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Head group ordering in the lyomesophases of the dipotassium hexadecanedioate–water system studied by ^{13}C and ^{2}H NMR

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Carbon-13 NMR measurements are reported for the hexagonal (hex) and lamellar (lam) mesophases formed by water and dipotassium hexadecanedioate (isotopically enriched in the carboxyl group). The average anisotropic ^{13}C chemical shift tensor in both mesophases has uniaxial symmetry and is almost independent of temperature with average values (relative to TMS) of $\langle\sigma_{\parallel}\rangle^{\text{hex}} = 171{\cdot}3$ ppm, $\langle\sigma_{\perp}\rangle^{\text{hex}} = 192{\cdot}4$ ppm, $\langle\sigma_{\parallel}\rangle^{\text{lam}} = 200{\cdot}2$ ppm, $\langle\sigma_{\perp}\rangle^{\text{lam}} = 177{\cdot}1$ ppm and $\sigma_{\text{iso}} = 184{\cdot}8$ ppm. These results together with earlier quadrupole interaction data of the α-methylene deuterons, and a simple model for the structure of the $-C^{\alpha}H_2COOK$ moiety are used to estimate the effective order parameters, n, of the disoap head groups along the direction normal to the water interfaces. The results are $n^{\text{hex}} \approx 0{\cdot}44$ and $n^{\text{lam}} \approx 0{\cdot}27$.

1. Introduction

In a recent series of publications [1–3] we have described the mesomorphic properties of mixtures of water with the disoap dipotassium hexadecanedioate (dipotassium thapsate, $KOOC(CH_2)_{14}COOK$, or in short $C_{16}K_2$). It was shown that, depending on the concentration of the disoap and the temperature, two types of uniaxial mesophases may exist. In the concentration range 40 to 55 wt% $C_{16}K_2$ a hexagonal phase is formed consisting of rod-like micelles in which the disoap molecules are stretched across the rods (see figure 1 (*a*)). At higher disoap concentrations the system exhibits two mesophases, (i) at low temperatures ($\leqslant 110^{\circ}$C) the same hexagonal phase as that observed below 55 wt% disoap and (ii) a lamellar phase at higher temperatures ($\geqslant 120^{\circ}$C). The latter phase consists of monolayers of disoap molecules interleaved with layers of water (see figure 1 (*b*)). Between the lamellar and hexagonal phases there is an intermediate isotropic phase which is, however, usually only observed on heating. The identification of the mesophases and information about their structure and ordering characteristics was obtained by extensive optical microscopy, X-ray and deuterium NMR measurements [1–3]. In particular deuterium NMR of deuteriated $C_{16}K_2$ was used to learn about the ordering of the alkyl chains of the disoap and the deuterium signal from the solvent D_2O provided information about the water ordering. These measurements did not, however, provide information about the

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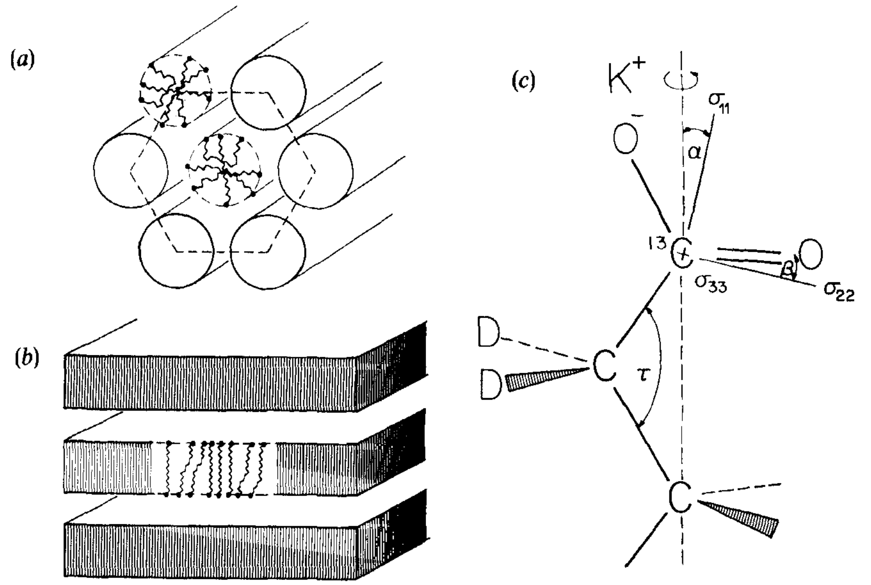

