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X-ray diffraction and deuterium N.M.R. of the lyomesophases of dipotassium hexadecanedioate-water mixtures

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Mixtures of water and the dipotassium thapsate form hexagonal and lamellar lyomesophases with structures similar to those found for monosoaps. X-ray diffraction from a high intensity synchrotron radiation source exhibits the first four reflections of the hexagonal phase and the first two from the lamellar phase yielding lattice parameters of about 28 Å and 22 Å, respectively. Within the stability range of the mesophases these parameters do not vary significantly with the disoap concentration and the temperature. An intermediate phase, found previously at about 120°C between the hexagonal and the lamellar phase was shown to be an isotropic liquid rather than a cubic mesophase. Combined X-ray diffraction and N.M.R. experiments on magnetically aligned samples showed that the lamellar and hexagonal phases have respectively negative and positive anisotropic magnetic susceptibilities. Samples which are allowed to equilibrate in the isotropic-mesophase boundary region for several hours, in the absence of a magnetic field, undergo surface-induced alignment. The lamellar phase aligns homeotropically while the hexagonal phase aligns homogeneously, but with the directors perpendicular to the capillary axis and with the hexagonal lattice vectors inclined at a constant orientation to the surface. Deuterium N.M.R. measurements on perdeuteriated disoap samples indicate that the amphiphile molecules in both mesophases are highly disordered, partly due to isomerization equilibria and partly due to orientational disorder. Based on the X-ray and N.M.R. results molecular models for both the lamellar and hexagonal phases are proposed. These models resemble very closely the corresponding mesophases of the monosoaps.

1. Introduction

Earlier X-ray measurements [1-2] on mixtures of dialkali salts of dicarboxylic acids with water indicated that mesophases similar to the lamellar phases of monosoaps [3-9] may be obtained from homologues containing between 16 to 22 carbons per molecule. More recently [10] we have reported an N.M.R. study on the water-dipotassium hexadecanedioate, $\text{KOO}(\text{CH}_2)_{14}\text{COOK}$ (dipotassium thapsate - C_{16}K_2) system, however unlike the X-ray study [2], these measurements indicated the presence of at least two lyomesophases as shown in the schematic binary phase diagram of figure 1. This diagram is a modified version of the protonated C_{16}K_2 - D_2O system of [10] and is based on additional N.M.R. observations made upon heating rather than cooling, as well as on X-ray results to be described later. Although the structure of the mesophases could not be determined from the N.M.R. results,

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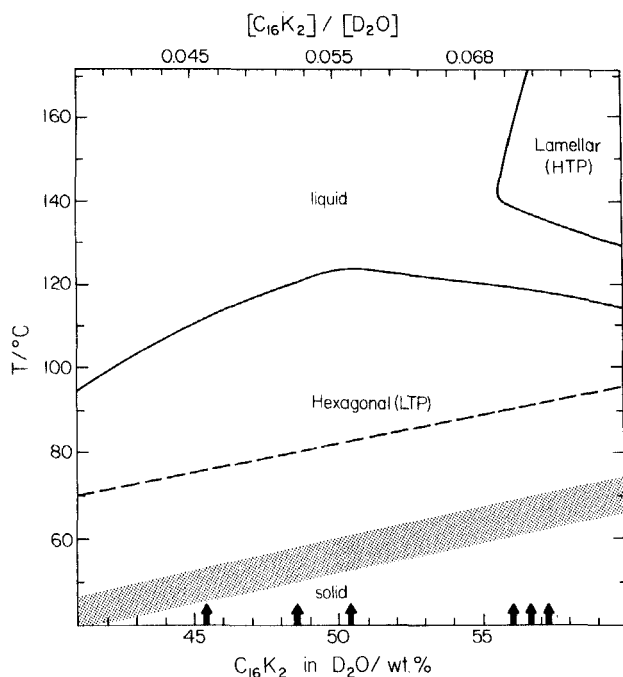


Figure 1. Schematic representation of the phase diagram for the binary $C_{16}K_2$ -water system based on the results of [10] (phase separation zones are not indicated). The shaded band gives the boundary between the solid and the hexagonal phase as determined by N.M.R. on cooling [10]. The dashed line is a suggested true solid-mesophase boundary based on X-ray measurements below which the hexagonal phase is in a supercooled state. The intermediate isotropic liquid at high concentrations is usually observed only on heating; upon cooling we normally obtain a supercooled lamellar phase at this region. The arrows at the bottom of the diagram indicate the compositions of the samples at which the X-ray diffraction measurements were performed.

qualitative arguments based on the deuterium spectrum of the solvent D_2O suggested that the mesophase observed at high disoap concentrations and high temperatures is lamellar, while the other mesophase is hexagonal. At concentrations between 56 and 60 wt % of $C_{16}K_2$ an intermediate phase with isotropic N.M.R. signals and no optical birefringence was usually observed upon heating from the hexagonal to the lamellar mesophase (at around $120^\circ C$). It was not clear, however, whether this intermediate phase corresponds to a (reentrant [11]) isotropic liquid or perhaps to a cubic [12-14] mesophase.

In the present work we use X-ray diffraction in order to substantiate the N.M.R. results on the $C_{16}K_2$ -water system, and to obtain structural information related to the various mesophases. The results largely confirm the earlier conclusions and provide quantitative geometrical data on the interlamellar and intercolumnar spacings in the lamellar and hexagonal mesophases. They also indicate that the intermediate phase observed by N.M.R. is not a cubic mesophase but rather an isotropic liquid. Complementary N.M.R. measurements on deuteriated $C_{16}K_2$ which pertain to the conformation equilibria and the orientational order of the disoap molecules are also reported.

2. Experimental

2.1. Material and sample preparation

The X-ray measurements were performed on mixtures of isotopically normal $C_{16}K_2$ and D_2O , while deuterium N.M.R. measurements on the deuteriated disoap were performed using partially (46 at %) perdeuteriated $C_{16}K_2$ in H_2O . The normal and the deuteriated compounds and the sample preparation procedures were as described previously [10]. Specimens for the X-ray measurements were prepared by transferring the desired disoap-water mixture into a 1.5 mm quartz capillary to a height of approximately 2 cm and the sample was flame sealed. In several cases the water content was checked by opening the capillary (after completion of the experiments) and determining the weight loss resulting from drying the sample to constant weight. No significant changes in the composition were found due to manipulation of the samples.

