relaxation rate at two different counterion proton sites upon addition of a relaxation agent, one can obtain orientational information of the counterion, related to the nitroxyl–proton distance. The use of nitroxides as spectroscopic probes in hydrocarbon assemblies and the interpretation of any results has been a matter of considerable controversy in the past. In particular, the actual location of the nitroxide group in microheterogenous systems has been much debated. Mukerjee et al.[20-22] have presented arguments for an exclusive location of the nitroxide group in the water–micelle region as based on arguments about microenvironmental polarities and band shifts in the UV and visible region. On the other hand, ESR data have been interpreted to be consistent with a location of the nitroxide group in the micellar hydrocarbon core.[23] Symons and Pena-Nuñez in a very recent paper summarize much of the earlier literature and present a study on di-*tert*-butyl nitroxide (DTBN) solvation in various solvent systems,[24] where they suggest that nitroxides in micelles and membranes are monohydrated.

In any case, one must expect the location of the solubilized nitroxides to differ with nitroxide type. A bulky or aromatic molecule may be difficult to physically incorporate into the hydrocarbon chain environment and such nitroxides may be forced to reside at the micellar surface. In the case of polyfunctional molecules one must also consider any specific interactions between the nitroxyls and the functional groups.

Figures 1–4 demonstrates that the excess relaxation rate is higher for the amphiphile part of the surfactant than for the counterion, both for the methylene and the methyl protons. This is partly due to the partial dissociation of the counterions from the micelle, but even for pentanoate for which $\beta = 0.87$ there is a significant difference between the counterion and amphiphile excess relaxation rates. This observation would indicate that the nitroxide group is not completely located in the water–micelle region.

The data of Figures 1–4 show that the orientation of butanoate and pentanoate differ from that of propanoate and isobutanoate. The methyl excess relaxation rate is higher than the α-methylene excess relaxation rate for butanoate and pentanoate, but the reverse is observed for propanoate and isobutanoate. If we assume that the paramagnetic relaxation contribution is higher inside the micelle, as the amphiphile relaxation rate excess measurements indicate, this would lead to the conclusion that it is more likely to find the methyl group inside the micelle than the methylene group for butanoate and pentanoate. This means that the hydrocarbon tails of butanoate and pentanoate would be located inside the micelle to a greater extent than those of isobutanoate and propanoate, corresponding to more of a mixed micelle situation. The still unresolved question of the actual location of the probe in the micelle makes it hazardous to draw firm conclusions from the measurements, however. Nevertheless, a comparison of the results found for the examined counterions demonstrate that there is a relative orientation difference between butanoate and pentanoate on one hand, and the less hydrophobic counterions on the other.

Conclusions

It is demonstrated that the degree of counterion association is affected by several counterion characteristics. Hydrophobic interactions between the micelle and the counterion are demonstrated to be important contributions to the ion–micelle attraction and a correlation is found between the degree of counterion association and the aggregation behavior of the amphiphile, even though the longer unbranched counterions seem to be less efficient in promoting a low cmc than the smaller and less hydropobic counterions. The excess relaxation measurements indicate that there are differences in the orientation of the micellarly bound counterions with regard to the micellar surface. The alkyl chains of butanoate and pentanoate most probably aggregate with the decylammonium surfactant part so as to form a mixed-micelle-like situation.

Registry No. Tempo, 2564-83-2; decylammonium propanoate, 39108-01-5; decylammonium chloropropanoate, 104875-20-9; decylammonium butanoate, 73702-94-0; decylammonium isobutanoate, 104875-21-0; decylammonium pentanoate, 104875-22-1; decylammonium trimethylacetate, 104875-23-2; hexamethyldisiloxane, 107-46-0.

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Nuclear Magnetic Relaxation in Micellar Systems. Influence of Micellar Size

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An extensive ^2H NMR relaxation study for hexadecyltrimethylammonium chloride micelles, with spin–lattice relaxation rates measured at nine magnetic field strengths and spin–spin relaxation rates at three magnetic field strengths, is presented. The measured relaxation rates show a strong dependence upon the magnetic field strength, and the data are analyzed with the "two-step" model of relaxation. A comparison is made with previously reported relaxation data for dodecyltrimethylammonium chloride micelles and the two-step model proves to be an excellent description of NMR relaxation in spherical micellar systems. Moreover, the motion causing the frequency dependence in the NMR relaxation can be described with an exponential correlation function with a correlation time that increases with the size of the spherical micelles.

