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## Liquid Crystals

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### Deuterium and potassium-39 N.M.R. and optical microscopy of the dipotassium hexadecanedioate-water mesophases

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## Deuterium and potassium-39 N.M.R. and optical microscopy of the dipotassium hexadecanedioate-water mesophases

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Mixtures of the dipotassium salt of thapsic acid (dipotassium hexadecanedioate,  $\text{KOO}(\text{CH}_2)_{14}\text{COOK}$ ) and water exhibit lyomesophases at disoap concentrations between 40 and 65 wt % and temperatures above *c.* 50°C. The phase diagram of this system has been studied by deuterium and potassium-39 N.M.R., and by optical microscopy. Mixtures of the disoap and water were studied as a function of concentration and temperature, in ordinary bulk samples, and in rectangular cells packed with parallel glass plates to allow measurements on oriented samples. The main features of this system are: between *c.* 40 and 55 wt % disoap, on cooling from the isotropic liquid, a single uniaxial phase appears with  $\Delta\chi > 0$ , while cooling solutions with disoap concentrations between 55 and 65 wt %, yield two phases separated by a first order transition; a high temperature phase (HTP) with  $\Delta\chi < 0$ , and a low temperature phase (LTP) with  $\Delta\chi > 0$ . The latter phase is identified with that observed at lower disoap concentrations. On heating the more concentrated solutions (> 55 wt %) an additional phase appears at the boundary between the LTP and HTP which is optically isotropic and exhibits single deuterium and potassium-39 N.M.R. peaks. It is suggested that the HTP is lamellar and corresponds to the phase studied earlier by Gallot. The LTP appears to have a two dimensional structure similar to the middle phase of monosoaps, while the intermediate isotropic mesophase is most likely cubic. The N.M.R. splitting pattern of the aliphatic deuterons is quite different to that found in monosoaps, and is discussed in terms of possible conformations of the disoap molecules within the mesophases.

### 1. Introduction

A considerable amount of work has been published on the anhydrous and hydrated mesophases of the alkali monocarboxylic soaps [1]. These systems are characterized by a high degree of polymorphism exhibiting a variety of phases with lamellar, hexagonal and even cubic structures. Much less work was done on the dialkali salts of  $\alpha,\omega$ -dicarboxylic acids and their lyomesophases. In both forms these disoaps are reported to exhibit a single type of mesophase with lamellar structure [2-4]. In the disoap-water systems the polar groups of the amphiphile molecules form two interfaces between the hydrocarbon regions and the water layers. Low angle X-ray measurements show [3] that the thickness of the amphiphile layers is

significantly smaller than the length of the extended disoap molecules, indicating that a certain degree of disorder must be associated with the arrangement and conformation of the disoap in the mesophase.

Deuterium N.M.R. can provide information on the molecular arrangements and conformations [5, 6] in ordered systems and many investigations have been published on monosoap-water mixtures [7-9] using this technique. A closely related investigation is the study of diacids incorporated into several liquid-crystalline lamellar systems [10]. Here we present a deuterium N.M.R. study on one member of the potassium- $\alpha,\omega$ -dicarboxylate series, viz. the dipotassium hexadecanedioate (dipotassium thapsate)-water system ( $C_{16}K_2$ )  $KOOC-(CH_2)_{14}-COOK$ . The purpose of the study is to construct the phase diagram and deduce as much as possible about the structure and ordering of the various phases. The deuterium measurements were made on solutions of the isotopically normal disoap dissolved in  $D_2O$ , as well as on solutions of various deuterated  $C_{16}K_2$  species in  $H_2O$ . Additional information was obtained from potassium-39 N.M.R. of the potassium ions and from optical microscopy observations on the same system. The low sensitivity of the potassium N.M.R. signal renders its application more difficult and so far has been applied to very few lyotropic systems [11, 12].

Before presenting the results we briefly comment on the basic principles of quadrupolar nuclei (such as  $^2H$  and  $^{39}K$ ) N.M.R. in liquid-crystalline mesophases. We limit the discussion to uniaxial systems, and refer to [13] for a more general discussion. The N.M.R. spectrum of a quadrupolar nucleus with spin  $I$  in a single uniaxial domain consists of  $2I$  peaks centred around the Larmor frequency. This corresponds to a 1:1 doublet for the deuteron ( $I = 1$ ), and a 3:4:3 triplet for  $^{39}K$  ( $I = 3/2$ ). The splitting between neighbouring transitions of the multiplet in frequency units is given by

$$\begin{aligned}\Delta\nu &= \frac{3(e^2qQ/h)}{2I(2I-1)} \langle F(\alpha\beta\gamma) \rangle \frac{1}{2} (3\cos^2\theta - 1) \\ &= \frac{1}{2} \nu_Q (3\cos^2\theta - 1),\end{aligned}$$

where  $e^2qQ/h$  is the principal component of the quadrupole interaction tensor in the molecular frame,  $\theta$  is the angle between the director and the magnetic field and  $\langle F(\alpha\beta\gamma) \rangle$  is a parameter which depends on the average orientation of the principal quadrupolar tensor with respect to the molecular axes and on the motional constants of the particular species [13, 14]. When fast isomerization or other dynamical processes take place further averaging is required over the various internal motions. The principal axes of the deuterons in  $D_2O$  can be identified in a straightforward manner, since the molecule is highly symmetric and rigid, but because of the low symmetry of the  $C_{16}K_2$  molecule and the possibility of having several conformational isomers this is not as simple for the disoap species. For potassium-39 the quadrupolar tensor in a lyomesophase results from small distortions of the hydration sphere due to various interactions with the amphiphile molecules. Consequently its magnitude and direction cannot in general be determined in such systems. The analysis of the N.M.R. results will therefore mainly involve phenomenological characterization of the mesophases, and the discussion of the molecular ordering will only be qualitative.

## 2. Experimental

### 2.1. Materials

The various isotopic species of dipotassium thapsate were prepared from the corresponding thapsic acid by neutralization with potassium hydroxide in ethanol, followed by precipitation with ether and drying under vacuum at 100°C to constant weight. Isotopically normal acid was obtained commercially. The  $\alpha$ -deuteriated acid was prepared from normal thapsic acid by base catalysed exchange with D<sub>2</sub>O at 200°C in a stainless steel bomb for 4 days, followed by neutralization with DCl [15]. Two samples of perdeuteriated acids were obtained from CEA Service des Isotopes Stables, CEN, Saclay. Their deuteration levels, as determined by N.M.R., was 46 and 90 at. %. Proton N.M.R. of these species, dissolved in trifluoroacetic acid, shows that the deuterium labelling is not evenly distributed along the chain. This is particularly apparent in the sample with 46 per cent deuteration where the  $\alpha$ -methylene was found to be significantly more enriched with deuterium than the rest of the methylene groups. The various deuteriated disoap species will be referred to as C<sub>16</sub>K<sub>2</sub>-*d* <sub>$\alpha$</sub> , C<sub>16</sub>K<sub>2</sub>-*d*<sub>46</sub> and C<sub>16</sub>K<sub>2</sub>-*d*<sub>90</sub>, respectively. Combustion analysis of the isotopically normal C<sub>16</sub>K<sub>2</sub> gave hydrogen and carbon contents to within 0.3 percent of the expected values. The potassium content, as determined by gravimetric analysis, was about 3 per cent below the stoichiometric ratio.

