Decylammonium chloride/ammonium chloride aqueous solutions A Raman scattering study

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Decylammonium chloride/ammonium chloride aqueous solutions
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Aqueous solutions of decylammonium chloride and decylammonium chloride/ammonium chloride between 20 and 50 per cent of DACl have been studied by Raman scattering. The spectral behaviour was followed as a function of temperature and phase transitions were observed for all samples. We have focused our study on the intensity variations of both the symmetric and the antisymmetric stretching vibration modes of CH_2 groups situated in the region 2800–3000 cm^{-1}. The study of the high frequency part of the spectrum showed the characteristics of order disorder transitions already studied for other materials. We have observed that the existence of a nematic phase in the ternary systems is caused by the addition of the salt.

1. Introduction

Ionic surfactants are important as models for biological membranes, as cleansing agents, etc. They belong to the amphiphile family, they possess a long hydrophobic, hydrocarbon chain and a hydrophilic, polar headgroup. In a polar solvent and at a certain concentration (the critical micellar concentration (CMC)) these molecules associate to form micelles. When the concentration increases further they can form liquid crystal phases.

Decylammonium chloride (DACl) has been the subject of recent papers [1–8]. The crystal phase of DACl from low temperature to room temperature is perfectly ordered with chains in the all-trans configuration and which form an interdigitated bilayer. It is known [1] to be monoclinic with two molecules per unit cell, and belongs to the space group C_2^2. Very few papers exist about DACl solutions [9, 10]. With X-ray scattering and NMR spectroscopy Holmes and Charvolin [9] observed the structural changes at the lamellar–nematic phase transition in the ternary mixtures (DACl/ NH_4Cl water). Following optical microscopy experiments, Rizzatti and Gault [10] also found a nematic phase for the binary system (DACl/water) in the concentration range 42 to 49 per cent of DACl by weight. In this paper, we report a study DACl and DACl/NH_4Cl aqueous solutions using Raman spectroscopy covering a composition range from 20·2 to 50 per cent (by weight) of DACl from liquid nitrogen temperature to nearly 380 K. We have chosen this concentration range because it might include the nematic phase domain.

Many studies have been made in the past few years to understand the molecular interactions inside lyotropic mesophases [11, 12] but very few Raman studies have been performed on aqueous solutions of surfactants [13–21]. Nevertheless, many

investigations both experimental and theoretical [22–26], have been performed on long chain molecules. These results have been used to interpret the Raman spectra of phospholipids or biomembranes [27,28]; we shall use them to interpret our experimental work.

The Raman spectra of a surfactant is dominated by the vibrational modes of the hydrocarbon chain as described hereafter. In the low energy part we can find a longitudinal acoustical mode (LAM) due to the extended chain. The LAM frequency depends on the length of the chain; the longer is the chain, the lower is the frequency. At higher frequency we have the skeletal vibrational modes (C–C stretching modes between 1050 and 1150 cm^{-1}), near 1160 cm^{-1} we find the CH_2 rocking mode, the CH_2 twisting mode is around 1300 cm^{-1} and the CH_2 bending modes between 1430 and 1460 cm^{-1}. The high energy part between 2800 and 3000 cm^{-1} contains the C–H stretching vibrational modes. We can find also some features due to the polar headgroup with generally low intensity. The high energy part is the most complex of the spectrum. It is interpreted as the combination of C–H stretching fundamental modes of the crystal and the Fermi resonance interactions of these modes with the overtones of the CH_2 bending modes. This Fermi interaction in the crystal is also affected by the coupling between the CH_2 bending modes of adjacent chains. This produces a greater dispersion of these modes and results in a broadening of the bands. The main features of the high energy part are the peaks at 2850 cm^{-1} and 2885 cm^{-1} respectively attributed to the symmetric (s) and the antisymmetric (as) CH_2 stretching modes. In the solid phase (low temperature) the antisymmetric mode is more intense (if we compare the peak heights) than the symmetric one. In the liquid phase, the heights of these two peaks are inverted. The peak height ratio I(as)/I(s) is generally used to measure the lateral order and gives information on the chain packing and the chain mobility [27,28]. This ratio decreases if there is an increasing chain disorder.

The C–C stretching vibration modes region between 1050 and 1150 cm^{-1} is characterized in the solid phase by two intense peaks near 1065 and 1120 cm^{-1} due to the C–C vibrational modes in the all-trans configuration (respectively the anti-symmetric and symmetric modes). Another band, at 1080 cm^{-1}, appears in the high temperature phases (crystal–liquid phases or isotropic liquid phases) and is due to the C–C vibrational modes in the presence of gauche conformations. Meanwhile, the 1120 cm^{-1} band reduces its intensity and the peak at 1065 cm^{-1} becomes a shoulder in the band due to gauche conformations [28–32]. The C–C stretching vibrational modes are affected by the intrachain disorder and give information about the trans-gauche isomerization.

After the description of the experimental procedure we describe the samples studied and discuss the results.

2. Experimental procedure

The Raman spectroscopy experiments were performed on a Jobin–Yvon Ramanor HG2S double spectrometer, using a Spectra Physics Ar^+ laser. We used the 514·5 nm laser line with a power of 400 mW. The spectral resolution was 4 cm^{-1}.

A small cryostat with nitrogen circulation and temperature regulation was used for the variable temperature experiments. For technical reasons, the platinum resistance is quite far from the focusing point of the laser beam, and the error in the temperature measurements was found to be 2 K. The sample was allowed to equilibrate for 15 min to stabilize the temperature before recording each spectrum.

The scattering light, detected at right angle from the incident light, was collected on the photocathode of a cooled photomultiplier and amplified by a DC operational amplifier. In the polarization measurements the incident light was polarized by a half-wave plate; a polaroid analyser and a scrambler were placed in front of the entrance slit of the monochromator.

All the samples were enclosed in sealed 1 mm diameter capillaries. Decylammonium chloride was prepared according to the method of Radley and Saupe [33]. The mixture with deionized water was made by sonication and centrifugation and we checked the homogeneity of the sample by successive heating and cooling processes between crossed polarizers. Depending on the concentration, the domain of existence of the nematic phase lies between 280 and 345 K [9, 10]. We studied our samples, therefore, from 77 K to nearly 350 K. We followed the same experimental procedure for all of the samples. We started the cooling process from the isotropic liquid phases (micellar phase) at high temperature to liquid nitrogen temperature at a rate of 5 K min^{-1}. Then slowly heating the samples to more or less 350 K step by step in order to record the spectrum at each temperature. Then cooling slowly step by step to 240 K. This cycle was made two or three times in order to verify the reproducibility of our results. Peak heights were measured by drawing a straight baseline between 2800 and 3050 cm^{-1}.

3. Results and discussion

We now present the results for the different concentrations studied. The concentrations are expressed in weight of DACl or NH$_4$Cl to the weight of solution. As indicated in the Introduction, the I(as)/I(s) peak height ratio of the CH stretching modes gives information on the chain packing and we mainly analysed this spectral feature. First we present the main results for the low temperature phase of the solutions (solid phase I) which is common to all of the samples.