Introduction

Nuclear magnetic resonance (NMR)[1] relaxation studies have been used extensively in the study of isotropic surfactant systems, e.g. micellar systems. In particular, ^{13}C T_1 and nuclear Overhauser enhancements have proven very valuable in this regard.[2-5] A general result of these studies is that several different types of

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(1) Abbreviations used: NMR, nuclear magnetic resonance; C_{12}TACl, dodecyltrimethylammonium chloride; C_{16}TACl, hexadecyltrimethylammonium chloride; C_{16}TAF, hexadecyltrimethylammonium fluoride.
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motions occurring on widely different time scales have to be invoked to rationalize the observed frequency dependence in the relaxation data. Several motional models have been proposed in order to explain the data.[2,3,6,7] When testing these motional models against the experimental ^{13}C data one runs into a major problem, namely that the experimental ^{13}C data can only be obtained at a few different, rather high field strengths, and it is thus difficult to differentiate between the different models. In what is probably the most extensive study of ^{13}C relaxation in this regard, Brown and co-workers[8] have measured T_1 for phospholipid vesicles at seven field strengths. Yet, it is difficult to differentiate between the different suggested models[9] on the basis of the ^{13}C data alone.[10] One further disadvantage with the ^{13}C nucleus is the difficulty of measuring accurately the spin–spin relaxation time (T_2) for this nucleus. We have therefore turned to deuterium relaxation measurements of specifically deuterated surfactants, since for this nucleus it is relatively easy to perform measurements at low field strengths by simply varying the static magnetic field on an NMR spectrometer equipped with an iron-core magnet. Two further advantages with ^2H is that it is easy to measure T_2 for this nucleus and that its relaxation expressions appear to be better "tuned" to the dynamics of many surfactant systems than ^{13}C.[11] We have previously reported a field-dependent ^2H NMR relaxation study on micelles formed by specifically deuterated dodecyltrimethylammonium chloride ($C_{12}TACl$)[11,12] and concluded that by invoking two motions (one fast motion in the extreme narrowing regime and one slow causing the frequency dependence of the relaxation) the observed NMR relaxation data could be explained. The slow motion could very accurately be described by a single exponential correlation function and it was suggested that its origin was the combined effect of tumbling of the micelle and surfactant diffusion over the curved micellar surface. Thus, the experimentally obtained correlation time was in good agreement with the one predicted for these motions. However, this could be a coincidence and we have therefore thought it worthwhile to study the influence of the micellar size on the relaxation data and present in what follows ^2H relaxation data for micelles formed by specifically deuterated hexadecyltrimethylammonium chloride ($C_{16}TACl$), i.e. the C_{16} analogue of $C_{12}TACl$ in water at nine different field strengths. In addition, the quadrupolar splitting measured at one concentration in the hexagonal phase formed at higher concentrations by $C_{16}TACl$ is also presented.

Experimental Section

Materials. $C_{16}TACl$-*1,1-*^2H was synthesized from hexadecanoic acid chloride which was reacted with dimethylamine to produce the corresponding amide which was then reduced with $LiAl(^2H)_4$. The resulting α-deuterated hexadecyldimethylamine was then reacted with CH_3I to obtain hexadecyltrimethylammonium iodine. To get $C_{16}TACl$, the iodine was finally exchanged for chlorine on an ion-exchange column. $LiAl(^2H)_4$ was purchased from Fluka and was of +99% ^2H atomic purity. High-resolution proton NMR showed no detectable trace of protons in the α-position. One sample was made by weighing $C_{16}TACl$-*1,1-*^2H and triply distilled water directly into an NMR tube that was subsequently sealed. The concentration of the sample was 13.0 % (wt/wt) $C_{16}TACl$. One sample in the hexagonal phase was made by weighing the components into a glass ampule that was then flame sealed. The sample was then equilibrated by repeated centrifuging back and forth.

Methods. ^2H NMR measurements were performed at 8.50, 5.99, and 2.11 T on a Nicolet 360 spectrometer, a homebuilt spectrometer equipped with an Oxford wide-bore superconducting magnet and a Bruker CXP 100 spectrometer equipped with a flux stabilizer HS 90. var. In addition to these measurements, further experiments were performed at field strengths below 2.11 T by varying the field strength on the Bruker CXP system.