The optical microscopy observations were made using a Zeiss Universal polarizing microscope equipped with a Mettler FP52 hot stage. The samples were contained in 2 × 0.1 mm rectangular capillaries, inserted into 4 × 0.4 mm capillaries which were flame sealed, or directly in flame sealed 4 × 0.2 mm capillaries.

### 2.2. Sample preparation

Solutions of the disoap were prepared by mixing weighed amounts of dry C<sub>16</sub>K<sub>2</sub> with H<sub>2</sub>O or D<sub>2</sub>O and allowed to equilibrate at around 140 to 160°C for several days. The concentration of the solutions is expressed in wt % defined as 100 × (weight of C<sub>16</sub>K<sub>2</sub>)/(weight of C<sub>16</sub>K<sub>2</sub> + weight of water). Two types of samples which we refer to as bulk and plate were used. The bulk samples were prepared in flame sealed 9 mm o.d. vials. The plate samples consisted of square (7 × 7 mm) glass tubes containing stacks (22 mm high) of 50 to 55 glass plates (cut from microscope coverglasses of approximately 0.1 mm thickness). The mixtures were prepared in the small void above the plates and then carefully flame sealed. To check for any change in composition, weights were taken before and after sealing. The sealed cells were then heated to the isotropic phase to allow the material to flow into the interplate spaces. The samples were rigidly fitted into 10 mm N.M.R. tubes and attached to a home-built goniometer for rotation experiments.

### 2.3. N.M.R. measurements

N.M.R. measurements were performed on Bruker AM 400 and CXP 300 spectrometers operating respectively at 61.43 and 46.07 for deuterium and at 18.7 and 14.0 MHz for potassium-39. Usually, single pulses were used for both nuclei. Some of the deuterium spectra of the labelled disoaps were recorded by the quadrupole echo method [16]. Up to 500 accumulations were required for the deuterium signal of D<sub>2</sub>O, while for the signals from the deuteriated soap this figure was well over 1000. The potassium-39 spectra were recorded by single, short pulses (25  $\mu$ s). The repetition time ranged between 0.04 to 0.2 s. About 10 000 or more scans were required to obtain reasonable signal-to-noise ratios.

Several deuterium experiments were performed in which the samples were rotated with respect to the magnetic field. These were performed with a home-made goniometer on a Bruker WH 90 or a BKR 322S spectrometer which employs resistive magnets, allowing easy rotation of the sample tube with respect to the magnetic field in the normal experimental configuration.

The temperature was adjusted using a precalibrated Bruker B-ST 100/700 temperature control unit. The accuracy of the temperature readings is estimated to be  $\pm 1^\circ\text{C}$ . The usual procedure was first to heat the sample within the magnetic field of the N.M.R. spectrometer into the isotropic phase (or at high soap concentrations, to around  $160^\circ\text{C}$ ) followed by slow cooling ( $\sim 0.5^\circ\text{C}$  per minute) to the desired temperature. As discussed later the results depended somewhat on the history of the sample.

### 3. Results and interpretation

The N.M.R. measurements were performed on disoap-water systems containing between 40 and 65 wt %  $\text{C}_{16}\text{K}_2$  in water. Below 40 wt % disoap no mesophase was found, as evidenced by the lack of splitting of the  $\text{D}_2\text{O}$  signal. We first describe deuterium N.M.R. measurements performed on solutions of isotopically normal  $\text{C}_{16}\text{K}_2$  in  $\text{D}_2\text{O}$ , where the solvent signal was studied in both bulk and plate samples. These results enabled us to construct a phase diagram for the system and to study the alignment of the mesophases with respect to the magnetic field. Similar, although less extensive, measurements were made on potassium-39. The results of these measurements are in general agreement with those of the water deuterons and they substantiate the phase diagram derived from the latter. We then describe deuterium N.M.R. measurements on solutions of deuteriated  $\text{C}_{16}\text{K}_2$ , which provide some information on the ordering of the disoap molecules in the various phases.

#### 3.1. Deuterium spectra of solvent $\text{D}_2\text{O}$ in bulk samples

Examples of deuterium N.M.R. spectra obtained by slowly cooling bulk samples of normal  $\text{C}_{16}\text{K}_2$  in  $\text{D}_2\text{O}$  from the isotropic phase are shown in figure 1. It can be seen

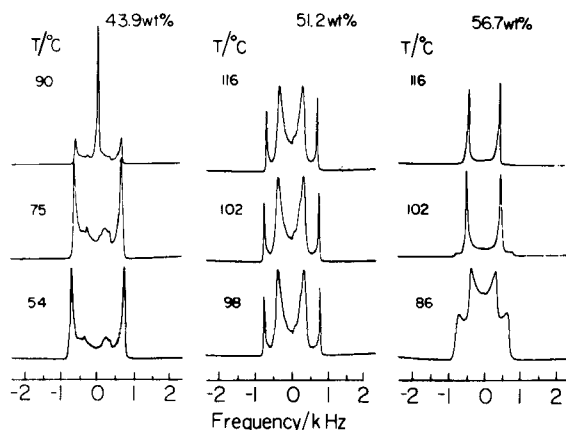


Figure 1. Deuterium N.M.R. spectra (at 46 MHz) in the mesophase region of the  $\text{C}_{16}\text{K}_2$ - $\text{D}_2\text{O}$  system at the temperatures and concentrations indicated. The solutions were contained in bulk samples and allowed to cool within the magnetic field from the isotropic liquid.

that at low concentrations (cf. sample with 43.9 wt % disoap) a biphasic, isotropic-mesophase, region is first obtained followed on further cooling by a region whose spectrum is dominated by a sharp doublet due to well ordered domains and a weaker powder-like signal. At higher disoap concentrations the fraction of the powder spectrum increases and eventually becomes predominant (cf. the centre column and the bottom trace from the right-hand column in figure 1). Sample rotation experiments indicate that the strong doublet represents the parallel features of a uniaxial phase whose director aligns parallel to the magnetic field (i.e.  $\Delta\chi > 0$ ). However once aligned the sample does not realign after rotating it in the magnetic field. The sharp features of the powder-like component are separated by exactly one-half the splitting of the main doublet suggesting that they correspond to the perpendicular features of disordered domains belonging to the same phase. On further cooling the sample solidifies. This is manifested by the appearance of a central isotropic  $D_2O$  peak (not shown in the figure) at the expense of the mesophase spectrum. It appears therefore that solidification is accompanied by phase segregation into a solid (perhaps hydrated) disoap, and an isotropic micellar solution.