2.2. X-ray diffraction measurements

Low-angle X-ray diffraction measurements were performed both with a conventional X-ray apparatus employing a rotating anode source [15] and with the high power synchrotron radiation source at LURE [16]. The general geometry of the X-ray experiment is shown schematically in figure 2. In the rotating anode equipment which employed a partially monochromated $Cu K_\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) the scattering was detected using a two dimensional detector of the delay line type. The detector was placed at a distance of 250 mm from the sample, at which point the beam diameter was $700 \mu\text{m}$. The temperature of the samples was regulated using a furnace which consisted of a copper and teflon cavity equipped with a triac temperature control ($\pm 0.5^\circ\text{C}$). Some measurements were also made using a Searl camera equipped with Franks optics and the scattering was detected by direct exposure film (Kodak). The X-ray diffraction experiments at LURE were performed using a monochromatized beam of $\lambda = 1.30 \text{ \AA}$ and recording the scattering on a photographic plate 247 mm behind the sample. The temperature was regulated by circulating warm oil through the sample holder and monitored by a thermocouple positioned close to the capillary.

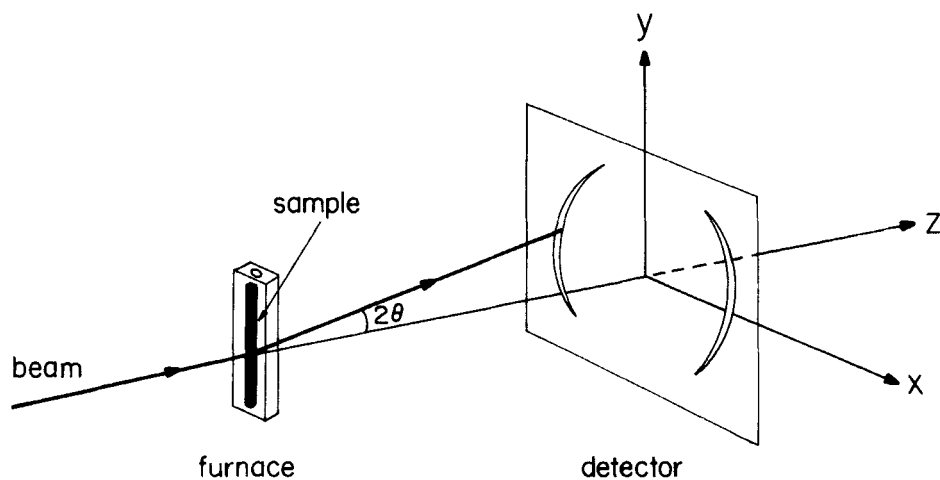


Figure 2. Schematic representation of the X-ray diffraction experiment.

To determine the alignment effect of magnetic fields some experiments were made (using the rotating anode apparatus) on samples prealigned in a strong field and the degree of alignment checked by recording the deuterium N.M.R. of the D_2O constituent. The X-ray capillary was fitted into the narrow internal lock N.M.R. tube that was in turn inserted into a 10 mm tube containing ethyleneglycol which ensured temperature stability. The sample was placed in the N.M.R. probe at the desired temperature with the magnetic field (7.0 T) parallel to the capillary axis. After alignment and recording the N.M.R. spectra the sample was transferred at constant temperature to the X-ray equipment.

2.3. N.M.R. measurements

Deuterium N.M.R. measurements were made on a Bruker CXP300 spectrometer operating at 46.07 MHz. For recording the D_2O spectrum single pulses (15 μs) were used, while for the signals of the deuteriated $C_{16}K_2$, the quadrupole echo method was employed [17] (using $\pi/2$ pulses of 2.4 μs , time interval between pulses 30 μs , repetition time 0.1 s). Usually 500 scans were accumulated for the D_2O signals and about 5000 for the deuteriated $C_{16}K_2$ before Fourier transformation.

3. Results and interpretation

3.1. X-ray measurements

X-ray measurements were performed on a limited number of $C_{16}K_2$ -water solutions in two regions of the phase diagram as indicated by the heavy arrows on the bottom of figure 1.

3.1.1. Low disoap concentrations

Low angle X-ray diffractions obtained with the intense synchrotron source on samples containing less than 55 wt % $C_{16}K_2$ provide conclusive identification of the mesophase observed in this concentration range as hexagonal. A diffraction pattern obtained for the 48.5 wt % sample at 81°C showing a series of four spotty rings with relative d spacings of $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$, as expected for a two dimensional hexagonal array, is depicted in plate (d) of figure 3. The corresponding lattice parameter for this sample is $a = 2d_{10}/\sqrt{3} = 28.3 \text{ \AA}$, where $d_{10} = 24.5 \text{ \AA}$ is the spacing corresponding to the innermost ring. This d_{10} spacing was measured over a wide range of concentrations (not all of them explicitly indicated in figure 1) and temperatures on the rotating anode apparatus and the results are summarized in the table. Considering the uncertainty in these results ($\pm 0.5 \text{ \AA}$) no significant dependence of the d spacing on either the temperature or the concentration within the stability range of the mesophase can be claimed. Measurements at wide diffraction angles exhibit a diffuse ring at around 4.5 \AA (see figure 3 (e)). Its position is characteristic of

Figure 3. Left: X-ray diffraction patterns from the $C_{16}K_2$ -water system obtained using the intense synchrotron radiation source (a)-(d) and the rotating anode source (e). Exposure times were 1/2 to 2 hours for the synchrotron source and 16 hours for the rotating anode apparatus. Right: Tracings of the diffraction rings. Rings 1 and 2 in (a) correspond to the lamellar diffraction. The rings numbered 1 to 4 in (c), (d) and (e) correspond to diffraction maxima of the hexagonal phase, while rings 1' and 2' in (d) are due to solid particles. The diffuse ring in (b) corresponds to a diffraction maximum at 23.4 \AA from the isotropic liquid intermediate, and the outer ring in (e) is the 4.5 \AA diffraction of the hexagonal phase. The sample to film distance was 24.7 cm for (a)-(d) and 3.7 cm for (e).

