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Articles

Dynamic Structure of *n*-Hexadecane Solubilized in a Nonionic Surfactant Bilayer Measured by Deuteron Magnetic Resonance

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A ²H NMR study was made of the order parameters of *n*-hexadecane molecules solubilized up to 55% (w/w) in a lyotropic lamellar liquid crystal of tetraethylene glycol *n*-dodecyl ether and water for a range of compositions of varying water and hydrocarbon content. The NMR data supported a model with only a small amount of penetration of the hydrocarbon between the amphiphilic molecules and a rapid exchange on the ²H NMR time scale between the penetrated segments and the nonpenetrating molecules which latter are essentially isotropic.

Introduction

Numerous studies have been made of surfactant phase equilibria as a result of their importance in many varied fields.¹⁻⁵ The lamellar liquid-crystalline phase is a prominent feature in all such systems. Its area dominates the phase diagram in systems in which water is combined with an ionic surfactant and a more hydrophobic amphiphile, with an OH group, such as long-chain alcohols,¹ carboxylic acids,¹ or, to an even large extent, polyethylene glycol alkyl ethers with a low number of oxyethylene groups.⁶ The lamellar liquid-crystalline phase is the dominating feature in systems with surfactants with two alkyl chains^{5,7} and is also the decisive factor limiting the stability of micro-emulsion systems.⁸ In spite of this wide importance, comparatively few studies have been made of the solubilized material in lamellar phases.

The act of "solubilization" implies inclusion within the structure of the host species. This inclusion necessarily has an effect on the location and order of both the host amphiphile and the guest molecule. The case of a guest molecule being strongly amphiphilic such as that of a long-chain alcohol has been classified both as to location and order. Low-angle X-ray investigations¹ left no doubt of the guest molecule being anchored at the interface with its polar group, and order parameter determinations using ²H NMR investigations⁹ showed such a guest molecule to display a degree of order along the hydrocarbon chain closely resembling that of the host amphiphile.¹⁰⁻¹³ Solubilization of fatty acid molecules in lipid bilayers^{14,15} gave a variation of the order parameter similar to the host amphiphile but had significantly lower values.

In the second case, the solubilization of a hydrocarbon has not been investigated to a similar extent possibly because early investigations¹ indicated only a minute solubilization and because the order parameters should show only nondistinctive variation along the chain¹⁰ for short

hydrocarbons. For longer hydrocarbons such as hexadecane, some divergency in opinion about location has been expressed.^{16,17} White¹⁶ discusses a model in which the lipid chains are coiled down to nearly close-packed state with no significant overlap with the amphiphilic chains in the central CH₃ region of bimolecular membranes. Gruen¹⁷ on the other hand, contends an overlap between solubilized and amphiphilic hydrocarbon chains at the midsection of the membrane of approximately 40%, pointing out the agreement between his model for bilayers¹⁸ and experimental results¹⁹⁻²¹ on bilayers and liquid crystals giving an organization of the lipid chains in a membrane similar to the state in a liquid alkane. The liquidlike state of the molecules and the considerable overlap in the midplane

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region would allow hexadecane molecules to span the midplane region since no actual handicap on a configuration would be felt by the solubilized molecule.

We found recent results from solubilization of aliphatic hydrocarbons²² in a lamellar liquid crystal of water and polyethylene glycol dodecyl ethers to contain sufficiently new information to give a more complete experimental description of the conditions in membrane bilayers and lamellar liquid crystals with solubilized hydrocarbons. The main factor is the fact that, contrary to the case for the lamellar structures based on lecithin,^{16,17,19-21} these liquid-crystalline phases solubilized large amounts of hydrocarbons; a maximum hydrocarbon percentage of 55% of total weight was reached.²²

The low-angle X-ray results²² indicated the hydrocarbon to be localized mainly as an oil layer between the surfactant layers with little or no penetration between the surfactant molecules. A preliminary study of the order of the solubilized hydrocarbon molecules by ²H NMR²³ revealed a complex order parameter variation both with the location of the groups along the hydrocarbon chain and with the concentration of hydrocarbon in the structure. Since these results obviously gave a different opinion about the state of solubilized hydrocarbon that was possible from earlier exploratory investigations,¹⁰ we found these systems with extremely high oil content to be a valuable tool for the clarification of the problem of the lamellar structure and also of pronounced interest per se.

