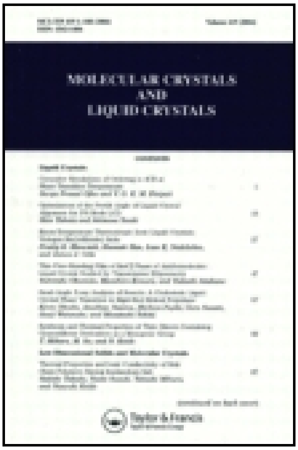

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Thermotropic Mesophases of the C_8, C_{10}, C_{12} and C_{16} n-Alkyl Ammonium Chlorides

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Thermotropic Mesophases of the C_8, C_{10}, C_{12} and C_{16} n-Alkyl Ammonium Chlorides

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Liquid crystalline and solid phases of the title compounds were studied by optical microscopy, differential scanning calorimetry and X-rays. Transition temperatures, heats and layer spacing were determined. In all the compounds the isotropic liquid is preceded by a neat (bilayer smectic A) phase, which in turn is preceded by an intermediate phase which is separated from the room temperature crystalline phase by 2 to 4 first order phase transitions. The intermediate phase has a structure consisting of disordered hydrocarbon chains held in place by their ionic heads ($-NH_3^+$), with the chains perpendicular to the ionic layers. This phase which is shown to be uniaxial by convergent light observations, may be best described as also being a liquid crystal.

INTRODUCTION

Decyl ammonium chloride (DACl) is one of the best known surfactants for use in lyotropic liquid crystalline studies.[1,2,3] While comparing the melting point of successive recrystallizations of this compound on the polarizing microscope, mesophases were observed in the interval from slightly above room temperature to 258°C; the texture of the highest temperature mesophase (188°C–258°C) being very similar to that of the "oily streaks" of the neat (smectic) lyomesophases[3] [Figure 1 (a)]. When a literature search did not locate any previous work on the high temperature mesophases of the alkyl ammonium chlorides, the present study was undertaken.

The major objective was to investigate the possibility of obtaining information which would elucidate the structure of the lyomesophases, especially bilayer structure. In the lyotropic phases the repeat

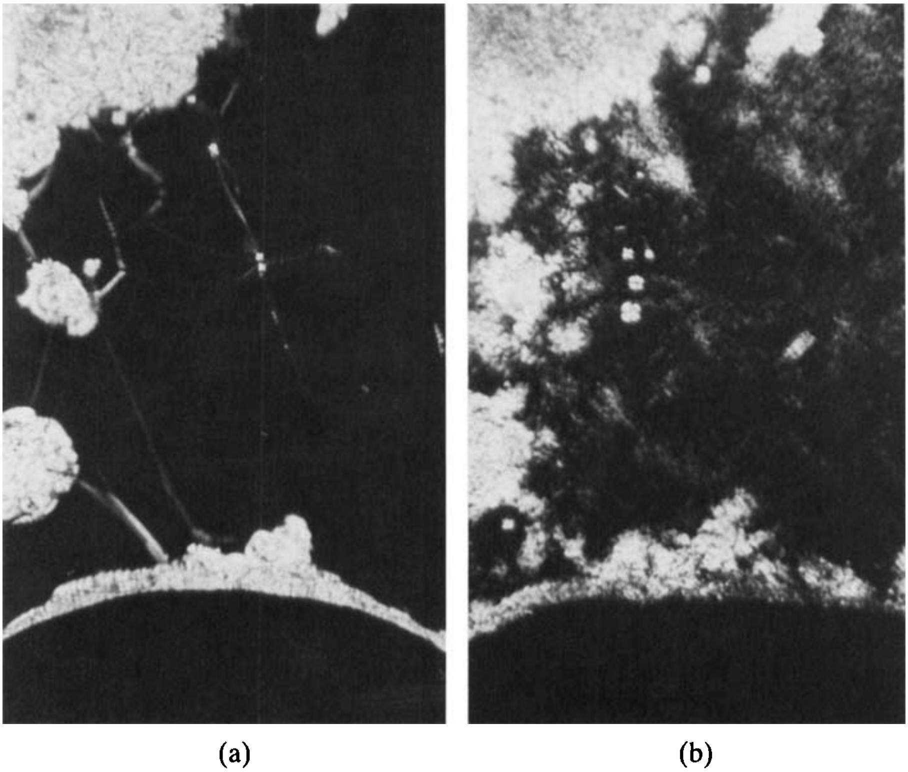
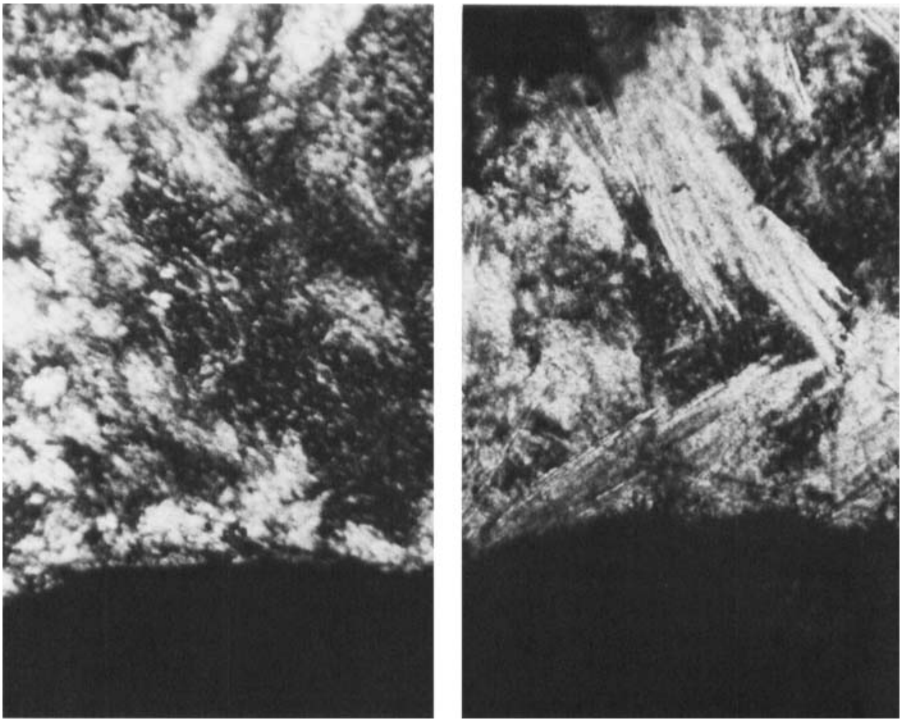