At 77 K all of the samples have a solid structure with the chains in the all-trans configuration as can be seen in figures 1 (*a*), 2 (*a*), 3 (*a*) and 4 (*a*). At low frequency (220 cm^{-1}) we find the LAM mode (see figure 1 (*a*)) with important shoulders at 208 and 228 cm^{-1}. This band at 228 cm^{-1} is due to the hexagonal I$_h$ structure of ice [34]. The LAM is found at 217 cm^{-1} in anhydrous DACl [8] and at 232 cm^{-1} in solid *n*-decane. The frequency for the solutions in the solid state is in agreement with an ordered alkyl chain with a heavy group at one extremity, as studied by Minoni and Zerbi on dimeric even-numbered fatty acids [35]. The small shift (+3 cm^{-1}) is probably due to changes in hydrogen bonding between head-to-head molecules as analysed by Minoni *et al.* [36]. As these authors have found, an increasing frequency is consecutive to an increase of the hydrogen bonding strength. We also think that the mode at 208 cm^{-1} is a LAM mode but due to molecules with a smaller hydrogen bonding strength.

The CH$_3$ rocking mode is situated at 890 cm^{-1} and another mode, observed at 943 cm^{-1}, is probably due to the stretching vibration of the last C–NH$_3$ bond of the alkyl chain. The antisymmetric C–C mode (see figure 2 (*a*)) is located at 1066 cm^{-1} while the symmetric one is at 1120 cm^{-1}. The mode at 1080 cm^{-1}, characteristic of gauche conformers, is not present in this phase showing that the chains are in the all-trans conformation.

The CH$_2$ rocking and twisting modes are at 1163 and 1296 cm^{-1}, respectively (see figure 3 (*a*)). We can observe the main features of the bending modes: 1435, 1450, 1453, 1460 and 1483 cm^{-1}. At least eight bands (1420, 1433, 1447, 1453, 1460, 1470,

16   M. Picquart *et al.*
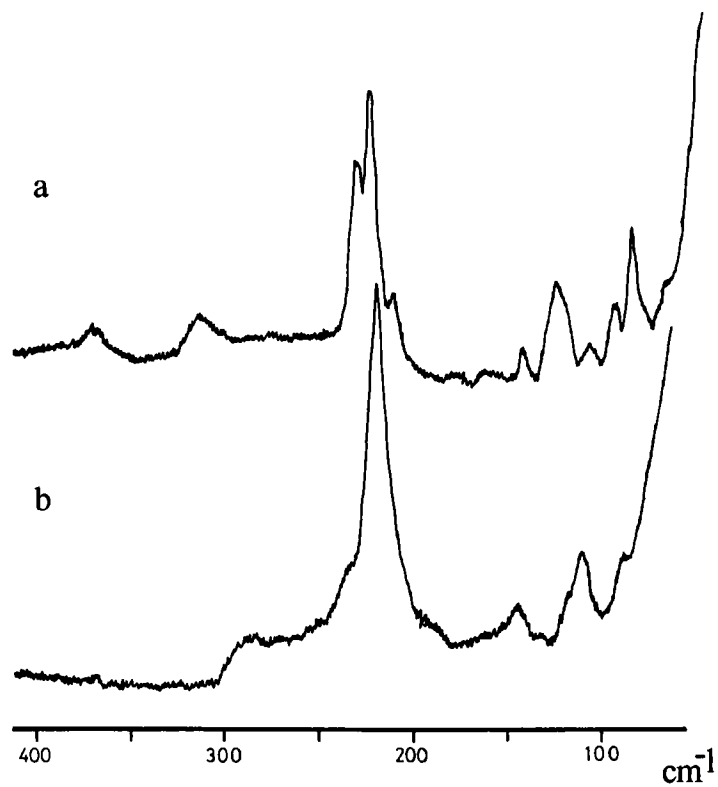

Figure 1.   Low frequency Raman spectrum of (*a*) solid phase I at 79 K and (*b*) solid phase II
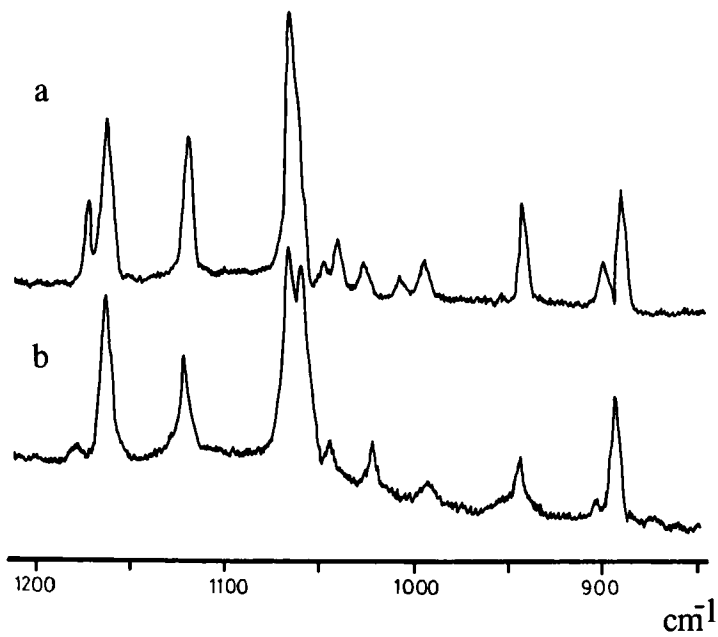at 260 K.

Figure 2.   Raman spectrum in the frequency range 850–1200 cm^{-1} of (*a*) solid phase I at 79 K
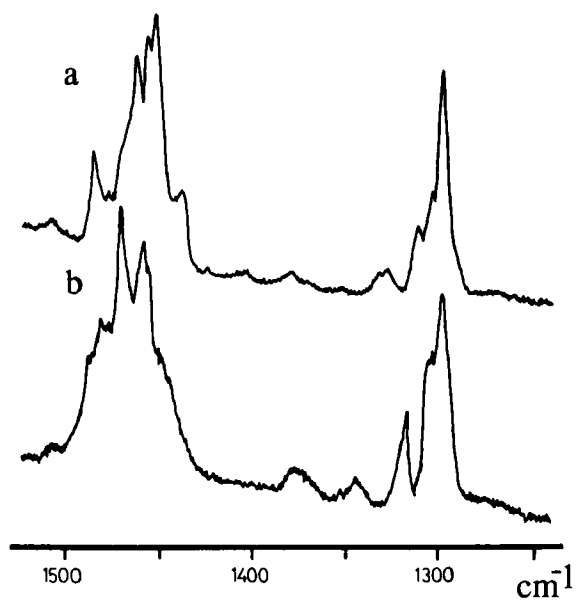and (*b*) solid phase II at 260 K.

Figure 3. Raman spectrum in the frequency range 1250–1500 cm^{-1} of (a) solid phase I at 79 K and (b) solid phase II at 260 K.
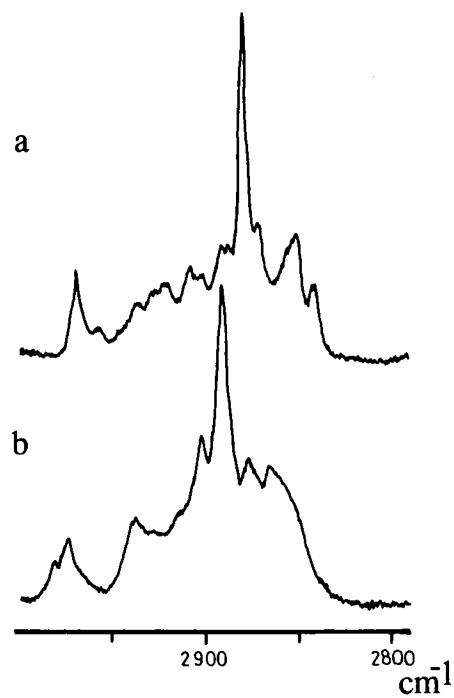

Figure 4. Raman spectrum in the CH stretching region of (a) solid phase I at 79 K and (b) solid phase II at 260 K.