In the present article, we publish a more comprehensive treatment of the ordering, penetration, and location of the solubilized hydrocarbon chains in the lamellar liquid-crystalline structure in order to lay a foundation for a later treatment of the puzzling question of the stability of a liquid-crystalline structure with such a thickness of the oil layers.

Experimental Section

Tetraethylene glycol *n*-dodecyl ether (C₁₂E₄) was obtained from Nikko (Japan) Ltd. and was >98% pure by GLC criteria. Perdeuterated *n*-hexadecane (lot no. 1344-H and 218-H) were obtained from MSD Isotopes and used without further purification. Deuterium oxide (99.8% isotope purity) was used as received from Stohler isotopes and *n*-hexadecane (Aldrich Chemical Co., Inc., gold label) was passed through an alumina column prior to use.

Samples were prepared by weighing the components in sample bottles, mixing thoroughly, and centrifuging to remove air bubbles. This procedure was repeated until the sample appeared homogeneous when viewed between crossed polars (a minimum of 2 times was usually required). Portions of the samples were then centrifuged into glass tubes for the NMR observations. ²H NMR spectra were obtained either on a spectrometer operating in the FT mode built at the Chemistry Department, UMSL, by one of the authors (D.W.L.) or on a Bruker CXP-200 spectrometer at 30 °C. The number of transients required varied in the range 10³ to 5 × 10⁴, depending upon the sample composition. Standard *T*₁ measurements indicated the values of the *T*₁'s to lie in the range 40–90 ms ((4 × 10⁻²)–(9 × 10⁻²) s); therefore, a pulse-repetition rate of 0.5 s or longer was used in order to eliminate saturation effects in the observed spectra.

Results

The ²H NMR spectra of perdeuterio-*n*-hexadecane solubilized in the aqueous lamellar phase of C₁₂E₄ were previously²³ found to be complex. Each spectrum comprises eight overlapping powder spectra, and a typical spectrum with its simulation is shown in Figure 1.²³

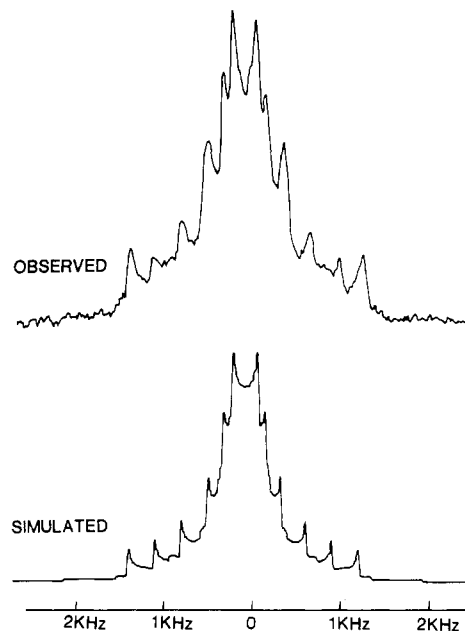


Figure 1. Typical ²H NMR spectrum of perdeuterated hexadecane solubilized in a lamellar liquid crystal prepared from water and tetraethylene glycol dodecyl ether.²³ Observed spectrum (top) and simulated spectrum of eight overlapping powder patterns (bottom).

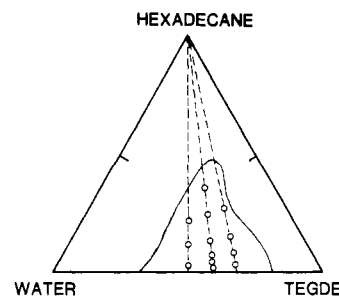


Figure 2. Lamellar liquid crystal area in the tetraethylene glycol dodecyl ether/water/hexadecane system and compositions of samples investigated.