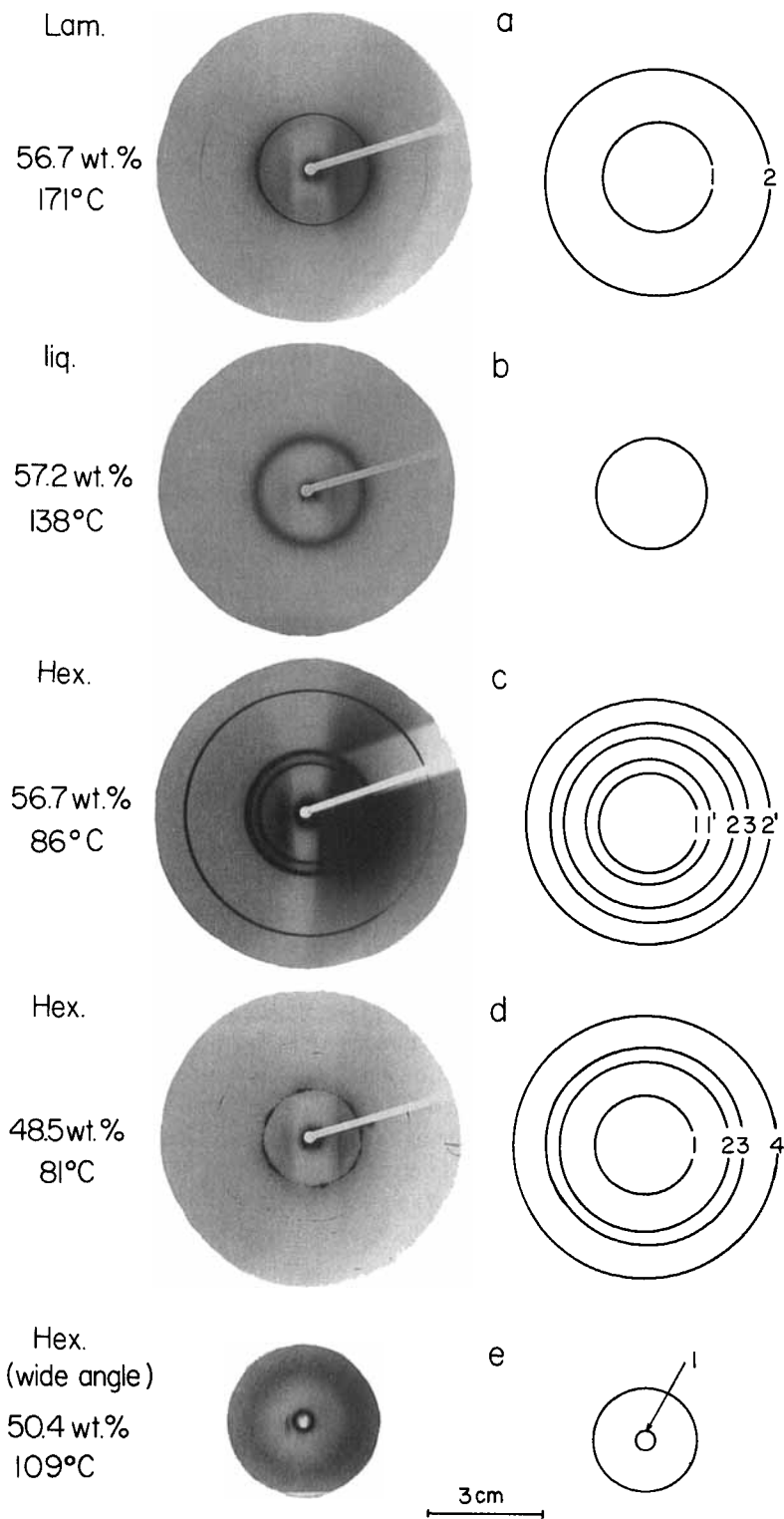


Figure 3.

d_{10} spacings in Å in the hexagonal phase for different $C_{16}K_2$ -water mixtures at three different temperatures, measured in the rotating anode apparatus. The estimated uncertainty in d is ± 0.5 Å.

| $t/^\circ\text{C}$ | Conc./wt % | | | | | | | | |
|--------------------|------------|------|------|------|------|------|------|------|------|
| | 43.8 | 45.0 | 45.4 | 45.5 | 48.5 | 49.8 | 50.4 | 54.2 | 56.0 |
| 80 | 24.8 | 24.4 | 24.0 | 24.1 | 24.5 | 24.6 | 24.8 | 24.3 | 24.6 |
| 90 | — | 23.9 | — | — | — | 24.4 | 25.1 | 24.2 | 24.1 |
| 100 | — | 23.8 | 24.0 | — | 24.2 | 24.1 | 25.6 | 24.1 | 23.5 |

packed hydrocarbon chains and its diffuseness suggests that in the hexagonal phase these chains are highly disordered [18].

In several experiments upon cooling the sample within the hexagonal phase sharp diffraction rings appeared at about 70 – 80°C whose positions agreed with those obtained for the solid phase at room temperature [1]. Their appearance reflects the onset of crystallization at a considerably higher temperature than indicated by the solid-mesophase boundary (40 – 60°C) determined by N.M.R. (see the shaded band in figure 1). Apparently solidification of the mesophase is slow and therefore part of the region in the phase diagram previously attributed to the hexagonal phase [10] actually corresponds to a supercooled state. Small amounts of solid will easily escape detection by N.M.R. in the presence of the mesophase, whereas due to the sharpness of the diffraction rings from solids, X-ray is especially sensitive to even small amount of crystals. We have indicated this region where crystallization is first observed by X-ray with the dashed line in figure 1.

3.1.2. High disoap concentrations

Above 55 wt % disoap the $C_{16}K_2$ -water system is polymorphic, exhibiting on heating the solid, first the hexagonal, then an isotropic intermediate phase (usually not observed on cooling) and finally the lamellar phase. Figure 3(a) shows the X-ray diffraction pattern obtained, using the synchrotron source, from a 56.7 wt % solution in the lamellar phase at 171°C . It reveals two diffraction rings with a d spacing ratio of 2:1. This result is consistent with a lamellar structure, and confirms the earlier identification made by Gallot [2] on high concentration samples at high temperatures. The d spacing for the particular diffraction shown in the figure corresponds to 22.0 Å. Temperature dependence measurements of this d spacing showed a very small negative slope corresponding to a thermal expansion coefficient [9] of $\alpha = -0.6 \times 10^{-3} \text{K}^{-1}$, which is about half of that determined by Gallot [2] ($-1.4 \times 10^{-3} \text{K}^{-1}$) in a 57 wt % disoap in H_2O solution. As for the hexagonal phase a diffuse ring is also observed in the high angle diffraction region of the lamellar phase, due to scattering from the hydrocarbon chains.

To measure the X-ray diffraction from the intermediate isotropic region in the phase diagram between the lamellar and the hexagonal phases the sample was first cooled into the hexagonal phase and then reheated to about 120 – 140°C . The low-angle diffraction from this intermediate phase (see figure 3(b)) exhibits a highly diffuse ring (corresponding to $d = 23.4$ Å) but no additional sharp Bragg reflections which would indicate a periodic structure. This strongly suggests that this intermediate region is not a cubic mesophase but rather an isotropic liquid as indicated in the phase diagram of figure 1. A similar diffuse ring corresponding to 23.4 Å is also observed in the isotropic region of the more dilute solutions above the clearing temperature of the hexagonal phase. Since this intermediate phase is obtained on heating and remains

stable at 120°C for long periods of time, we regard it as a thermodynamically stable reentrant isotropic liquid phase.