1473 and 1486 cm^{-1}) were observed in this region for anhydrous DACl [8]. These were due to a splitting caused by the interdigitation of the chains. In particular the band at 1420 cm^{-1} which appears also as in orthorhombic structures observed in decylamine [8], or in odd-numbered alkanes [37]. In this solid phase of the solutions such a band is not observed.

In anhydrous DACl a small band exists [8] at 1433 cm^{-1}. In the bending modes of figure 3 (*a*), we can observe a band at 1435 cm^{-1} but there is no band at 1420 cm^{-1}. The bending modes of the solution at low temperature look like the spectrum of orthorhombic *n*-alkanes but with a shift of nearly 15 cm^{-1} to higher frequencies, which cannot be due to a thermal effect.

At higher frequencies (see figure 4 (*a*)) the band at 2850 cm^{-1} (with a shoulder at 2842 cm^{-1}) is the CH$_2$ symmetric stretching mode and the CH$_2$ antisymmetric mode is at 2878 cm^{-1}. At 2969 cm^{-1} we find a band due to the terminal CH$_3$ stretching modes. The triclinic structure is characterized by the splitting of the CH$_2$ symmetric stretching mode [22], but generally the two bands have the same intensity. Here, the band at 2842 cm^{-1} is much smaller than the band at 2850 cm^{-1}. In the powder, some unusual splitting of both the antisymmetric skeletal vibrational mode and the symmetric C–H stretching mode were observed [8] and attributed to the interdigitation of the chains. Such a splitting of the skeletal mode is not observed in the solid phase I of DACl solutions.

From all of these observations and taking into account the results yet known [22] we decide, therefore, in favour of a non-interdigitated structure. But to decide about the structure it is necessary to study the other solid phase which appears when we heat the sample.

3.1. *Binary aqueous solutions*

3.1.1. *Sample with 20·2 per cent of DACl*

Between 77 and 255 K we have the solid phase I presented previously. Above 255 K the sample exhibits another solid phase (solid phase II) with vibrational frequencies quite different from the first as we can see in figures 1 (*b*), 2 (*b*), 3 (*b*) and 4 (*b*). The LAM mode is shifted to 218 cm^{-1} (see figure 1 (*b*)) and the shoulders are less intense than previously. In this phase the spectral region of the LAM is comparable to that of anhydrous DACl [8]. This suggests that all of the head-to-head molecules have the same interaction constant. The C–C antisymmetric mode is split in two components with comparable intensities: 1059 and 1064 cm^{-1} (see figure 2 (*b*)) and the band due to the gauche conformation does not exist in this phase, as in DACl powder.

We note also some differences in figure 3 (*b*) in the CH$_2$ twisting and bending modes: a new band at 1314 cm^{-1} and bands at 1456, 1469, 1480 cm^{-1} with shoulders at 1445 and 1485 cm^{-1}. The twisting band region is quite analogous to that of anhydrous DACl, however the 1417 cm^{-1} band is not observed here in the bending modes. If we compare figures 3 (*a*) and (*b*) it seems that the band at 1435 cm^{-1} merges into the band at 1456 cm^{-1} as happens in the transition between the orthorhombic and the α phase of odd numbered *n*-alkanes [37]. In this case the bands observed at 1435 and 1453 cm^{-1} of solid phase I would originate from a splitting due to the crystal effect suggesting an orthorhombic sublattice.

The CH stretching modes (see figure 4 (*b*)) are also different, we have only one band at 2863 cm^{-1}, the band at 2878 cm^{-1} collapses and the 2890 cm^{-1} band becomes the most intense. We must emphasize that this change is progressive, when we made

this experiment we could observe the two bands evoluting at the same time. This region is also nearly identical to that of DACl powder. The I(2890)/I(2863) peak height ratio is used in this phase to follow the evolution of chain packing. Our conclusion from these observations is that the structure of solid phase II is monoclinic with interdigitated chains. Nevertheless we note some differences between the spectra of solid phase II and the powder. These differences are probably due to different chain packing, in particular different tilt angles between the chains and the polar head or only partial interdigitation. It has to be noted that the transition solid phase I-solid phase II is not reversible: when the samples are cooling from this second solid phase they stay in solid phase II until liquid nitrogen temperature. It is possible that solid phase I is metastable, but until now we have not observed any slow transformation between solid phase I and solid phase II at 79 K.

Figure 5 shows the ratio I(2878)/I(2850) = I(as)/I(s) (I(2890)/I(2863) for solid phase II) for the peak heights plotted against temperature. We can see several discontinuities corresponding to structural phase transitions. The black circles were obtained by increasing temperature from 77 to nearly 350 K and the open circles by cooling the sample. We can observe that there is no complete superposition between the two sets of experimental points. The discrepancy is due to differences between the transition temperatures caused by some supercooling effect but also to differences in the structures which give different I(as)/I(s) ratios. We can see that the I(as)/I(s) ratio has the value of 2·6 at low temperature and decreases slowly with increasing temperature to 1·8 at 254 K. Then, due to the solid phase transition it increases to 2·2 at 255 K, and then decreases to 0·8 at 284 K, and keeps this value for higher temperatures.

Above 284 K the sample is in the isotropic micellar phase as we can see from the spectrum presented on figure 6 (a). This is confirmed by observation between crossed polarisers. The LAM mode becomes a broad band with low intensity centred near 250 cm^{-1} at the base of the central diffusion peak as for the liquid *n*-alkane of the same
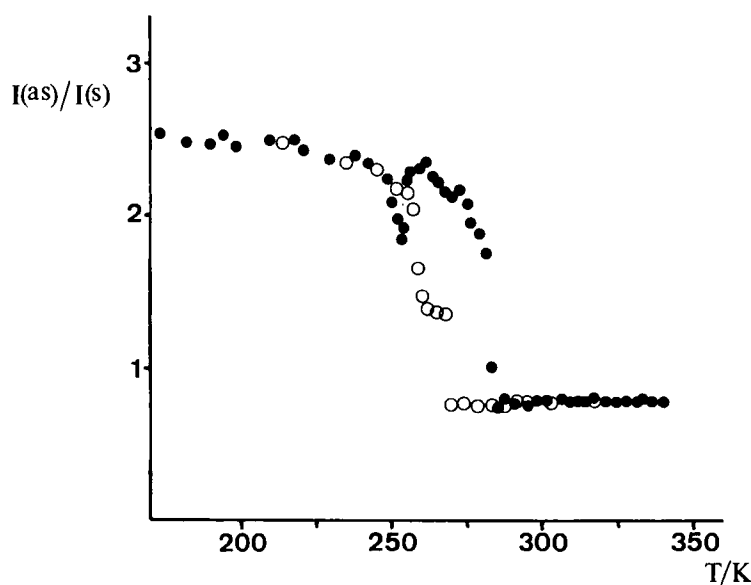