Spin–lattice relaxation times (T_1) were measured with the standard inversion recovery method. The spin–spin relaxation times (T_2) were measured at 8.50, 5.99, and 2.11 T with the Carr–Purcell–Meibom–Gill method (at 5.99 T) or deduced from the ^2H bandwidths after suitable corrections for the magnetic field inhomogeneities. The measurements below 2.11 T were performed without a field/frequency lock. Therefore, the magnetic field inhomogeneities are quite large, making measurements of T_2 below 2.11 T very uncertain. Consequently, we have chosen not to report any T_2 values below 2.11 T. Data evaluation was performed as described in ref 4. All given error limits in evaluated quantities correspond to an approximately 80% level of confidence, taking only random errors into account. The temperature in all experiments was 27 ± 0.5 °C.

Theoretical Considerations

In the so-called motional narrowing regime, the deuterium spin–lattice and spin–spin relaxation rates (i.e., $1/T_{1,2}$) are given by

$$R_1 = (3\pi^2/40)\chi^2(2\tilde{J}(\omega_D) + 8\tilde{J}(2\omega_D)) \quad (1)$$

$$R_2 = (3\pi^2/40)\chi^2(3\tilde{J}(0) + 5\tilde{J}(\omega_D) + 3\tilde{J}(2\omega_D)) \quad (2)$$

Here χ is the quadrupolar coupling constant, and $\tilde{J}$ is the reduced spectral density function, evaluated at zero frequency, at the Larmor frequency, and at twice the Larmor frequency. It is implied in eq 1 and 2 that the asymmetry parameter of the electric field gradient is zero. That this is indeed the case has been verified both experimentally[13] and theoretically.[14]

Given a function form for the spectral densities derived from a particular motional model, that model can then be tested against experimental relaxation data by using eq 1 and 2. We have previously shown[11,12] that by considering two motions (one rapid, slightly anisotropic motion in the extreme narrowing regime and one slower isotropic motion) it is possible to rationalize frequency-dependent NMR relaxation for a number of different isotropic surfactant systems. For such a case the spectral density can be shown, under some rather general conditions, to be given by[7,15]

$$\tilde{J}(\omega) = (1 - S^2)2\tau_c^f + S^2\tilde{J}^s(\omega) \quad (3)$$

where superscript "f" and "s" refer to the fast and slow motions, respectively. S is defined as $S = (1/2)\langle 3\cos^2\theta - 1\rangle_f$. Here θ is the angle between the C–D vector and the normal to the surfactant aggregate and subscript "f" denotes that the average should be taken so as to average over the fast motion but not over the slow motion. S is completely analogous to the order parameter measured by ^2H NMR in anisotropic liquid crystals and hence we shall use the term order parameter for S in what follows. τ_c^f is the (effective) correlation time for the fast motion. In ref 11, ^2H NMR relaxation data for $C_{12}TACl$ micelles could be explained if the slow motion was assumed to be described with a single exponential correlation function, which leads to a Lorenzian spectral density function, viz.

$$\tilde{J}^s(\omega) = 2\tau_c^s/(1 + (\omega\tau_c^s)^2) \quad (4)$$

We end this section by noting that the relaxation model implied

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TABLE I: Results of the ^2H Relaxation Experiments for $C_{16}TACl$

field strength, T	Larmor freq, MHz	R_1, s^{-1}	R_2, s^{-1}
0.306	2.00	116.6 ± 0.34[a]	
0.536	3.50	114.8 ± 2.5	
0.765	5.00	107.0 ± 2.3	
1.071	7.00	93.5 ± 1.7	
1.377	9.00	83.7 ± 2.1	
1.683	11.00	73.5 ± 1.6	
2.112	13.80	63.7 ± 0.8	99 ± 4
5.989	39.14	27.9 ± 0.7	62.8 ± 1.2
8.497	55.53	21.9 ± 0.1	60 ± 3

[a] Quoted error limits correspond to an approximately 80% level of confidence taking only random errors into account.