FIGURE 1 Microphotographs of DACl in a sealed 0.4 mm microslide after the temperature was raised into the isotropic and lowered. (a) 190°C, (b) 175°C, (c) 75°C, (d) 20°C. Magnification is 50×.

distance, measured by X-ray diffraction, includes both a surfactant and a water layer and it is often difficult to assign with confidence, a thickness to each of these two component layers. The bilayer thickness as measured in the pure surfactant (thermotropic liquid crystal), could be similar to that in the lyotropic phase.

The existence of a liquid crystalline phase in surfactants is well known. Demus, Demus and Zaschke in their "Flüssige Kristalle in Tabellen" show many surfactants with the neat phase, and these are known to be double lamellar structures.[4] Historically, early workers with soaps identified several phases between the neat phase and room temperature. For the sodium soaps ($C_nH_{2n+1}COONa$) the sequence is, in increasing temperature, crystalline, subwaxy, waxy, superwaxy, subneat, neat and isotropic.[5]



(c) (d)

FIGURE 1 *Continued*

Several of the metal n-alkyl ammonium halide salt crystals are known to have a structure in which the hydrocarbon chains are sandwiched between layers of ionically bound chloride and nitrogen atoms. In these studies,[6,7] the ionic layer is seen as a stable grid which holds the hydrocarbon chains as these melt, a process which often takes place in several progressive steps.

Professor Ivo Vencato of our department has made available to us a room temperature crystal structure determination of DACl which will soon be published. This structure has a 1.2 Å thick layer in which each chloride atom is bounded to 3 nitrogen atoms and each nitrogen to 3 chlorides; bond distances are about 3 Å, the hydrocarbon chains forming an angle of 21° with this plane. The chain length (last carbon to nitrogen) is 12.4 Å. The availability of this structure information was another strong incentive and a valuable asset for the present study.

EXPERIMENTAL

All the ammonium chlorides used in this study were prepared from their respective amines by the addition of 48 percent hydrochloric acid, and were recrystallized from a tetrahydrofurane-ethyl alcohol mixture, until their transition temperatures showed no difference from one recrystallization to the next. Transition temperatures were determined with a polarizing microscope and a differential scanning calorimeter.

Microscopic observations were done on a Leitz Ortholux polarizing microscope with a Mettler FP 52 hot stage. At room temperature the crystals (which in bulk had the appearance of soap powder) were clear, flat and brightly colored between crossed polarizers. Upon heating a very broken texture was observed which still showed color. This change was irreversible, the original texture not being obtained upon cooling. At still higher temperatures, the color disappeared, the texture becoming very dark. The temperatures of the lowest transitions on the heating of a virgin crystal were often quite different than those on successive reheatings (see Figure 2 and Table I). From microscopic observations, the transition below that labeled phase I on Figure 3 was thought at first to be melting, but the X-ray results showed the phase to be relatively highly structured.

