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THE THERMAL BEHAVIOUR OF MIXED LONG CHAIN ALKYLAMMONIUM TETRACHLOROMANGANATES(II)

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ABSTRACT

The results of a calorimetric and structural investigation of mixtures of layer compounds of the kind $(RNH_3)_2MCl_4$, R being a long chain *n*-alkyl group, show that the low-temperature forms are solid solutions, mainly ordered from the conformational viewpoint, in which chains of different length are more or less randomly arranged on the surface of the anionic layers. The observed high enthalpy solid—solid phase transitions correspond to the "melting" of the hydrocarbon layers, giving solid solutions in which the conformational freedom of the alkyl chains is similar to that of hydrocarbon substances in the liquid state.

INTRODUCTION

Transition metal complex salts of the kind $(RNH_3)_2MCl_4$, with M = Mn, Cu, Fe, Hg, and R a long chain *n*-alkyl group, can exist in a solid crystalline modification in which two-dimensional macroanions of composition MCl_4^{2-} are sandwiched each between two conformationally ordered alkylammonium layers. The hydrocarbon regions of the structure in this modification consist of double layers of alkyl chains, mainly in the all *trans* conformation, with their methyl ends facing each other (Fig. 1) [1—4].

All these compounds show, at temperatures between 270 and 400 K, solid—solid high enthalpy phase transitions which are associated with a partial "melting" of the hydrocarbon regions, the conformational freedom of the chain segments in the high-temperature solid modifications being not very different from that in liquid hydrocarbons at the same temperature [5—7].

It can be easily foreseen that such an unusual kind of disordered solid will have peculiar and interesting properties. In a previous paper [8] we suggested, for instance, that compounds with M = Mn and different alkyl groups can mix in the high-temperature disordered polymorphs to give solid solutions with a continuously variable composition. We want to confirm our previous suggestion by showing the results of a calorimetric and structural investigation of materials with composition $(n\text{-}C_{14}H_{29}NH_3)_{2x_{14}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{14}}MnCl_4$ and $(n\text{-}C_{12}H_{25}NH_3)_{2x_{12}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{12}}MnCl_4$, x_{14} and x_{12} being the mole fractions of tetradecylamine and dodecylamine, respectively.

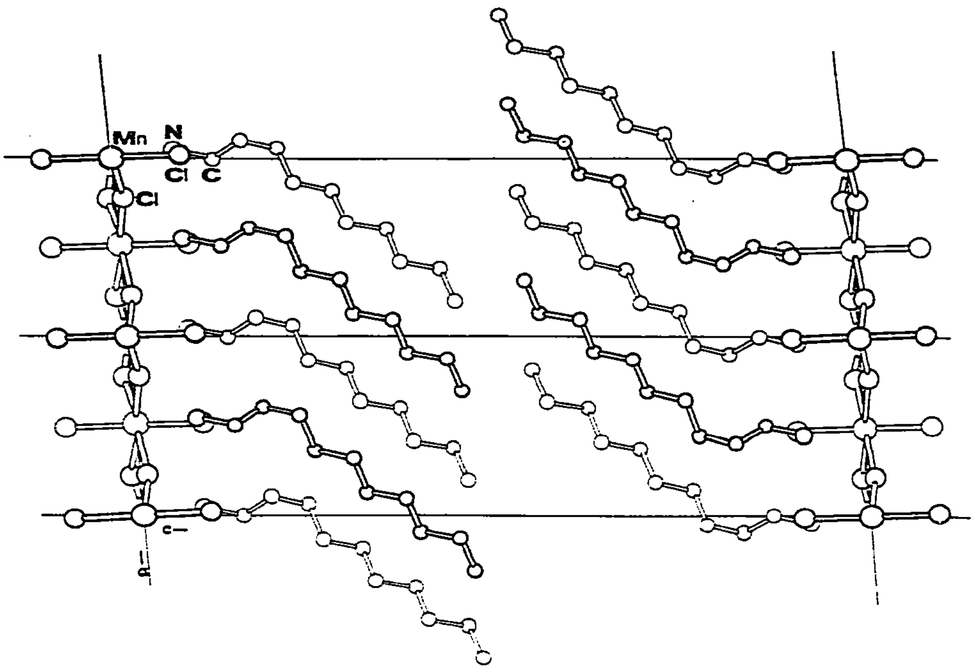


Fig. 1. An example of a transition metal complex salt of the kind $(RNH_3)_2MCl_4$ with macroanionic inorganic regions: the structure of the compound $(n\text{-}C_{10}H_{21}NH_3)_2MnCl_4$ [10].

