The Alignment of Lyotropic Liquid Crystals Formed by Hexadecyltrimethylammonium Bromide in D_2O in a Magnetic Field

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The alignment of lyotropic liquid crystals formed by hexadecyltrimethylammonium bromide (CTAB, where C stands for cetyl) with D_2O was studied by the use of ^2H NMR. At CTAB/D_2O concentrations between 1.01 and 1.29 mol/kg, liquid crystal domains aligned in the magnetic field within a few hours. The dependence of the characteristic alignment time on concentration and temperature has been determined. At higher concentrations, no alignment took place due to the high viscosity of the system. At lower concentrations, the alignment could not be observed by ^2H NMR. The addition of sodium salicylate (NaSal), at equal molar concentrations of CTAB and NaSal, changed the orientation of the micelles from parallel to the magnetic field to perpendicular to the field. Line-shape simulations were carried out to give estimates on the rate of exchange between free D_2O molecules and those bounded to the micelles, as well as on the deuterium quadrupole splittings for D_2O molecules bound to micelles. The dependence of the characteristic alignment time on the strength of magnetic field was also studied.

Introduction

Hexadecyltrimethylammonium bromide (CTAB, where C stands for cetyl) is a cationic surfactant that has been widely studied. It can form micelles in aqueous solution as well as in some organic solvents above the critical micelle concentration (cmc).[1] At concentrations above 0.7 mol/kg and temperatures above 25 °C, CTAB forms liquid-crystalline phases.[2] Ternary systems of water, CTAB, and organic salts such as sodium salicylate (NaSal)[3] or sodium 3-hydroxynaphthalene-2-carboxylate (NaHNC)[4] have also been studied extensively, because the aromatic anions cause the CTAB micelles to elongate and form viscoelastic systems at low concentrations.[3] It has been suggested that the hydrophobic part of the anions inserts into the CTAB micelles.[3a,4]

It is well-known that the liquid-crystalline domains in the hexagonal phase can be aligned in a magnetic field.[5] The orientation order of water molecules and hence the magnetic alignment of surfactant molecules can be easily studied by the use of deuterium, ^2H, NMR.[5,6] The NMR spectra of nuclei with quadrupole moments in an ordered mesophase exhibit splittings caused by nonzero time averaging of their quadrupolar interaction.[7] The quadrupole splittings observed in liquid crystals reflect the degree of order of molecular segments and give information on the orientation of the director of the mesophase.[5,8] For D_2O in ordered lyotropic liquid crystals, there is usually a rapid exchange between D_2O molecules aligned at the surface of the surfactant assembly and the unbound D_2O molecules in the bulk that tumble isotropically. Therefore, a time-averaged quadrupole splitting is observed in the ^2H NMR spectrum.

If a liquid crystal is not aligned in a magnetic field, a powder pattern is observed as a result of the random orientation of the liquid-crystal domains and, hence, the random distribution of directors in space. Upon alignment, the micelles orient either parallel or perpendicular to the magnetic field. If the diamagnetic anisotropy of the surfactant micelles is positive ($\Delta\chi = \chi_{\parallel} - \chi_{\perp} > 0$), the mesophase is called type I.[5] This is the case for discotic or cylindrical micelles of surfactants that contain aliphatic hydrocarbon chains and no aromatic rings. Because the aliphatic chains prefer to orient perpendicular to the field, the micelles would orient with their principal axes parallel to the field for type I mesophase. If $\Delta\chi$ is negative, the mesophase is called type II and the principal axes of the micelles orient perpendicular to the field.[5] For type I mesophases, the two peaks in the oriented spectrum correspond to the wings of the powder pattern; for type II mesophases they correspond to the "peak" region of the powder spectra.[5,9] Several NMR studies, including ^2H, ^{13}C, ^{14}N, ^{17}O, and ^{35}Cl, have been made on lyotropic liquid crystals formed from CTAB,[10] hexadecyltrimethylammonium chloride,[11] and hexamethyltriethylammonium bromide[9] in water. All of these studies reported the steady-state NMR spectra. Before reaching the steady state in a magnetic field, the rate of alignment of the domains in a lyotropic liquid crystal depends on the concentration of the surfactant, the strength of the magnetic field, and the temperature. Therefore, a study of the deuterium NMR spectra as a function of time gives proper information on the alignment process. In this paper, we report such a study on CTAB/D_2O systems under different conditions and in the presence of two organic salts, NaSal and NaHNC.

Experimental Section

CTAB was purchased from Aldrich Chemicals, recrystallized using an ethanol/ethyl acetate solvent system, and then dried in a vacuum oven at ~40 °C. Sodium salicylate (NaSal) was prepared by adding the required amount of alcoholic NaOH solution to a solution of salicylic acid in ethanol. The solvent

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was removed, and NaSal was dried in a vacuum oven at ~40 °C. The salt was recrystallized from ethanol. Sodium 3-hydroxy-2-naphthalene carboxylate (NaHNC) was prepared by adding the required amount of alcoholic NaOH solution to a solution of 3-hydroxynaphthalene-2-carboxylic acid in ethanol. The solvent was removed, and NaHNC was dried in a vacuum oven at ~40 °C.