Values of the associated quadrupolar splittings, $\Delta\nu_i$, obtained either by simulation or direct reading from the spectra, were in good agreement, and were typically ≤ 1500 Hz. The largest splittings are assigned to the central chain segments, by analogy to observations made with a selectively deuterated alkane.²³ The smallest splittings are assigned to terminal methyl segments. The variations of $\Delta\nu_i$ with position in the chain were constructed assuming monotonic behavior between the extremes.

The compositions studied varied along lines with constant water/surfactant ratio in the phase diagram,²² as shown in Figure 2. Figure 3a–c presents the observed splittings as a function of hydrocarbon/surfactant content at fixed water/surfactant content, with the splittings assigned to specific chain positions as described above.

The series with the lowest surfactant fraction, 50.6% (Figure 3c), showed an enhanced ordering with increased oil content for all positions on the chain. The next level of surfactant 60% (Figure 3b) gave maxima in the observed splittings for hydrocarbon contents of approximately 10–15% for all positions except that of the chain middle (position 1). The series with the highest surfactant content, 67.7% (Figure 3a), displayed monotonically decreasing splittings with oil content for all positions on the hydrocarbon chain.

Observations of phases comprising C₁₂E₄/D₂O/C₁₆H₃₄ showed the ²H NMR spectrum of the aqueous component

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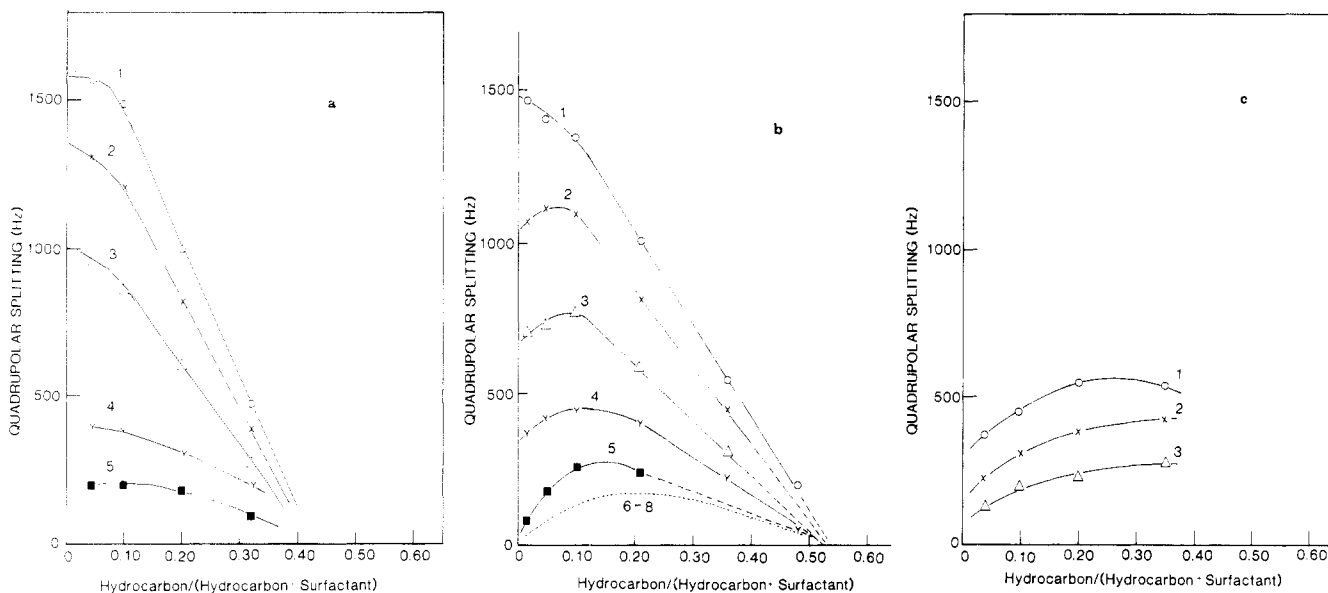