When the concentration of the disoap is increased to above 55 wt %, two different mesophases are observed on cooling; a high temperature phase (HTP) which gives rise to a sharp doublet, and a low temperature phase (LTP) which gives rise to a powder-like spectrum. The latter phase is identified with that observed in the more dilute disoap solutions. The transition from the HTP to the LTP is first order as indicated by the discontinuous change in the lineshape and by the presence of a biphasic region (cf. the centre trace in the right hand column of figure 1). Rotation experiments on the HTP indicate that this phase is also uniaxial but contrary to the LTP aligns perpendicular to the magnetic field, i.e.  $\Delta\chi < 0$ . Based on these assignments, the  $v_Q$ s, of the  $D_2O$  signal in the various solutions were determined. The results for a number of mixtures as a function of temperature are plotted in figure 2. It is noted that for solutions with less than 55 wt %  $C_{16}K_2$  the splitting varies monotonically with temperature while in solutions with more than 55 wt % disoap the  $v_Q$  plots exhibit a discontinuous change corresponding to the HTP to LTP transition (cf. the curve for the 56.7 wt % solution).

The temperature dependence (cf. figure 2) of  $v_Q$  within the LTP varies with the concentration of the disoap; below 55 wt % it decreases with increasing temperature, while at higher concentrations the effect is opposite and in the intermediate region ( $\sim 55$  wt %)  $v_Q$  passes through a maximum. The temperature dependence of  $v_Q$  reflects a number of competing effects such as the change of the overall ordering of the phase and redistribution of water molecules between several hydration sites with different orientational characteristics. Depending on the orientation and on the fractional population of the  $D_2O$  molecules in these sites,  $v_Q$  can vary over wide ranges and can be positive or negative. Because of the fast diffusion of the water between different sites only a single doublet is observed with  $v_Q$  values representing the weighted average of the splittings in the various sites [17]. There are insufficient data, however, to allow a quantitative analysis of these complex equilibria.

From results of the type depicted in figures 1 and 2 the phase diagram shown in figure 3 was constructed. It shows, in addition to the HPT and LTP regions, also biphasic regions consisting of the isotropic and either the LTP or HTP, as well as a region where both mesophases (HTP and LTP) coexist. The boundary between the LTP and solid is indicated by a dotted area. It was determined by the disappearance of the LTP signal and the appearance of an isotropic peak caused by segregation of

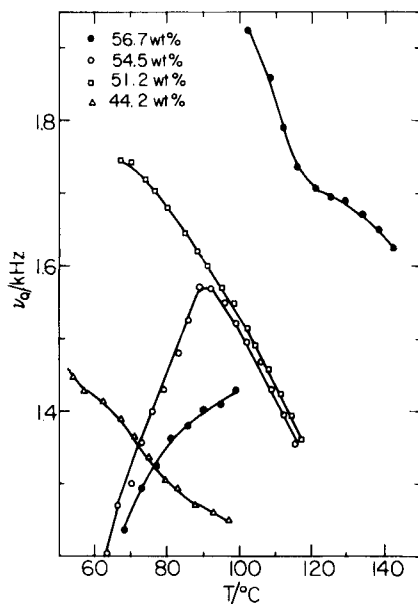


Figure 2. The average deuterium quadrupolar interaction in the mesophase region of a number of  $C_{16}K_2$  solutions in  $D_2O$  as a function of temperature. Note that  $\nu_Q$  is plotted and not the observed splitting.

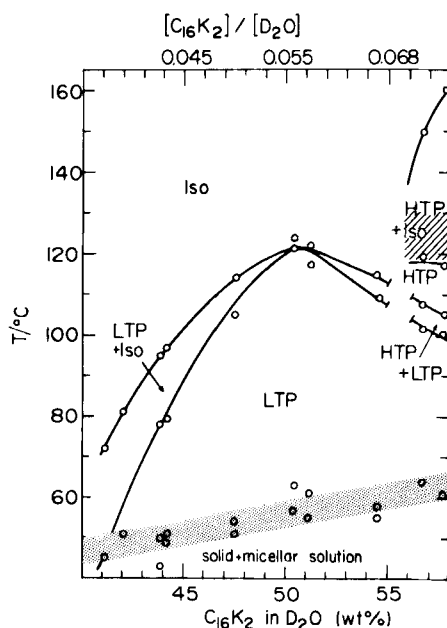


Figure 3. The phase diagram of the  $C_{16}K_2$ - $D_2O$  system as determined from the solvent  $D_2O$  N.M.R. results of the type shown in figures 1 and 2. The cross hatched area corresponds to the region in which the cubic phase appears.

the latter into a solid and an isotropic micellar solution. This transition occurs over a temperature range of about 5°C. From the phase rule this boundary should be sharp and at constant temperature over the composition coordinate, contrary to the experimental observations. The discrepancy may, in part, be due to supercooling but results more likely from the presence of some impurities, in particular a small amount of unneutralized acid. It is also possible that several different solid phases are formed, corresponding to different disoap hydrates.

The phase diagram in figure 3 was derived from experiments in which the solutions were cooled from the isotropic liquid into the mesophase region. The behaviour is, however, not exactly reproducible on heating. In addition to some supercooling (or superheating) across the phase transitions we have observed that in solutions which exhibit the HTP (i.e. above ~55 wt % disoap) heating of the LTP results in what appears to be an isotropic mesophase. This is evidenced by the appearance of a singlet within the temperature range of the liquid-crystalline region, as shown in figure 4. The spectra in the left-hand column were obtained on cooling the sample from the isotropic liquid. The top three traces are due to the HTP and exhibit spectra of a relatively well aligned sample, and a central peak due to a small amount of isotropic liquid. The bottom trace is a powder spectrum of the LTP which, at this concentration, is not orientated by the magnetic field. Upon heating the sample back into the HTP (see traces on the right-hand side of figure 4) a single peak appears which at

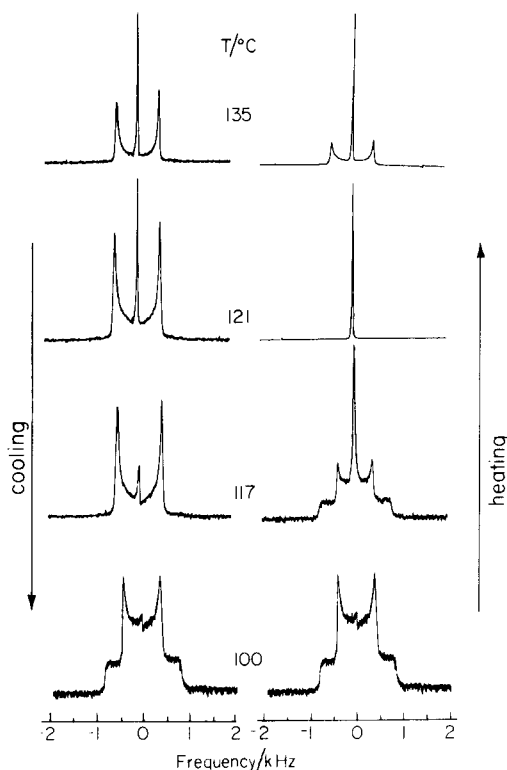


Figure 4. Deuterium N.M.R. spectra (at 13.82 MHz) in the mesophase region of a 57.8 wt %  $C_{16}K_2$  solution in  $D_2O$ . The spectra in the left-hand column were obtained by slow cooling a bulk sample from the isotropic liquid down to 100°C. Those in the right-hand column were obtained upon heating back to the isotropic liquid.