All the compounds studied rapidly decomposed when exposed to air at temperatures corresponding to the isotropic phase, therefore samples for microscopic observation were sealed in a 0.4 mm microslide. This permitted prolonged high temperature observations with very little sample discoloration and no detectable change in transition temperatures during several heating cycles. Figure 1 shows a sequence of microphotographs taken upon cooling a DACl sample contained in a 0.4 mm microslide. When the temperature is lowered from the isotropic, many batonettes form, move rapidly about, then disapear leaving the texture shown in 1(a) (oily streak). The dark area is homeotropic, conoscopic observations with a gypsum full wave plate show it to be optically positive. When the temperature is lowered into the phase I region, a new texture can be observed (1b) but conoscopic observation shows it to still be uniaxial. As the temperature is lowered in phase I, the alignment deteriorates (evidence of this can be seen in Figure 1c and also in the decrease in the definition of the cross in convergent light) but the birefringence increases to a point where at 50°C more than one interference ring can be seen. some biaxiality may be present at the lower temperatures of phase I, but if so it is very slight and as the microslide can also show some

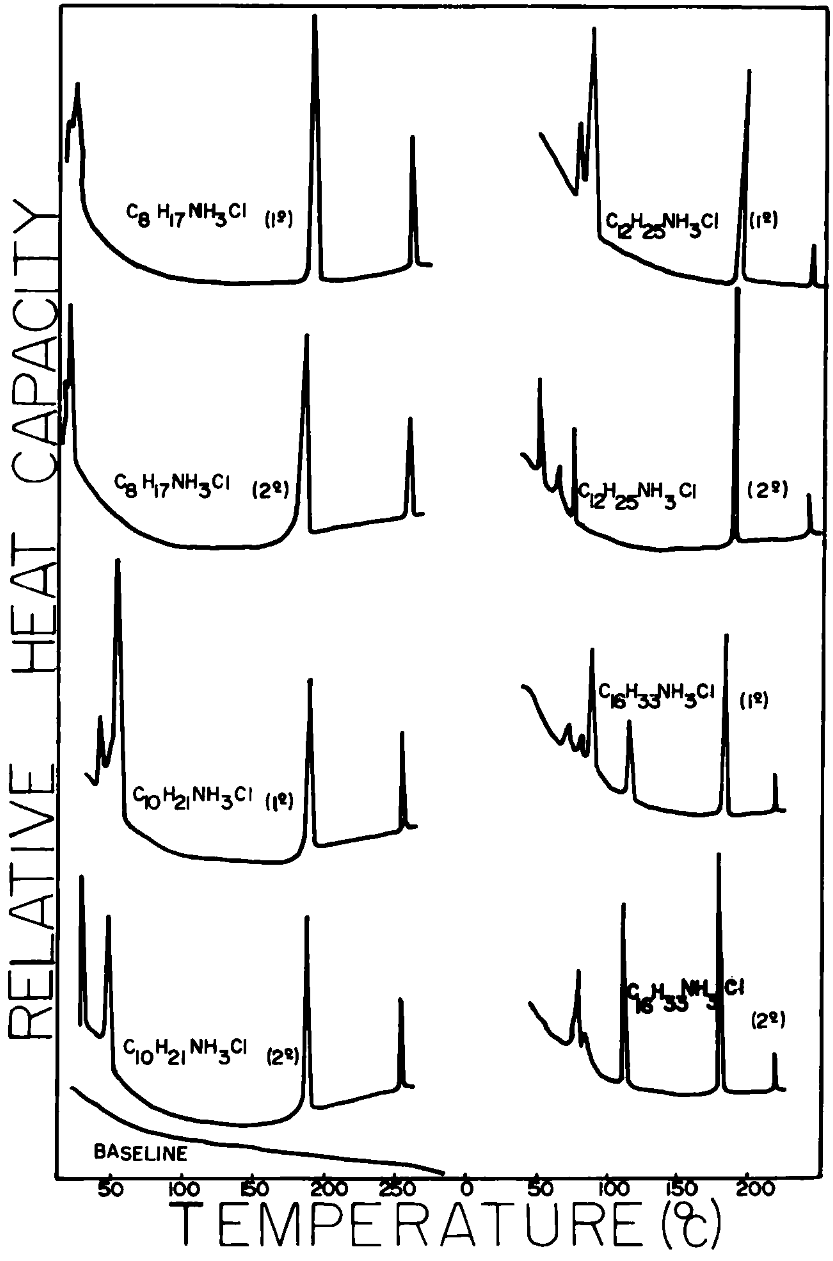


FIGURE 2 Differential scanning calorimeter curves of the virgin and reheated crystals of the n-alkyl ammonium chlorides. Heating rate was 10°/min, curves are not corrected for different sample weights.

