to prepare, by annealing mechanical mixtures of the pure components, solid solutions of composition $(Cm)_x(Cn)_{1-x}M$ $(0 \leqslant x \leqslant 1)$ in which bilayers of *n*-alkylammonium groups with differing chain lengths, positionally and conformationally disordered, alternate with crystalline ionic layers (modification β', Figure 10).

When the ionic layers are polymeric, solid solutions are obtained on cooling from modification β' in which the polymethylenic chains of the alkylammonium groups, while maintaining positional disorder, are partly crystallized (Figure 11), even when differing in length for more than two CH_2 units. Analogous structures, in the absence of polymeric layers to which the chains are linked, usually are unstable and give demixing into the pure components. The planar macroanions are in the same time a support to the migrating alkylammonium cations and a hindrance to their demixing on crystallization. In some respects, the situation in these systems is intermediate between mixtures of *n*-alkanes and double chain lipids[25] or 'comb-like' polymers[26] with side chains of different length.

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