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^{2}H NMR study on the lyomesophases of the system hexaethylene glycol dodecyl methyl ether/water Temperature dependence of quadrupole splittings

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The liquid-crystalline phases of the system hexaethylene glycol n-dodecyl methyl ether ($C_{12}E_6C_1$)/water are studied by deuteron NMR spectroscopy. Information about the molecular orientation is derived from the quadrupole splittings of two selectively deuteriated derivatives of $C_{12}E_6C_1$, one deuteriated at the α-position of the alkyl chain, the other at the methoxy group. The temperature dependence of the quadrupole splittings reveals a continuous decrease of orientational order on approach to the macroscopic phase transformations. This behaviour is explained by an increase of defects and fluctuations in the microstructure of the mesophases.

1. Introduction

Over the past few years the polymorphism of lyotropic liquid crystals [1, 2] has attracted the interest of researchers from diverse fields, extending from mathematics to the life sciences. For instance, the possible mesophase structures are derived by decurving surfaces in non-euclidian curved space [3–5] and the role of cubic phases in fusion and transport processes of biological membranes is investigated [6, 7]. Although innumerable studies on surfactant systems have been published, many questions remain about the relationship between lyotropic polymorphism and molecular behaviour, in particular transformation between phases of different symmetry. Recent publications indicate that the microscopic phase structure of lyotropics changes more or less continuously with both concentration of the components [8] and temperature [9]. In order to analyse the molecular origin of such changes, we performed NMR studies on selectively deuteriated hexaethylene glycol n-dodecyl methyl ether ($C_{12}E_6C_1$). This amphiphilic molecule is a typical representative of the class of the non-ionic oligo(ethylene oxide surfactants, $C_nH_{2n+1}(OCH_2CH_2)_mOR$, in short C_nE_m for R=H and $C_nE_mC_1$ for R=CH_3 [9–23]. $C_{12}E_6C_1$ shows a sequence of three different mesophases. With increasing surfactant concentration, a hexagonal H_1 phase, a narrow cubic V_1 phase, and a lamellar L_α phase are observed [16]. The methylated surfactant was chosen to avoid specific effects arising from the hydrogen bonds of the hydroxy group. $C_{12}E_6C_1$ shows the same sequence of mesophases as its unmethylated analogue, $C_{12}E_6$, but the upper transition temperatures of the mesophases and the clouding point of the micellar solution phase, L_1, are considerably lower in $C_{12}E_6C_1$ [16]. Oligo(ethylene oxide) alkyl ethers have the advantage that the sizes of both their hydrophobic and their hydrophilic part can be modified over a wide range. To explore the relationship between the size and shape of a surfactant on the one hand and its phase diagram on the other, not only the length of the chains can be varied but also branched moieties can be introduced [23].

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Among the NMR methods used to investigate lyotropic systems [11–13, 15, 17–19, 24–26], deuteron NMR spectroscopy, which probes the orientation of individual bonds via the quadrupole coupling of the spins, is certainly the most direct technique for the study of molecular orientation and order. Because of the synthetic effort involved with the isotopic labelling of the surfactant molecules, to date most ^{2}H NMR studies on ethylene oxide surfactants have been on binary mixtures where the second component, namely water, was deuteriated [13, 15]. A recent example for a ^{2}H NMR study of the surfactant itself is the work by Ward and collaborators [17]. These authors reported the order profile, that is the quadrupole splittings for all the different deuterium positions along the chain, for $C_{12}E_4$ in the lamellar phase.

The work presented here deals with $C_{12}E_6C_1/H_2O$, where the surfactant is selectively deuteriated in either one of two positions: at the α-position of the alkyl chain ($C_{12}E_6C_1$-d_2) or at the methoxy group at the outer end of the hydrophilic moiety ($C_{12}E_6C_1$-d_3). These positions were selected to provide probes both for the orientational order of the surfactant molecule as an entity (α-position) and for the hydrophilic head group (methoxy position), with a minimum of synthetic work.