TABLE I

Transition temperatures, enthalpies and entropies of the n-alkyl ammonium chlorides and related compounds

				Virgin Cryst.[b]		
Compound	Temp (°C)	ΔH (KJ/mol)	ΔS (J/°K-mol)	Temp (°C)	ΔH (KJ/mol)	Ref.
$C_8H_{17}NH_3Cl$	27[a]	5.0[a]	17[a]	27.0	8.3	*
	30.7[a]					
	201	8.8	18.6			
	272	2.1	3.9			
$C_{10}H_{21}NH_3Cl$	32.5[a]	14.6[a]	47.8[a]	41.2	24	*
	48.1[a]	(5.4)[+]	(16.8)[+]			
	188.0	8.8	19.1			
	258.0	1.7	3.2			
$C_{10}H_{21}N(CH_3)_3Br$	96.5	32.4	88			
$(C_{10}H_{21}NH_3)_2MnCl_4$	35.0	35	113			
$C_{12}H_{25}NH_3Cl$	45.0	5.5	17.3	57.5	31	*
	58.0	2.4	8.8			
	60.0	(0.3)[+]	(0.9)[+]			
	68.0	2.4	8.5			
	180	9.2				
	236	1.3				
$C_{12}H_{25}N(CH_3)_3Br$	97.4	42.3	114			7
$C_{12}H_{25}N(CH_3)_3Cl$	84.2	29.6	83			7
$(C_{12}H_{25}NH_3)_2MnCl_4$	59	49.8	149			6
	63	6.3	19			
$(C_{12}H_{25}NH_3)_2CuCl_4$	57	41.6	127			
	65	8.0	24			
$C_{16}H_{33}NH_3Cl$	63.5[a]	14.4[a]	42.8	55	31	*
	67.0[a]					
	101	7.1	24.1			
	167	10.6	2.1			
	204	1.0				
$C_{16}H_{33}N(CH_3)_3Br$	103	51.5	138			7
$C_{16}H_{33}N(CH_3)_3Cl$	95.4	41.8	113			7

*This work

[a] Peaks not resolved, enthalphy is the sum of more than one transition.

[b] ΔH includes the sum of all transitions below phase I, temperature is of the first peak.

[+] Estimate of enthalpy of second unresolved peak.

biaxiality, a definite conclusion is difficult. Figure 1d shows the room temperature phase, which is the only one that does not align sufficiently to show a conoscopic pattern. Upon reheating, black lines appear at about 35°C and the whole sample darkens at 45°C.

The DSC data were taken in sealed pans under a flow of nitrogen gas on a Perkin Elmer DSC-2. The heating curves of the virgin crystals of any sample were quite different from those of successive runs, the temperature of the first observed peak being as much as 10° higher (C_{10}, C_{12}) and the heats of transition much greater (see Figure 2 and Table I). The first heating curves sometimes showed an exothermic peak just below the onset of the liquid crystalline phase. The temperatures and transitions heats are repeatable on the reruns to within instrument accuracy, showing that decomposition is negligible. If the samples are left at room temperature for several months, the first heating again shows a greater value of ΔH but not as great as the virgin crystal. The areas of the peaks were determined by planimetry, the heats and temperatures being standardized with indium, lead and tin. Temperature accuracy is ±1°C, accuracy in ΔH is 5% for peaks whose baselines are well defined. In the first heating curves the variations in the baseline of the lower temperatures transitions make accurate planimetry impossible, and the peaks were often not well resolved, therefore the accuracy in the determination of ΔH on these curves is much less.

The X-ray measurements were done with the samples in 1 mm diameter capillaries in a temperature controlled furnace (±1°C). Filtered copper radiation was used, with a sample to flat camera distance of about 7 cm. Sample history was important as very low angle peaks were observed in room temperature data if the sample had been ground prior to filling the capillary or if the sample had been preheated. Exposition time varied from 2–6 hours. In the liquid crystalline phase there was considerable decomposition, therefore it was not possible to study the variation of layer thickness within this phase as a function of temperature.

DISCUSSION

Figure 2 gives both the first heating of the virgin crystal and the reheating DSC curves. Table I gives the values of the transition temperatures and heats, which are also plotted on Figures 3 and 4. Unless otherwise noted, the values are for previously heated samples.