approximately 120°C is the only one in the spectrum. This peak is apparently due to an intermediate cubic phase since on further heating, the signals of the HTP reappear. Subsequent experiments showed that this peak sometimes also occurs on cooling. The cross hatched area in figure 3 represents the region at which this isotropic phase appears. Insufficient data were, however, available to map exactly the contact region of the HTP, LTP and isotropic phases, hence the gap in the phase diagram in this region.

Observations with a polarizing microscope are consistent with the phase diagram derived from the N.M.R. results and provide some indication of the possible structure of the various phases. Examples of pictures taken on heating a sample containing 60 wt % C<sub>16</sub>K<sub>2</sub> are shown in figure 5. The bottom part, taken at 104°C, corresponds to the LTP and shows typical fan-like structures of the type often found in the middle phase of monosoaps. Similar pictures for the LTP were also obtained for samples with less than 55 wt % disoap. The upper part of the figure corresponds to the same sample in the HTP (189°C). It shows oily streaks and clover-leave structures characteristic of lamellar phases. In the intermediate region (centre pictures taken at 114 and 110°C) the isotropic mesophases and the transition to this phase from the LTP are shown. The lack of birefringence is consistent with the absence of a quadrupole splitting in this region.

### 3.2. Deuterium spectra of D<sub>2</sub>O plate samples

Several complementary experiments were performed with plate samples [18]. It turned out that, independent of the orientation of the magnetic field during cooling from the isotropic liquid, the HTP always aligns with the director perpendicular to the glass surface, giving well resolved doublet spectra. The angular dependence of the doublet splitting follows, very accurately, a  $\cos^2\theta$  dependence as expected for a uniaxial phase.

In the LTP region it appears that two types of domains are formed on the plates. This may be seen from the spectra depicted in figure 6. When the magnetic field is perpendicular to the glass plates (bottom trace) two sharp doublets are observed with relative splittings 2 : 1. They must therefore correspond to domains whose directors align parallel (outer doublet) and perpendicular (inner doublet) to the field direction. We may associate the former with homeotropic domains and the latter with domains aligned parallel to the glass plates in a two dimensional planar distribution. This is supported by the spectra taken with the magnetic field parallel to the glass plate (cf. the upper trace in figure 6). It shows an inner doublet, due to the homeotropically aligned domain, superposed on a powder pattern, characteristic of a two dimensional distribution. The spectral behaviour of these signals confirms the uniaxial nature of the LTP, at least within the accuracy of the N.M.R. results.

### 3.3. Potassium-39 N.M.R. in bulk samples

As indicated in the introduction some potassium-39 N.M.R. measurements were also performed on the C<sub>16</sub>K<sub>2</sub>-water system. These were made on bulk samples and the results are in general agreement with those derived from the deuterium spectra. In figure 7 are shown potassium-39 spectra of 45, 50 and 56 wt % disoap solutions in the LTP region. In the 45 wt % solution (lower trace in figure 7) in addition to the intense  $-1/2 \rightarrow 1/2$  central peak, sharp satellites due to the parallel features of the  $\pm 3/2 \rightarrow \pm 1/2$  transitions are observed (cf. the lower trace in figure 7). The

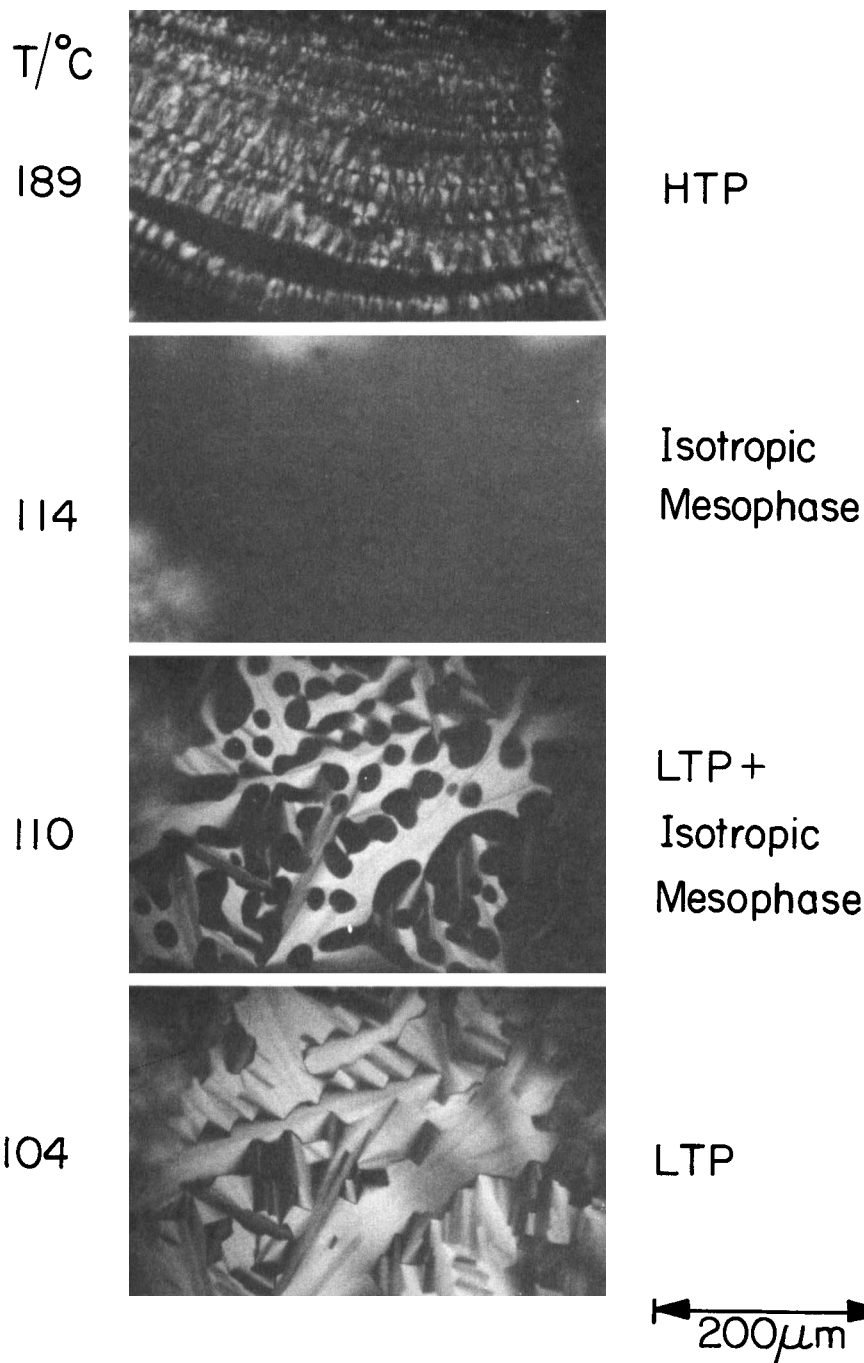


Figure 5. Optical textures of the HTP, isotropic and LTP obtained by heating a sample containing 60 wt %  $C_{16}K_2$  in  $D_2O$  to the temperatures indicated.