The required amounts of CTAB, NaSal, NaHNC, and D_2O were added to 5-mm (o.d.) NMR tubes. The tubes were sealed. The samples were mixed at elevated temperatures until the solution was homogeneous. The following samples were prepared: CTAB in D_2O with concentrations 0.83, 0.96, 1.01, 1.07, 1.19, 1.29, 1.50, 1.67, and 2.44 mol/kg (23.1, 26.0, 27.0, 28.1, 30.2, 32.0, 35.3, 37.8, and 47.1% CTAB in D_2O by weight, respectively); 1.01 mol/kg of CTAB in D_2O and CTAB/NaSal mole ratios of 1.0, 1.7, 1.8, 2.0, 2.5, 3.0, and 3.9; 1.01 mol/kg CTAB in D_2O with CTAB/NaHNC mole ratios of 0.8, 1.4, 2.0, and 3.0.

Alignment measurements were carried out on Varian VXR-500S and Varian XL-300 NMR spectrometers.

Results and Discussion

Spectral Characteristics of CTAB/D_2O Systems. The alignment of the hexagonal liquid-crystal domains of the CTAB samples in a magnetic field was investigated at 30, 40, and 50 °C by the use of ^2H NMR. In this temperature range, all samples studied are in the hexagonal phase.[3] Samples with a CTAB/D_2O concentration between 0.83 and 0.96 mol/kg show liquid crystallinity under the polarizing microscope, but only a single peak was observed in the ^2H NMR spectra of these samples at 11.7 T because the peaks might be broader than the deuterium quadrupole splitting. The ^2H spectra of samples with CTAB concentration $\geq$1.5 mol/kg show powder patterns that did not change with time, indicating that there was no re-alignment in the magnetic field, which is probably a result of the high viscosity of the system. At concentrations between 1.01 and 1.29 mol/kg, alignment could be observed by the use of ^2H NMR. When the samples were inserted into the magnet only a few hours after preparation, a singlet or a powder pattern was observed (Figures 1 and 2), and it changed into an asymmetric doublet over time. The origin of the asymmetry will be explained in the Spectral Simulations section. When these samples were left at 30 °C for at least 5 days before being inserted in the magnet, an initial powder pattern was observed (Figure 3). The spectral width of the powder pattern is quite small because of rapid solvent exchange between the ordered and the "free" states. The powder pattern gradually changes into an asymmetric doublet, indicating that the liquid-crystal domains align in the magnetic field. For samples with concentrations of 1.19 and 1.29 mol/kg, an initial asymmetrical powder pattern was observed (Figure 4), and it also changed into an asymmetric doublet over time.

To account for the differences in the ^2H NMR for these systems, the following explanation is offered. Initially the CTAB molecules form ropelike micelles that entangle with each other. If the micelles are not long enough, they cannot form lyotropic liquid crystals. Then, a singlet is observed in the deuterium NMR spectra. When the sample is placed in a magnetic field, the long micelles can align even though the system is not in a liquid-crystalline phase. This argument is based upon a well-known observation that even small molecules in the isotropic phase can be aligned in a high magnetic field.[12] As a result of this alignment, a doublet was observed in the spectrum. On the other hand, when the sample is left at 30 °C for several days before being put in the magnet, the micelles grew in length to reach an equilibrium state, which is a hexagonal liquid-crystalline phase with randomly oriented domains. Therefore, the ^2H NMR spectra show a powder pattern, which gradually changes into a doublet when the domains align in the magnetic field. At concentrations of at least 1.19 mol/kg CTAB, the micellar length is long enough to form liquid crystals immediately after sample preparation, even though equilibrium has not been reached. Therefore, the initial NMR spectra show a powder pattern (Figure 2), but the pattern is different after the samples are left at 30 °C to reach equilibrium before being put in the magnetic field (Figure 4). This is probably the result of a difference in the dynamics of the exchange process.[13] Nevertheless, the final splittings of the doublets are essentially the same for the aligned samples at the steady state in the magnetic field.

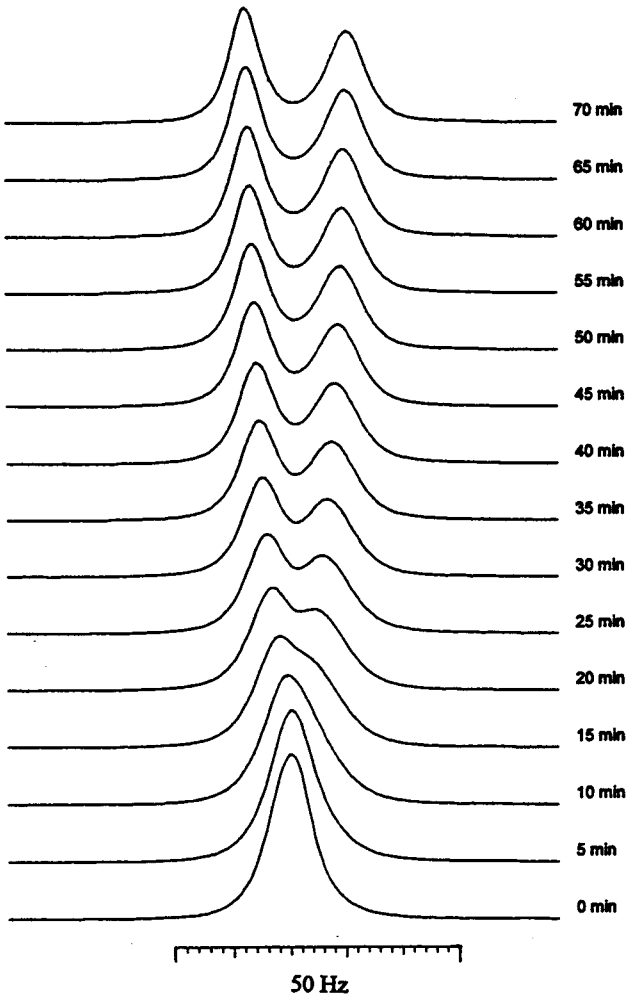

Figure 1. Time-dependent ^2H NMR spectra of 1.01 mol/kg CTAB in D_2O at 30 °C in a magnetic field of 11.74 T. The sample was put in the magnet immediately after thorough mixing in a sealed NMR tube.