In the following section, the theoretical background of deuteron NMR spectroscopy on lyotropic mesophases is reviewed. That section is followed by a brief description of the synthetic and experimental procedures. After that, the experimental data are discussed. The main result, an unexpected temperature dependence of the quadrupole splittings, is explained by changes in the microstructures of the lyotropic mesophases.

2. Deuterium NMR spectra of lyomesophases

The line shape of ^{2}H NMR spectra is dominated by the quadrupole coupling of the spin $I=1$ nucleus with the electric field gradient [27]. For aliphatic C–^{2}H bonds, the electric field gradient tensor is axially symmetric with its principal axis along the bond direction, thus providing a convenient probe for molecular orientations. When no molecular motions are present, for example, for crystalline surfactants at low temperature, the NMR frequencies $\nu_\pm$ of the two transitions are given by

$$\nu_\pm = \nu_0 \pm \delta \tfrac{1}{2}(3\cos^2\theta - 1), \tag{1}$$

where ν_0 is the Larmor frequency, $\delta = 3e^2qQ/4h$, and θ is the angle between the magnetic field and the principal axis of the electric field gradient tensor (the C–^{2}H bond). For aliphatic C–^{2}H bonds, the quadrupole coupling constant (e^2qQ/h) has a value of about 167 kHz.

In the case of rapid motions with correlation times $\tau_c < 10^{-6}$ s, the quadrupole splitting of the two satellite lines, $\Delta\nu = \nu_+ - \nu_-$, is given by the time average (in the following indicated by angular brackets) over the C–^{2}H bond orientations. For molecular motions in a uniaxial liquid-crystalline phase, the averaged splitting $\langle\Delta\nu\rangle$ depends on the angle β between the phase axis (director) **n** and the magnetic field and on the bond order parameter $S_{CD} = \tfrac{1}{2}\langle 3\cos^2\alpha - 1\rangle$, where α is the angle between the C–^{2}H bond direction and the phase axis **n**

$$\langle\Delta\nu\rangle = \delta S_{CD}(3\cos^2\beta - 1). \tag{2}$$

Both director fluctuations and changes of δ due to the motion are assumed to be small and will not be considered. The bond order parameter S_{CD} can take values between $-\tfrac{1}{2}$ and 1.

If the internal motions, namely interconversions between different conformations, and the tumbling of the surfactant molecules are faster than the surfactant diffusion along the hydrophobic/hydrophilic interface, the averaging can be performed in two steps and the bond order parameter can be factorized

$$S_{CD}=\tfrac{1}{2}\langle 3\cos^2\gamma-1\rangle\tfrac{1}{2}\langle 3\cos^2\varepsilon-1\rangle. \qquad (3)$$

Here γ is the angle between the C–^{2}H bond and the normal **a** of the hydrophobic/hydrophilic interface, and ϵ is the angle between **a** and the director **n**.

In an ideal lamellar phase, **a** is parallel to the director ($\varepsilon=0°$) and in an ideal hexagonal phase, consisting of parallel cylinders, **a** is perpendicular to the director ($\varepsilon=90°$). Therefore, $|S_{CD}|$ (and thus the quadrupole splitting) in hexagonal phases should be about half the value observed in lamellar phases. In both cubic mesophases and isotropic micellar solutions S_{CD} vanishes and the spectrum collapses to a single narrow line.

Since the quadrupolar frequency splitting depends on the director orientation, cf. equation (2), the orientational distribution of the crystallites or domains in non-cubic mesophases can be derived from the deuteron NMR line shape [28]. Uniformly oriented samples (single crystals) yield a doublet of narrow lines. The spectrum of an orientationally completely disordered (polycrystalline) sample, on the other hand, is a powder pattern [29], which is narrowed by a factor of S_{CD} compared to the spectrum in the rigid limit. Another characteristic line shape often observed for lyotropic mesophases is the spectrum of a planar director distribution. An example for such a spectrum will be discussed below.

