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# Phase Equilibria of the System Hexadecyltrimethylammonium Fluoride-Water Studied by $^2\text{H}$ , $^{14}\text{N}$ , and $^{19}\text{F}$ Nuclear Magnetic Resonance

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The binary phase diagram of hexadecyltrimethylammonium fluoride ( $\text{C}_{16}\text{TAF}$ ) in  $^2\text{H}_2\text{O}$  is determined by studies of  $^2\text{H}$  and  $^{14}\text{N}$  NMR.  $\text{C}_{16}\text{TAF}$  forms a hexagonal liquid crystalline phase between 40% and 60%  $\text{C}_{16}\text{TAF}$  and this phase is stable from 300 to 400 K. A cubic liquid crystalline phase appears between 328 and 383 K in the water-poor region between 74% and 85%  $\text{C}_{16}\text{TAF}$ . This phase is presumably built up of rodlike aggregates. Measurements of  $^{14}\text{N}$  transverse relaxation rates,  $T_2^{-1}$ , and isotropic chemical shifts of  $^{19}\text{F}$  show that the aqueous ( $^2\text{H}_2\text{O}$ ) solutions of  $\text{C}_{16}\text{TAF}$ , like those of  $\text{C}_{16}\text{TABr}$  and  $\text{C}_{16}\text{TACl}$ , undergo a transition from globular to rodlike micelles and this transition takes place at about 0.7  $m$  for the  $\text{C}_{16}\text{TAF}$ - $^2\text{H}_2\text{O}$  system. The water orientation in the hexagonal phase increases with the amphiphile concentration as well as with the temperature.

## Introduction

Amphiphiles undergo self-association in aqueous solutions forming micellar aggregates of various sizes and shapes, and they form different types of liquid crystalline phases. Studies of the phase equilibria of binary and ternary amphiphilic systems have been reported by Ekwall and co-workers,<sup>1</sup> and a large number of phase diagrams are available in their work. For biological lipids, phase diagrams have been presented by Luzzati and Tardieu.<sup>2</sup> Recently we showed that NMR can be conveniently used for determining phase diagrams<sup>3-5</sup> and also for studies of the structure of the aggregates in the phases.<sup>6-8</sup> This technique is nondestructive and avoids the often cumbersome separation of different phases existing in the sample.

Here we have studied the binary phase equilibria at different temperatures for the system hexadecyltrimethylammonium fluoride ( $\text{C}_{16}\text{TAF}$ )-heavy water. The phase diagram has been constructed by observing mainly quadrupole splittings of heavy water<sup>3</sup> and also from splittings of  $^{14}\text{N}$ . The binding and the orientation of water and fluoride ions in the liquid crystalline structures have also been investigated. Previously, it has been shown,<sup>9,11</sup> that micelles of hexadecyltrimethylammonium cations having bromide ( $\text{C}_{16}\text{TABr}$ ) or chloride ( $\text{C}_{16}\text{TACl}$ ) as counterions undergo a change of shape from globular to rodlike aggregates with increasing amphiphile concentration. A similar study has also been performed in this work

with fluoride as the counterion.

## Experimental Section

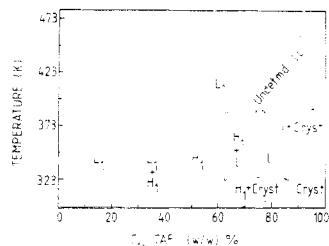
Hexadecyltrimethylammonium bromide  $\text{C}_{16}\text{TABr}$  was purchased from Th. Suchardt, München, West Germany.  $\text{C}_{16}\text{TABr}$  was converted to the hydroxide form by ion exchange on Dowex 21K. The  $\text{C}_{16}\text{TACl}$  was immediately neutralized with either  $\text{HCl}$  to  $\text{C}_{16}\text{TACl}$  or  $\text{HF}$  to  $\text{C}_{16}\text{TAF}$ , to pH 4-5. The solution was lyophilized and a white crystalline product was obtained after drying.