The upper temperature limit at which quadrupolar splitting could be observed in the ^2H NMR spectra was 54 °C for 1.01 mol/kg of CTAB in D_2O, 60 °C for 1.07 mol/kg, 74 °C for 1.19 mol/kg, and 91 °C for 1.29 mol/kg. Above these temperatures, only a singlet was observed. These temperatures are somewhat lower than the hexagonal-to-isotropic transition temperatures for the same molar concentrations (expressed in a unit of mole ratio) of CTAB in H_2O.[2] To explain this difference, we suggest that the deuterium quadrupole splitting at high temperatures might not be observed because it is not large enough compared to the line width.

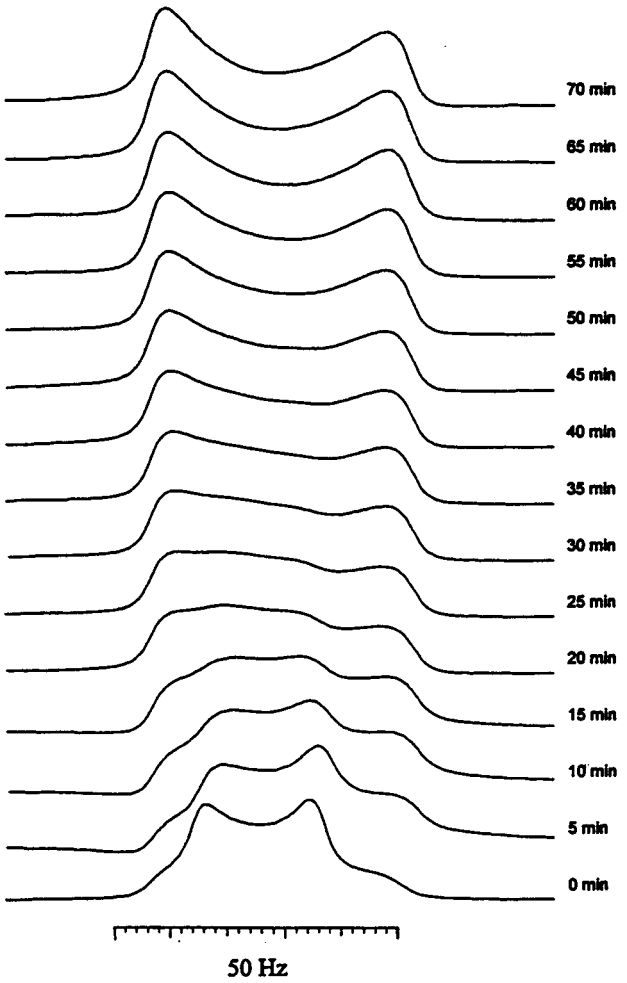

Figure 2. Time-dependent ^2H NMR spectra of 1.29 mol/kg CTAB in D_2O at 30 °C in a magnetic field of 11.74 T. The sample was put in the magnet immediately after thorough mixing in a sealed NMR tube.

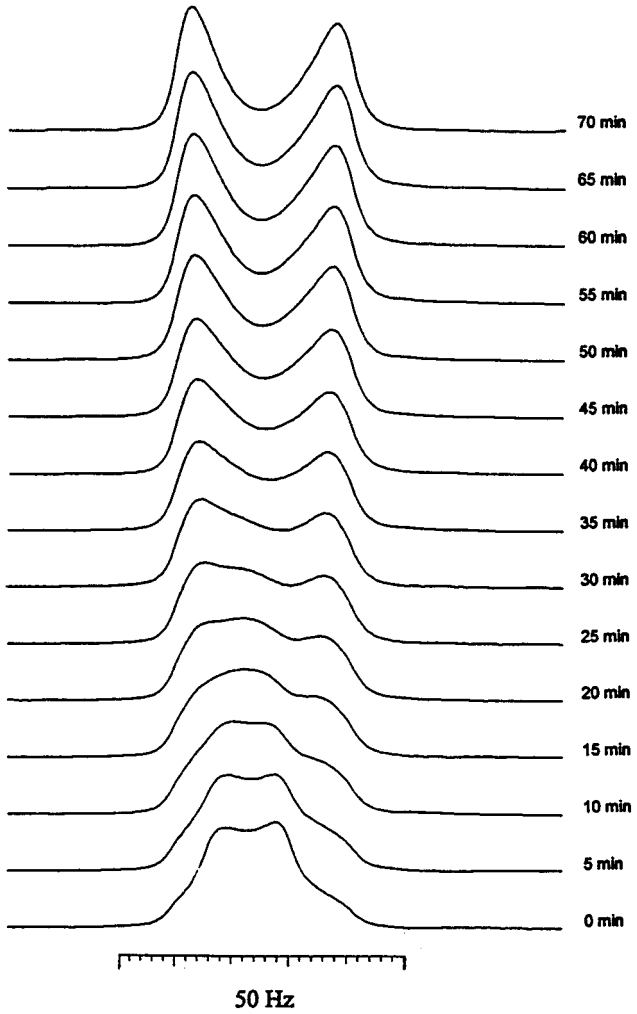

Figure 3. Time-dependent ^2H NMR spectra of 1.01 mol/kg CTAB in D_2O at 30 °C in a magnetic field of 11.74 T. The sample was thoroughly mixed and then equilibrated for 5 days at 30 °C before being put inside the magnet.