EXPERIMENTAL

Compounds of the kind $(n\text{-}C_nH_{2n+1}NH_3)_2MnCl_4$ can be obtained as pale pink platelets by mixing hot ethanolic solutions of $MnCl_2$, HCl and the alkylamine in a 1 : 2 : 2 molar ratio, slowly cooling down to room temperature and filtering the precipitate [1,2,9]. We used a slightly modified method to prepare the mixed materials investigated in this work, since the hot ethanolic solutions containing $MnCl_2$, HCl and the two-component alkylamines in stoichiometric amounts were dried in vacuo, in order to avoid losses of one of the components, and the resulting crystalline materials kept at 350 K for 12 h.

Thermograms were registered between 270 and 380 K in a running N_2 atmosphere on a Perkin-Elmer DSC-2 differential scanning calorimeter at the scanning rate of 5 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 ($\Delta H = 28.5$ J g^{-1}).

X-Ray powder diffraction patterns were obtained with a Philips PW-1011 diffractometer using the FeK_α radiation (Mn filter).

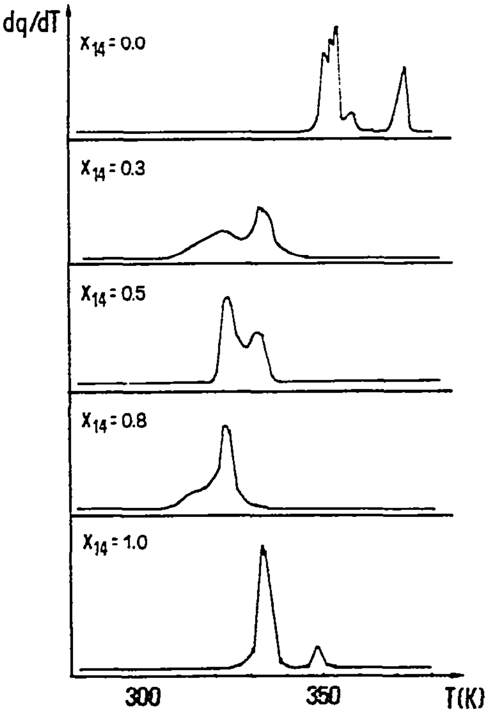
Infrared spectra were registered with a Perkin-Elmer 457 spectrometer equipped with a variable temperature sample cell.

RESULTS

All the mixed materials prepared with the previously described method and with different mole fractions of the component amines show, at temperatures between 300 and 380 K, solid—solid phase transitions which are associated with unusually large enthalpic effects. In Figs. 2 and 3 we show a comparison of the thermograms of some of these materials with those of the pure salts of the component amines. The pure complex salt $(n\text{-}C_{18}H_{37}NH_3)_2MnCl_4$ has been prepared and characterized for the first time in this work.

In Tables 1 and 2 we report the transition temperatures, enthalpies and entropies for mixed materials with various mole fractions of tetradecylamine and dodecylamine, respectively. The transition temperatures of Tables 1 and 2 are mean weighted values, while enthalpies and entropies are total values, corresponding to the overall endotherm. All the thermograms are completely reproducible even after 36 h of heating and cooling scans throughout the transition points.

Figure 4 shows the low-frequency region of the IR spectrum of the mixed material with $x_{12} = 0.5$ taken at room temperature (a) and at 380 K (b). Figure 5 reports the low-angle region of the X-ray powder diffraction patterns of some of the mixed materials taken at room temperature.