Figure 1. Schematic diagrams of the structures of the hexagonal (*a*) and lamellar (*b*) mesophases of the dipotassium hexadecanedioate–water system. (*c*) The structure and relevant parameters used in the analysis of the head group ordering in the mesophase.

interfacial region between the carboxyl groups of the disoap and the water. Here we attempt to fill in this gap using carbon-13 NMR of $C_{16}K_2$ molecules specifically labeled at the carboxyl head groups as well as earlier deuterium NMR results of the α-deuterons [2]. The approach we adopt is similar to that used earlier for ^{31}P and ^{13}C NMR of polar head groups in lyotropic liquid crystals and membrane systems [4–10]. So far there appears to be only very few studies of the carboxyl carbon in soaps where the carboxylic head group is ionized [11–13]. Long and Goldstein [11] measured the ^{13}C chemical shift anisotropy of the alkyl and carboxyl carbons in the lyomesophases of potassium laurate and analysed these data together with deuterium quadrupole interaction splittings measured on the same system in terms of chain ordering and chain conformation. Delikatny and Burnell [12, 13] investigated the ordering of the $-C^{\alpha}H_2COOK$ head group in the lamellar lyomesophase of potassium palmitate. They performed a detailed analysis of the ordering of this group based on the dipolar interaction between the α-protons and the 1-^{13}C with additional information from the quadrupole interaction of the α-deuterons. Since we are unable to obtain the dipolar interaction in $C_{16}K_2$ our analysis is somewhat more qualitative and is mainly based on the average chemical shift tensor of the carboxyl ^{13}C and the average quadrupole interaction of the α-deuterons as was done by Long and Goldstein [11]. Nevertheless using suitable approximations, useful information about the ordering of the $-C^{\alpha}H_2COOK$ head group in the two lyomesophases of $C_{16}K_2$ could be obtained.

2. Experimental

Dipotassium thapsate labelled with ^{13}C at the two carboxyl groups ($C_{16}K_2$-1,16-^{13}C) was prepared by neutralization of the corresponding ^{13}C labelled diacid with KOH in a methanol solution. The starting material for the preparation of the hexadecanedioic acid-1,16-^{13}C was 1,14-dibromotetradecane which was obtained by bromination of tetradecane-1,14-diol (Aldrich) using red phosphorus and bromine [14]. The dibromide was converted to the 1,14-dicyanotetradecane by reaction with potassium cyanide-^{13}C in an ethanol–water mixture under reflux according to the procedure of Vanino [15]. The desired compound was obtained, without isolation of the dinitrile, by hydrolysis with concentrated sulphuric acid. After several ether extractions pure hexadecanedioic acid-1,16-^{13}C (70 per cent yield) was obtained (mp 122–124°C) with 80 at.% ^{13}C at each carboxylic group.

Two solutions were studied containing (I) 50·5 and (II) 57·0 wt% $C_{16}K_2$ in D_2O. The disoap used consisted of a mixture of isotopically normal $C_{16}K_2$ (82 per cent) and $C_{16}K_2$-1,16-^{13}C (18 per cent), so that the ^{13}C enrichment was about 15 at.% for each head group. The solvent D_2O was chosen in order to allow independent observation of the ordering of the samples by ^{2}H NMR. The low concentration solution (I) exhibits only the hexagonal phase, and shows the phase sequence,

Solid 63°C Hex 120°C Iso,

while the more concentrated solution (II) exhibits the hexagonal and lamellar phases, and may also exhibit an intermediate isotropic phase,

Solid 63°C Hex 115°C interm. Iso 130°C Lam 160°C Iso.