Spectral Characteristics of CTAB/NaSal/D_2O Systems. The temperature range in which alignment of the liquid-crystal domains can be observed by the use of ^2H NMR is lowered by the addition of NaSal (the reason for this will be discussed later). For different CTAB/NaSal molar ratios at a CTAB concentration of 1.01 mol/kg, only a singlet was observed above 32 °C and the spectra did not change with time.

For CTAB/NaSal = 1.0, a powder pattern was observed at 22 °C. It gradually changed into a doublet when the samples were left in the magnetic field (Figure 5). The inner peaks of the powder pattern grew to give the doublet, while the outer wings disappeared. This was opposite to the pure CTAB−water samples, for which the outer wings finally turned into the doublet and the inner ones disappeared (Figures 2−4). It means that the CTAB−NaSal−water system is a type II lyotropic liquid crystal, while CTAB−water is of type I.[5,9] In other words, the ropelike CTAB micelles prefer to align parallel to the magnetic field B_0, but the alignment changed to perpendicular to B_0 in the presence of salicylate. Since compounds with aromatic rings have positive $\Delta\chi$ and align with the planes of the ring parallel to the magnetic field, the result implies that the salicylate ions would insert into the micelle with the phenyl ring perpendicular to the principal axis of the micelle[3a] rather than being parallel. It is well-known that the contribution of aromatic rings to $\Delta\chi$ is positive and that of aliphatic chains is negative, but the former is much large in absolute value.[14] Therefore, at high enough concentrations of NaSal the overall orientation of the micelle is defined by the salicylate anions. Therefore the higher the concentration of NaSal is, the larger is the final splitting, because a higher concentration enforces a greater orientation of the micelles perpendicular to the field (Table 1).

For CTAB/NaSal = 1.7 and 1.8 at 22 °C, the samples were allowed to reach equilibrium for 2 weeks before being placed in the magnet. The initial deuterium NMR spectra showed a superposition of a singlet and a powder pattern; they also gradually changed into an asymmetric doublet.

For samples with molar ratios of CTAB/NaSal between 1.8 and 3.9, a singlet was observed at temperatures between 22 and 50 °C. The spectrum did not change with time. At these NaSal concentrations, the overall $\Delta\chi$ of the CTAB liquid-crystalline system could be close to zero, so that there is no uniform alignment either parallel or perpendicular to the field.

For all of the CTAB−NaHNC−D_2O systems studied, a singlet was observed, which did not change with time. It became broader with increasing NaHNC concentration. Since HNC^- has a greater $\Delta\chi$ than Sal^- and is expected to insert into the micelles the same way,[4] it would change the orientation of the micelles in a magnetic field from type I to type II more easily. However, the samples were not homogeneous at molar ratios of 2.0 and lower. An examination of the samples under the polarizing microscope showed that there were mixtures of crystals and liquid, but no liquid-crystalline phase was present. Therefore a broad singlet was observed.

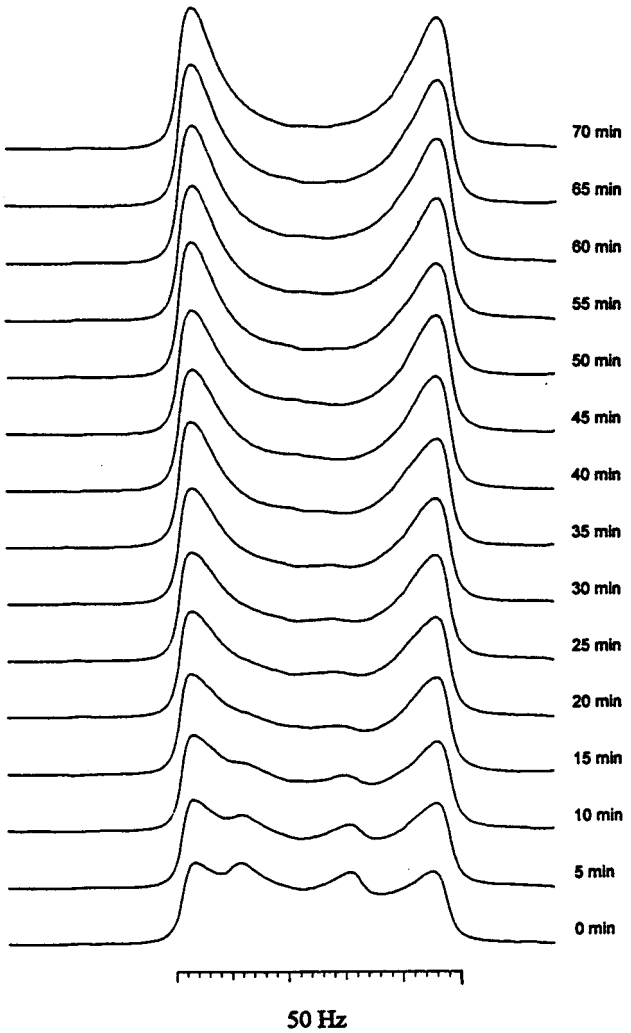

Figure 4. Time-dependent ^{2}H NMR spectra of 1.29 mol/kg CTAB in D_2O at 30 °C in a magnetic field of 11.74 T. The sample was thoroughly mixed and then equilibrated for 5 days at 30 °C before being put inside the magnet.