Figure 5. I(as)/I(s) peak height ratio versus temperature for the solution containing 20·2 per cent DACl.
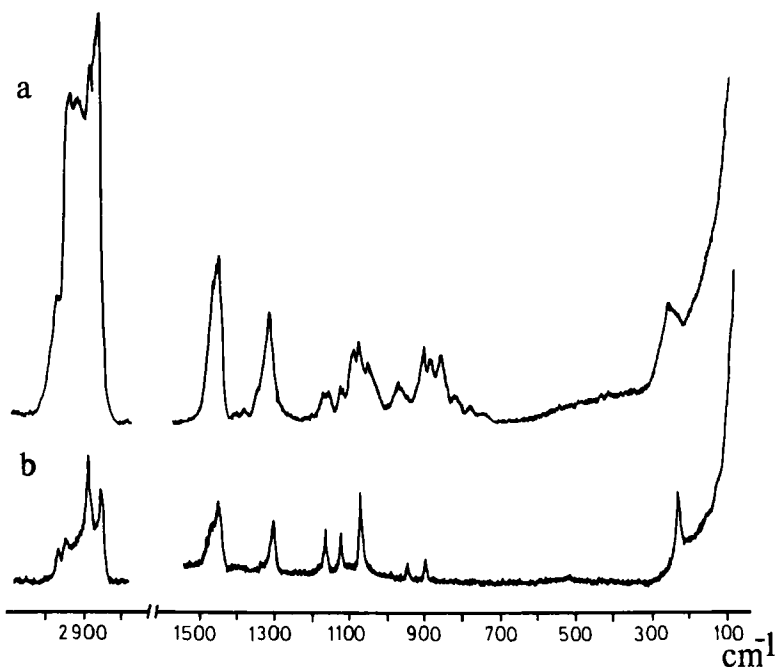
Figure 6.   Raman spectrum of (*a*) the micellar liquid phase at 320 K and (*b*) the coagel phase at 265 K.

chain length. This mode, called the 'pseudo-LAM' [25], is an envelope due to parts of the chains with shorter lengths.

The skeletal modes due to the all-trans conformation decrease and the band at 1080 cm^{-1} increases indicating the presence of gauche conformers in the sample. We observe also two broad bands at 845 and 871 cm^{-1} which characterize the tg$^{\pm}$t$_{n-5}$ and g$^{\pm}$t$_{n-4}$ conformations, respectively [22]. At the same time the symmetric CH stretching mode at 2855 cm^{-1} is more intense and the antisymmetric band broadens, decreases in intensity and shifts to 2905 cm^{-1}.

Cooling the sample from 320 K, the isotropic phase exists until 270 K as we can see in figure 5 (open circles). At this temperature a new solid phase appears as seen in figure 6 (*b*): the main change with respect to the other solid phases are in the CH stretching modes. The two main bands (located at 2850 and 2880 cm^{-1}) now have quite comparable intensities, and interactions between adjacent chains are lower than in the solid phase as can be deduced from an intensity ratio of 1·4. This late structure is very well known [22] and the spectrum is characteristic of a lamellar phase with molecules on a bidimensional hexagonal array. This is the so-called coagel phase also called by spectroscopists the α phase or the spaghetti-like phase which can be found in the odd numbered n-alkanes [37]. When cooling the sample, it exhibits a transition to solid phase I at 260 K. On heating the sample, the cycle described here starts again.

3.1.2. *Samples with 39, 44 and 48 per cent DACl*

From 77 to 255 K, the sample with 39 per cent DACl presents the same solid phase I as the previous one. The LAM mode is found at 221 cm^{-1} with shoulders at 210 and

228 cm^{-1}. As in the previous sample, this last frequency corresponds to the hexagonal ice but the two others correspond to LAM frequencies with higher hydrogen bonding strength. The skeletal modes are at 1066 and 1120 cm^{-1} and the CH stretching modes at 2850 cm^{-1} (shoulder at 2843 cm^{-1}) and 2879 cm^{-1}. In figure 7 we present the I(as)/I(s) peak height intensity ratio which permits us to determine the transition temperatures and to characterize the phases.

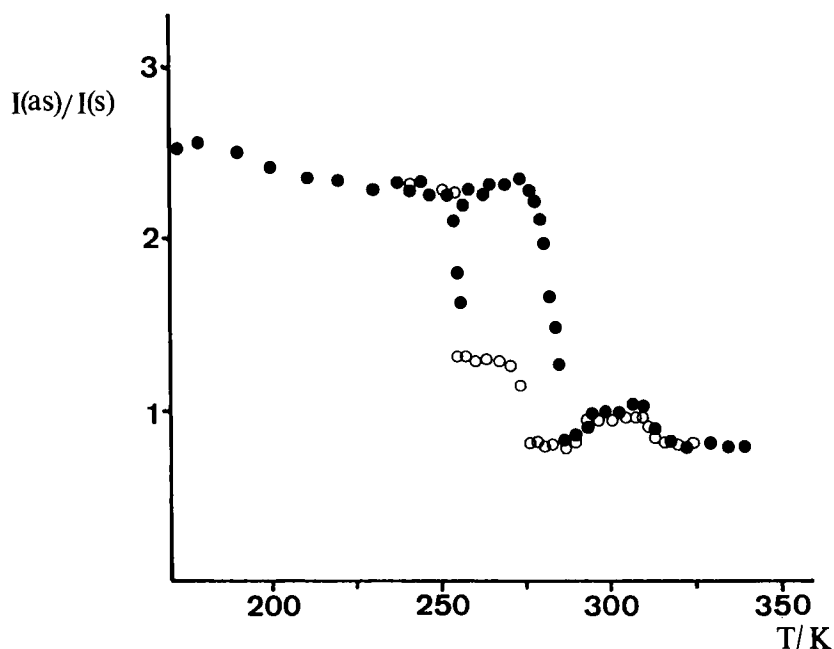Figure 7. I(as)/I(s) peak height ratio versus temperature for the solution containing 38·8 per cent DACl.

From 257 to 286 K we find solid phase II with the LAM mode at 218 cm^{-1}, the skeletal modes are at 1057, 1063 and 1120 cm^{-1}, and the stretching modes at 2862 and 2890 cm^{-1}. The behaviour is quite identical to the previous sample.

At 286 K the sample exhibits a transition to another phase nearly identical to the liquid phase of the previous sample. If we observe this phase between crossed polarizers, it is isotropic. The bands are at 235 cm^{-1} for the LAM mode, 1065, 1080 and 1117 cm^{-1} for the skeletal modes and 2855 and 2905 cm^{-1} for the stretching modes. The value of the pseudo-LAM frequency is smaller than that of the micellar isotropic phase of the previous sample. This could indicate that the kinks in the chains are not in the same position. The spectrum is presented in figure 8 (*a*) and is apparently identical to that of the micellar liquid phase where the molecules form spherical micelles except that the CH stretching modes are more intense in the micellar phase when compared with the CH twisting mode, for example. These differences could be an argument for the existence of an isotropic phase, but not micellar, between solid phase II and the next one. Other experiments with different techniques are necessary to elucidate this point.