3. Experimental

3.1. *Synthesis of the deuteriated surfactants and sample preparation*

Hexaethylene glycol n-dodecyl methyl ether-1,1,1-d_3 (**1**): Hexaethylene glycol (**2**) was prepared by a Williamson ether synthesis from diethylene glycol and di(1-chloroethylene) ether [30]. Hexaethylene glycol mono-*n*-dodecyl ether (**3**) was synthesized from **2** and *n*-dodecyl bromide [20]. The deuteriated surfactant **1** was prepared by reaction of **3** with iodomethane-d_3 [16].

Hexaethylene glycol n-dodecyl methyl ether-21,21-d_2 (**4**): Hexaethylene glycol mono methyl ether (**5**) was obtained by coupling of triethylene glycol with diethylene glycol (1-chloroethyl) methyl ether [20]. Dodecanol-1,1-d_2 was prepared by reduction of ethyl laureate with $LiAlD_4$ [31] and subsequently reacted to dodecyl 4-toluene sulphonate (**6**) [32]. The deuteriated surfactant **4** was obtained by etherification from **5** and **6** [20].

Several mixtures of the deuteriated surfactants with bidistilled water were prepared by homogenization in a Perkin–Elmer vibrating mill [21]. The phase transition temperatures of these mixtures, which cover the region of liquid-crystalline phases, were determined by differential scanning calorimetry, optical microscopy, and NMR spectroscopy. The transition temperatures were found to agree with the previously published phase diagram [16].

3.2. *Differential scanning calorimetry*

DSC measurements were performed with a Perkin–Elmer DSC 7 calorimeter. Heating scans with scanning rates of $1\,\mathrm{K\,min^{-1}}$, $1{\cdot}5\,\mathrm{K\,min^{-1}}$, and $2\,\mathrm{K\,min^{-1}}$ were recorded. The phase transition temperatures were obtained by extrapolation to zero heating rate [22, 33].

3.3. *Optical microscopy*

The liquid-crystalline mesophases were characterized by their features [34] observed by a Leitz Ortholux II Pol BK polarizing microscope equipped with a Mettler FP 80/82 hot stage.

3.4. *NMR measurements*

The ^2H NMR spectra were recorded on a Bruker CXP 300 spectrometer operating at a deuterium resonance frequency of 46·073 MHz. The measurements at various angles to the magnetic field were performed with a home-made goniometer probe head. All data were obtained applying a $90^0_x - \tau - 90^0_y - \tau$ pulse sequence [35] with full phase cycling to minimize artifacts. Typically, 128 transients were averaged before Fourier transformation. The 90° pulse length was 3·3–3·6 μs and the pulse separation τ was 40 μs. The sample temperature was kept constant to ± 1 K by a Bruker BVT 100 temperature unit. Absolute sample temperatures were determined independently from the data acquisition by calibration with a Pt 100 thermocouple placed directly in the coil of the NMR probe head.

4. Results and discussion

4.1. *Deuterium NMR spectra of oriented samples*

Figure 1 shows the orientation dependence of the ^2H NMR spectra of macroscopically oriented $C_{12}E_6C_1$-d_2/H_2O samples. The top spectra are from samples which were aligned in the magnet by slow cooling from the isotropic phase and subsequent