Figure 3. (a) Variation of ^2H NMR quadrupolar splittings for hexadecane solubilized in a water/TEGDE liquid crystal as a function of hydrocarbon/surfactant fraction. The surfactant/(surfactant + water) = 0.677. (b) Variation of ^2H NMR quadrupolar splittings for hexadecane solubilized in a water/TEGDE liquid crystal as a function of hydrocarbon/surfactant fraction. The surfactant/(surfactant + water) = 0.600. (c) Variation of ^2H NMR quadrupolar splittings for hexadecane solubilized in a water/TEGDE liquid crystal as a function of hydrocarbon/surfactant fraction. The surfactant/(surfactant + water) = 0.506.

to be a simple powder spectrum as expected for such unoriented lamellar dispersions. The variation of $\Delta\nu_{\text{D}_2\text{O}}$ with water content was found (Figure 4) to be essentially independent of the hydrocarbon/surfactant ratio.

In this model it is assumed that the central peak (Figure 1) is degenerate, an assumption based on our earlier results.²³ The alternative of the outer peak degenerate would change the order parameter functions in Figure 3a-c to a shape with a less pronounced maximum. The relative height of the outer peaks may, at first, indicate a support for this alternative; an interpretation along this line must take line broadening into account due to different T_2 values. Awaiting further experimental evidence, we would prefer the original interpretation.

Attempts to obtain values for the ^2H T_1 relaxation times of the solubilize by the usual inversion recovery technique were complicated by the need for deconvolution of partially relaxed, partially resolved spectra. It appears that there is a significant variation of T_1 (a factor of 2 or more) with chain position, but further work using selectively deuterated oils is needed to obtain reliable data.

Discussion

The study of the molecular organization and intramolecular order in lyotropic lamellar phases of lipids and soaps by NMR methods is well established¹⁰⁻¹³ and only the most brief review will be given. In particular, ^2H NMR has proved useful in the study of these systems since the dipolar couplings between ^2H nuclei are negligible and the system is one of uncoupled spins; thus, different molecular groups may be distinguished by differences in the motional averaging of the quadrupole coupling constant for their C-D bonds. For a superposition of randomly oriented domains of bilayers with motions described by symmetry axes, a characteristic doublet "powder spectrum"²⁴ is obtained for a specific ^2H site, characterized by a splitting

$$\Delta\nu = \frac{3}{4} \frac{e^2qQ}{h} |S|$$

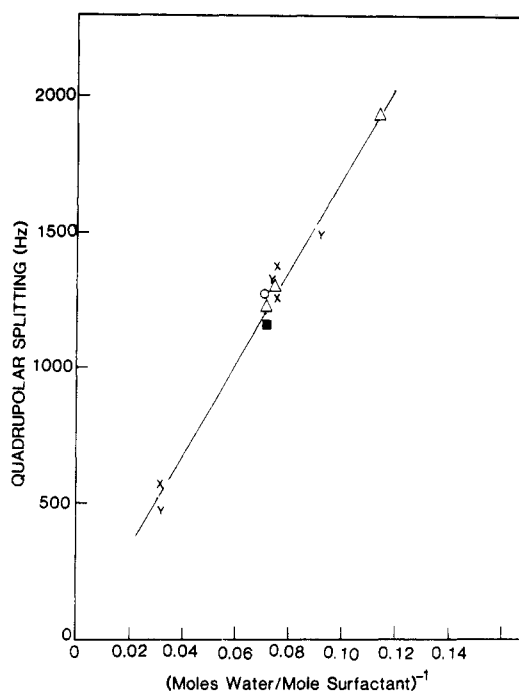


Figure 4. Variation of the ^2H NMR quadrupolar splitting of water (D_2O) in the lamellar phase as a function of inverse water/surfactant molar ratio. The data correspond to hydrocarbon/(hydrocarbon + surfactant) fractions: O, 0.0; X, 0.49; Δ , 0.20; Y, 0.35; \square , 0.375.