At 298 K a new transition occurs, with the LAM mode at 230 cm^{-1}. This frequency corresponds to an intermediate frequency between the mode of an ordered
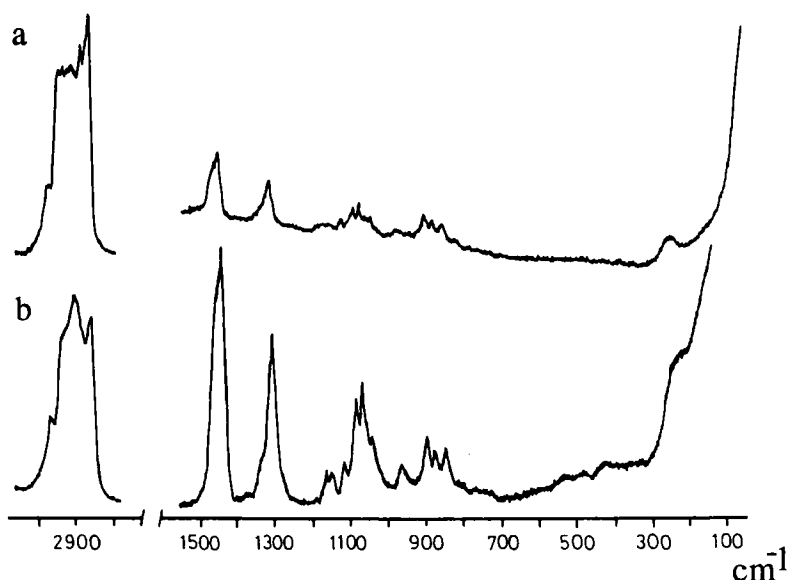
M. Picquart *et al.*

Figure 8. Raman spectrum of (*a*) the isotropic intermediate phase at 284 K and (*b*) the hexagonal phase at 265 K.

chain and the mode of a disordered chain as observed in liquid *n*-alkanes. The skeletal modes are at 1066, 1081 and 1115 cm^{-1} and the CH stretching modes at 2854 and 2896 cm^{-1}, their intensity ratio is nearly 1. This phase is not isotropic when it is observed between crossed polarizers. The Raman spectrum is shown in figure 8 (*b*). We have observed such a phase [21] for SDS and it was a hexagonal phase (H$_\alpha$). In this case it would be made of cylindrical micelles of molecules with their chains toward the centre. These micelles are parallel and their axes form a hexagonal structure. This phase is different from the coagel phase where the chains form a bilayer and are in a hexagonal array in each layer. Rizzatti and Gault [10] have observed this hexagonal phase by optical microscopy.

At 312 K the sample has a last transition to an isotropic phase (micellar phase) analogous to that presented in figure 6 (*a*) with a broad band at 245 cm^{-1} for the LAM which corresponds to the frequency of a disordered chain of 12 carbon atoms and peaks at 1070, 1080 and 1115 cm^{-1} for the skeletal modes and at 2855 and 2905 cm^{-1} for the CH stretching modes. Cooling the sample, at 311 K, it exhibits a transition from the isotropic liquid phase to the non-isotropic hexagonal phase shown in figure 8 (*b*). At 298 K it goes to the isotropic phase shown in figure 8 (*a*), and at 274 K it exhibits a transition to the coagel phase also observed on the previous sample (see figure 6 (*b*)). The CH$_2$ peak height ratio is then 1·3, finally, it passes to solid phase I at 254 K.

The I(as)/I(s) peak height ratio of samples containing 44–48 per cent DACl are not given here. Their behaviour is quite identical to that of the sample containing 39 per cent DACl when it is heated. We have a first transition to solid phase II at 262 K, then a transition to the intermediate isotropic phase at 280 K instead of 286 K, a transition to the non-isotropic hexagonal phase (H$_\alpha$) at 289 K instead of 298 K and to the micellar phase at 353 K instead of 312 K.

When the sample is cooled, the hexagonal phase appears at 345 K instead of 311 K, the intermediate isotropic phase at 296 K (instead of 298 K), the coagel phase at 273 K (instead of 274 K) and solid phase I at 254 K. There is no difference between these last two samples and the previous one. Contrary to Rizzatti and Gault [10] we do not observe a nematic phase on the last two samples.

3.1.3. *Samples with 50 per cent, or more, DACl*

The I(as)/I(s) peak height ratio is given in figure 9. For these samples, we observe solid phase I until 259 K, from 259 to 288 K we have solid phase II. At 288 K the isotropic liquid micellar phase appears until higher temperatures. When cooling the sample, a phase appears at 310 K. The CH stretching region looks like that shown in figure 8 (*b*), however it seems that the spectrum is globally less intense and that the I(as)/I(s) peak height ratio is nearly 1. The sample passes from a disordered liquid phase to a partially ordered phase. It means a mixture of domains of spaghetti-like molecules coexisting with liquid-like domains or long chains containing just a few kinks. This phase is analogous to that observed for concentrated SDS solutions [21] and is called the lamellar phase (L_α), it was also observed by Rizzatti and Gault for these samples [10]. In this lamellar phase, the DACl molecules do not form a hexagonal array. The coagel phase appears at 278 K and, at 252 K, solid phase I appears.

To summarize, we list in table 1 the transition temperatures and phases for three binary solutions. These temperatures indicate the appearance of each phase. We can observe the increase of the transition temperature between the two solid phases as the concentration increases.
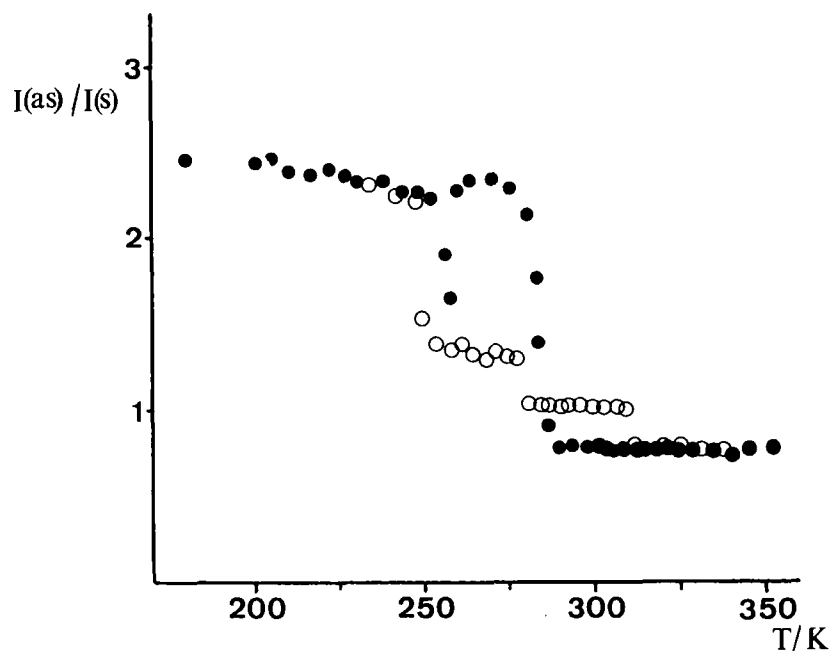

Figure 9. I(s)/I(as) peak height ratio versus temperature for the solution containing 50 per cent DACl.

Table 1.   Transition temperatures for three binary solutions (C_1 = solid phase I; C_2 = solid phase II; M.I. = micellar isotropic; H_α = hexagonal; L_α = lamellar). Temperatures are the outset of the indicated phase.