perpendicular features at half splitting are barely seen indicating good alignment of the LTP in this sample. In the 50 wt % solution (middle trace) the perpendicular  $\pm 3/2 \rightarrow \pm 1/2$  satellites are much more intense and the overall lineshape is consistent with a disordered sample. The pattern remains at higher concentrations of the LTP

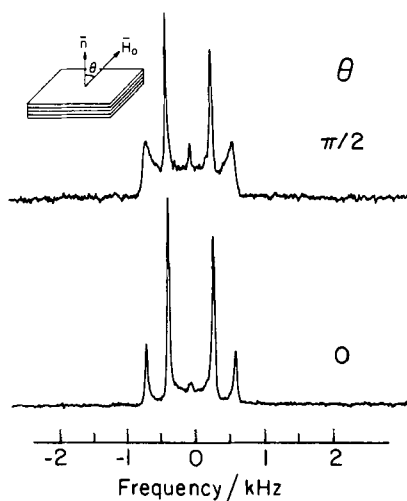


Figure 6. Deuterium N.M.R. spectra (13.82 MHz) of a glass plate sample in solutions containing 56.7 wt %  $C_{16}K_2$  in  $D_2O$  in the LTP ( $86^\circ C$ ) at orientations as indicated in the figure.

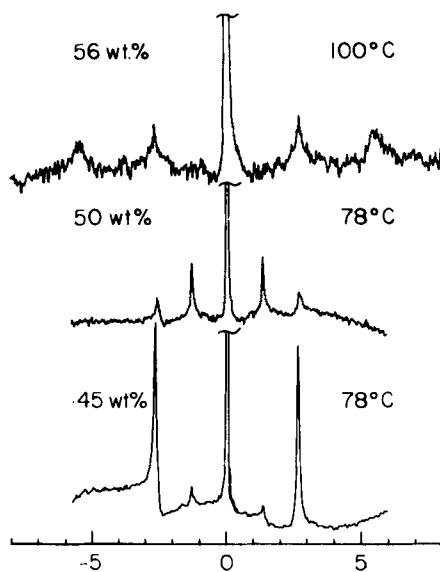


Figure 7. Potassium-39 N.M.R. spectra in the LTP region of  $C_{16}K_2$ -water mixtures at the concentrations and temperatures indicated.

as may be seen in the upper trace of figure 7; the latter spectrum corresponds to 56 wt % and was recorded at  $100^\circ C$ .

On heating samples containing more than 55 wt % disoap the transformation to the isotropic mesophase and HTP are observed. Figure 8 shows spectra for the 56 wt % solution at  $100^\circ C$ ,  $117^\circ C$  and  $138^\circ C$ . The transition to the isotropic mesophase is clearly manifested by the presence of a central narrow peak, and by the complete absence of satellites (cf. the middle trace at  $117^\circ C$ ). Further heating to the HTP results is a sharp triplet, characteristic of a well aligned sample. On cooling,

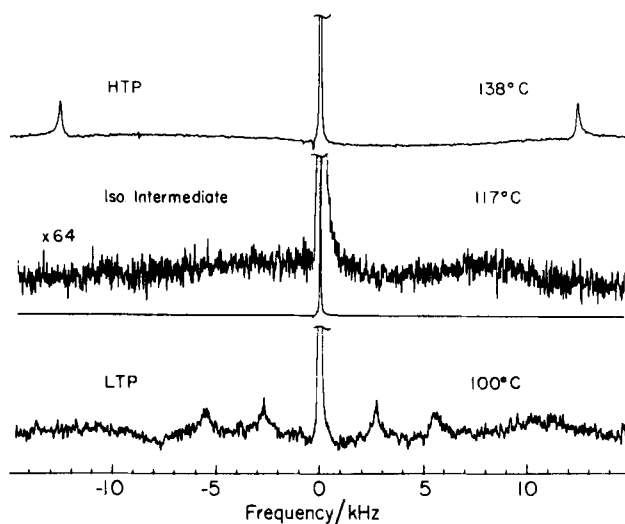


Figure 8. Potassium-39 N.M.R. spectra of a 56 wt %  $C_{16}K_2$  solution as function of temperature, obtained on heating the sample from the LTP.

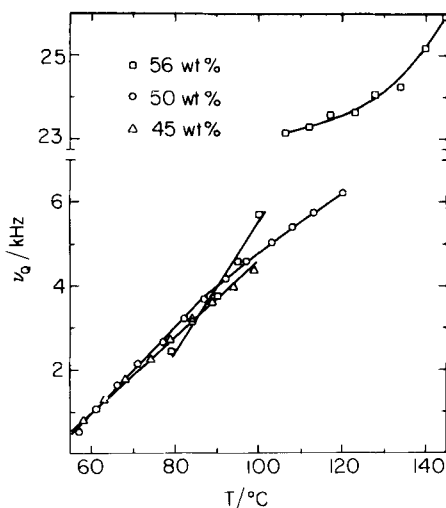


Figure 9. The potassium-39 average quadrupolar interaction parameter in the mesophase region of  $C_{16}K_2$ -water mixtures as function of temperature and concentration.

this spectrum transforms directly to that of the LTP, as was also observed for the deuterium spectra.

The average quadrupolar interaction parameter,  $\nu_Q$ , of the potassium-39 as determined from spectra of the type shown in figures 7 and 8 is plotted in figure 9 as a function of temperature. It may be seen that the LTP yields small  $\nu_Q$ s, essentially independent of the disoap concentration but strongly dependent on temperature. In the HTP the splitting is larger but the relative change of  $\nu_Q$  with temperature is much smaller. In both phases  $\nu_Q$  increases with temperature indicating that the splitting is not simply related to the degree of ordering of the mesophase.

Similar behaviour was found in the potassium oleate–water system and was interpreted in terms of multiple binding sites for the potassium ions [12].