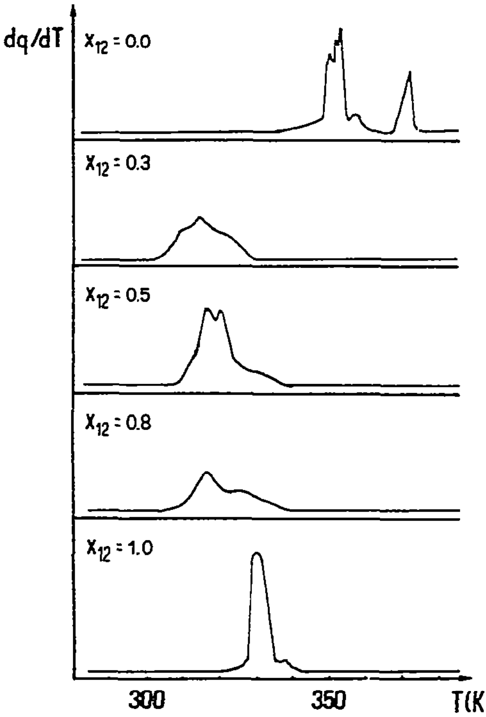


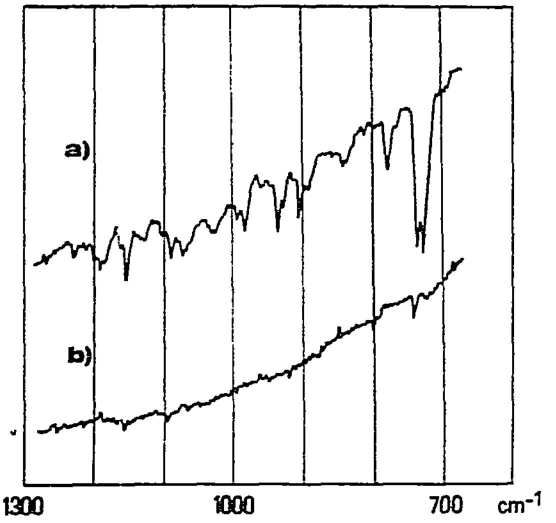
Fig. 2. Heating thermograms of some mixed materials of the type $(n\text{-}C_{14}H_{29}NH_3)_{2x_{14}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{12}}MnCl_4$ and of their pure component salts.

Fig. 3. Heating thermograms of some mixed materials of the type $(n\text{-}C_{12}H_{25}NH_3)_{2x_{12}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{12}}MnCl_4$ and of their pure component salts.

TABLE 1

Solid—solid transition temperatures, enthalpies and entropies for mixed materials of composition $(n\text{-}C_{14}H_{29}NH_3)_{2x_{14}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{14}}MnCl_4$ with various mole fractions of tetradecylamine, x_{14}.

x_{14}	T (K)	ΔK (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
0.0	355	64	180
	376	16	43
0.1	345	34	98
0.2	335	37	110
0.3	329	32	97
0.4	325	35	107
0.5	328	35	106
0.6	322	33	102
0.7	322	23	71
0.8	319	23	72
0.9	326	24	73
1.0	336	45	134
	348	7	20