TABLE II: Results for $C_{16}TACl$ from Fitting the Two-Step Model to the Relaxation Data in Figure 1

τ_c^f, ps	τ_c^s, ns	S
42 ± 1	7.6 ± 0.34	0.186 ± 0.003

TABLE III: Results for $C_{12}TACl$ from Ref 11

τ_c^f, ps	τ_c^s, ns	S
37 ± 3	3.9 ± 0.4	0.17 ± 0.01

TABLE IV: Results for the Hexagonal Phases of $C_{12}TACl$ and $C_{16}TACl$

system	composition, wt % surfactant in water	S
$C_{12}TACl$	64.3	0.196 ± 0.003[a]
$C_{16}TACl$	55.8	0.192 ± 0.003

[a] Data from ref 11.

by eq 1–4 has been termed a "two-step" model since the relaxation is assumed to occur in two steps.

Results

Presented in Table I and Figure 1 are the results of the deuterium relaxation studies. The solid lines in Figure 1 are the fit of the "two-step" model (i.e., eq 1–4) to the experimental data. The obtained parameters from this fit are given in Table II. For the sake of comparison, we present in Table III values for the corresponding $C_{12}TACl$/water system (data from ref 11). Finally, values for the quadrupolar splitting in the hexagonal phases formed in the $C_{16}TACl$/water and $C_{12}TACl$/water systems are presented in Table IV. When extracting these parameters, we have used a value for the quadrupole coupling constant, χ, equal to 167 kHz. The use of this value deserves a few comments. Recently, Greenfield and co-workers[16] have, on the basis of ^2H experiments on an alkane/urea clathrate, suggested that a value of $\chi > 185$ kHz would be more appropriate, while one of us has suggested the value $\chi = 181$ kHz for sodium octanoate and sodium hexanoate.[17] The reason for this is basically that χ should only be averaged over motions that are too fast to contribute to the NMR relaxation. The value of 167 kHz originates from solid-state ^2H NMR techniques[13] and, in this case, is averaged by any motions that are more rapid than the inverse of the quadrupolar splitting, i.e. motions with frequencies more rapid than of the order of 100 kHz. That is to say, motions that can contribute to the NMR relaxation have also been included in the averaging of χ. One further complication noted by Greenfield et al. is that, since the presence and rates of low-frequency vibrational motions in the molecules would depend on which particular molecule one is studying, χ may very well vary from one system to another. Therefore, χ may perhaps best be looked upon as an adjustable parameter. Our choice of 167 kHz is dictated by the fact that we want to compare data for $C_{16}TACl$ with data for $C_{12}TACl$ from ref 11, where this value for χ was used. Presumably, there should be little difference in χ for $C_{12}TACl$ and $C_{16}TACl$. It should be remarked that the absolute value of χ does not influence the goodness of the fit of the relaxation expressions to the experimental data. However, the values of S and τ_c^f are influenced (S and τ_c^f decrease by slightly less than 10% if a value of $\chi = 181$ kHz is used instead of 167 kHz) while τ_c^s remains independent of χ, since this parameter is determined by the inflection point in the graphs of $R_{1,2}$ vs. frequency.

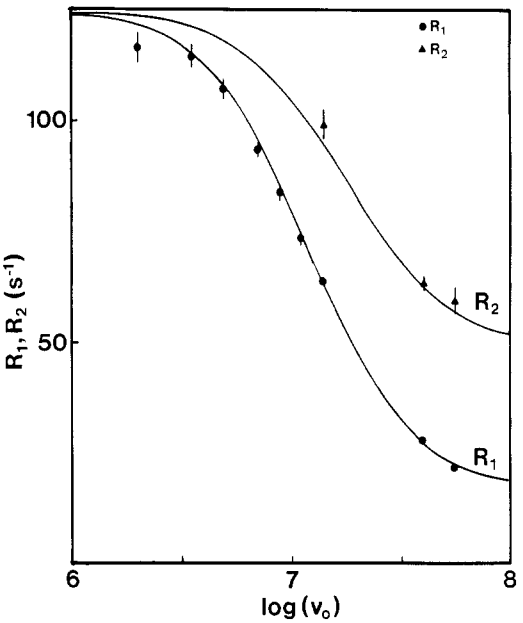

Figure 1. ^2H spin–lattice (●) and spin–spin (▲) relaxation data as functions of the logarithm of the Larmor frequency (expressed in Hz) for $C_{16}TACl$ micelles. The solid lines are the result of fitting eq 1–4 to the data.