Cooling to the hexagonal phase yields the diffraction pattern shown in figure 3 (c). It exhibits two sets of diffraction rings; one set labelled (1, 2, 3) can be indexed on a hexagonal lattice with a lattice parameter $a = 28.2 \text{ \AA}$, essentially identical to that determined in the more dilute (48.5 wt %) sample. This supports the earlier assignment that the whole low temperature region in the phase diagram corresponds to the same hexagonal phase. The second set of lines in figure 3 (c) consists of two sharp reflections (1', 2'), whose d spacings coincide with reflections found in solid disoap [1]. Hence we associate the appearance of these reflections with the onset of solidification and, as for the low concentration region, we have shifted the solid-mesophase boundary in the phase diagram to higher temperatures as indicated by the dashed line of figure 1.

3.2. Alignment characteristics

In the earlier work, using the N.M.R. spectrum of the D₂O deuterons, it was noted that both glass surfaces and magnetic fields exert alignment forces on the mesophases of the disoap system [10]. Thus, when disoap samples were prepared between stacked glass plates the lamellar phase was found to orient homeotropically, i.e. with the lamellae lying parallel to the surface, while the hexagonal phase gave a homogeneous distribution with the directors of the various domains randomly oriented in a plane parallel to the surface. In larger bulk samples magnetic forces often caused partial or even complete alignment of the mesophases, particularly during their formation from the isotropic liquid. Analysis of these alignment effects indicated that the hexagonal and lamellar phases are characterized by positive and negative anisotropic magnetic susceptibilities, respectively. To confirm these observations and study further the alignment characteristics of the disoap mesophases we have performed X-ray diffraction experiments on the same samples used in the previous experiments but after various alignment treatments. These experiments were performed on the rotating anode apparatus, which due to its weaker X-ray intensity (compared to the synchrotron source) allowed only the first order diffraction peaks to be detected in each of the mesophases.

3.2.1. Alignment of the lamellar phase

When a C₁₆K₂ solution is cooled from the isotropic liquid or the biphasic liquid-lamellar region and the X-ray diffraction of the lamellar mesophase measured shortly thereafter, diffraction rings appear as expected for randomly distributed domains. An example of the first order diffraction ($d = 23.1 \text{ \AA}$) obtained under such conditions for a 57.2 wt % solution contained in a 1.5 mm quartz capillary is shown in the upper left hand trace of figure 4. To determine the effect of magnetic field alignment on this phase the sample was placed in the N.M.R. spectrometer with the capillary axis parallel to the field (7 T), then heated to 140°C, equilibrated for approximately 1 hour and allowed to cool within the magnetic field to 118°C. The deuterium N.M.R. spectrum recorded at this temperature shows a sharp doublet (upper trace in column (d)), indicating that the sample is well aligned. When the X-ray diffraction of this sample was recorded, with the capillary axis along the y direction, it exhibited two diffraction peaks lying symmetrically along the x axis, (upper trace in column (c)). This is consistent with the diffraction expected from domains of layers whose reciprocal lattice vectors are distributed within the xz plane. Such a distribution would have just these two intersections (for the first order diffraction) with the Ewald sphere,

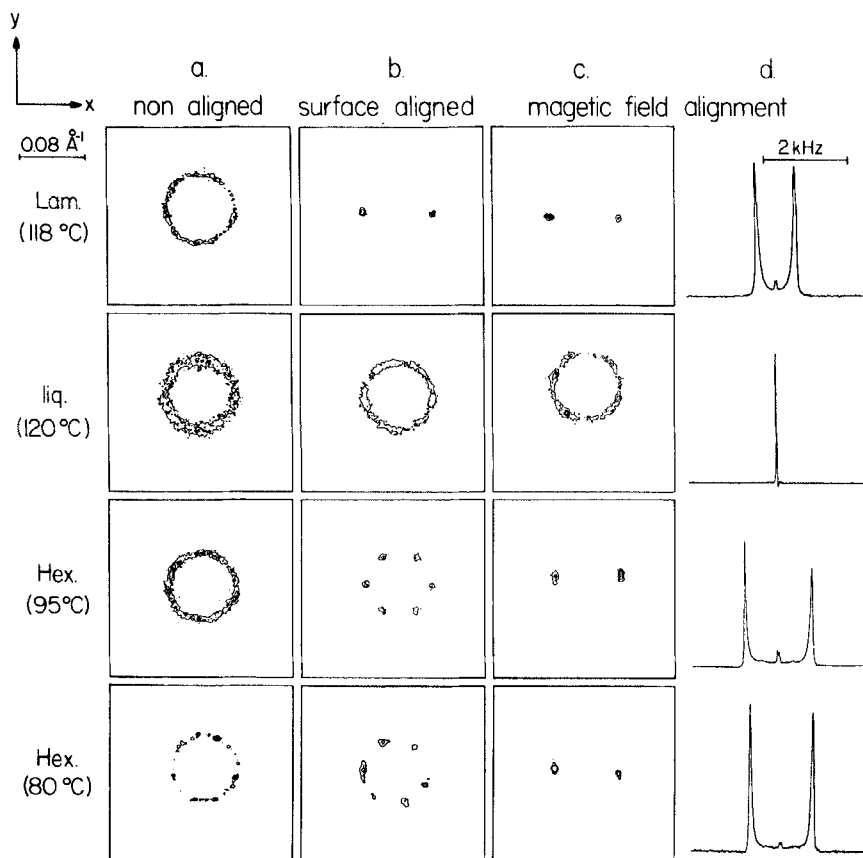


Figure 4. X-ray diffraction patterns obtained using the rotating anode source. The results in the three upper rows correspond to the high concentration range (56 and 57 wt %), while the bottom row to a low concentration sample (48.5 wt %). Column (a) exhibits the diffraction pattern of unaligned samples, column (b) of surface aligned samples and column (c) of samples aligned in a magnetic field (7 T). The diffraction intensities were recorded using a two dimensional array detector and are displayed as contours plots. The contouring was usually done at 3–5 equal intervals up to maximum intensity. Column (d) shows the deuteron N.M.R. spectra of the corresponding samples used to acquire the X-ray diffractions of column (c).

confirming the conclusion derived from the N.M.R. experiment that $\Delta\chi$ of the lamellar phase is negative.

A similar pattern is also observed from disordered samples which are allowed to equilibrate at about 150–160°C followed by slow cooling over a period of many (5 to 15) hours. As an example the X-ray diffraction of a 56 wt % sample so equilibrated and measured at 120°C is shown in the top trace of column (b). This result suggests that during the lengthy sample equilibration surface alignment produces a domain distribution very similar to that induced by a magnetic field oriented parallel to the capillary axis. It is consistent with a homeotropic alignment, as was also found by the earlier N.M.R. experiments in samples consisting of stacked thin glass plates.