The main features observed in the deuterium  $D_2O$  spectra of the bulk samples are well reproduced by the potassium-39 results; the appearance of a low temperature phase which is well aligned at low concentrations but becomes disordered at higher concentrations, the appearance of a well aligned high temperature phase at higher concentrations of disoap ( $> 55$  wt %), the appearance of an isotropic mesophase in the boundary region between the LTP and the HTP (usually only upon heating), and the discontinuity of the  $^{39}K$   $\nu_Q$  at the phase transition, with larger values for the HTP than for the LTP.

#### 3.4. Deuterium spectra of deuteriated $C_{16}K_2$ species

Three species of deuteriated  $C_{16}K_2$  were studied, i.e. specifically deuteriated  $C_{16}K_2-d_\alpha$  and randomly deuteriated  $C_{16}K_2-d_{46}$  and  $C_{16}K_2-d_{90}$ . We show in figure 10 examples of spectra from samples prepared from the perdeuteriated disoaps. The traces in the right-hand column are of  $C_{16}K_2-d_{46}$  bulk samples, and exhibit spectra due to a well aligned HTP and a disordered LTP. Considerably better resolution for the LTP was obtained with glass plates, as shown for a  $C_{16}K_2-d_{90}$  in the left-hand column. The most striking difference between the HTP and LTP disoap spectra is the multitude of splittings observed in the latter as compared to just two doublets in the HTP. In both spectra we have identified the outer doublet as due to the  $\alpha$ -deuterons by comparison with spectra from specifically deuteriated  $C_{16}K_2-d_\alpha$ . The strong inner doublet in the HTP spectrum must therefore correspond to all other deuterons in the molecule. In the plate sample of the LTP, six well resolved doublets are observed, one of which with double the intensity of the others. Since the  $C_{16}K_2$  molecule has seven distinct pairs of methylenes this result suggests that each of the peaks corresponds to one pair of methylenes, except for the more intense peak which corresponds to two. We have tentatively assigned the various peaks sequentially from the outer  $\alpha$ -pair towards the inner ones [7] and plotted the various  $\nu_Q$ s as function of these numbers in figure 11.

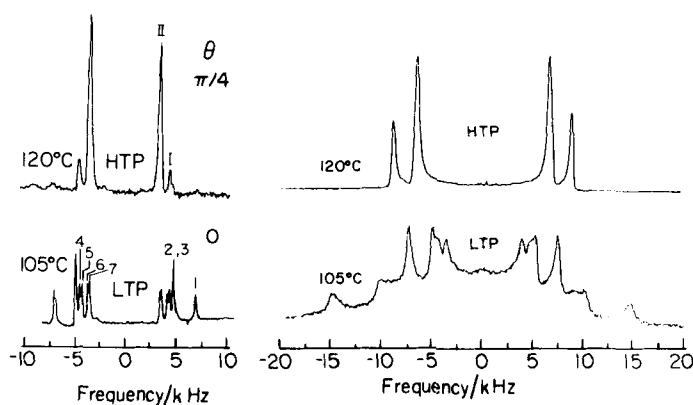


Figure 10. Deuterium N.M.R. spectra of deuteriated  $C_{16}K_2$  in  $H_2O$ . The spectra on the right-hand side are for a bulk sample containing 60.2 wt %  $C_{16}K_2-d_{46}$  in  $H_2O$  at the temperatures indicated. The spectra on the left-hand side are for a 64 wt % solution of  $C_{16}K_2-d_{90}$  in a plate sample at the temperatures and orientations indicated. The spectra on the left-hand side were recorded by single pulses, while those on the right-hand side were obtained by the quadrupolar echo method.

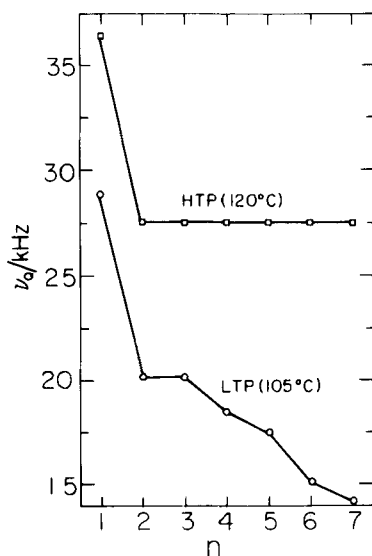


Figure 11. A plot of  $\nu_Q$  for the various peaks observed in a plate sample of a 64 wt % solution of  $C_{16}K_2-d_{90}$  in  $H_2O$ . The labelling of the peaks ( $n$ ) is as in figure 10.

We have measured the spectrum of  $C_{16}K_2-d_{46}$  in a number of bulk samples and obtained similar results to those shown in figure 10 except that the resolution in the LTP was considerably poorer, so that the 4–5 and 6–7 pairs of peaks were not resolved in most cases. The corresponding  $\nu_Q$ s for a number of solutions are plotted as function of temperature in figure 12. Based on these results a phase diagram was constructed as shown in figure 13. This diagram is in fair agreement with that obtained from the  $D_2O$  spectra (cf. figure 3) although the transition temperatures are not exactly the same. In part this may be due to the deuterium isotope effect on the

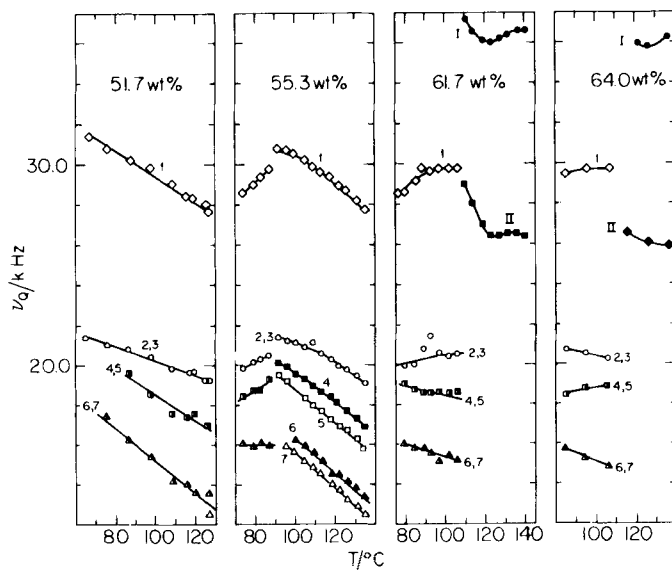


Figure 12. Plots of  $\nu_Q$  for the various deuterium signals of deuteriated  $C_{16}K_2$  species.

transition temperatures [19], but it may also be due to experimental effects such as hysteresis. At any rate it is probably less accurate than the one depicted in figure 3 because of the difference in the N.M.R. sensitivity of the  $D_2O$  signals compared with those of the  $C_{16}K_2-d$  species. Note that the deuterium results of  $C_{16}K_2-d$  in the 55.3 wt % solution (cf. figure 12) are somewhat exceptional in that they are better resolved and also appear to exhibit a small discontinuity at about  $90^\circ C$ . A similar discontinuity was observed in the 57.1 wt % solution but not in other samples. The effect may be related to the appearance of maxima in the  $\nu_Q$  plots of the  $D_2O$  signal in this concentration range (cf. figure 2).