Spectral Simulations. The asymmetric ^{2}H NMR spectra observed for the CTAB−D_2O systems (Figures 1−5) are rather unusual. The following model is offered for their interpretation.

In a lyotropic liquid-crystalline system there is a rapid exchange of water molecules between two unequally populated sites—the bound and the free D_2O molecules. Because the spin states of ^{2}H nuclei do not alter during the exchange, the following treatment can be used.

Let us designate "*a*" for the $|1,2\rangle \rightarrow |1,0\rangle$ transition for the bound site and "*f1*" for the same transition for the free site, and "*c*" and "*f2*", respectively, for the corresponding sites for the $|1,0\rangle \rightarrow |1,-1\rangle$ transition. The molecules in sites *a* and *f1*, as well as those in sites *c* and *f2*, exchange rapidly. The two exchange processes are simultaneous, and they determine the overall line shape of a ^{2}H spectrum. Since transitions *a*, *f*, and *c* have different resonance frequencies and each exchange process results in a singlet, a doublet is observed, with a splitting much less than that expected for only bound water molecules. For CTAB−water samples, the peak at higher frequency has lower intensity. The opposite behavior was observed for CTAB−NaSal−water systems. The following line-shape simulations show that this asymmetry can be explained by a difference in the chemical shifts of free and bound D_2O molecules.

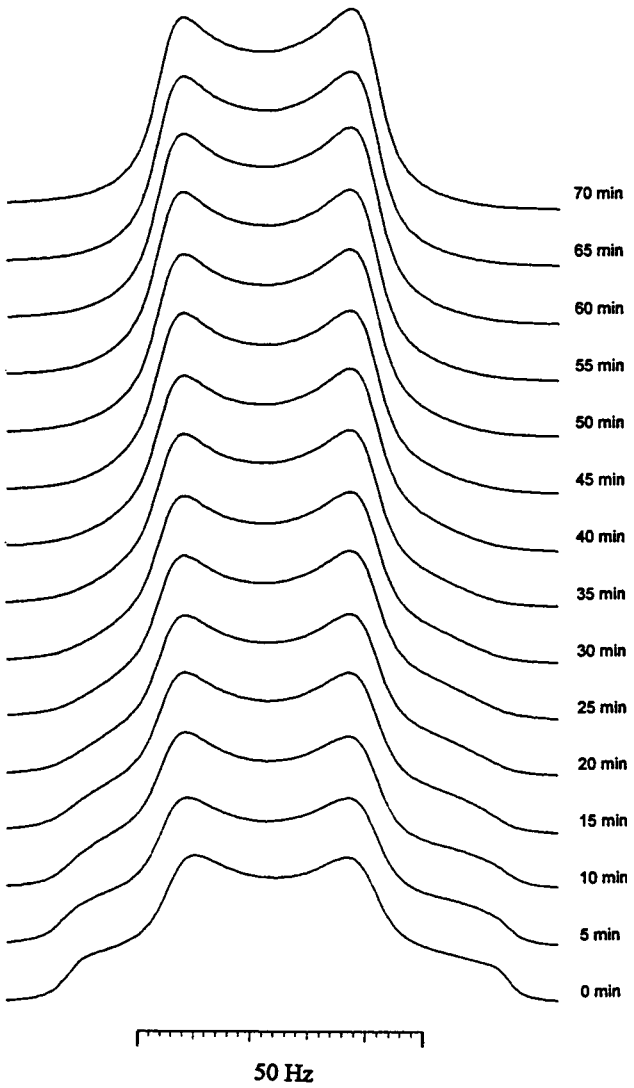

Figure 5. Time-dependent ^{2}H NMR spectra of 1.01 mol/kg CTAB in D_2O with a CTAB/NaSal mole ratio of 1.0. The sample was thoroughly mixed and then equilibrated for 5 days at 25 °C before being put inside the magnet. The spectra were taken at 22 °C in a magnetic field of 11.74 T.

TABLE 1: Lifetimes of D_2O Molecules at a Given Site and Transition Frequencies Obtained from Line-Shape Simulation[a,b]

CTAB in D_2O (mol/kg)	lifetime (s) $\tau_a = \tau_c$	lifetime (s) τ_f	frequency (Hz) ν_a[a]	frequency (Hz) ν_c[b]
1.01	2.0×10^{-4}	1.6×10^{-3}	−595	635
1.07	1.5×10^{-4}	1.0×10^{-3}	−575	605
1.19	1.5×10^{-4}	0.9×10^{-3}	−620	640

[a] ν_a is the frequency for the $|1,1\rangle \rightarrow |1,0\rangle$ transition of the bound water molecules. [b] ν_c is that for $|1,0\rangle \rightarrow |1,-1\rangle$ transition; ν_f for the unbound D_2O molecules is set to zero.