where the order parameter characterizes the orientational order of the C-D bond according to

$$S = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle$$

θ is the angle between the C-D bond and the strong magnetic field, and $\langle \rangle$ represents an average over all conformations of the molecule. The remaining factors in the expression for the splitting is the coupling constant. These measured quadrupole coupling constants in lamellar soap and liquid phases are much smaller than that of the static C-D bond, i.e., ca 167 kHz,²⁵ and the values of S may

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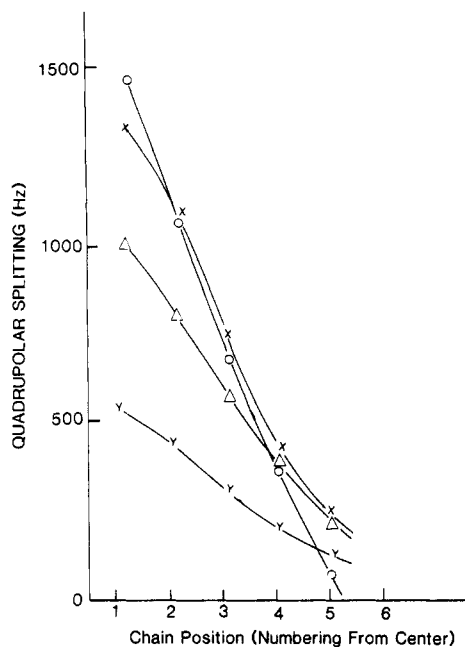


Figure 5. Variation of the ^2H NMR quadrupolar splitting profile of hexadecane solubilized in a water/TEGDE (40/60) lamellar liquid crystal. Hydrocarbon/(hydrocarbon + surfactant) values: O, 0.016; X, 0.102; Δ , 0.215; Y, 0.358.

be directly obtained by division of the values in Figures 3a-c with 1.67×10^5 ; also, a characteristic variation in order parameter with position on the amphiphile chain has been found for a large variety of bilayer systems.¹¹⁻¹³ This variation shows little or no change in $|S|$ for chain segments near the head group located at the bilayer interface, with a large and rapid decrease from the chain center to the terminal methyl segments located in the middle of the bilayer. Since the splittings are distinct, the amplitudes of the motions must vary along the chain, with the largest variations being for the terminal segments.

An alternative presentation of the experimental data in Figure 3a-c is a series of plots of observed splittings vs. chain position. Figure 5 shows such splitting profiles for $n\text{-C}_{16}\text{D}_{34}$ solubilized in the $\text{C}_{12}\text{E}_4/\text{H}_2\text{O}$ lamellar phase for a variety of oil contents at one of the fixed soap/water ratios studied. The values for position 6-8 are all small and not significant for this discussion. Monotonic variation of splittings is assumed for all profiles. The plots in Figure 5 are roughly linear with slight sigmoidal character for chain positions 1-5. However, each plot is characterized by a different slope which demonstrates the complex dependence of order parameter on oil content. It should also be noted that there is an abrupt change in shape of the plot at chain position 5 for the lowest hydrocarbon content studied by Figure 5. The terminal segments (6-8) have splittings too small to be clearly resolved and assigned. In addition, the observed $\Delta\nu_i$ are 1-2 orders of magnitude smaller than those found typically¹¹⁻¹³ for C-D bonds of amphiphilic chains in lamellar phases.