3.2.2. Alignment of the hexagonal phase

In similar experiments in which the hexagonal phase is formed by rapid cooling of either a non-oriented lamellar phase (at high $C_{16}K_2$ concentrations) or of the

isotropic liquid (at low concentrations), the resulting X-ray diffraction consists of an evenly distributed, sometimes spotty, ring (cf. the bottom two traces in column (a) of figure 4). When, however, the hexagonal phase is formed by slow cooling within the magnetic field of the N.M.R. spectrometer (with the capillary axis parallel to the magnetic field direction) an oriented sample is obtained, as may be seen from the N.M.R. spectra of two such samples (containing 56.0 wt % and 48.5 wt % $C_{16}K_2$) in the third and fourth traces of column (d) of figure 4. The corresponding X-ray diffraction patterns, shown in column (c), exhibit two spots along the x axis, indicating that the sample consists of an ensemble of hexagonal domains all having their C_6 axes parallel to the y direction, but with a random distribution of the lattice axes in the transverse plane. In this configuration all the reciprocal lattice vectors are confined to the same (xz) plane and will give just two intersections with the Ewald sphere, as observed experimentally. This confirms the assignment of positive $\Delta\chi$ for the hexagonal phase.

We have also observed effects on the domain distribution of the hexagonal phase after lengthy equilibration and slow passage into the mesophase region. The diffraction pattern observed in such aligned samples consisted of a few isolated spots around the first diffraction ring. Very often an array of spots occupying the corners of a hexagon were obtained, as shown for example in the two bottom traces of column (b), figure 4 obtained respectively on slow cooling from the lamellar phase (third trace for a 56 wt % solution) and from the isotropic liquid (fourth trace, 48.5 wt %). Although these diffraction patterns may appear to reflect the symmetry of the hexagonal phase, this is not necessarily so and could, in principle, arise from some special packing of domains. Several models of domain distributions which are consistent with the experimental X-ray results come to mind. For example, (i) the very unlikely situation that a single domain is formed perpendicular to the capillary axis and the X-ray beam is fortuitously oriented parallel to its C_6 axis (see figure 5(a)). If the diffraction spots are sufficiently broad, e.g. due to director fluctuations or mosaicity, this will result in a symmetric, six spot diffraction. (ii) A similarly unlikely situation in which the sample consists of three ensembles of domains, (not necessarily hexagonal), each with a common director but random orientations of the two dimensional lattice vectors. For the particular situation in which the directors of the three sets are inclined at 120° to each other in a plane perpendicular to the X-ray beam (see figure 5(b)), a hexagonal pattern as found experimentally should be observed. (iii) The sample consists of a two dimensional distribution of domains whose directors are perpendicular to the capillary (y) axis, but with the lattice vectors inclined at a constant angle to this axis. For the high concentration sample where the hexagonal phase evolves from the lamellar phase this distribution of domains could be visualized as resulting from the homeotropic alignment already present in the lamellar phase (see figure 5(c)). A similar situation was encountered in the case of dihexadecylphosphatidylethanolamine-water system in which a hexagonal phase was obtained by heating a lamellar phase [19]. For the interpretation of the present results we must assume that the rods of the hexagonal phase are formed circumferentially, i.e. with their long axes perpendicular to y and in such a way that the planes of the lamellar phase transform into the $\{10\}$ planes of the hexagonal phase. This results in one planar and one conical (inclined at 30° to y) distribution of reciprocal lattice vectors yielding six symmetrical intersections with the Ewald sphere. Similar epitaxial relations have been invoked to explain the X-ray and neutron diffraction results in the

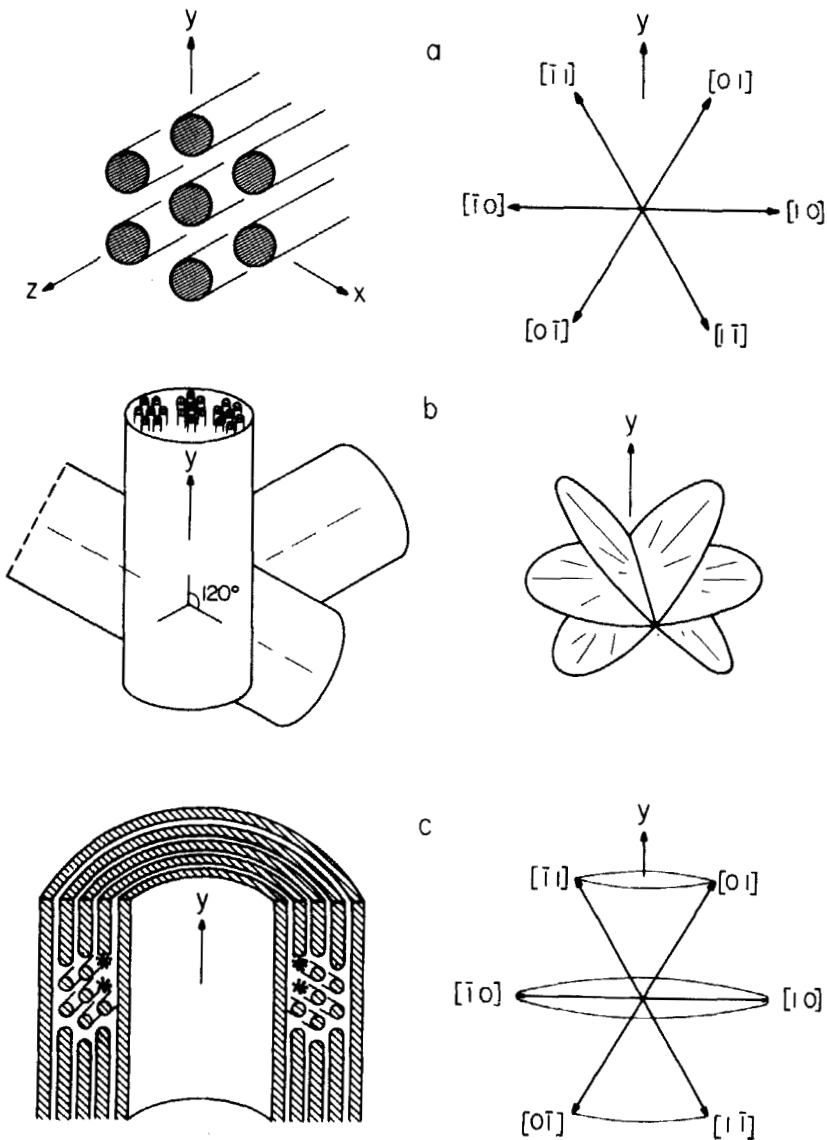


Figure 5. Possible surface-induced domain distributions formed in the hexagonal phase which are compatible with the six spot diffraction patterns shown in column (b) of figure 4. The drawings on the left correspond to real space while those on the right to reciprocal space (with corresponding indices of the k vectors). (a) A single hexagonal domain aligned perpendicular to the capillary axis and parallel to the X-ray beam. (b) A set of three ensembles of domains each with a common director but random distribution of the transverse lattice vectors, and oriented at 120° to each other. (c) A two dimensional distribution of domains with directors perpendicular to the capillary y -axis, but with fixed orientations (relative to y) of the transverse lattice vectors.