The other chemicals used were as follows:  $^2\text{H}_2\text{O}$  (99.7 at. %  $^2\text{H}$ ), Ciba-Geigy, Switzerland;  $\text{NaF}$  and  $\text{HCl}$ , Merck, West Germany;  $\text{HF}$  and Dowex 21K ion-exchange resins, BDH Chemicals Limited, Poole, England.

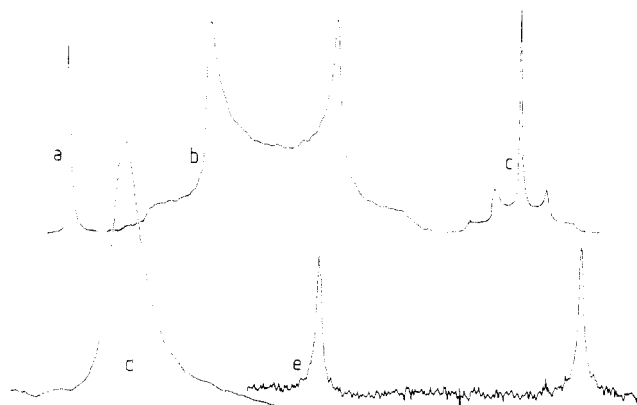
The samples were prepared by weighing appropriate amounts of  $\text{C}_{16}\text{TA}$  salts and  $^2\text{H}_2\text{O}$  into glass tubes which were sealed off immediately. The mixing of liquid crystalline samples was done by repeated heating and centrifuging for 2-3 days. The samples were kept standing at ambient temperature for at least 1 week before any NMR measurements were made.

$^2\text{H}$ ,  $^{19}\text{F}$ , and  $^{14}\text{N}$  (quadrupole relaxation only) NMR studies were made at 15.351, 94.077, and 7.224 MHz, respectively, with a modified Varian XL-100-15 pulsed spectrometer working in the Fourier transform mode using an external lock.  $^{14}\text{N}$  quadrupole splittings were studied at 18.45 MHz on a home-built Fourier transform spectrometer equipped with an Oxford Instruments 6-T wide-bore superconducting magnet. The  $^{19}\text{F}$  isotropic chemical shifts ( $\sigma_0$ ) for micellar solutions were measured at 300 K relative to solutions of  $\text{NaF}$  in  $^2\text{H}_2\text{O}$  at infinite dilution. The transverse relaxation rates,  $T_2^{-1}$  ( $=\pi\nu_{1/2}$ ), of  $^{14}\text{N}$  were obtained at 300 K from the line width at half-height ( $\nu_{1/2}$ ) of the resonance signal. The  $^2\text{H}$  and  $^{14}\text{N}$  quadrupole splittings were respectively measured as the distance between the two peaks in the spectra.  $^2\text{H}$  NMR of the liquid crystalline samples was also studied as a function of the temperature. A variable temperature control unit was used to control the temperature at the airflow in which the 12-nm (i.d.) NMR tube containing the sample tube was placed in the NMR probe. The sample was thermally equilibrated for at least 1 h before the spectrum was traced. The temperature of the probe was

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**Figure 1.** Temperature-concentration phase diagram of the system  $C_{16}TAF-H_2O$ : (L) aqueous isotropic liquid; (H<sub>1</sub>) hexagonal liquid crystalline phase; (I) cubic liquid crystalline phase; (C) crystalline  $C_{16}TAF$ ; (---) approximative boundary lines of phases.



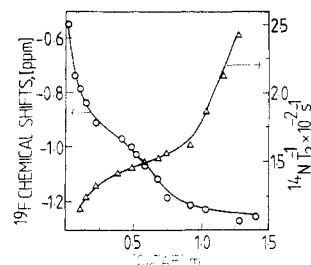
**Figure 2.** Examples of NMR spectra obtained for the system  $C_{16}TAF-H_2O$ .  $^2H$  NMR spectra for (a) 75%  $C_{16}TAF$  at 346 K, (b) 40%  $C_{16}TAF$  at 346 K, and (c) composition b at 389 K.  $^{14}N$  NMR spectra for (d) composition a at 346 K and (e) composition b at 300 K.

measured with a thermometer. The NMR measurements of some liquid crystalline samples were repeated after about 2 months. No significant change was observed. The samples in the liquid crystalline phases were also investigated by polarizing microscopy. The hexagonal and cubic phases were easily recognized. The structure interpretations were confirmed by low-angle X-ray diffraction.