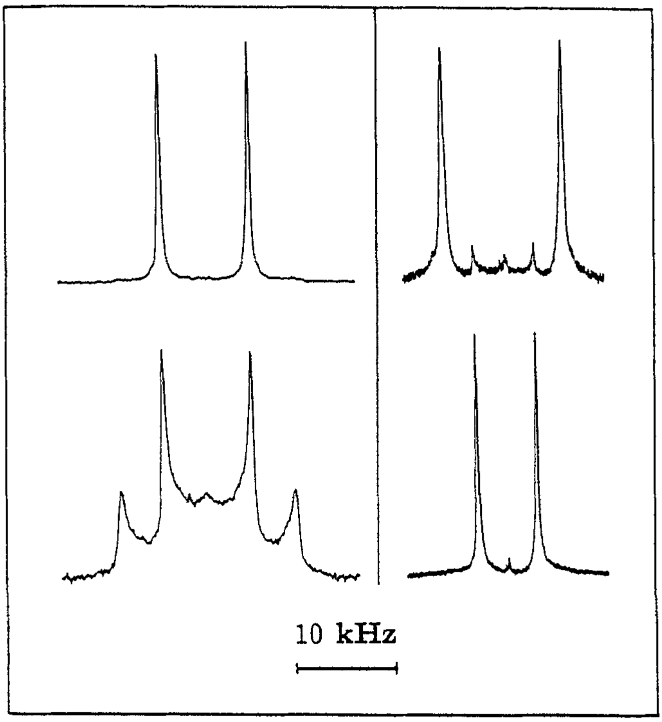

Figure 1. ^2H NMR spectra of oriented $C_{12}E_6C_1$-d_2/water samples. Left: lamellar phase (299 K, 71·6 wt% surfactant), right: hexagonal phase (290 K, 53·2 wt% surfactant). The top spectra are from aligned samples obtained by slow cooling of the sample in the magnet from the isotropic phase, the bottom spectra are from the same samples after a rotation by 90° about an axis perpendicular to the magnetic field.

annealing in the biphasic region. As can be seen from the sharp doublets in these NMR spectra, almost complete orientation of the mesophases is achieved for both the L_α phase (left spectra in figure 1) and the H_1 phase (right spectra in figure 1). Unaligned portions of the samples contribute to the spectral line shapes in the form of small powder patterns underneath the doublets. This is most obvious in the spectrum for the 0° sample orientation of the hexagonal phase (top right spectrum in figure 1), where the peaks of the powder pattern appear as a small doublet in the middle of the spectrum. To decide whether the director orientation, obtained by cooling, is parallel or perpendicular to the magnetic field, spectra for at least one other orientation of the aligned samples with respect to the magnetic field are required. We find that, once the temperature is lowered to the pure mesophase region, the ethylene oxide surfactant mixtures can be reoriented in the presence of the magnetic field without any realignment of the directors, so that the orientation dependence of the line shapes can be measured. Even after several hours and repeated sample rotations, no realignment of the directors is observed and the line shapes for the different sample orientations can be reproduced exactly.

The spectra at the bottom of figure 1 are from aligned samples rotated by 90° about an axis perpendicular to the magnetic field. The line shape of the rotated lamellar sample (bottom left), with its characteristic inner and outer doublet, whose splittings are related by a factor of 1/2, results from a planar director distribution [28] when the magnetic field vector is coplanar with the directors. From the spectral line shapes of the lamellar phase, we conclude that the magnetic field-induced alignment leads to a planar distribution of directors perpendicular to the field. Since, in the lamellar phase, the molecules are on average parallel to the director, the field-induced director alignment perpendicular to the field shows that the diamagnetic anisotropy of the ethylene oxide surfactant molecules is negative, in agreement with other surfactant systems containing alkyl chains [26, 36].

From the orientation dependence of the main doublet in the spectra of the hexagonal sample, shown on the right of figure 1, an alignment of the directors (the hexagonal axes) parallel to the magnetic field is inferred. Thus the surfactant molecules, which in the hexagonal phase are on average perpendicular to the director, have the same preferred orientation with respect to the magnetic field as in the lamellar phase. From a detailed analysis of the orientation dependence of the width of the doublet lines, which shows a maximum when the sample is rotated by 45° from its initial orientation (not shown) and minima for sample orientations of 0° and 90°, the static orientational disorder in the aligned part of the samples can be derived.

4.2. *Temperature dependence of the quadrupole splittings*

In figure 2, the quadrupole splittings $\langle \Delta\nu \rangle$ of the α-deuteriated ($C_{12}E_6C_1$-d_2) and the methoxy-deuteriated ($C_{12}E_6C_1$-d_3) surfactant in the different $C_{12}E_6C_1/H_2O$ mixtures are shown as a function of temperature. The splittings shown for the α-deuteriated surfactant were obtained upon heating. For the methoxy-deuteriated surfactant, the $\langle \Delta\nu \rangle$ values are very small and could not be evaluated from the powder spectra observed upon heating. Therefore, the quadrupole splittings shown in figures 2 (*e*)–(*h*) are from partially oriented samples obtained upon cooling, after the magnetic field had been carefully shimmed on the signal from the samples in the isotropic phase. In general, the values from a cooling series are somewhat larger than those from the corresponding heating series, indicating effects from supercooling.