C12EO6-water mixtures [16], where the planes of the lamellar phase evolve into the $\{10\}$ planes of metastable hexagonal phase (which in turn transforms into a cubic mesophase). This epitaxial growth model does not strictly apply to the low concentration region of the phase diagram where the hexagonal phase lies below the isotropic liquid. It is possible, however, that the similar behaviour of the low concentration solutions reflects the presence of molecular aggregates in the isotropic liquid just

above the hexagonal phase. Of the three models described the latter appears the most plausible, although it is difficult to understand why the rods prefer to align perpendicular to the y axis. Considerations of elastic energy would, if at all, prefer a parallel alignment [20]. We could, in fact, suspect that the director is randomly distributed on the surface of the capillary [21] (with a constant azimuthal phase) and that due to misalignment the X-ray beam passes very close to one side of the capillary surface. This should also lead to a six spot pattern but with the horizontal peaks much more intense than the others, contrary to the experimental observations.

For completeness we have also performed similar alignment experiments on the isotropic intermediate phase. As may be seen from the diffraction pattern in the second row of figure 4, no orientation effects were observed by the magnetic field or by equilibration, supporting the identification of this phase as a liquid rather than a cubic mesophase.

3.3. Deuterium N.M.R. of perdeuteriated $C_{16}K_2$

Additional information about the ordering of the disoap molecules in the two mesophases could be obtained from deuterium N.M.R. measurements on a $C_{16}K_2-H_2O$ preparation containing perdeuteriated (46 at %) $C_{16}K_2$. The sample contained 62 wt % disoap and thus formed both the lamellar and the hexagonal phases. They were obtained by first equilibrating the sample at a high temperature ($\sim 160^\circ\text{C}$) within the magnetic field, followed by slow cooling through the lamellar to the hexagonal phase. Spectra recorded as a function of temperature are depicted in figure 6. At 158°C a spectrum due to a well aligned lamellar phase (perpendicular to the magnetic field) exhibiting four doublets (in addition to the HDO and an isotropic centre peak) is observed. The outer doublet was identified as due to the α -deuterons (carbon no. 2) by comparison with spectra obtained from a specifically labelled $C_{16}K_2$ molecule at the α carbons. The other three doublets were assigned in pairs to successive methylenes in the chain as indicated in the figure. This tentative assignment is based on the assumption that as in monosoaps the quadrupole splitting in the aliphatic chain decreases monotonically from the carbonyl group in pairs along the chain (even-odd effect) [6, 22–24]. Note that in $C_{16}K_2$ there are seven pairs of chemically distinct methylenes. Since the average degree of deuteration was 46 at % not all sites were equally labelled. In particular the degree of deuteration of the α -carbon was significantly higher than of the rest of the sites.

As the temperature is lowered within the lamellar phase region the splitting of the α -deuterons remains fairly constant while the signals of the other deuterons slowly merge into a single doublet. At 115°C signals due to the hexagonal phase start to appear and at 111°C they dominate the spectrum completely. Since this phase is not as well aligned as the lamellar phase, both parallel features of the aligned domains as well as perpendicular peaks due to the unaligned part of the sample are observed. As for the spectra of the lamellar phase we have labelled the perpendicular features in decreasing, pairwise, order starting with the α -methylene which was identified by independent measurements using specifically labelled $C_{16}K_2$ in the α -position.

The average quadrupole interaction parameters, $\langle \nu_Q \rangle$, as measured from the frequency spacing between the perpendicular features in both phases for the various $C_{16}K_2$ deuterons are plotted in figure 7 versus temperature. It may be noted that the deuterons bonded to the α -carbons exhibit a considerably higher splitting than the rest of the deuterons, for which the ν_Q s are rather similar. Also there is a sharp discontinuous drop in the splitting by a factor of about 0.7 on going from the lamellar to

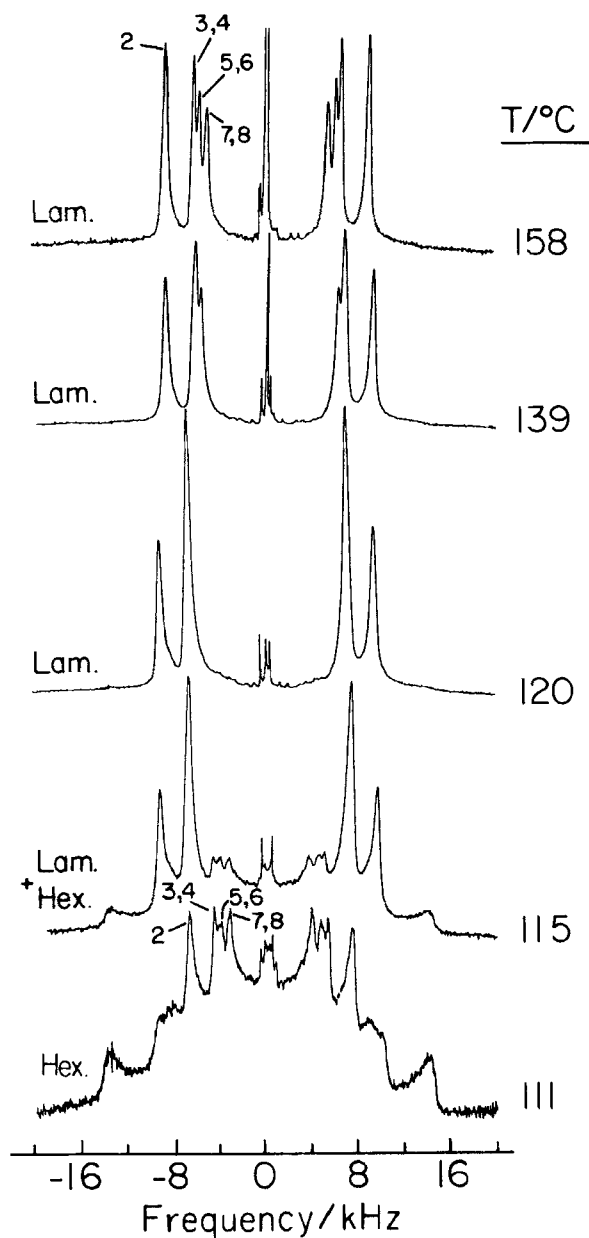


Figure 6. Deuterium N.M.R. spectra of $C_{16}K_2$ (62 wt %) perdeuterated to 46% in the disoap-water mesophase region at the temperatures indicated. The lamellar phase is aligned perpendicular to the magnetic field direction while the hexagonal phase is only partially aligned (parallel to the field).