The liquid crystal-isotropic transition temperature decreases with the number of carbon atoms in the hydrocarbon chain (n), as does the transition heat. The temperature of the onset of phase I increases with n as does its enthalpy of formation, but the temperature range of its existence decreases. The formation of phase I from the crystal is complex, with as many as 4 separate transitions, all included in the region between intermediate I and the crystal phase on Figure 3. In this figure the line which separates these phases from the crystal is

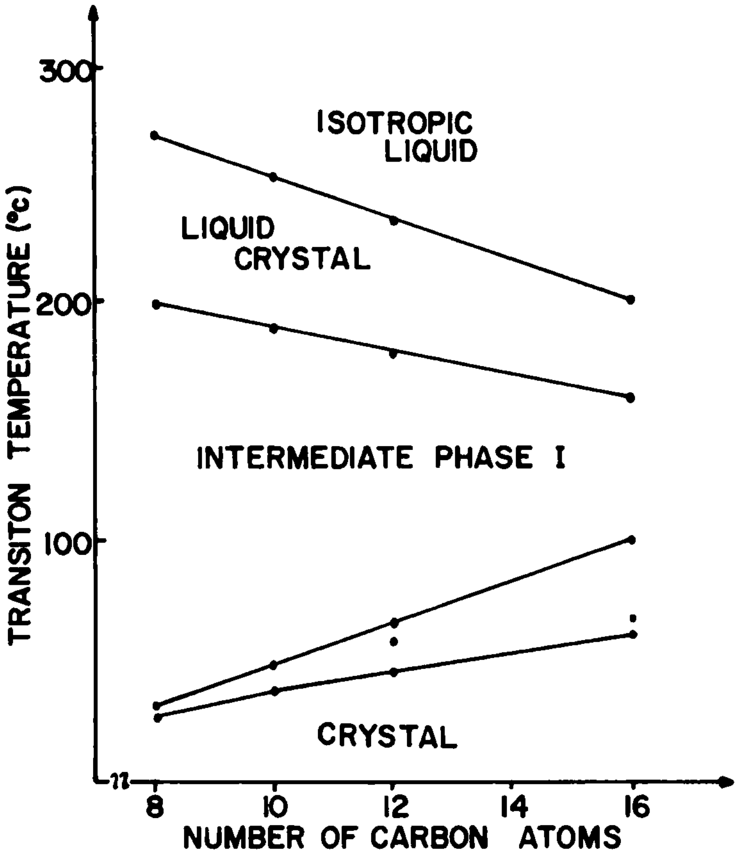


FIGURE 3 The variation of transition temperatures with the number of carbons in the aliphatic chain of the n-alkyl ammonium chlorides.

TABLE II

Bilayer spacing as determined by X-rays for the neat and preheated room temperature phases

No of C atoms	Temperature (°C)	Layer spacing (Å)
8	20	22.7
8	210	20.4
10	20	27.3
10	198	24
12	200	26
16	20	34
16	175	30

that observed for the reheated crystal, if virgin crystal data were used this line would move toward higher temperatures.

The X-ray data show those phases below the liquid crystal phase to be quite solid-like, with several reflections always observed (Figure 5a). It was very disconcerting to note the presence of an internal ring corresponding to an interlayer spacing of 27 Å in the room temperature DACl sample, as this should not have been present in the structure as determined by Vencato. The ring (identical to that in Figure 5a) however was found to be present only when the sample