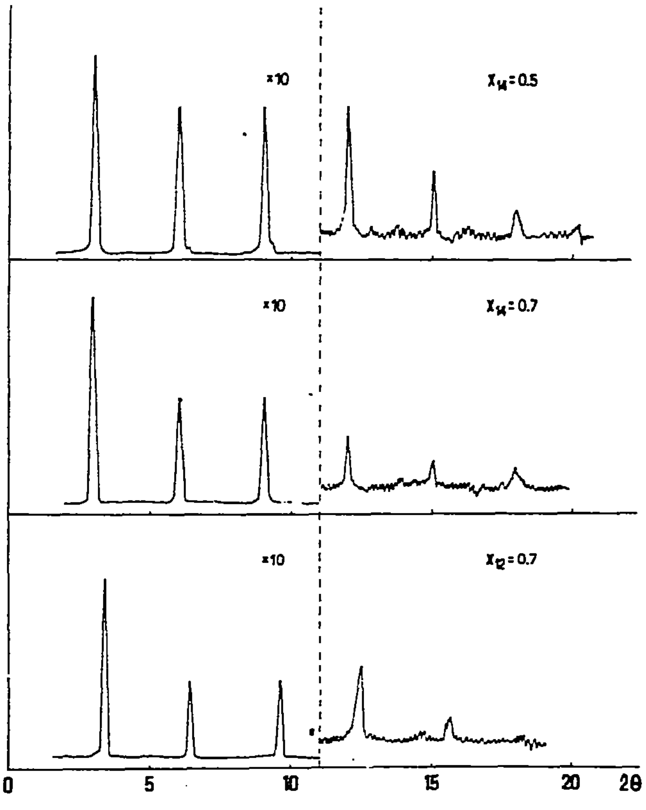


Fig. 4. Low-frequency region of the IR spectrum of the mixed material $(n\text{-}C_{12}H_{25}NH_3)(n\text{-}C_{18}H_{37}NH_3)MnCl_4$ at room temperature (a) and at 380 K (b).

Fig. 5. Low-angle region of the room-temperature X-ray powder diffraction patterns for some of the mixed materials investigated in this work, x_{14} and x_{12} being the mole fractions of tetradecylamine and dodecylamine, respectively.

TABLE 2

Solid—solid transition temperatures, enthalpies and entropies for mixed materials of composition $(n\text{-}C_{12}H_{25}NH_3)_{2x_{12}}(n\text{-}C_{18}H_{37}NH_3)_{2-2x_{12}}MnCl_4$ with various mole fractions of dodecylamine, x_{12}.

x_{12}	T (K)	ΔH (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
0.0	355	64	180
	376	16	43
0.1	339	36	106
0.2	340	29	85
0.3	319	19	60
0.4	314	22	70
0.5	317	22	69
0.6	313	21	67
0.7	313	18	58
0.8	317	18	57
0.9	317	16	50
1.0	332	41	123

DISCUSSION

The most relevant features of the thermograms of the mixed materials investigated in this work, as compared with those of the pure component salts, can be summarized as follows.

(a) All the thermograms show high enthalpy transitions which are always associated with solid—solid phase changes.

(b) In the case of the mixed materials the solid—solid transition peaks are spread over relatively large temperature intervals (usually 20—30 K).

(c) The higher temperature solid—solid transition peaks found for the pure octadecylammonium and tetradecylammonium salts are systematically absent in the thermograms of all the mixed materials.

(d) The mean weighted solid—solid transition temperatures observed for the mixed materials are always lower than the transition temperature of their most abundant pure component salt.

These features suggest the hypothesis that the high enthalpy phase transitions of the mixed materials are of the order—disorder kind and very similar to the analogous phase transitions observed for the pure salts. This hypothesis is confirmed by the IR spectra of Fig. 4. It may be seen that the low-frequency region of the spectrum taken below the solid—solid transition point (Fig. 4a) is indicative of strong correlations among successive chain segments of the same chain (the methylene twisting absorption is split, in the region 1200—1300 cm^{-1}, in several absorption peaks, due to the presence of sequences of CH_2—CH_2 bonds in the *trans* conformation) and of different neighbouring chains (the methylene rocking absorption is present as a strong and sharp doublet at 719 and 730 cm^{-1}, due to the presence of two non-equivalent alkyl chains in the crystallographic unit cell). The general aspect of the same spectral region at temperatures above the solid—solid transition point is, on the other hand, similar to the spectrum of hydrocarbon substances in the liquid state (Fig. 4b) [5].

The observed transitions are then of the order—disorder kind, and the hydrocarbon parts of the crystal structure of the mixed materials are, at temperatures above the transition points, in a liquid-like state similar to that of the pure salts in the analogous disordered solid polymorphs.

The thermal behaviour of all the compounds investigated in this work has been found to be reproducible even after a very large number of thermal cycles throughout the transition points, showing that the local composition of these materials does not vary with the thermal history.