The general line-shape equation[15] for the system studied involves terms that describe two exchange processes, one between *a* and *f1* and another between *c* and *f2*. Because the transition frequencies and the other NMR properties are the same for *f1* and *f2*, the indices 1 and 2 are omitted for the sake of simplicity. Then, the line-shape equation can be written as:

$$V = \gamma B_1 M_0 (V_{af} + V_{fc}) \qquad (1)$$

Here the terms V_{af} and V_{fc} describe line-shape functions due to deuteron exchange between the sites *a* and *f* and the sites *f*

and *c*, respectively, and can be written as

$$V_{ij} = \frac{\left[1 + \frac{\tau_{ij}}{2}\left(\frac{p_i}{T_{2j}} + \frac{p_j}{T_{2i}}\right)\right]P_{ij} + R_{ij}Q_{ij}}{P_{ij}^2 + R_{ij}^2} \quad (2)$$

($i,j = a, f,$ or c) where

$$\frac{1}{\tau_{ij}} = 2\left(\frac{1}{\tau_i} + \frac{1}{\tau_j}\right) \quad (3)$$

$$P_{ij} = \frac{P_i}{T_{2i}} + \frac{P_j}{T_{2j}} + \frac{\tau_{ij}}{2}\left\{\frac{1}{T_{2i}T_{2j}} - \left[\frac{\omega - (\omega_i + \omega_j)}{2}\right]^2 + \left(\frac{\omega_i - \omega_j}{2}\right)^2\right\} \quad (4)$$

$$R_{ij} = \left(\frac{\omega - (\omega_i + \omega_j)}{2}\right)\left[1 + \frac{\tau_{ij}}{2}\left(\frac{1}{T_{2i}} + \frac{1}{T_{2j}}\right)\right] + \frac{\tau_{ij}}{4}(\omega_i - \omega_j)\left(\frac{1}{T_{2i}} + \frac{1}{T_{2j}}\right) - \frac{1}{2}(p_i - p_j)(\omega_i - \omega_j) \quad (5)$$

$$Q_{ij} = \frac{\tau_{ij}}{2}\left[\omega - \frac{\omega_i + \omega_j}{2} + \frac{(\omega_i - \omega_j)(p_i - p_j)}{2}\right] \quad (6)$$

where τ_i is the time that a molecule stays at the *i*-th site, p_i is the population, ω_i is the Larmor frequency, and T_{2i} is the transverse relaxation time of D_2O molecules at the *i*-th site.

The following obvious constraints

$$p_a + p_f = 1 \quad (7)$$

$$p_a = p_c \quad (8)$$

$$\tau_a p_f = \tau_f p_a \quad (9)$$

$$\tau_a = \tau_c \quad (10)$$

$$T_{2a} = T_{2c} \quad (11)$$

reduce the number of independent variables in eq 1 to seven.

Since eq 1 contains 10 variables (the factor $\gamma B_1 M_o$ is only a scaling factor for the total intensity), the result of simulations is far from being unambiguous. Therefore, certain assumptions have to be made to narrow down the number of possible combinations of the parameters to give physically sensible results. First, we know that $p_{f1} = p_{f2} > p_a = p_c$ because there are more water molecules in the bulk phase than those bound to the CTAB molecules, but the population ratio of free to bound D_2O molecules must be estimated. Canet and co-workers[16] found that the number of D_2O molecules bound to a CTAB surfactant molecule in a micelle is about 10, and their result is used here. Second, since $T_1 \approx T_2$ for free water molecules, the transverse relaxation time for free D_2O at 30 °C T_{2f} was taken to be equal to the longitudinal relaxation time T_1 at that temperature, 0.53 s.[17] The values of T_{2a} and T_{2c} are expected to be considerably shorter, but they cannot be determined experimentally. Therefore, we assume that the relaxation time T_2 for bound water is approximately one tenth of that for free water, i.e., $T_{2a} = T_{2c} = T_{2f}/10 = 0.053$ s. Using these assumptions, the asymmetric spectra can be simulated, and the results of two typical cases are shown in Figure 6. The asymmetric powder patterns arise from superposition of these asymmetric doublets with spatial distribution of the liquid-crystalline domains, but we did not attempt spectral simulations for such a system because of the uncertainties involved.

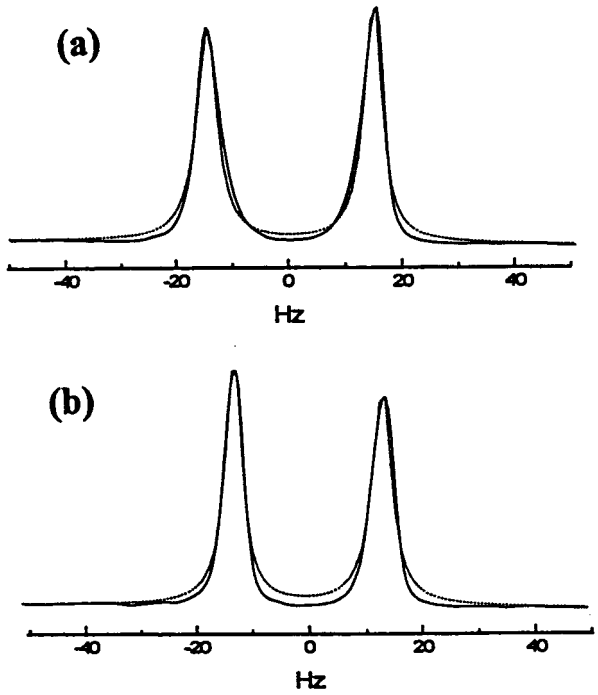

Figure 6. Steady-state ^2H NMR spectra of 1.01 mol/kg CTAB in D_2O, — experimental, --- simulated. (a) No NaSal added, at 30 °C. (b) With a mole ratio of CTAB/NaSal = 1.7, at 22 °C.