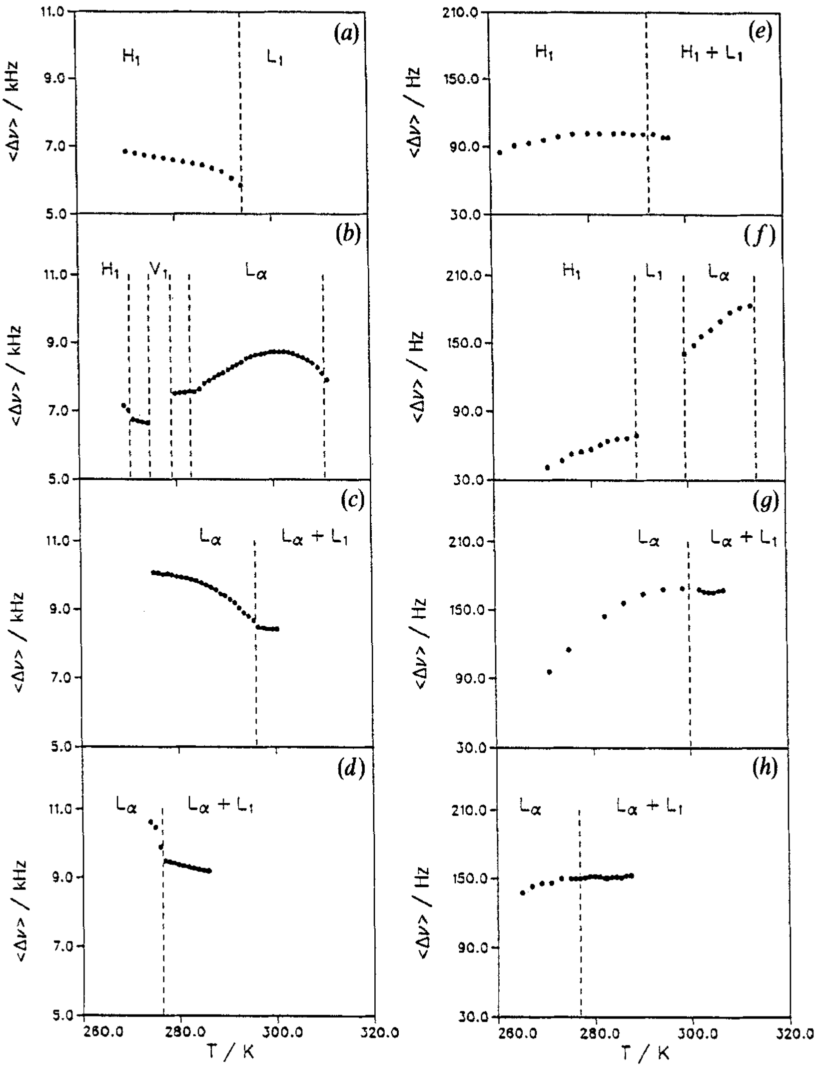

Figure 2. Quadrupole splittings ⟨Δν⟩ of $C_{12}E_6C_1/H_2O$ mixtures as a function of temperature for different surfactant concentrations. Left: α-deuteriated surfactant, right: methoxy-deuteriated surfactant. (*a*) 53·2 wt% surfactant, (*b*) 65·5 wt% surfactant, (*c*) 71·1 wt% surfactant, (*d*) 79·5 wt% surfactant, (*e*) 47·7 wt% surfactant, (*f*) 60·5 wt% surfactant, (*g*) 70·4 wt% surfactant, (*h*) 79·6 wt% surfactant.