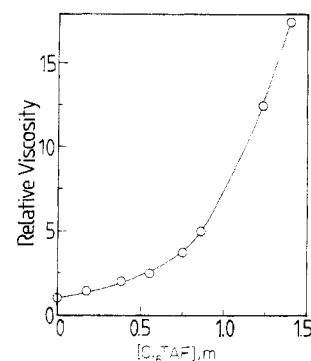
## Results and Discussion

**Phase Diagram.** Hexadecyltrimethylammonium fluoride ( $C_{16}TAF$ ) forms micellar solutions in water up to a concentration of 30% (w/w). A two-phase region consisting of a liquid crystalline phase and the isotropic solution phase exists between 30% and 40%  $C_{16}TAF$ . The liquid crystalline phase begins to form at 40%  $C_{16}TAF$  and continues up to 60%  $C_{16}TAF$  above which concentration the liquid crystalline phase appears along with crystals of  $C_{16}TAF$ . The phase behavior was determined at 300 K (27 °C) from the studies of  $^2H$  and  $^{14}N$  NMR spectroscopy and by polarizing microscopy as previously described<sup>5</sup> (Figure 1).

The samples in the liquid crystalline region are transparent and stiff and have in the polarizing microscope the simple, nonstriated type of nongeometric texture, 231 in the classification of Rosevear.<sup>10</sup> This texture is typical for a hexagonal liquid crystalline phase. X-ray diffraction showed that the size of the two-dimensional hexagonal unit cell increased with the lipid content from 49 to 59 Å. If we assume the density to be unity this means that the diameter of the rod aggregates forming the structure increased from 33 to 49 Å and the area per polar group at the interface between polar and nonpolar regions decreased from 62 to 48 Å<sup>2</sup>. The  $^2H$  and  $^{14}N$  NMR for the samples in this region produces a quadrupole splitting for each of these nuclei (Figure 2, b and e). The liquid crystalline phase does not change its microscopic texture or the nature



**Figure 3.** Composition of  $C_{16}TAF$ , against  $^{19}F$  isotropic chemical shifts, and  $^{14}N$  quadrupole transverse relaxation rates, for the micellar solutions of the  $C_{16}TAF-H_2O$  system at 300 K: (O)  $^{19}F$  isotropic chemical shift ( $\sigma_0$ ); ( $\Delta$ )  $^{14}N$  transverse relaxation rates ( $T_2^{-1}$ ).



**Figure 4.** Relative viscosity vs.  $C_{16}TAF$  concentration ( $m$ ): temperature, 25 °C; reference,  $H_2O$ . The measurements were made with an Ostwald viscometer.

of the quadrupolar splitting except with respect to its magnitude with increasing temperatures until it is converted to an isotropic solution where the NMR spectra for  $^2H$  and  $^{14}N$  give a sharp single peak (Figure 2, a and d). Similar quadrupole splittings are also observed at 300 K for samples in the two-phase region above 60%  $C_{16}TAF$ . The gross appearance of the samples in this region is white at 298 K, in contrast to the transparent one of the liquid crystalline phase. The microscopic studies show the existence of two different birefringent textures in this region, one having the texture of the hexagonal phase and the other one that of crystalline  $C_{16}TAF$ . Samples with compositions between 74% and 85%  $C_{16}TAF$  become transparent, optically isotropic, and highly viscous when heated between 328 and 383 K. The cubic structure was confirmed by X-ray low-angle diffraction. However, as only three reflections were obtained the indexing of them was uncertain but a primitive cubic structure with a unit cell dimension of about 69 Å fitted best with experimental data. The sample in this temperature region produces singlets for  $^2H$  and  $^{14}N$  NMR, respectively, similar to those obtained for these nuclei in the micellar solution (Figure 2 a and d). A  $^2H$  quadrupole splitting together with a central sharp peak is obtained (Figure 2c) for the two two-phase regions. Based upon the above observations, the phase diagram was determined for the temperature region 300–473 K (27–200 °C) (Figure 1).