Discussion

Before discussing the results, the following background information is needed. The critical micelle concentration (cmc) of $C_{16}TACl$ is around 1 mM,[18] while the concentration used in the present study is 0.4 M. Thus, any contribution from monomeric $C_{16}TACl$ may safely be neglected. Secondly, $C_{16}TACl$ forms spherical micelles from cmc up to its solubility limit.[19] As is evident from Figure 1, the fit of the relaxation expressions to the data is excellent (see also the uncertainty in the determined parameters in Table II). Thus we may safely assume that a single exponential correlation function is sufficient to account for the observed frequency dependence in R_1 and R_2. It has been suggested that collective fluctuations around the aggregate director contribute to the relaxation in micellar systems[20,21] and vesicle[9] systems. The correlation function for these motions gives rise to a spectral density which is proportional to $1/B_0^{1/2}$. Indeed, for phospholipid vesicles, Brown and co-workers have suggested that such a dependence on magnetic field strength is at hand. Recently, Marqusee et al.[22] have pointed out that, since vesicles are two-dimensional systems rather than three-dimensional systems, the spectral density should be proportional to $1/B_0$. In Figure 2 we present the relaxation data plotted vs. $1/B_0$ and $1/B_0^{1/2}$, respectively. Clearly, the data deviate from these proposed dependences on B_0. This does not necessarily mean that director fluctuations (or, equivalently, micellar shape fluctuations) are absent in mi-

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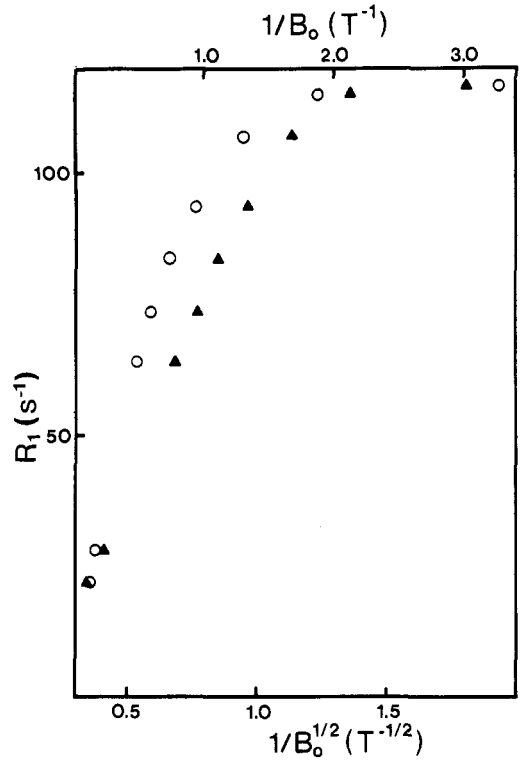

Figure 2. ^2H spin–lattice relaxation data for $C_{16}TACl$ micelles as functions of $1/B_0$ (○) and $1/B_0^{1/2}$ (▲), respectively.

celles. Any motion that is slower than the fastest isotropic motion which in this case is proposed to be the tumbling of the spherical micelle and diffusion of the surfactant over the curved micellar surface (see further the discussion below) does not contribute to the NMR relaxation.[11,23] Director fluctuations with frequencies smaller than the inverse of the obtained value for τ_c^s that is smaller than around 100 MHz may very well be present. Moreover, if the director fluctuations have very small amplitudes, they can be present with higher frequencies, since in such a case their contribution to the relaxation will be small. Thus, it would appear that in this regard the charged micelles differ from phospholipid vesicles, where substantial contributions to the NMR relaxation of fluctuations occurring in the nanosecond time regime have been reported to occur.[8,9]

Turning to the individual values of the parameters presented in Table I, we start by considering the correlation time for the slow motion τ_c^s. As was pointed out in the Introduction, we have previously ascribed the motion(s) causing the frequency dependence in the relaxation data to the combined effect of micellar tumbling and surfactant diffusion over the curved micellar surface. The effect of these motions can, since they are statistically independent and both can be described by exponential correlation functions, be described by an exponential correlation function with an effective correlation time, viz.