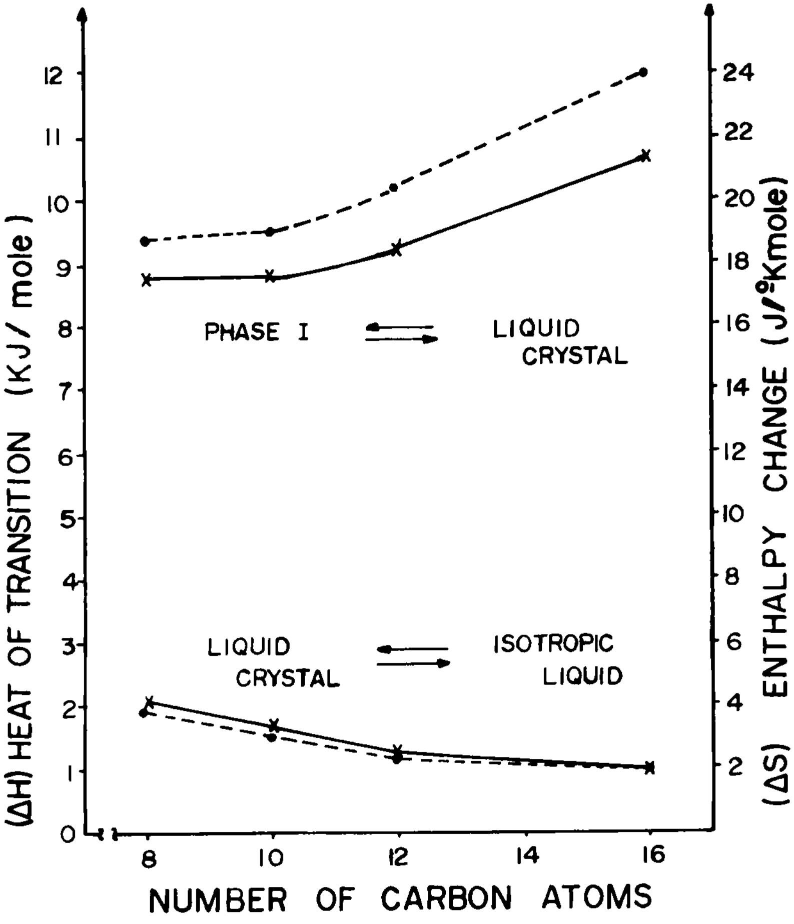
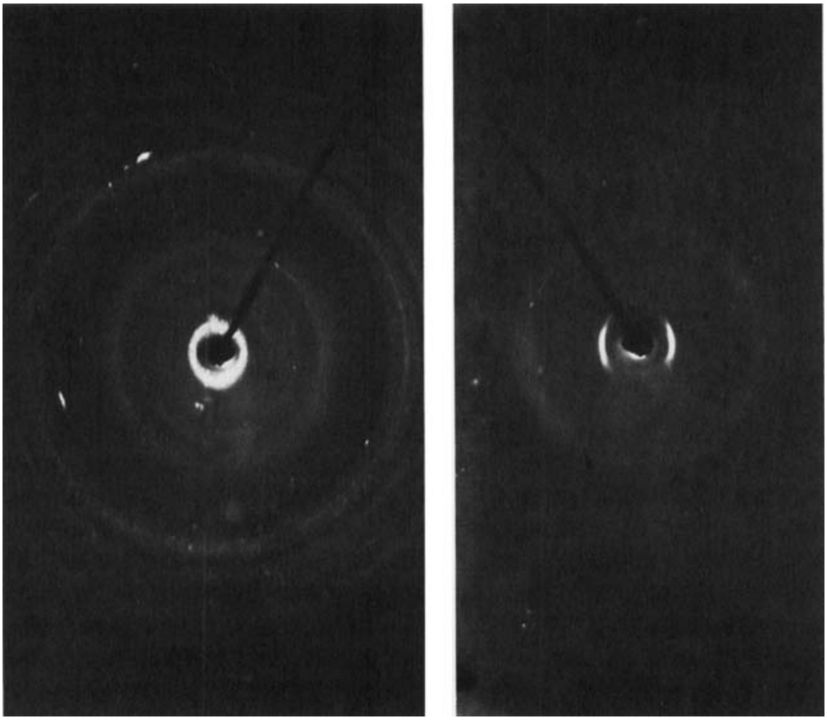


FIGURE 4 Variation of transition heats (solid line) and entropies (dashed line) with the number of carbon atoms in the aliphatic chain of the n-alkyl ammonium chlorides.

was ground prior to filling the capillary tubes, or it could also the made to appear by preheating the sample. Table II gives the spacing of this inter ring at room temperature and in the liquid crystalline phase. In all cases the interlayer spacing was considerably greater at room temperature than in the liquid crystalline phase, with this difference diminishing for longer hydrocarbon chains. (As can be clearly seen in Figure 6.) Because of the width of the room temperature reflections, the error in our determination of the layer spacing, d, could well be greater than an Angstrom. Figure 5b shows the diffraction pattern for the neat phase of a DACl sample which has spontaneously aligned. The outer ring in this figure (also present in Figure 5a) is due to the Mylar window of the sample holder. The complete absence of an external ring shows that no order exists within the layer.



(a) (b)

FIGURE 5 X-ray photographs of DACl at (a) 70°C and (b) 205°C. The external ring present in both photographs is an artifact of the sample holder window (Myllar).