Concentration	Transition temperatures and phases
20·2 per cent	77 K ⟶ 255 K ⟶ 284 K ⟶
	C_1 C_2 M.I.
	⟵ 260 K ⟵ 270 K ⟵
	C_1 Coagel
39 per cent	77 K ⟶ 257 K ⟶ 286 K ⟶ 298 K ⟶ 312 K ⟶
	C_1 C_2 Isotropic H_α M.I.
	⟵ 254 K ⟵ 274 K ⟵ 298 K ⟶ 311 K ⟵
	C_1 Coagel Isotropic H_α
50 per cent	77 K ⟶ 259 K ⟶ 288 K ⟶
	C_1 C_2 M.I.
	⟵ 252 K ⟵ 278 K ⟵ 310 K ⟵
	C_1 Coagel L_α

3.2. Ternary aqueous solutions

3.2.1. Samples with 20 per cent of DACl and 2 per cent of NH₄Cl

At 77 K the sample has solid phase I observed for the binary solutions (see figures 1 (a), 2 (a), 3 (a) and 4 (a)). We do not observe any important change in the frequency of the modes.

In figure 10 we show the I(as)/I(s) peak height ratio plotted against temperature for this sample. As in the binary solutions, several discontinuities are observed corresponding to structural phase transitions. Black triangles indicate increasing temperature and open triangles denote cooling the sample from nearly 350 K. On heating the sample we observe, at 252 K, the first transition to solid phase II identical to that of the binary solutions. At 285 K the sample goes to the micellar liquid phase shown in figure 6 (a). On cooling the sample, the micellar phase exists until 277 K, where the coagel phase is formed (see figure 6 (b)) and at 260 K the sample passes to solid phase I. The behaviour of this sample is quite identical to that containing 20·2 per cent DACl without salt, described in the previous section.

3.2.2. Samples with 34–38 per cent DACl and 3·4–3·8 per cent NH₄Cl

We have studied two samples in this concentration range. Both have the same behaviour, and we present only the results for the sample with 38 per cent DACl. The sample with 34 per cent DACl has only a shift of 1 or 2 K in the transition temperatures.

As it can be seen in figure 11, from 77 to 258 K the sample is in solid phase I, then it transforms to solid phase II until 293 K. At this temperature the sample is in the isotropic, micellar liquid phase. On cooling the sample from the micellar liquid phase, this phase is observed until 293 K where a new phase appears. The spectrum between
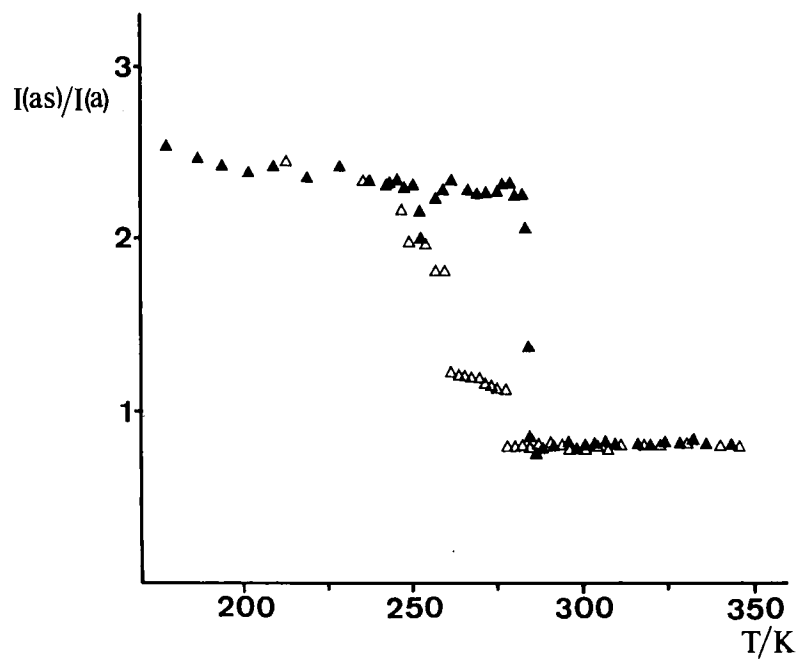
Figure 10.   I(as)/I(s) peak height ratio versus temperature for the solution containing
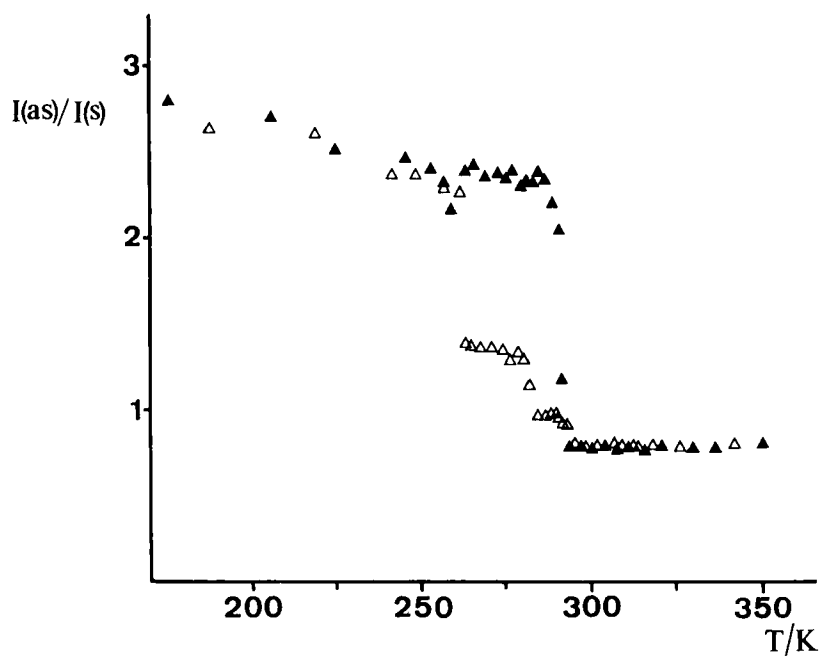20 per cent DACl and 2 per cent NH_4Cl.

Figure 11.   I(as)/I(s) peak height ratio versus temperature for the solution containing
34·7 per cent DACl and 3·47 per cent NH_4Cl.

50 and 1500 cm^{-1} apparently does not change, but little change is observed in the CH stretching region: the band at 2850 cm^{-1} collapses and the antisymmetric CH stretching mode is shifted to 2900 cm^{-1}. Zerbi *et al.* [37] have shown that introducing gauche defects into the chain the CH$_2$ antisymmetric mode shifts towards higher frequency, loses intensity and broadens. This broad band near 2900 cm^{-1} can be seen as composed of two bands, one due to trans segments at lower frequency and the other due to gauche conformers at higher frequency. The shift of the maximum is due to the relative proportion of each components. The I(as)/I(s) ratio is now 0·97 (see figure 12 (a)). This structure stays until the temperature reaches 282 K where the coagel phase is observed. At 262 K it passes to solid phase I. The structure observed between 293 and 282 K is supposed to be the nematic, discotic phase (N$_D$) which has been observed previously for these ternary compounds [9, 10]. This phase is only observed on cooling this sample.
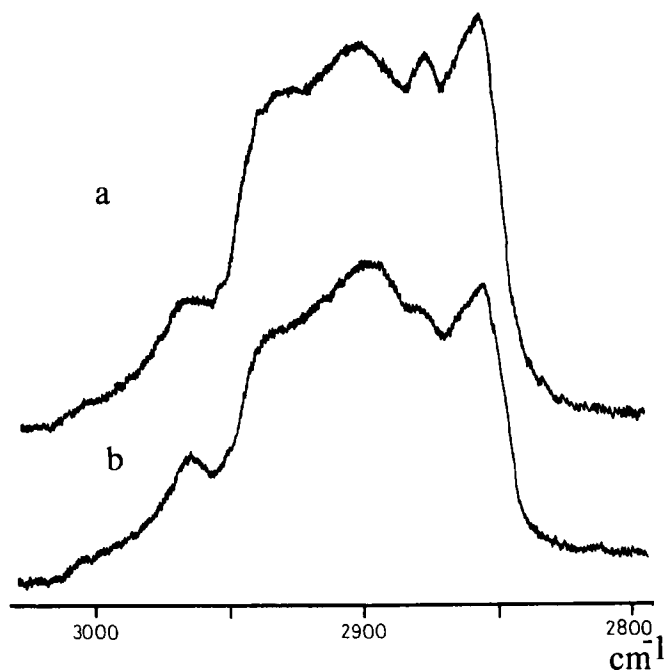