TABLE 2: Lifetimes of D_2O Molecules at a Given Site and Transition Frequencies Obtained from Line-Shape Simulation[a,b]

mole ratio of CTAB/NaSal	*T* (°C)	lifetime (s) $\tau_a = \tau_c$	lifetime (s) τ_f	frequency (Hz) ν_a[a]	frequency (Hz) ν_c[b]
1.67	30	3.0×10^{-4}	2.36×10^{-3}	−566	564
1.67	25	3.0×10^{-4}	2.36×10^{-3}	−558	512
1.67	22	1.0×10^{-4}	0.75×10^{-3}	−660	575
1.8	22	2.0×10^{-4}	1.58×10^{-3}	−537	523

[a] ν_a is the frequency for the $|1,1\rangle \rightarrow |1,0\rangle$ transition of the bound water molecules. [b] ν_c is that for $|1,0\rangle \rightarrow |1,-1\rangle$ transition; ν_f for the unbound D_2O molecules is set to zero.

By using this procedure, all spectra of the fully aligned CTAB−D_2O systems studied were simulated.[18] The parameters obtained from the best fits to the experimental spectra at 30 °C are listed in Table 1. The results show that $(\nu_a + \nu_c) > 0$, implying that the deuterons in the bound D_2O molecules are less shielded than those in the free D_2O molecules. The quadrupole splitting of the bound D_2O molecules ($\Delta\nu = \nu_c - \nu_a$) increases with CTAB concentration, as expected. There is no apparent trend for lifetime, τ, with respect to CTAB concentration.

For the ternary CTAB−NaSal−D_2O system, fitting parameters used to simulate the experimental spectra are listed in Table 2. The CTAB/D_2O mole ratio was kept constant (1.01 mol/kg) for these systems. In contrast to the pure CTAB systems, $(\nu_a + \nu_c) < 0$ here. It means that the deuterons in the bound D_2O molecules are less shielded than those in free D_2O molecules. The quadrupole splitting of the bound D_2O molecules ($\Delta\nu = \nu_c - \nu_a$) decreases with increasing temperature and decreasing NaSal concentration, as expected. The only exception was found for CTAB/NaSal = 1.7 at 25 °C, and the reason is likely to be the uncertainty in lifetime, for which no trend with respect to

NaSal concentration or temperature is apparent from the lineshape simulation.

Under the assumptions involved, the parameters in Tables 1 and 2 are only order-of-magnitude estimates. The ratio of $p_f/p_a = p_f/p_c = 10$ (10 D_2O molecules bound to each CTAB headgroup[16]) may not be completely valid, especially when the CTAB micelles transform from globular to ropelike. The assumption of $T_{2a} = T_{2c} = T_{2f}/10$ is rather arbitrary. The experimental spectra can also be simulated using other ratios of p_f/p_a and T_{2f}/T_{2a}.[16] Nevertheless, the major conclusion from the simulation should be valid: the asymmetry of the ^2H NMR spectra is a result of different chemical shifts of the bound and free D_2O molecules.

Alignment Kinetics. The alignment of a ropelike micelle in a magnetic field can be qualitatively described as follows. The magnetic energy of a micelle with an anisotropy of the magnetic susceptibility of $\Delta\chi$ in a magnetic field with strength B can be estimated as

$$\Delta E(\theta) = -\Delta\chi B^2 V \cos\theta \tag{12}$$

where θ is the angle between the director of the micelle and the magnetic field and V is the volume of the micelle. Then, the magnetic moment that affects the molecule at a small θ is

$$P = \mathrm{d}E/\mathrm{d}\theta \approx \Delta\chi B^2 V\theta \tag{13}$$

(here we assume that $\Delta\chi > 0$, otherwise the definition of θ should be changed). The moment makes the major axes of the micelles rotate by an angle $\mathrm{d}\theta$. According to Stokes' law, the force of friction is $F = -\sigma\mu v$, where σ is Stokes' constant, μ is the viscosity of the medium, and v is the velocity of the particle. For a ropelike micelle, we can rewrite (13) as

$$P = \int F\mathrm{d}r = -\sigma\mu\int v\mathrm{d}r \tag{14}$$

(the integration is carried out over the length of the micelle).

Because $v = r(\mathrm{d}\theta/\mathrm{d}t)$ and $\int v\mathrm{d}r = (1/2)L^2(\mathrm{d}\theta/\mathrm{d}t)$, where L is the length of the micelle, (14) can be rewritten as

$$\frac{1}{2}\sigma\mu L^2(\mathrm{d}\theta/\mathrm{d}t) = -\Delta\chi B^2 V\theta \tag{15}$$

or $\theta = \theta_0 \exp(-t/2t_a)$, where

$$t_a^{-1} = 4\Delta\chi B^2 V/\sigma\mu L^2 \tag{16}$$

The quadrupole splitting in the ^2H NMR spectrum can be written as

$$\Delta\nu \propto (3\cos^2\theta - 1)/2 \tag{17}$$

For small θ it can be expanded into $\Delta\nu \propto (1 - 3\theta^2/2)$, or

$$\Delta\nu \propto [1 - (3/2)\theta_0^2 \exp(-t/t_a)] \tag{18}$$

Thus, under the assumption of small θ, the dynamics of micelle rotation in a magnetic field can be expressed by the simple eq 16, which can be rewritten in a more conventional form

$$\Delta\nu = D_0\left[1 - \exp\left(\frac{t_0 - t}{t_a}\right)\right] \tag{19}$$

where D_0 is the final splitting at $t\rightarrow\infty$, t_a is given by (16), and $t_0 = t_a\ln(3\theta_0^2/2)$. The physical meaning of t_0 is the lagging time after which the above model becomes valid. The fitting parameters for various samples are listed in Table 3. Because t_0 is dependent on the time between the insertion of the sample into the magnet and the start of data collection, its values are not directly related to the properties of the systems. Therefore, they are not listed in the tables. The indicated errors only refer to the fitting, but do not include experimental ones that give rise to more severe uncertainty when the doublets are not completely resolved. Therefore, the actual errors can be more than those given in Table 3.