As a point of discussion, we start with a simplified description of the solubilized alkane. For an alkane, each segment of the alkane chain proceeding in the direction away from its center may be expected to have greater orientational freedom than the preceding one, which is different from chains with groups that may be anchored at the amphiphile/water interface. The flexibility of a free chain, therefore, does not yield a plateau in the order parameter profile such as expected for the host chains,

barring some special situation where intermolecular packing restraints lead to motional restriction. The high degree of orientational disorder as manifested by the very low S values (10^{-2} - 10^{-4}) of the *n*-hexadecane compared to that expected for host chains is also most likely a direct result of the absence of any effects arising from anchoring one end of the solubilize in the region of the bilayer interface. This is supported by the observation of almost linear dependence of splitting with position in the alkyl chain of lamellar potassium palmitate when heated to high temperature,²⁶ resulting from the loss of the head-group anchoring effect due to increased thermal motion.

The absence of any connection between the solubilized chains and the polar part of the amphiphilic host membrane is also indicated by the fact that the amount of solubilized hydrocarbon had no influence on the linear relationship between $\Delta\nu_{\text{D}_2\text{O}}$ and $(\text{mol water/mol soap})^{-1}$ (Figure 4). Such a relation is expected for a simple fast exchange between water molecules "bound" by the surfactant and water molecules that are essentially isotropic so that $\Delta\nu_{\text{D}_2\text{O,obsd}} = P_{\text{bound}}\Delta\nu_{\text{D}_2\text{O,bound}}$.²⁷ These observations are, therefore, consistent with the previous observation²⁸ of no contact between solvent and hexadecane solubilized in nonionic surfactant normal micelles, indicating the solubilize to be located almost entirely within the hydrophobic region of the amphiphilic chains.

Hydrocarbons solubilized in bilayer environments are subject to interactions with the amphiphile chains. Calculations of chain order parameters have been made under various assumptions. For example, calculations based upon the statistical distribution of chain segments in saturated alkane lipid bilayers have been reported.^{17,18} These calculations gave the distribution of the chains in terms of volume fractions and the order parameter profile across the bilayer. Segments, which are located at the center of the hydrophobic part, will have very small order parameters whereas those located closer to the soap/water interface will have large order parameters. The profile observed by us (Figure 5) is qualitatively the same as the thermodynamically averaged order parameter profile calculated¹⁷ in that the highest order parameters are predicted for the chain center, and these fall to small values for the terminal segments.

It is thus tempting to rationalize observed oil splittings in terms of specific locations and/or orientations within the bilayer; however, the composition dependence observed in Figure 3a,b suggests that such an approach may not be justified. We observe linear behavior over wide enough ranges of composition so as to suggest that simple extrapolation to isotropic behavior ($\Delta\nu = 0$) is justified. The extrapolation for each chain position predicts isotropic behavior at the same composition for all chain segments of the hydrocarbon. The extrapolated isotropic behavior occurs at hydrocarbon/surfactant ratios of 42:58 (Figure 3a) and 55:45 (Figure 3b). This result is obtained empirically, devoid of a specific model for the hydrocarbon interaction with the amphiphile chains. The conclusion is that at the stated compositions, *all* the solubilized hydrocarbon in the sample exhibits splittings consistent with isotropic motion. This, in turn, means that any amphiphile

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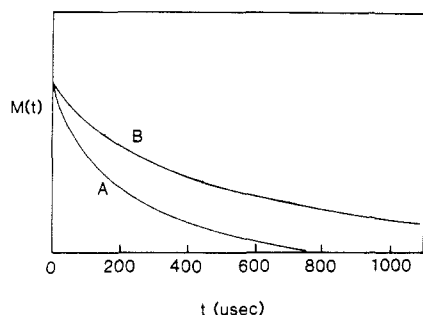


Figure 6. Proton Bloch decays for $D_2O/E_4C_{12}/C_{16}D_{34}$ samples. Compositions: (A) surfactant/ D_2O , 61.6:38.4; (B) surfactant/ $D_2O/C_{16}D_{34}$, (43, 26.8):30.2. In (B), surfactant to water ratio is same as in (A), but 30.2% of $C_{16}D_{34}$ is added.

chain segments in contact with the hydrocarbon have no ordering influence at the specific compositions corresponding to the extrapolation; i.e., the terminal amphiphile chain segments themselves must be classified as isotropic at that composition. A comparison with Figure 2 shows the extrapolations to zero quadrupolar splitting (Figure 3a,b) to signify points in a triangle in which the stability of the lamellar liquid-crystalline phase disappears.