Samples were prepared in short, sealed 5 mm o.d. tubes and placed in a coaxial position into 10 mm tubes for the NMR measurements. NMR measurements were performed on a Bruker AM 400 WB spectrometer operating at 100·62 MHz for ^{13}C and 61·43 MHz for ^{2}H. A dual 10 mm ^{13}C-^{2}H low power probe was used which allowed measurements of both the ^{13}C and ^{2}H signal of all samples at all temperatures without removing the sample from the spectrometer. The spectra were recorded using single pulses (12 μs width for ^{13}C and 15 μs for ^{2}H) followed by Fourier transformation. The ^{13}C spectra were measured with proton broad band decoupling. This was essential for obtaining reasonable signal-to-noise and accurate lineshape for the ^{13}C nuclei. Usually 500 to 1500 scans were necessary (with 2 s delay time) for the ^{13}C signals and 40 to 120 (with 0·1 s delay) for the ^{2}H signal of the D_2O solvent. The chemical shifts of ^{13}C are reported relative to TMS. They were measured relative to the narrow methylene central line, which itself was determined separately relative to TMS in an isotropic solution.

3. Results and discussion

From our previous NMR measurements on the lyomesophases of $C_{16}K_2$ [1–3] we know that bulk samples of the lamellar phase undergo spontaneous alignment in the magnetic field of the NMR spectrometer with the director aligning perpendicular to the field direction ($\Delta\chi < 0$). Thus in this phase only the perpendicular components of the magnetic tensors (chemical shift for ^{13}C and quadrupole splitting for ^{2}H) can be measured. The hexagonal phase, on the other hand, which is the only one to exist in the more dilute solution (I) and also appears at low temperatures in the more concentrated solution (II), does not spontaneously align. In fact at high concentrations of $C_{16}K_2$ the domains of the hexagonal phase will remain randomly distributed even at the high magnetic field of our NMR spectrometer, but at low concentrations partial alignment is usually observed, with more domains orienting preferentially parallel to the magnetic field direction ($\Delta\chi > 0$). This alignment becomes more pronounced as the concentration of $C_{16}K_2$ is decreased and the temperature increased. In order to ensure that the domains in the hexagonal phase, in the two solutions (I) and (II) are as close to random distribution as possible the following procedure for recording the spectra was adopted. The sample was first heated to above 120°C into the isotropic liquid (for solution I) or to the lamellar phase (for solution II), then allowed to cool to room temperature into the (supercooled) hexagonal phase outside the magnetic field of the NMR spectrometer. Only then was the sample inserted into the NMR probe at the lowest desired temperature, followed by spectra recording as a function of increasing temperature.

3.1. *The hexagonal phase (solution I) and the low temperature region of solution (II)*

Carbon-13 and ^{2}H NMR spectra for solutions (I) and (II), are shown in figures 2 and 3 respectively at several temperatures. It may be seen that both samples, in the hexagonal region, indeed exhibit powder patterns. In the low temperature (73°C) spectrum of solution (I) the lineshape of both the ^{13}C and ^{2}H spectra are typical of a random distribution of domains with axial symmetry. As the temperature is increased a small asymmetric signal develops on top of the parallel features of the powder patterns indicating that partial alignment of domains takes place parallel to the magnetic field direction. Close to the clearing temperatures a sharp central peak appears which eventually dominates the spectrum. The spectrum of the hexagonal phase in solution (II) also indicates a small degree of partial alignment. On the basis of this interpretation it is straightforward to determine the principal values of the ^{13}C chemical shift tensor in the two solutions simply from the positions of the parallel and perpendicular features in