the hexagonal phase, despite the general expectation that low temperature phases are more highly ordered. This can be rationalized on the basis of the assumed molecular ordering in the two phases, i.e. that the long axes of the disoap molecules are on average parallel to the lamellae normal in the lamellar phase and transverse to the rods in the hexagonal phase. An approximate expression for the quadrupole interaction

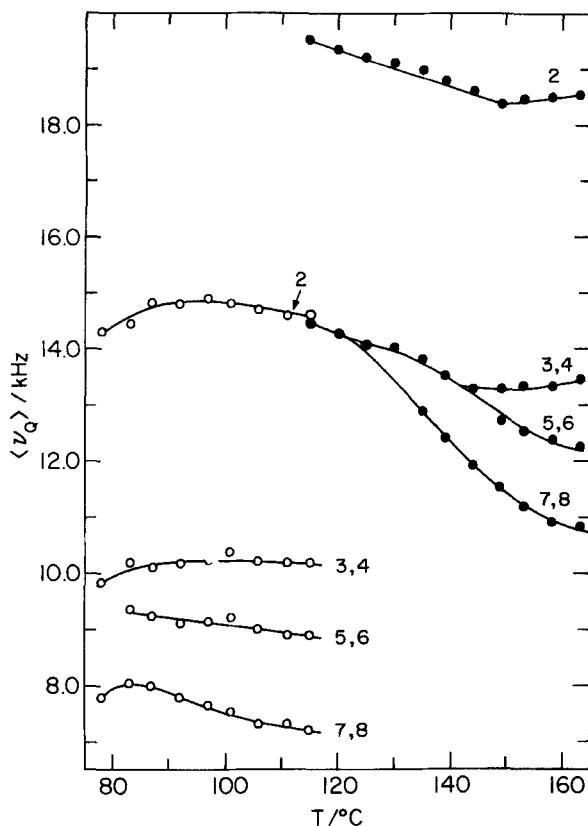


Figure 7. The average quadrupole interaction parameter, $\langle v_Q \rangle$, of the various deuterons in the same solution as described in the caption to figure 6. Note that $\langle v_Q \rangle$ is half the overall splitting of the parallel features (or the full splitting of the perpendicular features). Full circles, lamellar phase; open circles, hexagonal phase.

parameter, v_Q , in a uniaxial domain whose director makes an angle θ with the magnetic field can be written as follows [25]

$$\begin{aligned} v_Q &= v_Q(\theta) = \frac{3}{4} \frac{e^2 q Q}{h} S_m \left\langle \frac{1}{2} (3 \cos^2 \beta - 1) \right\rangle \frac{1}{2} (3 \cos^2 \theta - 1) \\ &= \langle v_Q \rangle \frac{1}{2} (3 \cos^2 \theta - 1), \end{aligned} \quad (1)$$

where S_m is the orientational order parameter of the molecules, assumed to have cylindrical (or at least three fold) symmetry, β the angle between the C-D bond direction relative to the molecule symmetry axis and the angular brackets indicate averaging over all the internal motions in the molecule. Besides the uniaxial symmetry this expression also assumes the presence of a single conformer, or alternatively that all conformers have the same orientational order. Although this is certainly a very crude assumption, it derives its justification from the likelihood that most conformers will deviate from the all-trans structure by only one or very few kinks (sequences of the type $t \dots t g^\pm t g^\mp t \dots t$) thus preserving the overall long dimension of the molecule [26, 27]. The motional averaging effect is thus divided into two parts, one reflecting the reorientation of the whole molecule, S_m , and a second part reflecting the

internal motions and conformational equilibria, included in the angular brackets of equation (1). In the lamellar phase the disoap molecules are on average aligned parallel to the director (normal to the layers) while the C–D bonds are approximately oriented perpendicular to the molecular axis. Fast reorientation of the molecules about their long axis will thus reduce the magnitude of the observed quadrupole interaction parameter to at most one half of its maximum value (i.e. from 120 to at most 60 kHz). In the hexagonal phase where the molecules lie on average with their long axes perpendicular to the rods, fast molecular reorientation perpendicular to the rod direction will reduce the quadrupole interaction parameter by another factor of two (i.e. to at most 30 kHz). This effect is probably the main reason for the smaller splitting observed in the hexagonal phase compared to that in the lamellar. The deviation from an exact factor of two and the reduction in ν_Q from the estimated maximum values must come from molecular ordering effects, and internal motions such as conformational isomerization.

It is difficult to estimate the relative importance of these two effects. We note however that in both mesophases, particularly in the lamellar phase, the splitting of the α deuterons is persistently somewhat larger than the other deuterons, which have very similar ν_Q s. One possible interpretation of this pattern of splitting is that the dominant conformations of the disoap chains involve besides the all-trans conformation, structures having predominantly one or very few kinks and that the kinks are equally distributed along the chain. Under these conditions the motional averaging of all methylene deuterons will result in similar quadrupole splittings except for the α -methylenes (since they are affected by kinks formed on one side only). Hsi *et al.* [25] developed a simplified model to account for the effect of kinks on the average quadrupole interaction in a mesophase. With these assumptions their model gives for the α deuterons

$$\langle \frac{1}{2}(3 \cos^2 \beta - 1) \rangle_{\alpha} = (1 - \frac{1}{2}p)Y_0^2\left(\frac{\pi}{2}\right) + \frac{1}{2}pY_0^2(\gamma). \quad (2)$$

and for the rest of the deuterons ($i \neq \alpha$)

$$\langle \frac{1}{2}(3 \cos^2 \beta - 1) \rangle_i = (1 - p)Y_0^2\left(\frac{\pi}{2}\right) + pY_0^2(\gamma), \quad (3)$$

where p is the (constant) kink probability at a methylene segment and Y_0^2 the spherical harmonic of order two. The angles $\pi/2$ and $\gamma = \frac{1}{2}(\pi - \tau)$ apply under the assumption that the long molecular axis is perpendicular to the planes of the CD₂ segments in the all-trans conformation and that all bond angles are tetrahedral (τ). From the ratio of the quadrupole splittings in the lamellar phase at about 115 to 120°C ($\nu_Q^s/\nu_Q^i \approx 1.34$) we may determine the kink probability per segment to be approximately 0.2. This is equivalent to an average of 2.7 kinks per disoap molecule and corresponds to an effective reduction of the molecular length from 21.5 to 18.1 Å. Once p and therefore $\langle \frac{1}{2}(3 \cos^2 \beta - 1) \rangle$ is known the molecular order parameter can be determined from the observed quadrupole splitting, yielding for the lamellar phase $S_m \approx 0.4$.