With this in mind, it appears reasonable to state that the nonspecific ordering influence of the amphiphile hydrocarbon chains on the solubilized hydrocarbon molecules is terminated at the point of instability of the lamellar structure.

The argument requires that at least a portion of the amphiphile chain (that near the middle of the hydrophobic layer) experiences variation in order as a function of hydrocarbon content. This is in contrast to the water behavior, which is independent of hydrocarbon content (Figure 4). Hence, the picture emanating is one of an enhanced disordering of the hydrocarbon part of the amphiphile with increased solubilization of hydrocarbon while the conditions in the polar chain part remain essentially identical.

Preliminary confirmation of this concept was found from gross changes in amphiphilic motion using 1H resonance. Two samples comprising (A) $C_{12}E_4/D_2O$ and (B) $C_{12}E_4/D_2O/C_{16}D_{34}$, with fixed surfactant/water ratio, were investigated. A single 1H NMR line was observed for the amphiphilic protons of the type described by Bloom et al.³¹ The longitudinal relaxation was found essentially exponential indicating either a spin diffusion or defect diffusion mechanism.³² A value of 0.29 s for the 1H spin-lattice relaxation time was observed for both samples, whereas the transverse relaxation time (T_2) was shorter for the sample without any solubilized hexadecane (A). The free

induction decays for the two samples (Figure 6) are of similar shape, but there is a factor larger than twice the difference in T_2 for the two curves. A detailed interpretation of the 1H relaxation results would entail a discussion of the anisotropic motion and spin diffusion along the chain. Such a treatment is beyond the scope of this paper; however, the conclusion that the amphiphilic head groups are unaffected by hydrocarbon content and the observed decreased T_2 at high oil content suggest increased amphiphile chain mobility. Assuming that the spin diffusion occurs on a time scale of ca 10^{-3} s, the observed doubling of T_2 corresponds to a large portion of the amphiphilic chain being characterized by an appreciably smaller transverse relaxation rate.

A second interesting feature of this system is the marked dependence of splitting variation on the water/surfactant ratio in the original liquid crystal structure (Figure 3a-c). At small water/surfactant ratio, minimum order is observed at low hydrocarbon content (Figure 3c). Intermediate behavior between these extremes, observed in Figures 3b and 5, illustrates this intermediate behavior in the splitting profiles. The three profiles for largest hydrocarbon content are indicative of behavior at small water/surfactant ratio. The smallest hydrocarbon content profile in Figure 5 is qualitatively different from the other three. It is almost linear and crosses the other three (sigmoidal) curves. This small hydrocarbon content curve is typical of large water/surfactant behavior.

Low-angle X-ray measurements of the interlayer spacing as a function of oil and water content were earlier²² interpreted as indicating a change in conformation and/or angle of packing of the amphiphilic molecules. Comparison between the calculated and experimental spacings at a water content corresponding to that of Figure 3b and 5 showed this change to be complete at an oil volume fraction of 0.175. This proposed structural change may thus be related to the maxima in $\Delta\nu_i$ observed in Figure 3b and to the qualitative change in splitting profile observed in Figure 5. In terms of the previous model,²² the initial rise in $\Delta\nu_i$ may be regarded as a result of an initial mixing of the solubilize with the amphiphile chains, resulting in the mixed segments adopting conformations with segment axes closer to the lamellar director. Intuitively, such a mixing/ordering would be expected to be more pronounced for the liquid-crystalline compositions with large water content.⁶ The observed trend in Figure 3a-c supports this assumption: i.e., for largest water content (Figure 3c), largest oil content gives maximum order; for intermediate water content (Figure 3b), intermediate behavior is observed; for smallest water content (Figure 3a), smallest oil content gives maximum ordering.

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