**Micellar Solution.** The isotropic ( $^2H_2O$ ) solutions of  $C_{16}TAF$  were investigated by following the  $^{19}F$  isotropic chemical shift ( $\sigma_0$ ) and  $^{14}N$  line widths ( $\nu_{1/2}$ ) as a function of amphiphile concentration. The results obtained are summarized in Figure 3. It can be inferred from this figure that  $\sigma_0$  decreases rapidly with increasing  $C_{16}TAF$  content and becomes constant at about 0.7  $m$   $C_{16}TAF$ . Similarly, the relaxation rate,  $T_2^{-1}$ , calculated from the line width through  $T_2^{-1} = \pi \nu_{1/2}$  shows a remarkable increase from about 0.7  $m$  to the concentration limit (1.4  $m$ ), where a two-phase region is formed.

TABLE I: Effect of  $\alpha$ -Methylnaphthalene ( $\alpha$ -mN) on <sup>14</sup>N NMR Line Widths ( $\nu_{1/2}$ ) in the Micellar Solution Region of C<sub>16</sub>TAF-<sup>2</sup>H<sub>2</sub>O (300 K)

C <sub>16</sub> TAF, <i>m</i>	$\alpha$ -mN, wt %	$\nu_{1/2}$ , Hz
0.50		46.5
0.45	0.95	63.5
0.41	1.6	205.5
0.49	1.7	271.0

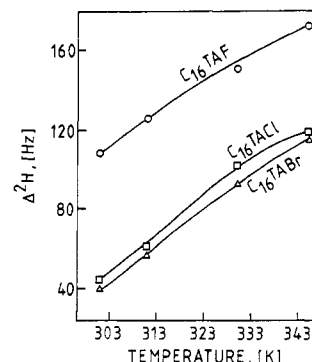
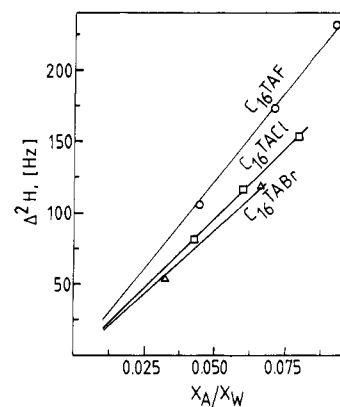
TABLE II: Effect of Temperature and Amphiphile Concentration on <sup>2</sup>H NMR Quadrupole Splittings ( $\Delta^2H$ ) of the Hexagonal Liquid Crystalline Phases for the Systems C<sub>16</sub>TAF-<sup>2</sup>H<sub>2</sub>O, C<sub>16</sub>TACl-<sup>2</sup>H<sub>2</sub>O, and C<sub>16</sub>TABr-<sup>2</sup>H<sub>2</sub>O

amphiphile	$X_A^a$	$\Delta^2H$ , Hz			
		301 K	311 K	330 K	346 K
C <sub>16</sub> TAF	0.04	65.8	76.3	97.2	105.2
C <sub>16</sub> TAF	0.07	108.5	126.3	151.0	173.5
C <sub>16</sub> TAF	0.09	142.0	165.6	205.4	234.7
C <sub>16</sub> TACl	0.04	27.3	39.7	61.6	78.2
C <sub>16</sub> TACl	0.06	40.0	57.4	93.7	116.2
C <sub>16</sub> TACl	0.07	56.0	78.1	128.4	155.3
C <sub>16</sub> TABr	0.03	22.8	32.3	49.8	52.8
C <sub>16</sub> TABr	0.06	44.6	61.3	102.6	119.9

<sup>a</sup> Mole fraction.

A preliminary study of the viscosity of the aqueous solutions also showed a marked rise in  $\eta_{rel}$  at about 0.7 *m* C<sub>16</sub>TAF (Figure 4). This may be taken as a sign for the formation above this concentration of rodlike micelles. This conclusion is supported by the finding that solubilization of  $\alpha$ -methylnaphthalene in aqueous solutions of C<sub>16</sub>TAF leads to dramatic increase in the <sup>14</sup>N line widths, as shown in Table I. It has been shown previously<sup>9</sup> that additives such as  $\alpha$ -methylnaphthalene favor the formation of rodlike micelles.