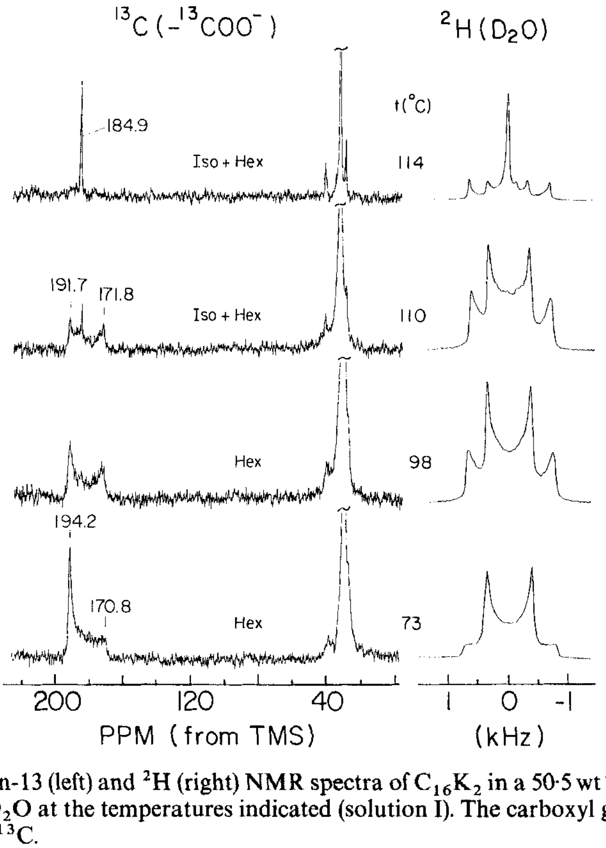

Figure 2. Carbon-13 (left) and ^{2}H (right) NMR spectra of $C_{16}K_2$ in a 50·5 wt % solution of the disoap in D_2O at the temperatures indicated (solution I). The carboxyl group is enriched to 15 at.% ^{13}C.

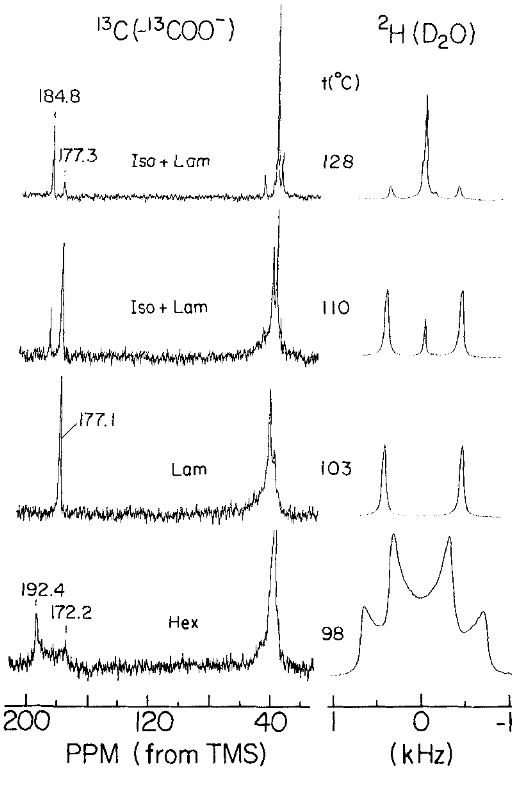

Figure 3. Carbon-13 (left) and ^2H (right) NMR spectra of $C_{16}K_2$ in a 57·0 wt % solution of the disoap in D_2O at the temperatures indicated (solution II). The carboxyl group is enriched to 15 at.% ^{13}C.

the spectra. The results for $\langle\sigma_\parallel\rangle^{\text{hex}}$ and $\langle\sigma_\perp\rangle^{\text{hex}}$ are plotted in figures 4 and 5 for solutions (I) and (II) respectively as a function of the temperature. It can be seen that the chemical shift tensor components in both solutions are almost identical and essentially independent of the temperature in the mesophase region.

3.2. *The lamellar phase (high temperature region of solution (II))*

As solution (II) is heated to above 115°C it passes through a narrow intermediate isotropic region, then (at ~130°C) a lamellar phase is formed which spontaneously aligns with the director orienting perpendicular to the magnetic field direction. In the temperature region of the lamellar phase the system is usually biphasic with part of the sample being isotropic. NMR spectra of this phase in solution (II) are shown in figure 3. These were actually obtained after cooling back from higher temperatures to the supercooled state of the lamellar phase. In general two peaks are observed, one very sharp at 184·8 ppm due to the isotropic solution and a second somewhat broader, shifted 7 to 8 ppm towards higher fields due to domains of the lamellar phase oriented in the perpendicular orientation. The chemical shift of these peaks are plotted in figure 5 over the temperature range measured. As may be seen the chemical shift for the lamellar phase is changed very little as a function of temperature.