All reported splittings correspond to director orientations of $\beta = 90°$. For both splittings and order parameters only absolute values are given. The phase transition temperatures are indicated by vertical lines in the diagrams.

The quadrupole splittings of the α-deuteriated surfactant ($C_{12}E_6C_1$-d_2) are between 7 and 11 kHz in the lamellar phase (see figures 2 (*b*)–(*d*)), and between 6 and 7 kHz in the hexagonal phase (see figures 2 (*a*) and (*b*). According to equation (2) with $\beta = 90°$, these splittings correspond to bond order parameters between *c*. 0·06 and 0·09, and between *c*. 0·05 and 0·06, respectively. These order parameters of bonds at the centre of the chain molecules are a measure of the overall molecular alignment, and it is quite instructive to compare them for different systems. For lyotropic systems, the comparison of S_{CD} at the α-position of surfactants with hydrophobic moieties of similar length exhibits a dependence of S_{CD} on the polarity of the head group: for example, the α-bond order parameters of the strongly polar dodecyl dimethyl amine oxide (DDAO) and of the ionic sodium decyl sulphate [8] in the lamellar phase at room temperature are about twice as large. The same holds for the bond order parameters of the inner methylene groups of alkanes dissolved in nematic liquid crystals. For example, at a temperature of *c.* 15 K below the isotropic–nematic phase transition, the C–^{2}H bond order parameter at the centre of the relatively short octane molecule is 0·16 and the innermost C–^{2}H bond order parameter of hexadecane is 0·22 [37]. These values illustrate that the orientational constraints in the methyl-capped oligo (ethylene oxide) system studied here are considerably lower than in the lyomesophases of more polar surfactants or in thermotropic nematic phases.

If the temperature dependence of the α-bond order parameter (cf. left column of figure 2) is dominated by the first factor of equation (3), that is by the intramolecular mobility and the molecular alignment with respect to the interface, a continuous decrease of the order parameter with increasing temperature is expected. A decrease is observed, indeed, for the hexagonal phase (see figures 2 (*a*) and (*b*)) and for the higher concentrations of the lamellar phase (see figures 2 (*c*) and (*d*)). For the 65·5 wt% sample (see figure 2 (*b*)), however, the order parameter of the lamellar phase initially increases with temperature, reaches a shallow maximum, and only then decreases as expected. This behaviour indicates that the second factor of equation (3), namely the orientation of the interface relative to the phase director, may play a significant role. We suggest the following explanation for the observed temperature dependence of the quadrupole splittings: the area of the hydrophilic head groups decreases with temperature because of a repulsion of the water molecules from the ethylene oxide chains [13, 15]. With decreasing head group area the curvature of the interface decreases, which leads to a gradual change of the mesophase structure. Within a distinct mesophase region, these changes are microscopical but at the phase transformations, they become apparent as a change of the macroscopic phase structure. For the microscopic changes which occur, for example, within the lamellar phase, we can imagine that initially, when the lamellae form from the cubic phase, a large number of defects exists. The lamellae are of limited size, because the surfactant head group is still too large to allow for extended planar micelle structures. With rising temperature, water molecules are repelled to the continuous aqueous phase between the surfactant layers, and the head group area becomes small enough to enable the formation of extended smooth lamellae. When the head group area becomes smaller than the optimum size for lamellar aggregates, the number of defects increases again. This leads to the decrease of the quadrupole splittings observed before the transformation to the isotropic L_1 phase. The defects causing the decrease of the splittings need not be static. X-ray and neutron scattering experiments on the similar lyotropic $C_{12}E_6$ system have shown that dynamic fluctuations of the phase structures occur close to the phase transformations [9].