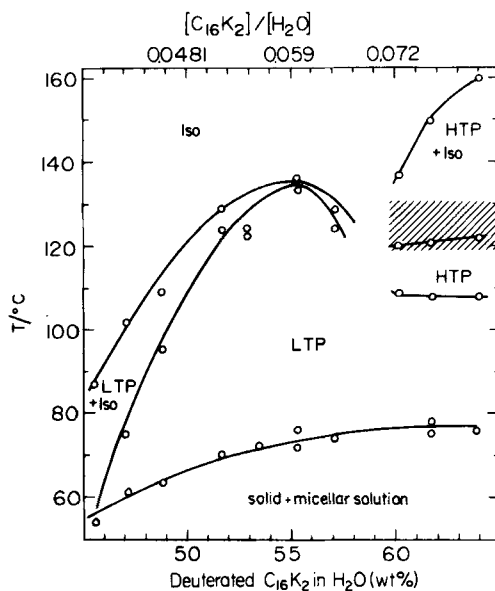


Figure 13. The phase diagram of the  $C_{16}K_2-H_2O$  system as determined from the deuterium spectra of deuterated  $C_{16}K_2$  species.

The  $\nu_Q$ s of the various  $C_{16}K_2$  deuterons in both the low and high temperature phases vary between 10 and 40 kHz. This must be compared with the splitting of a deuteron in a rigid C–D bond of *c.* 250 kHz. The reduction in the splitting reflects molecular orientational disorder, or averaging due to conformational equilibria, or a combination of both processes. The fact that all deuterons (except the  $\alpha$ s) show identical splittings in the HTP, may indicate that the disoap molecules are predominantly in the all-trans conformation, because in this state all deuterons are essentially perpendicular to the molecular long axis and should exhibit identical quadrupolar splittings. The deviation of the  $\alpha$ -deuteron splitting in this phase may reflect an intrinsically larger quadrupolar interaction of the  $\alpha$  C–D bond compared to the rest of the methylenes. Assuming free rotation of the molecules about their effective long axis and an average value of  $\nu_Q = 27$  kHz in the HTP gives for this model a molecular order parameter,  $S_{zz} \approx 0.22$ . This is quite low for a rod-like chain with 16 carbon atoms.

A more likely interpretation of the result is to assume that the reduction in the quadrupole splitting is dominated by chain melting, i.e. averaging over a distribution of chain conformations. The splitting profile in the HTP can then be explained in

terms of a dynamic equilibrium between the all-trans conformation and a series of kink conformations (sequences of the type  $t \dots tg^{\pm} tg^{\mp} t \dots t$ ). If these kinks are equally distributed along the chain we would predict [20] a constant reduction in all methylene splittings, except for the  $\alpha$ -deuterons (which can only participate partially in such conformations) as found experimentally. The real picture is probably a combination of the two mechanisms, i.e. orientational disorder of the whole molecule as well as conformational isomerism. A rough estimate of the effective length,  $\langle l \rangle$ , of the disordered disoap molecules can be made using an equation proposed by Schindler and Seelig [21]

$$\langle l \rangle = 1.25 \left[ \frac{n}{2} - \sum_{i=1}^n S_{zz}^i \right],$$

where  $n$  is the number of methylene segments [14]. Using the  $v_Q$ s of figure 11 for the HTP to calculate the  $S_{zz}^i$ s (and realizing that they must be negative) we obtain  $\langle l \rangle \sim 13 \text{ \AA}$  (at  $120^\circ\text{C}$ ). This result may be identified with the average length of the molecules in the lamellar layers, which was found by Gallot [3] to vary between 11 and  $13 \text{ \AA}$  in the temperature range  $98$  to  $130^\circ\text{C}$  for a 57 wt % disoap solution in  $\text{H}_2\text{O}$ . For a complete understanding of the aliphatic chain splitting profile more general models need be considered [22–24].

The dispersity of the methylene splittings in the LTP does not significantly alter the picture. It merely indicates that in this phase a somewhat wider distribution of conformations occurs involving, in addition to kinks also forms with single or multiple gauches of various combinations. However the near constancy of the methylene splittings is quite different from the situation in monosoaps where the tail end of the chains exhibit gradually decreasing quadrupolar order. In the present case the chains are attached at both ends to hydrophilic interfaces, and there are no loose ends, as in monosoaps. According to de Gennes [25] in such cases the quadrupolar order should be constant for all methylenes as is indeed found for the HTP, and very nearly also for the LTP. In both phases we cannot rule out completely the presence of molecules which are folded about their long axis. However if they occur their abundance must be low and in fast equilibrium (on the N.M.R. timescale) with the trans conformation, since only a single peak was observed for each deuterium. This is contrary to a previous observation by Seelig *et al.* [26] in the E.S.R. spectra of  $\alpha,\omega$ -dicarboxylic spin probes where separate signals were observed for the *U* and trans forms of the spin probe. It should be noted however that the time scale for the latter observation is longer by a factor of  $\sim 10^4$  compared to deuterium N.M.R.

As for the  $\text{D}_2\text{O}$  signal, the deuterium spectra of deuteriated  $\text{C}_{16}\text{K}_2$  also exhibited a signal due to an isotropic phase; on slow heating from the LTP at around  $120^\circ\text{C}$  the spectrum collapses to a single peak which only transforms again to give the characteristic HTP spectrum at about  $130^\circ\text{C}$ .

#### 4. Discussion

The results of both the optical microscopy and the N.M.R. experiments show that in the concentration range studied the  $\text{C}_{16}\text{K}_2$ -water system exhibits three mesophases.

(i) A HTP, which may be identified with the lamellar phase studied by Gallot [3]. It is characterized by  $\Delta\chi < 0$  and a constant quadrupolar order for the methylene deuterons. Optical microscopy of this phase exhibits features typical of lamellar



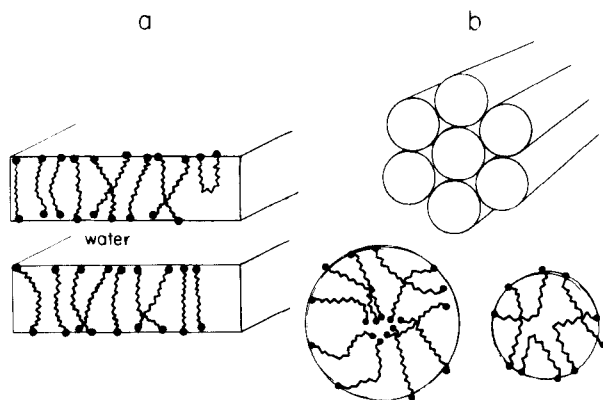


Figure 14. Schematic diagram for possible structures of the  $C_{16}K_2$ -water mesophases (a) Lamellar structure with alternate water and disoap layers proposed for the HTP. (b) Rod-like micelles forming the LTP. In the rod-like micelles the molecules can stretch from one side to the other, or they can be visualized as folded monolayers with inner hydrophilic regions.

structures, which in this case must be assumed to consist of monolayers (see figure 14(a)) bound on both sides by hydrophilic interfaces. The fraction of the lamellar spacing occupied by disoap molecules was estimated by Gallot [3] to range between 11.4 and 14.4 Å (depending on concentration) which is about 60 per cent of the length of an extended  $C_{16}K_2$  molecule. This is consistent with the observed quadrupolar splitting of the methylene deuterons from which an effective average length of  $\sim 13$  Å can be calculated.