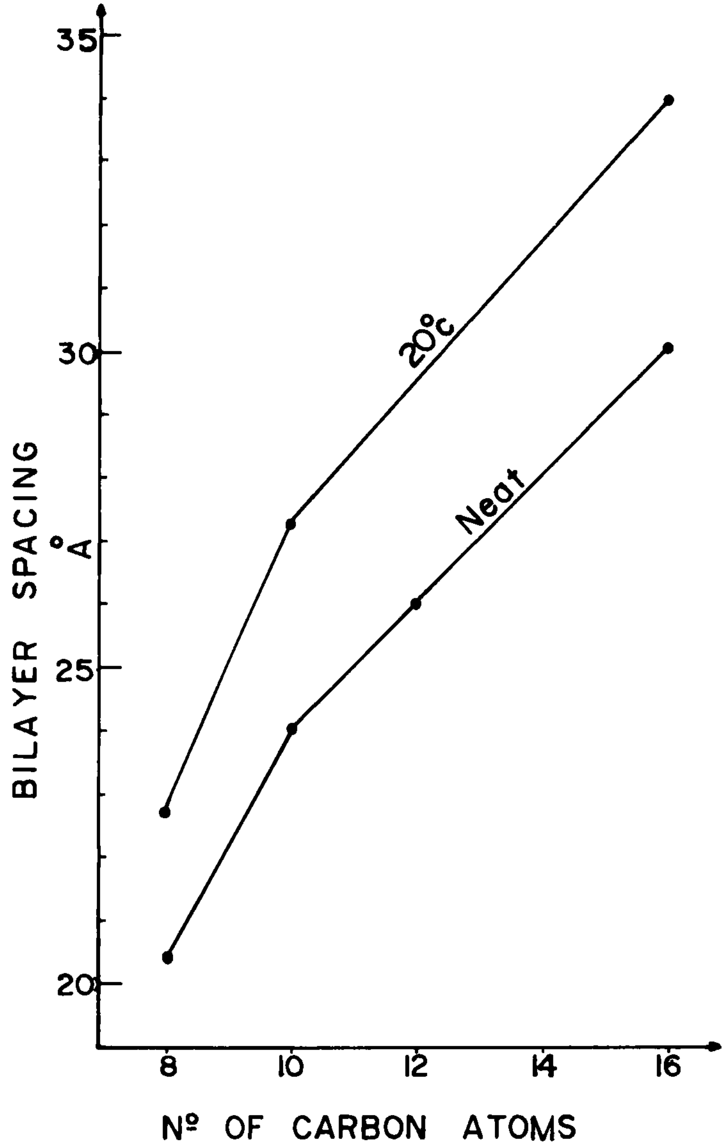


FIGURE 6 Bilayer thickness of the n-alkyl ammonium chlorides as determined by X-ray diffraction for the neat and preheated room temperature phase.

To help interpret our results, comparison will be made with previous studies on the trimethyl n-alkyl ammonium halides and the n-alkyl ammonium metal halides. In spite of the great similarity of the trimethyl substituted compounds in both molecular and crystalline structure to those we studied, the heats of transition and certain other aspects of the comportment of the metal halides are found to be closer to those of the n-alkyl ammonium chlorides.

Iwamoto, et al.[7] have studied the solid-solid phase transition in the trimethylalkylammonium halides (for n = 10,12,14,16 and 18) and came to 3 conclusions: (1) that these compounds have an endothermic solid-solid phase transition between 77°C and 127°C; (2) that this transition is the result of the melting of the hydrocarbon chains while the ionic layers remain practically unchanged and (3) a supercooled state is obtained on cooling with complete recovery of the original state being "practically difficult."

Needham and Willett[6] studied the solid-solid phase transitions of $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ salts with n = 12,14; (M = Mn, Cu, Cd). In these substances there are two phase transitions which they interpret as one associated with a separation of layers, allowing the chains to become nearly perpendicular to the layer (chain melting), and a second (with less associated energy) in which the chains become disordered and extend perpendicular to the layer.

The transition temperatures and energies are both higher for the trimethyl substituted salts than for our compounds. Iwamoto, et al. also found these compounds to have slightly greater and sharper DSC peaks on cooling than on heating. At the melting point of those compounds a transparent liquid is formed which decomposes rapidly i.e. they report no neat phase. The metal salts[6] have a thermal comportment much closer to those we studied, all have two peaks. These have a ΔH of 23 to 27 kJ/mole for each C_{12} chain, depending on the metal. These are quite similar to the value obtained upon heating virgin crystals of our C_{12} compound (31 kJ/mol at 57.5°C) but on the successive heatings only 11 kJ/mol, distributed in 4 peaks between 45° and 68° is observed (see Figure 2). After this sample set at room temperature for almost 2 months, 16 kJ/mol was obtained on the first reheating, the two lowest temperature peaks giving the increased contributions. Our values are within the expected for chain melting (500 cal per bond)[6] and support the hypothesis of ref. [7] that complete chain order is not recovered upon cooling.

Our X-ray data, especially when considered together with the DSC data, indicate that the crystalline structure of the virgin crystal is different from that which has been heated. In the crystal structure of

DACl as determined by Vencato, c = 15.5 Å. Therefore, in the virgin crystals of our compounds, unlike the metal or trimethyl ammonium salts, there is a very great overlap of the chains whose heads (NH_3^+) are in neighboring layers. For example, in DACl the layer thickness is 15.5 Å, with a chain length of about 13 Å, thus leading to an overlap of more than 10 Å. In the metal salts, whose bilayer corresponds to about twice the molecular length, there is difference in layer spacings (Δd) between the intermediate phase and that at higher temperatures which increases as the number of carbons in the chain increases, and this shorting of the chains is attributed to the chain melting. In our compounds, while d decreases from the room temperature phase I to the liquid crystalline phase, there is no increase of Δd with n, in fact a slight decrease is noted (but this is within experimental error).