The same arguments used above can explain the fact that the slopes of the $\langle \Delta\nu \rangle$ versus T curves often change abruptly when a biphasic region is reached. This is seen best in figures 2 (*b*)–(*d*). This phenomen can be explained, for example, for the L_α–V_1 transformation upon cooling as follows: when the lamellar phase is cooled down, the degree of hydration and hence the curvature of the interface increases. Up to the onset of the macroscopic phase transformation, the system can only respond by small changes within the given two dimensional phase structure, for example by a crumpling of the lamellae or a formation of holes. As soon as the second phase begins to form, another mechanism in order to retain the macroscopic phase structure becomes possible: the surplus of water from the L_α phase can be accommodated in the cubic phase, which is on the water-rich side of the L_α phase. As long as this process is possible, that is as long as both phases are present, the microscopic phase structure of the lamellae stays rather constant, so that nearly constant $\langle \Delta\nu \rangle$ values are observed in the biphasic region.

The growing number of defects and fluctuations on approaching a transformation to another phase also explains why the observed ratio $|S_{CD}(H_1)|/|S_{CD}(L_\alpha)|$ is considerably larger than $\frac{1}{2}$. It should be interesting whether a significant deviation from the ideal ratio is observed also for surfactants other than oligo(ethylene oxide) ethers. For DDAO, a surfactant with the same sequence of mesophases, which exist over a larger temperature range than in $C_{12}E_6C_1$, we found both a constant decrease of the quadrupole splittings as a function of temperature and a ratio close to 1/2.

For the methoxy-deuteriated surfactant ($C_{12}E_6C_1$-d_3), the observed splittings, shown in the right hand column of figure 2, are between 90 and 190 Hz in the L_α phase and between 40 and 100 Hz in the H_1 phase. These splittings correspond to bond order parameters of approximately 0·002 to 0·005 and 0·001 to 0·002, respectively. The calculation of the methoxy order parameters is based on rotating methyl groups, with $\langle \delta \rangle = \frac{1}{3}\delta$ as a reference. The data thus reflect the orientational order of the methoxy O–C bond. Values as small as those observed are expected because of the high conformational flexibility of the ethylene oxide surfactant molecules, which causes the bond order parameters to approach zero at the chain ends.

The temperature dependence of the methoxy bond order parameter shows an increase for all concentrations and mesophases. The interpretation of these data is more complex than in the case of the α-bond order parameter. Computer simulations of amphiphilic chain molecules consisting of short alkyl and ethylene oxide chains [38] in a uniaxial potential of mean torque [37, 39] have shown that the quadrupole splittings at the hydrophilic end of the chain may increase with temperature—a result which is not surprising, considering the complexity of the motional average. The fact that the observed increase of the quadrupole splittings is strongest in the lamellar phase, in particular at low concentrations (see figures 2(*f*) and (*g*)), where the abnormal behaviour of the α-bond order parameter is observed, however, supports the model of the gradual change of the phase structure: the repulsion of water molecules from the head groups goes hand in hand with a change of the statistical equilibrium of the ethylene oxide chain conformations, leading to the observed increase of the quadrupole splittings. In order to analyse the gradual change of the head group conformation in more detail, further experimental data are required.

5. Conclusions

From the orientational order and mobility of the surfactant molecules, which are probed by NMR spectroscopy, information about the microscopic phase structure can be obtained. The present data give firm evidence, (i), that the microstructure within a given lyotropic liquid-crystalline phase changes significantly with temperature and concentration, and (ii), that the temperature dependence of the interactions between the ethylene oxide moieties and the water molecules plays an important role in the aggregation behaviour of the surfactants. The degree of hydration, which depends on both concentration and temperature, determines the area of the head groups, which in turn affects the curvature of the hydrophobic/hydrophilic interface and thus the microscopic structures of the mesophases. Both an increase of temperature and an increase of surfactant concentration cause an effective dehydration of the ethylene oxide moiety. This is reflected in the phase diagrams of many ethylene oxide surfactants [14, 16, 21, 23]: the stability regions of the mesophases, in particular of the L_α phase, usually show a tilt from high surfactant concentration and low temperature towards low surfactant concentration and high temperature.

Further experiments on ethylene oxide surfactants with deuterium at other chain positions, which are presently under way, in combination with surfactant diffusion studies, will reveal more details about the relationship between the molecular behaviour and the phase structure.

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