Figure 12.   Raman spectrum in the CH stretching region of (a) the nematic discotic phase and (b) the lamellar phase.

3.2.3. *Sample with 45·3 per cent in DACl and 4·53 per cent NH$_4$Cl*

The I(as)/I(s) peak height ratio is presented on the figure 13, we note solid phase I from 77 to 262 K, then solid phase II from 262 to 293 K. Then from 293 to 325 K a new phase appears, the CH stretching region of which is shown on figure 12 (b). In this phase the antisymmetric mode is at 2895 cm^{-1}. Comparing with the nematic phase, and according to Zerbi *et al.* [38] it seems that the samples have more trans segments in this phase. It is the lamellar phase as observed by Holmes and Charvolin [9] and by Rizzatti and Gault [10].

Then from 325 to 340 K we have the nematic phase observed in the previous sample and for temperatures higher than 340 K we have the micellar liquid phase. On cooling the sample the nematic phase appears at 338 K, then at 323 K another phase
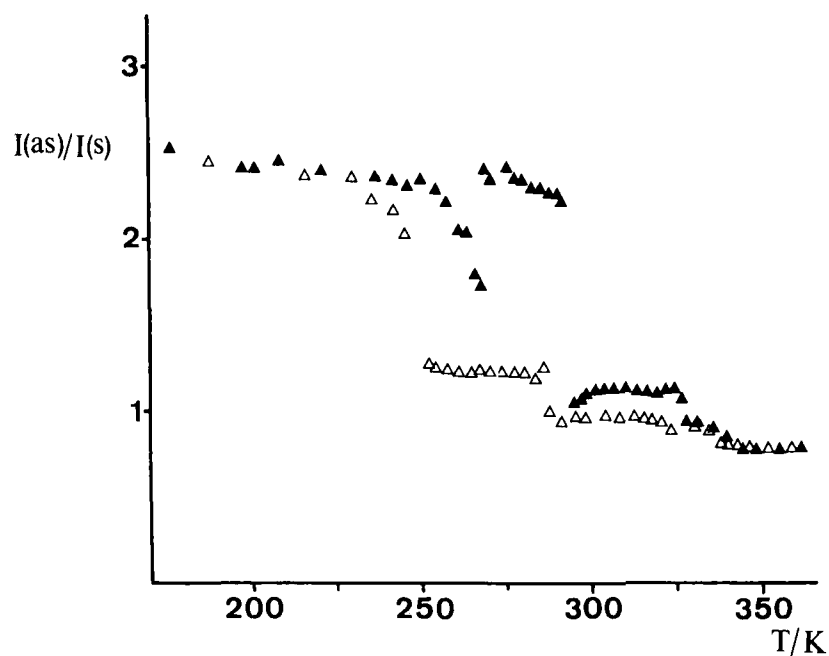
Figure 13. I(as)/I(s) peak height ratio versus temperature for the solution containing 45·3 per cent (DACl and 4·53 per cent NH₄Cl.

Table 2. Transition temperatures for four ternary solutions (N_D = nematic discotic; ? = unknown phase). Temperatures are the outset of the indicated phase.

Concentration	Transition temperatures and phases
20 per cent 2 per cent	77 K ⟶ 252 K ⟶ 285 K ⟶ 　　C_1　　　　　C_2　　　　M.I. ⟵ 260 K ⟵ 277 K ⟵ 　　C_1　　Coagel
38 per cent 3·8 per cent	77 K ⟶ 258 K ⟶ 293 K ⟶ 　　C_1　　　　　C_2　　　　M.I. ⟵ 262 K ⟵ 282 K ⟵ 293 K ⟵ 　　C_1　　Coagel　　N_D
45 per cent 4·5 per cent	77 K ⟶ 262 K ⟶ 293 K ⟶ 325 K ⟶ 340 K ⟶ 　　C_1　　　C_2　　　L_x　　　N_D　　M.I. ⟵ 248 K ⟵ 286 K ⟵ 323 K ⟵ 338 K ⟵ 　　C_1　　Coagel　　　?　　　N_D
50 per cent 5 per cent	77 K ⟶ 255 K ⟶ 289 K ⟶ > 350 K ⟶ 　　C_1　　　C_2　　　　L_x　　　　M.I. ⟵ 192 K ⟵ 271 K ⟵ 　　C_1　　Coagel

appears which seems intermediate between the nematic and the lamellar phases; it is therefore quite difficult to characterize it. Then the coagel phase appears at 286 K and at 248 K solid phase I. For this sample the nematic phase is observed either by heating or by cooling the sample.

3.2.4. *Sample with more than 50 per cent DACl and 5 per cent NH₄Cl*

The I(as)/I(s) peak height ratio is not shown here because it does not present any peculiar features. We observe solid phase I between 77 and 255 K, solid phase II until 289 K and a lamellar phase (L_α) until temperatures higher than 350 K. On cooling the sample the coagel phase appears between 271 and 192 K where the sample passes into solid phase I, instead of 252 K without salt. We do not observe the nematic phase for this sample.

To summarize, we give in table 2 the transition temperatures and phases for four different ternary mixtures. As we can see the salt strongly modifies the phases in the 38 to 45 per cent samples. It prevents the existence of the intermediate isotropic phase and the hexagonal phase and generates a nematic discotic phase.

4. Conclusion

We have studied the Raman spectrum of each phase of two series of aqueous solutions of DACl with or without addition of salt. We can see that the added salt is the cause of modifications to the phase diagram. This is probably due to a modification of the interaction between the polar head groups. At the concentration studied (NH_4Cl weight/DACl weight $= 1/10$), the salt prevents the formation of the hexagonal phase but gives rise to a nematic phase nearly 15 K wide.

Some phases which we have found were not observed either by Holmes and Charvolin [9] or by Rizzatti and Gault [10]. In particular they did not observe the two solid phases I and II because they did not work at low temperatures. From our observations and other studies [37] we concluded that solid phases I has an orthorhombic structure without interdigitation and that solid phase II is a monoclinic structure with partial interdigitation.