(ii) The second phase, LTP, occurs at lower concentrations and temperatures than those studied by Gallot [3]. Its optical microscopy features are similar to those of the monosoaps' middle phases. Within the accuracy of the N.M.R. measurements it is uniaxial with  $\Delta\chi > 0$ , and it exhibits deuterium and potassium-39 quadrupolar splittings considerably smaller than in the HTP despite the fact that it appears at lower temperatures. A possible model for this phase may accordingly be an hexagonal or rectangular phase consisting of rod-like micelles in which the disoap molecules are oriented perpendicular to the rods' axes. Several types of such rods may be imagined for example, with circular or elliptical cross sections [27] in which the molecules are stretched across the micelles, or rods made of folded monolayers with inner hydrophilic cores (cf. figure 14(b)). The rod model, with chains perpendicular to the rod direction, is consistent with the positive  $\Delta\chi$  found for this phase, and the reduction in the quadrupolar splitting may be ascribed to the diffusion of the molecules and ions around the micelles long axis thus provides an additional averaging mechanism for the quadrupole interaction not present in lamellar structures.

(iii) The third phase, about which we know the least, is the isotropic mesophase. It appears between the LTP and HTP and is characterized by  $\nu_Q = 0$  for both the deuterium and potassium nuclei, and lack of birefringence. The vanishing of these second rank tensorial properties could be interpreted in terms of a re-entrant isotropic phase, however we prefer the tentative assignment of a cubic phase, since such phases were previously found in other lyotropic systems [28]. Clearly more experimental work need be done to identify this phase fully.

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### References

- [1] EKWALL, P., 1975, *Advances in Liquid Crystals*, Vol. 1, edited by G. H. Brown (Academic Press), p. 1.
- [2] GALLOT, B., and SKOULIOS, A., 1968, *Kolloid-Z. Z. Polymere*, **222**, 51.
- [3] GALLOT, B. R., 1971, *Molec. Crystals liq. Crystals*, **13**, 323.
- [4] DANIELSSON, I., 1956, *Acta Acad. åbo. Math. Phys.*, **20**, 15.
- [5] DOANE, J. W., 1979, *Magnetic Resonance of Phase Transitions*, edited by F. J. Owens, C. P. Poole and H. A. Farach (Academic Press), p. 171.
- [6] DAVIS, J. H., 1983, *Biochim. biophys. Acta* **737**, 117.
- [7] SEELIG, J., 1977, *Q. Rev. Biophys.*, **10**, 353.
- [8] MELY, B., and CHARVOLIN, J., 1977, *Chem. Phys. Lipids*, **19**, 43. MELY, B., CHARVOLIN, J., and KELLER, P., 1975, *Chem. Phys. Lipids*, **15**, 161. CHARVOLIN, J., and HENDRIKX, Y., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (Reidel), p. 449.
- [9] FORREST, B. J., and REEVES, L. W., 1981, *Chem. Rev.*, **81**, 1.
- [10] FORREST, B. J., HECKER DE CARVALHO, L., REEVES, L. W., and RODGER, C., 1981, *J. Am. chem. Soc.*, **103**, 245.
- [11] LINDBLOM, G., and LINDMAN, B., 1973, *Molec. Crystals liq. Crystals*, **22**, 45.
- [12] BODEN, M., and JONES, S. A., 1983, *Israel J. Chem.*, **23**, 356. 1985 *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (Reidel), p. 473.
- [13] GOLDFARB, D., POUPKO, R., LUZ, Z., and ZIMMERMANN, H., 1983, *J. chem. Phys.*, **79**, 4035.
- [14] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1982, *J. Phys., Paris*, **43**, 421.
- [15] ATKINSON, J. G., CSAKVARY, J. J., HERBERT, G. T., and STUART, R. S., 1968, *J. Am. chem. Soc.*, **90**, 498.
- [16] DAVIES, J. H., JEFFREY, K. R., BLOOM, M., and VALIC, M. I., 1976, *Chem. Phys. Lett.*, **42**, 390.
- [17] ABDOLALL, K., BURNELL, E. E., and VALIC, M. I., 1977, *Chem. Phys. Lipids*, **20**, 115. TANG, W. W. S., BURNELL, E. E., and HIGGS, T. P., 1985, *J. phys. Chem.*, **89**, 4535.
- [18] DE VRIES, J. J., and BERENDSEN, H. J. C., 1969, *Nature. Lond.*, **221**, 1139.
- [19] PETERSEN, N. O., KROON, P. A., KAINOSHO, M., and CHAN, S. I., 1975, *Chem. Phys. Lipids*, **14**, 343.
- [20] HSI, S., ZIMMERMANN, H., and LUZ, Z., 1978, *J. chem. Phys.*, **69**, 4126.
- [21] SCHINDLER, H., and SEELIG, J., 1975, *Biochemistry*, **14**, 2283.
- [22] GRUEN, D. W. R., 1985, *J. phys. Chem.*, **89**, 146; 1985, *Ibid.*, **89**, 153.
- [23] LUCKHURST, G. R., 1985, *Recent Advances in Liquid Crystalline Polymers*, edited by L. L. Chapoy (Elsevier), p. 105.
- [24] SAMULSKI, E. T., 1983, *Israel J. Chem.*, **23**, 329; 1985, *Polymer*, **26**, 177. JANIK, B., SAMULSKI, E. T., and TORIUMI, H., 1987, *J. phys. Chem.*, **91**, 1842.
- [25] DE GENNES, P. G., 1974, *Physics Lett. A*, **47**, 123. ALEXANDER, S., 1977, *J. Phys., Paris*, **38**, 983.
- [26] SEELIG, J., LIMACHER, H., and BADER, P., 1972, *J. Am. chem. Soc.*, **94**, 6364.
- [27] ALPERINE, S., HENDRIKX, Y., and CHARVOLIN, J., 1985, *J. Phys. Lett., Paris*, **46**, L-27.
- [28] FONTELL, K., 1981, *Molec. Crystals liq. Crystals*, **63**, 59. GUTMAN, H., ARVIDSON, G., FONTELL, K., and LINDBLOM, G., 1984, *Surfactants in Solution*, Vol. 1, edited by K. L. Mittal and B. Lindman (Plenum Press) p. 143. CHARVOLIN, J., 1985, *J. Phys., Paris, Coll.*, **46**, C3-173.