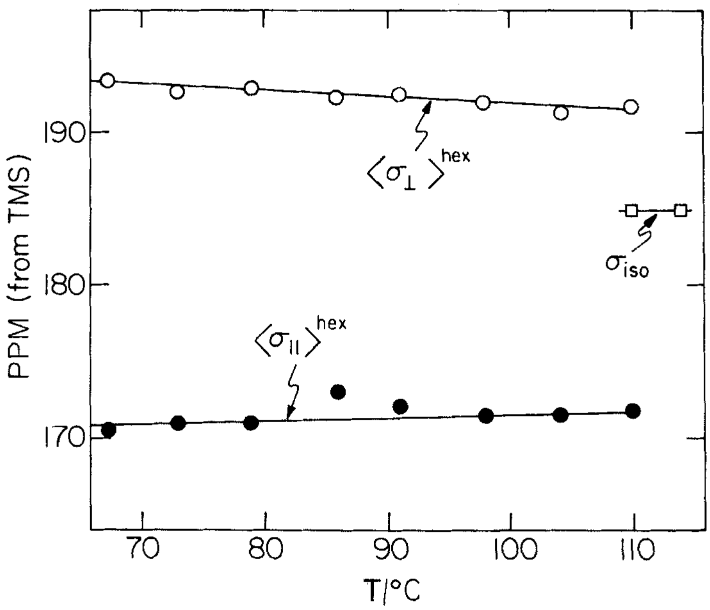

Figure 4. Plots of $\langle\sigma_\parallel\rangle^{hex}$, $\langle\sigma_\perp\rangle^{hex}$ and σ_{iso} as measured for the hexagonal and isotropic phases in solution (I) as a function of temperature.

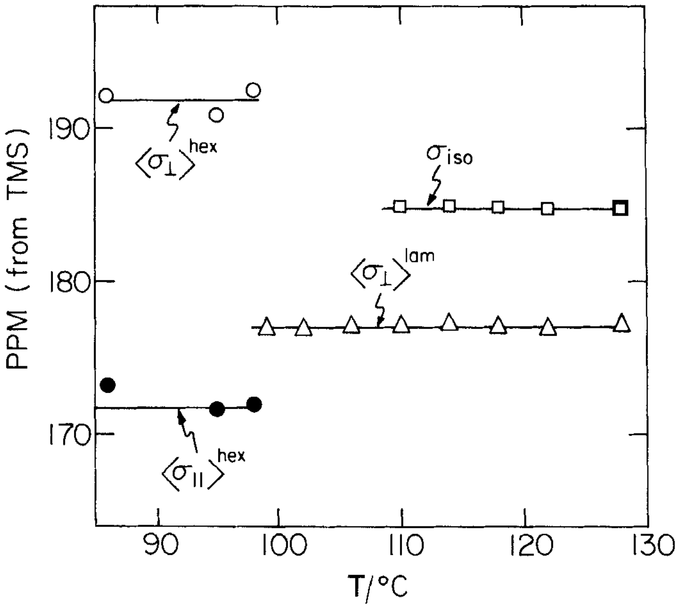

Figure 5. Plots of $\langle\sigma_\parallel\rangle^{hex}$, $\langle\sigma_\perp\rangle^{hex}$, $\langle\sigma_\perp\rangle^{lam}$ and σ_{iso} as measured for the hexagonal, lamellar and isotropic phases in solution (II) as a function of temperature.

The deuterium NMR spectra of the D_2O solvent confirm the interpretation of the ^{13}C results of the lamellar phase. They exhibit a sharp central peak due to the isotropic phase and a doublet corresponding to the average perpendicular quadrupole splitting due to the lamellar phase. More details on the splittings of the D_2O deuterons in both the hexagonal and lamellar phases and their temperature dependence may be found in [1].