A similar analysis for the hexagonal phase is less justified since the assumption of near constancy of the ν_Q s (for $i \neq \alpha$) does not hold. If, for the sake of comparison, we nevertheless apply this analysis using 14.6 kHz for the α -deuterons and an average of 9 kHz for the rest of the methylenes, we obtain $p = 0.28$ and $S_m \approx -0.33$, where the negative sign of S_m reflects the assumption that the molecules lie on average in a plane transverse to the rod direction. Thus perpendicular to the rod interface the

ordering of the molecules is 0.66 which must be compared with 0.4 in the lamellar phase. The reduced molecular length due to kink formation in the hexagonal phase is 16.9 Å, compared to 18.1 Å in the lamellar phase.

These numbers, regarding the ordering of the molecules and their conformations in the mesophases, should not be taken too seriously because of the many simplifying assumptions made in their calculation. Qualitatively, however, they give a consistent picture and provide a means for comparison between the ordering of the molecules in the various mesophases.

4. Discussion

To gain more insight into the structure of the mesophases at the molecular level we present some calculations relating the geometrical parameters determined from the X-ray experiments and the molecular ordering obtained from N.M.R. Assuming complete segregation between regions containing neat disoap and neat water, the lamellar phase can be viewed as alternating layers of disoap and water molecules (with widths d_a and d_w respectively) and the hexagonal phase as amphiphile rods (with diameter $2r$) imbedded in a water environment (see figure 8). In both cases an interface involving the carboxyl groups of the disoaps and water is formed. Following Luzzati [9] these quantities can be computed from the known densities ρ_a [1, 2] and ρ_w of the neat amphiphile and water, and the corresponding weight fractions, c_a and c_w of the two constituents:

$$d_a = d \left(1 + \frac{\rho_a c_w}{\rho_w c_a} \right)^{-1}, \quad d_w = d - d_a. \quad (4)$$

Similarly the average surface area, S_a , per carboxyl group at the layers interface is given by

$$S_a = \frac{M_a}{N_A \rho_a d_a}, \quad (5)$$

where M_a is the molecular weight of the disoap. Substituting the experimental values at 115°C: $d = 22.4$ Å, $\rho_a = 1.25$ g/ml, $\rho_w = 1.05$ g/ml, yields $d_a = 11.6$ Å, $d_w = 10.8$ Å and $S_a = 42$ Å². Within the temperature (100–170°C) and concentration (56–60 wt %) range in which the lamellar phase was studied these parameters are essentially constant. These results may be compared with those of Gallot [2] who obtained for the concentration range 53 to 68 wt % at 104°C $d = 24.1$ to 23.1 Å and accordingly $d_a = 11.4$ to 14.4 Å; $d_w = 12.7$ to 8.6 Å and $S_a = 42.4$ to 33.4 Å². The result of 11.6 Å

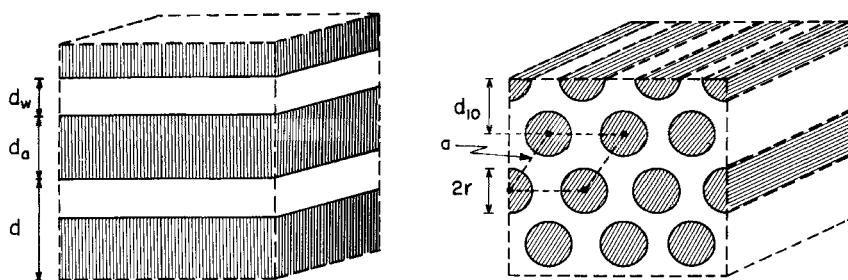


Figure 8. Schematic representation and definitions of geometrical parameters for the lamellar and hexagonal mesophases of the $C_{16}K_2$ disoap-water system.

for d_a may be related to the orientational order parameters derived from the N.M.R. measurements. If for simplicity we assume a rectangular distribution function for the disoap tilt angle in the lamellae, bounded between zero and a maximum allowed inclination angle, ε_{\max} , then taking $S_m = 0.4$ will give $\varepsilon_{\max} = 58^\circ$. This value corresponds almost exactly to the angle that an all-trans molecule has to tilt in order to be accommodated in the lamellae ($\varepsilon = 57.3^\circ$) with the carboxyl groups still occupying both interfaces.

An analogous analysis of the results for the hexagonal phase yields for the radius and head group area (S_a) of the amphiphile in the rods

$$r = d_{10} \left(\frac{2c_a \varrho_w}{\pi \sqrt{3(c_a \varrho_w + c_w \varrho_a)}} \right)^{1/2}, \quad S_a = \frac{M_a}{N_A \varrho_a r}. \quad (6)$$

Substituting the relevant parameters and the experimental value for d_{10} (24.5 Å) yields $2r \approx 19$ Å and $S_a \approx 49$ Å², again with very little variation within the temperature and concentration stability range of the hexagonal phase. On the other hand, considering the effect of kinks and molecular disorder, discussed in connection with the N.M.R. results, a projection of the molecular length on the transverse plane of the rod of 15–16 Å is calculated. This is consistent with a model in which the disoap molecules are stretched across the rod diameter, excluding for example a structure consisting of a cylindrically folded monolayer with the carboxyl groups forming both the centre core of the rods and their outer interface. Also excluded, on geometrical grounds, is a reversed hexagonal phase with water cylinders surrounded by disoap molecules. For such a phase the appropriate analogues of equations (6) yield very wide water cylinders ($2r = 20$ Å) leaving too little space to allow the disoap molecules to bend around the cylinders.

It appears therefore, although on the basis of only limited experimental data, that disoaps and monosoaps form very similar lyomesophases. The molecular organization in these mesophases, i.e. into lamellae and rods in the lamellar and hexagonal phases respectively, have essentially the same structures with interfaces consisting of carboxyl groups which form the boundary between the hydrophobic alkyl chains and the water regions. In fact both the lamellar and hexagonal phases of the disoaps can be visualized as resulting from monosoap molecules which have dimerized by covalently linking the methyl ends of the alkyl chains.

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