The crystal structure of $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) as shown in ref. [7] is very similar to that of DACl, as far as the ionic layer is concerned, with distances between the nitrogen and the halogen atoms agreeing very closely. It is interesting to note that except for the Br^- to Cl^- change, the only difference in these compounds is the substitution of the H by CH_3 in the head of the molecule, and that this increases the stability of phase I [101–167°C for $C_{16}H_{33}NH_3Cl$ and 103–260° for CTAB] and inhibits the formation of a liquid crystalline phase. The isotropic temperature of CTAB is more than 50°C higher than that of our C_{16} sample with its phase I going directly to the isotropic in contrast to our C_{16} compound which has a smectic (neat) phase over a temperature range of 37°C. We believe the addition of the methyl group inhibits the formation of hydrogen bonds, which occupy part of the charge, thus greatly weakening the ionic network, (however the increased polarizability of the Br^- with respect to Cl^- will also be responsible for part of the increase in the transition temperatures). The melting points of the trimethyl salts show no regular dependence on chain length in contrast to the very regular monotonic decrease with n that we observe.

A monotonic decrease as a function of n in the neat-isotropic transition temperatures is also seen in the sodium soaps, but these temperatures are about 100°C higher than ours (for $C_{10}H_{21}COONa$, 247°C < neat < 343°C[5]). These higher temperatures are probably due to the fact that the ionic layer in the soap crystals is an interlinked three dimensional bilayer which has greater stability than the staggered monolayer found in our compounds.[8]

After this work was completed, we became aware of that of Busica, Scopa and Vacello[9,10] on certain of the higher temperature phases of three of the compounds we studied. Their data agree well with ours, as do most of their conclusions; however their denomination of the disordered intermediate phase as a plastic crystal is in conflict with what we understand to be the normal use of this term as a crystal which "possesses long range positional order but is orientationally completely disordered."[11] (In this case the disorder is about only one axis.) While it may only be an exercise in semantics to speak of a very disordered solid or a highly ordered liquid crystal, we believe the latter probably best describes the phase in question. This is supported by the ease with which a cover slide can slipped when the crystal is in this phase and by the permanence of the uniaxial interference figure in convergent light during the transition from the neat phase to the phase in question.

CONCLUSIONS

The alkyl ammonium chlorides in this study have a solid structure in which layers of ionic bonds are sandwiched between layers of hydrocarbon chains. At room temperature the distance between ionic layers is only slightly greater than the chain length. At a temperature slightly above room temperature a phase transition takes place in which the layer spacing increases to that of a bilayer. This change is irreversible, the structure of the virgin crystal not being recovered upon cooling, though after several months at room temperature partial recovery of the original structure may take place. At temperatures below those of the neat phase an intermediate phase is formed in which the hydrocarbon chains are molten (or highly disordered), are perpendicular to the layers and are maintained in place by a layer of ionic bonds. The formation of this phase from that at room temperature is complex, involving as many as 4 phase transitions. At higher temperatures a bilayer liquid crystalline phase is formed with a decrease in layer spacing of about 10% over that at room temperature (intermediate phase). This is a bilayer smectic A (neat) in which no long range order exists within the layer showing that the long range order ionic net was destroyed.

We would like to thank prof. Ivo Vencato for access to the DACl crystal structure data and many helpful discussions. We also greatfully acknowledge fruitful discussions with profs. Abio Pinto and Ted Taylor. This project was made possible by Financial assistance from the Brazilian Organizations CNPq, FINEP and CAPES.

References

1. T. Haven, D. Armitage and A. Saupe, *J. Chem. Phys.*, **75**(1), 352 (1981).
2. M. R. Alcantara and J. A. Vanin, *Mol. Cryst. Liq. Cryst.*, **107**, 333 (1984).
3. M. C. Holmes and J. Charvalin, *J. Phys. Chem.*, **88**(4), 810 (1984).
4. D. Demus, H. Demus and H. Zaschke, *Flüssege Kristalle in Tabellen*, (VEB Deutscher Vereag für Grundstoffindustrie, Leipzig, 1974) pp. 310-317.
5. M. J. Vold, M. Macomber and R. D. Vold, *J. Am. Chem. Soc.*, **63**, 168 (1940).
6. G. F. Neddham, R. D. Willett, and H. F. Franzen, *J. Phys. Chem.*, **88**(4), 674 (1984).
7. K. Iwamoto, Y. Ohnuki, K. Sawada and M. Seno, *Mol. Cryst. Liq. Cryst.*, **73**, 95 (1981).
8. V. Vand, T. R. Lomer and A. Lang, *Acta Cryst.*, **2**, 214 (1949).
9. V. Busico, A. Scopa and M. Vacatello, *Z. Naturforsch A*, **37**, 1466 (1982).
10. V. Busico; P. Cernichlaro; P. Corradini and M. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1982).
11. G. W. Smith, *Advances in Liquid Crystals*, (Ed. G. Brown) Vol. 1, p. 191, Academic Press, New York, (1975).