We have mentioned that Rizzatti and Gault [10] observed, by optical microscopy, a nematic structure on binary solutions containing 32 to 49 per cent DACl. In our experiments we do not observe such a phase. Anyhow, these authors mentioned that the nematic phase is a metastable supercooled state which persists for only several hours. Recording each spectrum after 15 min stabilization we do not observe this phenomenon. This discrepancy may probably be due to differences in the preparation of the samples and perhaps in the quality of the water used, because as we have observed, ions are required for the existence of the nematic phase. In our experiments a nematic phase is only observed on ternary compounds containing 34 to 45·5 per cent DACl, in agreement with Rizzatti and Gault [10] and Holmes and Charvolin [9].

Apparently the local environment of the molecule in the lamellar and nematic phases are nearly identical as we can see from the CH stretching modes given in figure 12. This is in agreement with the nematic discotic model and the conclusions of Holmes and Charvolin [9] on these systems. The lamellar phase could be formed by the connection of the disks. The differences between the spectra could result from the number of curved lateral parts of the discoids which need more molecules in the nematic phase. But also, as we have discussed, it seems that there are more trans segments in the lamellar phase than in the nematic phase. However it can be

a source of difficulty in the interpretation of Raman spectra of such lyotropic compounds.

The transition between the hexagonal or nematic phase and the micellar phase is progressive as we can see on the I(as)/I(s) curves. It means that there is a biphasic region nearly 5 K wide between the two phases.

Salt also increases, at a given concentration of DACl, the transition temperature between solid phase II and the upper phase. As we know, salt in solutions screens the repulsive interactions between the polar heads, this leads to a more dense structures. This is probably the reason for the destruction of the hexagonal phase by adding salt. This phase is not compatible with a small area per polar head. The same reason causes the transition temperatures to the isotropic phases to increase, more energy is necessary to disrupt the structure.

Experiments with other techniques are needed to elucidate some of the new phases which we have observed. In particular, the intermediate isotropic phase observed for binary systems could be a cubic phase or more simply a micellar phase. But also the new phase observed between 323 and 286 K for a ternary mixture could simply be a biphasic region between the micellar phase and the coagel phase or could be a structured phase which we cannot determine at the present time.

References

[1] KIND, R., BLINC, R., AREND, H., MURALT, P., SLAK, J., CHAPUIS, G., SCHENK, K. J., and ZEKS, B., 1982, *Phys. Rev.* A, **26**, 1816.

[2] LOZAR, B., BURZAR, M. I., BLINC, R., KIND, R., and AREND, H., 1982, *Solid State Commun.*, **44**, 737.

[3] SELIGER, J., ZAGAR, V., BLINC, R., ARENDAD, H., and CHAPUIS, G., 1983, *J. chem. Phys.*, **78**, 2661.

[4] BUSICO, V., CERNICCHIARO, P., CORRADINI, P., and VACATELLO, M., 1983, *J. phys. Chem.*, **87**, 1631.

[5] CHAPUIS, G., SCHENK, K., and ZUNIGA, J., 1984, *Molec. Crystals liq. Crystals*, **113**, 113.

[6] CASAL, H. L., MANTSCH, H. H., and CAMERON, D. G., 1984, *Solid State Commun.*, **49**, 571.

[7] CASAL, H. L., CAMERON, D. G., and MANTSCH, H. H., 1985, *J. phys. Chem.*, **89**, 5557.

[8] PICQUART, M., and LACRAMPE, G., 1987, *Solid State Commun.*, **62**, 73.

[9] HOLMES, M. C., and CHARVOLIN, J., 1984, *J. phys. Chem.*, **88**, 810.

[10] RIZZATTI, M. R., and GAULT, J. D., 1986, *J. Colloid Int. Sci.*, **110**, 258.

[11] WENNERSTRÖM, H., and LINDMAN, B., 1979, *Phys. Rep.*, **52**, 1.

[12] TIDDY, G. J., 1980, *Phys. Rep.*, **57**, 1.

[13] OKABAYASHI, H., OKUYAMA, M., KITAGAWA, T., and MIYAZAWA, T., 1974, *Bull. chem. Soc. Japan*, **47**, 1075.

[14] OKABAYASHI, H., OKUYAMA, M., and KITAGAWA, T., 1975, *Bull. chem. Soc. Japan*, **48**, 2264.

[15] FAIMAN, R., and LONG, D. A., 1975, *J. Raman Spectrosc.*, **3**, 371.

[16] KALYANASUNDARAM, K., and THOMAS, J. K., 1976, *J. phys. Chem.*, **80**, 1462.

[17] ROSENHOLM, J. B., STENIUS, P., and DANIELSSON, I., 1976, *J. Colloid Int. Sci*, **57**, 551.

[18] ROSENHOLM, J. B., LARSSON, K., and DINH NGUYEN, N., 1977, *Colloid Polymer Sci.*, **255**, 1098.

[19] AMORIM DA COSTA, A. M., GERALDES, C. F. G. C., and TEXEIRA-DIAS, J. C., 1981, *J. Colloid Int. Sci.*, **86**, 254.

[20] BROOKER, M. H., JOBE, D. J., and REINSBOROUGH, V. C., 1984, *J. chem. Soc. Faraday Trans. 1*, **80**, 73.

[21] PICQUART, M., 1986, *J. phys. Chem.*, **90**, 243.
[22] SNYDER, R. G., HSU, S. L., and KRIMM, S., 1987, *Spectrochim. Acta* A, **34**, 395.
[23] SNYDER, R. G., and SCHERER, J. R., 1979, *J. chem. Phys.*, **71**, 3221.
[24] ABBATE, S., ZERBI, G., and WUNDER, S. L., 1982, *J. phys. Chem.*, **86**, 3140.
[25] SNYDER, R. G., STRAUSS, H. L., and ELLIGER, C. A. 1982, *J. phys. Chem.*, **86**, 5145.
[26] LIPPERT, S. L., and PETITCOLAS, W. L., 1972, *Biochim. biophys. Acta*, **282**, 8.
[27] SNYDER, R. G., SCHERER, J. R., and GABER, B. P., 1980, *Biochim. biophys. Acta*, **601**, 47.
[28] GABER, B. P., and PETITCOLAS, W. L., 1977, *Biochim. biophys. Acta*, **465**, 260.
[29] VELLIN, N., and LEVIN, I. W., 1977, *Biochim. biophys. Acta*, **489**, 177.
[30] SPIKER, R. C., and LEVIN, I. W., 1976, *Biochim. biophys. Acta*, **433**, 457.
[31] BULKIN, B. J., and KRISHNAMACHARI, N., 1972, *J. Am. chem. Soc.*, **94**, 1109.
[32] WONG, P. T. T., and MANTSCH, H. H., 1983, *J. phys. Chem.*, **87**, 2436.
[33] RADLEY, K., and SAUPE, A., 1978, *Molec. Crystals liq. Crystals*, **44**, 227.
[34] WONG, P. T. T., and WHALLEY, E., 1976, *J. chem. Phys.*, **65**, 829.
[35] MINONI, G., and ZERBI, G., 1986, *J. phys. Chem.*, **86**, 4791.
[36] MINONI, G., ZERBI, G., and RABOLT, J. F., 1984, *J. phys. Chem.*, **81**, 4782.
[37] ZERBI, G., MAGNI, R., GUSSONI, M., MORITZ, K. H., BIGOTTO, A., and DIRLIKOV, S., 1981, *J. chem. Phys.*, **75**, 3175.
[38] ZERBI, G., RONCONE, P., LONGHI, G., and WUNDER, S. L., 1988, *J. chem. Phys.*, **89**, 166.