$$(\tau_c^s)^{-1} = (\tau_c^r)^{-1} + (\tau_c^d)^{-1} \quad (5)$$

In eq 5 superscripts r and d denote micellar tumbling and surfactant diffusion, respectively. In turn, τ_c^r and τ_c^d are given by the Debye–Stoke–Einstein relation

$$\tau_c^r = (4\pi R^3\eta)/(3kT) \quad (6)$$

and the diffusion equation

$$\tau_c^d = (R^2)/(6D) \quad (7)$$

In eq 6 and 7, R is the micellar radius and D is the lateral diffusion coefficient of the surfactant in the aggregate. All the other quantities in eq 6 and 7 have their usual meaning. In using the same radius in eq 6 and 7 we have assumed that it is the electrostatic interactions in the headgroup region that determine the rate of surfactant diffusion. In ref 11 we computed R from τ_c^s by taking the diffusion coefficient from measurements in a cubic liquid crystalline phase. Here, we will proceed in a slightly different manner and compute D from τ_c^s. In order to do this we need to know the micellar radius. Now, theoretical considerations imply that the radius of a spherical micelle should be that of the length of an all-trans hydrocarbon chain.[24] This is equal to 16.7 and 21.7 Å from the terminal methyl group to the midpoint of the bond connecting the α-carbon to the nitrogen[25] for $C_{12}TACl$ and $C_{16}TACl$, respectively. Adding on another 2 Å for the headgroup we obtain R = 18.7 and 23.7 Å for $C_{12}TACl$ and $C_{16}TACl$, respectively. These values yield a lateral diffusion coefficient of $D = (4.6 \pm 0.8) \times 10^{-11}$ m^2 s^{-1} for $C_{12}TACl$ and $D = (4.1 \pm 0.5) \times 10^{-11}$ m^2 s^{-1} for $C_{16}TACl$. The values of D are of course dependent on the chosen value of R (for instance, increasing R by 2 Å for $C_{12}TACl$ nearly doubles the value of D). One conclusion that can be reached and which does not depend critically on the chosen value for R is that the lateral diffusion coefficient is independent of chain length, supporting the notion that the rate of diffusion is to a large extent determined by electrostatic interactions in the headgroup region. This follows since the micellar radii have been calculated in a "self-consistent" way, that is if we allow the value of R to change for one of the surfactants, we must also change the radius for the other surfactant correspondingly. That the surfactant lateral diffusion coefficient has only a slight dependence on the chain length for a given headgroup has been shown in liquid crystalline phases.[26] Returning to the chosen values of R, one could argue that a layer of hydration water and some hydrated counterions should be included in the value of R. See, for instance, the discussion by Hayter and Penfold[27] who discuss small-angle neutron scattering data in terms of two radii for the micelle; the first given by the ω-methyl group and a fraction of the methylene groups, and the second given by the first radius plus the remaining methylenes, the hydrated headgroups, and nonionized hydrated counterions. In the present authors' opinion one should, when using formulas such as eq 6, keep in mind that it is derived for solid spheres without any internal degrees of freedom, in a continuous medium. Thus using eq 6 for a micelle is in itself an approximation and any refinements such as including "bound" water, "bound" counterions, and so forth may be of little value. As a final remark we note that the values we have chosen for R correspond closely to the average of the two radii given by Hayter and Penfold for $C_{12}TACl$ and $C_{16}TACl$. To put the determined value of D into perspective they can be compared with those found by Eriksson and Lindblom[28] in cubic liquid-crystalline phases. Here, the extraction of the lateral diffusion coefficient D_L from the measured diffusion coefficient, D_{obsd}, depends on the structure of the cubic phase; for a phase consisting of lamellar units, $D_L = (3/2)D_{obsd}$ and for a phase consisting of rodlike aggregates, $D_L = 3D_{obsd}$. For both $C_{12}TACl$ and hexadecyltrimethylammonium fluoride ($C_{16}TAF$) a value of $D_{obsd} = 0.7 \times 10^{-11}$ m^2 s^{-1} at 26 °C is reported (the value for $C_{16}TAF$ has been obtained by extrapolating to 26 °C and assuming a simple activation process for the diffusion). For a cubic phase consisting of rodlike aggregates one obtains $D_L = 2 \times 10^{-11}$ m^2 s^{-1} and for one with lamellar aggregates, $D_L = 1 \times 10^{-11}$ m^2 s^{-1}. These values are a factor of two and four, respectively, smaller than those found in the micellar case. However, taking into account the difference in phase geometry and composition and the uncertainty as regards the proper value for the micellar radius, the difference is slight. That the lateral surfactant diffusion rate depends slightly on the phase geometry has been observed also in the decylammonium chloride/water and the phospholipid/sodium cholate/water systems.[29,30] If anything,

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the present study supports the conclusion reached by Eriksson and Lindblom that the geometry of the cubic phase is rod shaped.