3.3. *Analysis of the NMR results*

For a quantitative analysis of the ^{13}C results it is convenient to consider the average anisotropic components of the carboxyl carbon chemical shift tensors, $\langle\bar{\sigma}_i\rangle$, in the two mesophases. Taking the measured values in the centre of the mesophase region in solution (I) for the hexagonal phase ($\langle\sigma_\parallel\rangle^{\text{hex}} = 171{\cdot}3$ ppm, $\langle\sigma_\perp\rangle^{\text{hex}} = 192{\cdot}4$ ppm) and similarly the high temperature region of solution (II) for the lamellar phase ($\langle\sigma_\perp\rangle^{\text{lam}} = 177{\cdot}1$ ppm) we obtain

$$\begin{aligned}
\langle\bar{\sigma}_\parallel\rangle^{\text{hex}} &= \langle\sigma_\parallel\rangle^{\text{hex}} - \sigma_{\text{iso}} = -14{\cdot}1\text{ ppm},\\
\langle\bar{\sigma}_\perp\rangle^{\text{hex}} &= \langle\sigma_\perp\rangle^{\text{hex}} - \sigma_{\text{iso}} = 7{\cdot}0\text{ ppm},\\
\langle\bar{\sigma}_\perp\rangle^{\text{lam}} &= \langle\sigma_\perp\rangle^{\text{lam}} - \sigma_{\text{iso}} = -7{\cdot}7\text{ ppm},\\
\langle\bar{\sigma}_\parallel\rangle^{\text{lam}} &= 15{\cdot}4\text{ ppm},
\end{aligned}$$

where we have used $\sigma_{\text{iso}} = 185{\cdot}4$ ppm for the hexagonal phase, and $184{\cdot}8$ ppm for the lamellar phase and the relation $\langle\bar{\sigma}_\perp\rangle = -\frac{1}{2}\langle\bar{\sigma}_\parallel\rangle$. These anisotropic chemical shifts are considerably reduced with respect to the static principal values, $\bar{\sigma}_{ii}$, of the carboxylic carbon [16–19] and reflect, of course, the motional averaging and ordering of the disoap in the interface region. Note in particular the opposite sign of $\langle\Delta\sigma\rangle = \langle\sigma_\parallel\rangle - \langle\sigma_\perp\rangle$ in the hexagonal and lamellar phases as found also for the carboxylic carbon in the mesophases of potassium laurate [11] and for ^{31}P in corresponding phospholipid systems. In fact this behaviour of ^{31}P spectra has been used as a diagnostic tool for identifying lyotropic mesophases [4–7].

An estimate of the static anisotropic chemical shift tensor of the carboxyl carbon can be obtained from experimental measurements on alkyl salts and acids in the solid state [16–19]. We assume that the carboxyl group at the interface is not symmetric (see figure 1 (*c*)) so that the principal coordinate system of the chemical shift tensor of the carboxyl carbon is inclined with respect to the bisector of the OCO group. According to Veeman [20] suitable average values for the principal components, σ_{ii}, of this tensor are $\sigma_{11} = 245$ ppm, $\sigma_{22} = 169$ ppm and $\sigma_{33} = 105$ ppm, corresponding to the anisotropic components $\bar{\sigma}_{11} = 72$ ppm, $\bar{\sigma}_{22} = -4$ ppm and $\bar{\sigma}_{33} = -68$ ppm, and the (average) principal directions as shown in figure 1 (*c*), with $\beta = 12°$. These values are probably sufficiently close to the true ones for the COOK group to allow reliable estimates of the ordering characteristics of the disoap head groups to be made and are certainly suitable for comparing the two mesophases. We note that the isotropic chemical shift calculated from the average principal values of the static tensor, 173 ppm, is about 12 ppm smaller than the experimental value of 185 ppm found in the isotropic solution of $C_{16}K_2$. The discrepancy is, however, within the distribution range of σ_{iso} of the carboxyl carbon [20].

In addition to this ^{13}C chemical shift data we shall also use the earlier deuterium NMR measurements on $C_{16}K_2$ deuteriated at the α-carbons [2], which provide information on the average quadrupole interaction parameter of the α-methylene deuterons. In both mesophases this interaction was fairly constant, deviating by not more than 3·5 per cent from the corresponding mean values which were, $|\langle\Delta\nu_{\parallel}^{\alpha}\rangle^{\mathrm{hex}}| = 14{\cdot}5$ kHz in the hexagonal phase and $|\langle\Delta\nu_{\parallel}^{\alpha}\rangle^{\mathrm{lam}}| = 18{\cdot}8$ kHz in the lamellar phase. Here $\langle\Delta\nu_{\parallel}^{\alpha}\rangle$ refers to half of the full quadrupole splitting observed with the magnetic field along the director. Only the magnitude of the interactions are indicated since their signs cannot be determined from the experiments. These results should be compared with the deuterium static quadrupole interaction which we assume to be axially symmetric along the C$^{\alpha}$–D bond, with a major principal value of $\nu_Q = \frac{3}{4}(e^2qQ/h) \approx 125$ kHz.