The increase in relaxation rate  $T_2^{-1}$  (Figure 3) at about 0.7 *m* C<sub>16</sub>TAF is most probably due to rodlike aggregates, the length of which increases with amphiphile concentration. The reason for this conclusion is that, for quadrupolar nuclei like <sup>14</sup>N ( $I = 1$ ), the relaxation is dominated by the quadrupolar mechanism, where the electric quadrupole moment of the nucleus interacts with time-dependent electric field gradients present at the site of the nucleus. The changes of the <sup>14</sup>N relaxation rate obtained for the hexadecyltrimethylammonium ions in the micellar aggregates can be understood by considering the molecular motion occurring on different time scales in the aggregates.<sup>12</sup> In this treatment, one considers a fast local anisotropic motion and a second slower overall motion of the micellar aggregates. This model has been utilized in this study. Recently it was shown<sup>13</sup> that the correlation time for the slow motion increases rapidly with amphiphile concentration because of the formation of rodlike C<sub>16</sub>TABr micelles. Thus, the increase in  $T_2^{-1}$  (Figure 3) at about 0.7 *m* C<sub>16</sub>TAF is most probably due to rodlike aggregates, the length of which increases with amphiphile concentration. A similar result<sup>14</sup> has recently been reported from measurements of <sup>13</sup>C relaxations on the dodecyldimethylammonium chloride-<sup>2</sup>H<sub>2</sub>O system showing a sphere-rod transition in the presence of sodium chloride. The interpretation of a change in the micellar shape is further supported by the <sup>19</sup>F chemical shift data (Figure 3). Here

Figure 5. <sup>2</sup>H NMR quadrupole splittings ( $\Delta^2H$ ) vs. temperatures (*T*) of the hexagonal liquid crystalline phases for amphiphile-heavy water systems: (O) 51.9% ( $X_A = 0.07$ ) C<sub>16</sub>TAF; (□) 54.6% ( $X_A = 0.06$ ) C<sub>16</sub>TABr; (Δ) 49.1% ( $X_A = 0.06$ ) C<sub>16</sub>TACl.Figure 6. <sup>2</sup>H NMR quadrupole splittings ( $\Delta^2H$ ) vs.  $X_A/X_W$  where  $X_A$  is the mole fraction of the amphiphile and  $X_W$  is that of water at 346 K for the hexagonal liquid crystalline phases of amphiphile-heavy water systems.TABLE III: Slopes Obtained at Different Constant Temperatures from Plots of  $X_A/X_W$  vs.  $\Delta^2H$  (Figure 6) for the Hexagonal Liquid Crystalline Phases of C<sub>16</sub>TAX-<sup>2</sup>H<sub>2</sub>O ( $X = Cl^-$ ,  $Br^-$ , or  $F^-$ ) Systems

amphiphile	slope, kHz			
	301 K	311 K	330 K	346 K
C <sub>16</sub> TAF	1.52	1.76	2.21	2.44
C <sub>16</sub> TACl	0.67	0.95	1.55	1.93
C <sub>16</sub> TABr	0.68	0.96	1.56	1.76

also a marked change in  $\sigma_0$  is observed at about 0.7 *m* C<sub>16</sub>TAF.

To summarize, our experimental findings suggest that all of the amphiphiles, C<sub>16</sub>TAF, C<sub>16</sub>TABr, and C<sub>16</sub>TACl, form rod-shaped micelles in aqueous solution and the concentration of aggregate transition increases in the order  $Cl^- > F^- > Br^-$  (cf. ref 9).