The value for the fast correlation time is 42 ± 1 ps in C_{16}TACl and 37 ± 3 ps in C_{12}TACl. This value describes the complex, local motions that the C-D vector undergoes within the micelle, e.g. rotations around carbon-carbon bonds, torsions, protrusions from the micellar surface, and so forth. τ_c^f is thus an effective correlation time, i.e. the integral over a correlation function rather than a characteristic time scale for any one particular motion. That it shows so little dependence on chain length is not surprising since the rate of motions is presumably given by the features of the hydrophobic/hydrophilic interface which should be nearly identical for C_{16}TACl and C_{12}TACl.

Finally, the value of the order parameter is slightly greater for C_{16}TACl than for C_{12}TACl but the difference is marginal. In both cases the values in the hexagonal phases are slightly larger than in the micellar phase, but again the difference is very small. Thus the order parameter for the C_α-D bond depends neither on the chain length nor on the geometry of the phase.

Conclusions

The present data clearly indicate that the two-step model is an excellent description of the NMR relaxation in systems containing spherical micelles. The motion causing the frequency dependence in the relaxation data can to a high degree of accuracy be described with a single exponential correlation function with a correlation time that increases with the radius of the micelle. It is argued that the origin of this slow motion is a combination of micellar tumbling and surfactant diffusion over the curved aggregate surface. From the parameters obtained when fitting the two-step model to the relaxation data, it is maintained that both the amplitude (order parameter) and rate (effective correlation time) of the local fast motion(s) that the C_α-D bond undergoes depend marginally on the alkyl chain length. Furthermore, the amplitude of this local motion would not appear to depend on the phase geometry.

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Diffusion Studies in Liquid Crystalline Phases of Surfactant Solutions: A New Mass-Transport Approach. 1. Cetyltrimethylammonium Bromide/Water

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The optical microscopic mass transport (OMMT) approach was utilized to determine diffusion coefficients of the liquid crystalline phases in surfactant solutions. This approach is based on establishing a spontaneous bulk concentration gradient in a thin film of a concentrated isotropic solution of a surfactant/water binary mixture by spontaneous evaporation of water from one edge of the diffusion pathway. The diffusion profile was observed under polarizing microscope via the existing phase boundary lines in the texture, which are the interfaces between the existing isotropic and aniosotropic regions. The diffusion coefficients at the phase boundary lines were determined from their space-time analysis. The system studied was cetyltrimethylammonium bromide/water (CTAB/water), which with the increasing concentration exhibits hexagonal, cubic, and lamellar phases. The diffusion coefficients at the isotropic-hexagonal, hexagonal-cubic, and cubic-lamellar phase boundary lines were determined at temperatures between 30 and 75 °C. The results are within the same order of magnitude as those obtained for amphiphiles in water by the NMR method. The diffusion activation energies at the three liquid crystalline phase boundaries were obtained from typical Arrhenius plots with values in the range of 10-30 kcal/mol.

I. Introduction

Diffusion, or mass transport, is important in understanding drug solubilization, foam stability, cleaning, and digestion processes, among others. Mass-transport studies have provided information on the micellar size, shape, polydispersity, dynamics of liquid crystalline order, and structure of bilayers. This phenomenon is an irreversible dynamic process with similar physical foundations in both microscopic and macroscopic scales. The diffusion coefficient is determined either by transient techniques on a molecular scale, such as NMR and quasi-elastic light scattering methods, or by mass transport techniques on a macroscopic scale. In the former, the self-diffusion coefficient, which is correlated with the Brownian motion of the particles, is obtained at the molecular time scale in the absence of an overall bulk concentration gradient, whereas in the latter, the mutual and/or tracer diffusion coefficient, which is the outcome of the proportionality factor between the macroscopic material flux and the force gradient causing the flux, is determined on the basis of Fick's phenomenological laws.

In surfactant systems, the measurements of the diffusion coefficients in relatively dilute solutions, i.e., near the critical micelle concentration (cmc), have been reported with a number of well-developed techniques. These techniques include dynamic light scattering,[1-8] NMR,[9-15] capillary tracer,[16-19] polarography,[2]

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