TABLE 3: The Steady-State Deuterium Quadrupole Splitting, D_0, and Characteristic Alignment Time t_a (at B_0 = 11.74 T) for Equilibrated CTAB−D_2O Systems

CTAB in D_2O (mol/kg)	CTAB/NaSal mole ratio	T (°C)	D_0 (Hz)	t_a (min)
1.01		50	47.6 ± 0.1	9 ± 1
1.01		40	40.6 ± 0.1	23 ± 1
1.01		30	24.1 ± 0.3	25 ± 2
1.07		30	26.0 ± 0.3	28 ± 2
1.19		30	32.9 ± 0.2	37 ± 3
1.01	1.67	30	29.2 ± 0.4	49 ± 2
1.01	1.67	25	30.2 ± 0.3	50 ± 4
1.01	1.0	22	31.8 ± 0.8	101 ± 30
1.01	1.67	22	30.6 ± 0.2	31 ± 2
1.01	1.8	22	26.0 ± 0.2	25 ± 1

TABLE 4: Relation between Characteristic Alignment Time, t_a, and Magnetic Field Strength, B_0

CTAB in D_2O (mol/kg)	magnetic field B_0 (T)	characteristic alignment time t_a (min)	$B_0^2 \times t_a$ (10^3 T^2·min)
1.01	7.05	87 ± 9	4.3 ± 0.4
1.01	11.74	25 ± 2	3.4 ± 0.3
1.07	7.05	107 ± 13	5.3 ± 0.6
1.07	11.74	28 ± 2	3.9 ± 0.3

The parameter D_0 increases with CTAB concentration, because at higher concentration a larger fraction of D_2O molecules is bound to the micelles, leading to a larger average quadrupole splitting. It is also possible that the order parameter of ropelike micelles may become larger with higher CTAB concentration. Increasing the amount of NaSal also leads to a larger quadrupole splitting, because the salicylate anions bind to the CTAB micelles and favor type II alignment.

With an increase in temperature, the quadrupole splitting for the CTAB−D_2O samples increases, and the splitting for the CTAB−NaSal−D_2O samples decreases. At higher temperature, the quadrupole splittings of thermotropic liquid crystals usually decrease due to a decrease in the order parameter. However, a reverse trend has been observed for several lyotropic liquid crystals,[9] including the CTAB−D_2O system studied here. This could be due to a temperature dependence of the orientational distribution of the bound water molecules with respect to the director of the mesophase.[6] As for the opposite trend of the CTAB−NaSal−D_2O samples as compared with the CTAB−D_2O system, it should be noted that the macroscopic orientation of the CTAB micelles is now perpendicular to the field rather than parallel to it. Because of this difference in temperature dependence, the deuterium quadrupole splitting can be observed for CTAB−D_2O samples at much higher temperatures than that for CTAB−NaSal−D_2O samples (as mentioned above).

According to eq 16, the characteristic alignment time, t_a is expected to be the reciprocal of the square of the magnetic field. This was approximately the case for CTAB−D_2O samples at equilibrium (Table 4). The difference may be attributed to the uncertainties in the values of t_0, as discussed in the previous section.

Conclusion

^2H NMR has been used to monitor the alignment of lyotropic liquid-crystal systems in the magnetic field of 11.74 T. The liquid-crystalline domains of samples with CTAB/D_2O concentrations between 1.01 and 1.29 mol/kg were aligned in the magnetic field within a few hours. The characteristic alignment time and the final quadrupolar splitting increased with concentration. An increase in temperature made the characteristic alignment time shorter and the final splitting larger. At concentrations greater than 1.50 mol/kg, the viscosity of the system became too high for any alignment to be observed. The alignment could not be studied by ^2H NMR at concentrations less than 1.01 mol/kg because the quadrupolar splitting was less than the line width. The addition of NaSal changed the orientation of the ropelike micelles from the type I lyotropic system to the type II system at equal molar concentrations of NaSal and CTAB. This effect was not observed for NaHNC as a result of its low solubility. For CTAB−NaSal−D_2O samples, the steady-state quadrupole splitting decreased with a temperature increase, which was opposite to the trend observed for CTAB−D_2O samples. Line-shape simulations of the ^2H NMR spectra of completely aligned samples were carried out under the assumption of fast exchange between unequally populated sites. It gave order-of-magnitude information on the lifetime of D_2O molecules at the sites bound to micelles and their deuteron quadrupole splittings. The asymmetry in the ^2H NMR spectra was attributed to the difference in ^2H chemical shifts between the bound and free D_2O molecules: the molecules bound to the surfactant headgroup become less shielded in CTAB−D_2O systems and more shielded in CTAB−NaSal−D_2O systems.

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