For simplicity we assume that the –C$^{\alpha}$D$_2$COOK moiety has a plane of symmetry which includes the COO$^-$ group and the bisector of the C$^{\alpha}$D$_2$ segment (see figure 1 (*c*)) with $\angle$OCO = $\angle$CCO = 120° and $\angle$CCC = $\angle$DCD = 109·47° (the tetrahedral angle). Consequently only one principal direction of the ordering tensor is determined by the local symmetry of the head group, i.e. the direction perpendicular to the symmetry plane (x). A complete evaluation of the head group ordering matrix therefore requires the determination of the other principal directions (z, y), and two order parameters, e.g. S_{zz} and $S_{xx}-S_{yy}$, where $S_{ii} = \langle\frac{1}{2}(3\cos^2\gamma_i - 1)\rangle$ and γ_i is the instantaneous orientation of the ith principal direction of the ordering tensor and the director. Since, however, only two independent relevant experimental parameters are available ($\langle\bar{\sigma}_{\parallel}\rangle$ and $\langle\Delta\nu_{\parallel}^{\alpha}\rangle$) the problem is underdetermined and we need to resort to additional simplifying assumptions. In the most extreme simplification we assume that the –C$^{\alpha}$D$_2$COOK group has cylindrical symmetry with the unique axis (z) lying perpendicular to the CD$_2$ plane. With these approximations there is only one independent parameter, S_{zz}, and the observed anisotropic chemical shift of the carboxyl carbon and the quadrupole splitting of the α-deuterons become [21]

$$\langle\bar{\sigma}_{\parallel}\rangle^p = S_{zz}(\bar{\sigma}_{11}\cos^2\alpha + \bar{\sigma}_{22}\sin^2\alpha),$$

$$\langle\Delta\nu_{\parallel}^{\alpha}\rangle^p = S_{zz}\nu_Q\frac{1}{2}\left(3\cos^2\frac{\pi}{2} - 1\right),$$

where the superscript p stands for either the hexagonal or the lamellar phase and the angles α and $\pi/2$ correspond to the relative orientations of the principal component σ_{11} and the C$^{\alpha}$–D bond relative to the principal z-component of the ordering tensor. Substituting the experimental results for $\langle\bar{\sigma}_{\parallel}\rangle^p$ and $\langle\Delta\nu_{\parallel}^{\alpha}\rangle^p$, and the structural ($\beta$, $\angle$OCO, $\angle$DCD, $\angle$CCC) and magnetic ($\bar{\sigma}_{ii}$, ν_Q) parameters given here, yields $S_{zz}^{\mathrm{hex}} = -0{\cdot}22$ and $-0{\cdot}23$ from the ^{13}C and ^{2}H results, respectively, and 0·24 and 0·30 for S_{zz}^{lam}. In these calculations we have assumed $\langle\Delta\nu_{\parallel}^{\alpha}\rangle^{\mathrm{hex}} > 0$ and $\langle\Delta\nu_{\parallel}^{\alpha}\rangle^{\mathrm{lam}} < 0$ in order to make the results from the quadrupole interaction consistent with those of the chemical shift.

If instead of the assumed cylindrical approximation for the symmetry of the head group, we also admit a biaxial order parameter, $(S_{xx}-S_{yy})$, but still assume the same molecular fixed coordinate system with z along the perpendicular to the CD$_2$ plane and y along its bisector (i.e. assuming $S_{xy}=0$) the equations for $\langle\bar{\sigma}_{\parallel}\rangle^p$ and $\langle\Delta\nu_{\parallel}^{\alpha}\rangle^p$ become [21]

$$\langle\bar{\sigma}_{\parallel}\rangle^p = S_{zz}(\bar{\sigma}_{11}\cos^2\alpha + \bar{\sigma}_{22}\sin^2\alpha) + \tfrac{1}{2}(S_{xx}-S_{yy})[\bar{\sigma}_{11}\sin^2\alpha - \tfrac{1}{3}(\bar{\sigma}_{33}-\bar{\sigma}_{22})(1+\cos^2\alpha)],$$

$$\langle\Delta\nu_{\parallel}^{\alpha}\rangle^p = -\tfrac{1}{2}\nu_Q[S_{zz} - \tfrac{1}{3}(S_{xx}-S_{yy})].$$