**Liquid Crystalline Phases.** The magnitudes of the <sup>2</sup>H NMR quadrupole splittings ( $\Delta^2H$ ) for the hexagonal liquid crystalline phase of the C<sub>16</sub>TAF-<sup>2</sup>H<sub>2</sub>O system are dependent on concentrations as well as temperatures, as shown in Table II. For comparison, some values of NMR quadrupole splittings for the hexagonal liquid crystalline phases of C<sub>16</sub>TACl-<sup>2</sup>H<sub>2</sub>O and C<sub>16</sub>TABr-<sup>2</sup>H<sub>2</sub>O systems are included in the table. It can be seen from the table that  $\Delta^2H$  increases with increased amphiphile concentrations (36–58%) and temperatures (300–346 K), irrespective of the counterions employed. The magnitudes of  $\Delta^2H$  for C<sub>16</sub>TACl and C<sub>16</sub>TABr systems are approximately the same (120 Hz at 346 K, at 0.06 molar ratio), but the values are considerably smaller than those of the C<sub>16</sub>TAF system (e.g.,

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174 Hz at 346 K, at 0.08 molar ratio) (Figure 5).

The plot of  $X_A/X_W$  vs.  $\Delta^2H$  where  $X_A/X_W$  is the ratio of the mole fraction of the amphiphile to that of water, at a constant temperature, is a straight line passing through the origin (Figure 6). The slopes obtained for these three amphiphile systems at different constant temperatures are shown in Table III.

The deuteron, like  $^{14}\text{N}$  nucleus, has a spin quantum number of unity, and hence its NMR spectrum is dominated by the quadrupolar mechanism. In an anisotropic medium, the quadrupolar interaction becomes nonzero and its spectrum thus consists of a doublet having equal intensity in each component. The observed quadrupole splitting ( $\Delta^2H$ ) for a nonoriented powder sample is given by<sup>12</sup>

$$\Delta^2H = |\sum P_i \nu_{Q_i} S_i|$$

where  $P_i$  is the fraction of water molecules in site  $i$  characterized by the order parameter,  $S_i$ ;  $\nu_{Q_i}$  is the effective quadrupole coupling constant.

Applying a two-site model with free and bound water molecules having fast exchange between the sites,  $\Delta^2H$  obtained for a mesophase may be related to the molar ratio of amphiphile and water as<sup>15</sup>

$$\Delta^2H = (nX_A/X_W)|\nu_Q S|$$

where  $n$  is the average number of water molecules bound to each polar group. The  $\nu_Q$  for water is taken as 220 kHz.<sup>15</sup> The hexagonal liquid crystalline phases in the CTAX- $^2\text{H}_2\text{O}$  ( $X = \text{F}^-$ ,  $\text{Br}^-$ , or  $\text{Cl}^-$ ) systems follow the above model at different constant temperatures, as can be seen from Figure 6, where a plot of  $\Delta^2H$  vs.  $X_A/X_W$  gives a straight

line passing through the origin. The water splitting also increases markedly with increased temperatures (Figure 5, Table III). This may be due to the fact that an increased area per amphiphile polar end group is caused by thermal expansion leading to a change in the water orientation. However, since the quadrupole splitting increases as much as a factor of 2 or 3 for a change in temperature of 40 K, it is not likely that the whole effect can be ascribed to an alteration of the amount of bound water,<sup>16</sup> but, it may be suggested that also a change in the order parameter is responsible for this behavior. The large difference in the splitting between  $\text{C}_{16}\text{TAF}$  on one side and  $\text{C}_{16}\text{TACl}$  and  $\text{C}_{16}\text{TABr}$  on the other might be due to a difference in the hydration<sup>17</sup> of the halide counterions.

With an average value of  $n = 9$  obtained from the phase diagrams of  $\text{CTAF-}^2\text{H}_2\text{O}$  (Figure 1) and  $\text{CTABr-}^2\text{H}_2\text{O}$ <sup>18</sup> systems, we obtain a value of the order parameter,  $|S_{\text{hexagonal}}| = 10^{-3}$  at 346 K. The cubic liquid crystalline phase which appears in the phase diagram (Figure 1) in the water-poor region at high temperatures has been shown in the accompanying paper<sup>19</sup> to consist of continuous hydrocarbon regions in agreement with the structure proposed by Luzzati and Spegt<sup>20</sup> for some other cubic phases. In our study, different NMR methods were utilized, permitting also an estimation of the dimension of the cubic unit cell.<sup>19</sup>

**Acknowledgment.** This work was supported by a grant from the Swedish Natural Science Research Council.

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