Important evidence concerning the local composition can be obtained from the X-ray diffraction patterns of Fig. 5. These are very similar to the X-ray patterns obtained for the pure salts [1,2], showing that the main features of the crystal structure (layer structure with macroanions in the ionic regions) are preserved in the mixed materials. The presence in the diffraction patterns of a series of maxima at values of sin Θ which are integer multiples of the same quantity ($\sin \Theta = n\lambda/2d$) for each compound shows that the mixed materials are not a mixture of phases with a different composition in the low-temperature stable polymorphs; they are, on the contrary, true solid solutions with a continuously variable composition ranging from the pure octadecylammonium salt to the pure tetradecylammonium or dodecylammonium salts. These solid solutions are mainly ordered from the conformational viewpoint at low temperatures, as evidenced by the IR spectra. The observed solid—solid transitions correspond to a "conformational melting"

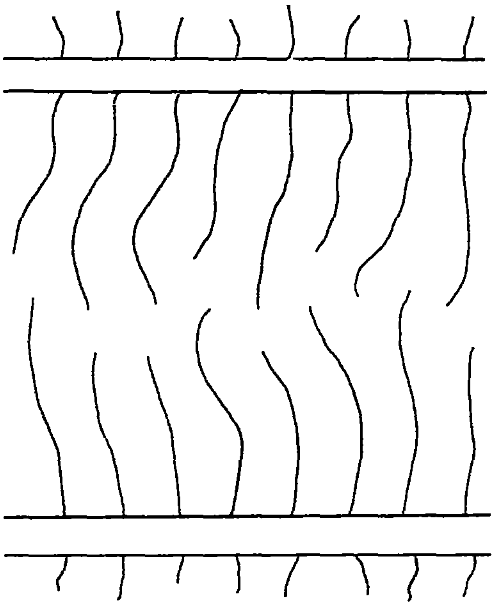


Fig. 6. Schematic view of a possible structural model of the disordered high-temperature phases of the mixed long chain alkylammonium tetrachloromanganates (II).

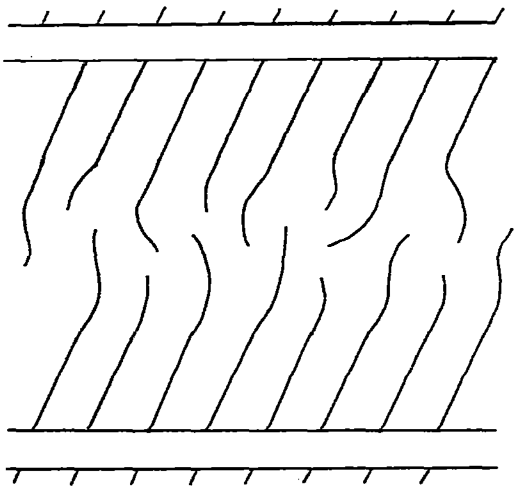


Fig. 7. Schematic view of a possible structural model of the low-temperature phases of the mixed long chain alkylammonium tetrachloromanganates (II).

of these solutions to phases which are the solid state layered equivalent of solutions of different hydrocarbons, the alkylammonium ions being more or less randomly arranged on the surfaces of the macroanions. A schematic view of a possible structural model of the disordered high-temperature phases is shown in Fig. 6.

It is interesting to underline at this point that the structural arrangement of the alkyl chains in the low-temperature conformationally ordered solid solutions cannot be easily understood only in terms of the positional disorder of the alkyl chains. The data of Tables 1 and 2 show, on the other hand, that the solid—solid transition enthalpy per mole of methylene group, for all the solid solutions investigated in this work, is of the order of half the corresponding value found for the pure components. This could be explained in terms of the persistence of some conformational disorder in the low-temperature forms. The model we propose in order to justify the enthalpic data and the stability of the low-temperature solid solutions is shown in Fig. 7, in which a conformationally disordered layer is present in the contact area between successive hydrocarbon layers.

We intend to perform a more thorough investigation of the relationships between crystal structure and chemico-physical properties of these materials, both in the low and high temperature modifications, and to extend this work to compounds with different metals and halogens, in order to understand the influence of the ionic parts of the structure on the behaviour of the hydrocarbon layers.

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