Using the same parameters as before we now obtain $S_{zz}^{\mathrm{hex}} = -0{\cdot}22$, $(S_{xx}^{\mathrm{hex}} - S_{yy}^{\mathrm{hex}}) = +0{\cdot}02$ for the hexagonal phase, and $S_{zz}^{\mathrm{lam}} = 0{\cdot}27$, $(S_{xx}^{\mathrm{lam}} - S_{yy}^{\mathrm{lam}}) = -0{\cdot}09$ for the lamellar phase.

Due to the limited experimental data we cannot place too much weight on the secondary order parameters ($S^p_{xx}-S^p_{yy}$) derived for the various phases, but the results obtained for S^p_{zz} seem quite consistent and in the following we shall limit the discussion to this parameter only using the average values $S^{\mathrm{hex}}_{zz}=-0{\cdot}22$, $S^{\mathrm{lam}}_{zz}=0{\cdot}27$.

3.4. *The ordering of the head groups in the interfaces*

To continue the discussion within this approximation it is appropriate to define an interface order parameter, n, which measures the degree of ordering of the polar heads along the interface normal [22]. For the lamellar phase clearly $n^{\mathrm{lam}}=S^{\mathrm{lam}}_{zz}$ since the interface normal is parallel to the director. For the hexagonal phase we take $n^{\mathrm{hex}}=-2S^{\mathrm{hex}}_{zz}$ to account for the fact that in this phase the director is perpendicular to the interface. In this way also the effect of fast lateral diffusion around the periphery of the rods is cancelled out. Taking these average values for S^{hex}_{zz} and S^{lam}_{zz} then yields $n^{\mathrm{hex}}=0{\cdot}44$ and $n^{\mathrm{lam}}=0{\cdot}27$. The higher value obtained for n^p in the hexagonal phase is probably partly due to the fact that it is stable at lower temperatures than the lamellar phase. The effect of temperature seems however to be secondary, as we have seen within each mesophase region that the orientational order is fairly constant with temperature. A more important factor affecting the head group orientation is most likely the difference in curvature of the interface region in the two mesophases. While in an ideal lamellar phase the interface is essentially flat, in the hexagonal phase it is highly curved. This would be expected to lead to a higher area per head group for the hexagonal compared to the lamellar phase and consequently to a lower order parameter, contrary to observation. This perhaps indicates that the lamellar phase is not strictly flat. For example it could have a ribbon structure where diffusion around the ribbon results in a reduction of the observed anisotropy. Clearly more work is required to clarify this point.

In the previous studies [2, 3] of the $C_{16}K_2$–water system by deuterium NMR of the perdeuteriated disoap the results were analysed in terms of a model in which the chain ordering is determined by two main factors; one that reflects the overall anisotropic motion of the chains due to orientational disorder S_m and a second due to conformational disorder. Despite the many approximations used in the analysis the results derived for S_m ($S^{\mathrm{hex}}_m\approx-0{\cdot}33$, $S^{\mathrm{lam}}_m\approx0{\cdot}4$) and in particular their ratios are quite similar to those obtained in the present work for the head group ordering S_{zz}.

A similar analysis of molecular ordering relative to the interface normal was performed on the lamellar and hexagonal phases of some monosoap–water systems using the deuterium quadrupole splittings in perdeuteriated samples [22]. In these cases however the reported degree of ordering (equivalent to our n^{hex} and n^{lam}) appear to be very similar in both phases, being slightly larger in the lamellar phase. It would be interesting to extend these studies using ^{13}C NMR of the carboxyl group in order to check whether the difference in the results obtained for mono- and disoaps is real or perhaps due to the procedure used in the analysis of the deuterium data. Despite the rich polymorphism and the many studies performed on the monosoap–water system only very few such investigations [11] have been reported so far.

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