obtained on the basis of ^{15}N chemical shifts correlations, and we recommend that barriers be determined by more direct methods, whenever possible.

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^{13}C Magnetic Relaxation in Micellar Solutions. Influence of Aggregate Motion on T_1

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Abstract: The ^{13}C T_1 NMR relaxation times of the carbon atoms in the alkyl chains of a micelle-forming amphiphile are discussed. A theoretical model for the relaxation process is developed. The relaxation in a $^{13}C^1H_2$ methylene group is treated in detail using a density matrix formalism. In modeling the molecular dynamics of the system the emphasis is placed on a separation between a fast local motion within the micelles and a slower overall motion associated with the aggregate itself. In applying the model to octanoate micelles it is shown that, using previously determined structural parameters, it is possible to obtain an a priori estimate of the contribution from the slow motion to T_1 of the individual carbons. Particularly for the carbons close to the polar group, the overall motion gives a substantial, and probably dominating, contribution to T_1. It also emerges that the T_1's should be frequency dependent. The predictions of the model are tested against experimentally determined T_1 values for four carbons in sodium octanoate micelles and a surprisingly good agreement is found. Particularly the observed frequency dependence of T_1 shows unequivocally that the slow micellar motion contributes to the spin–lattice relaxation. It also follows that the alkyl chain motion within the micelles is very rapid. The interior of the micelle is thus even more liquid-like than has been inferred previously from ^{13}C T_1 measurements.

In studying the properties of micellar solutions on a molecular level, nuclear magnetic resonance has proved to be one of the most versatile experimental techniques.[2a] The chemical shift and relaxation parameters of different magnetic nuclei in a micellar system are sensitive to different molecular properties and by a careful choice of method one is able to study a particular aspect of the problem of the molecular organization. For example, the size of micellar aggregates can be determined using ^1H[2b,3] and ^{14}N[4] NMR. By using ^{19}F chemical shifts one can accurately determine cmc values;[5] ^{23}Na, ^{35}Cl, and ^{81}Br NMR provide information on counterion binding.[6]

^{13}C T_1 measurements are particularly well suited for the study of alkyl chain motions.[7] In micellar systems the ^{13}C relaxation times give a picture of the dynamics of the (unperturbed) micellar interior. It was originally concluded from thermodynamic arguments[8,9] that the micellar interior is similar to a liquid hydrocarbon and the validity of these conclusions was later established through spectroscopic studies directly probing the molecular motion.[10,11] However, several problems regarding the details of the alkyl chain motions within the micelle are still unsolved. Are the motional time scales quite similar to those in a corresponding hydrocarbon system or are they an order of magnitude larger? How does the fact that the polar head is more or less fixed at the micelle surface influence the motional properties? The ^{13}C T_1 values of micellar systems are often significantly shorter than those characteristic of the monomer state.[12–18] This has usually been

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interpreted in terms of comparatively slow intramolecular motions[12-21] in analogy with what has been observed for phospholipid bilayer vesicles[22,23] and membrane fragments.[23] In the present paper we propose a different model for the interpretation of ^{13}C T_1 values, which emphasizes the separation between fast local motions of the alkyl chains and the overall motion of the micellar aggregate. The model is then used in the interpretation of T_1 values for sodium octanoate micelles.

Table I. Energies, Eigenfunctions, and Constants of Motion for the Eigenstates of H_0 in Equation 1[a]

eigenfunction	energy[b]	m_1	M_{23}	P_{23}
$\|1\rangle = \|\alpha\alpha\alpha\rangle$	$-(\omega_H + {}^1\!/\!_2\omega_C)$	$^1\!/\!_2$	1	1
$\|2\rangle = 1/\sqrt{2}\{\|\alpha\alpha\beta\rangle + \|\alpha\beta\alpha\rangle\}$	$-{}^1\!/\!_2\omega_C$	$^1\!/\!_2$	0	1
$\|3\rangle = \|\alpha\beta\beta\rangle$	$\omega_H - {}^1\!/\!_2\omega_C$	$^1\!/\!_2$	−1	1
$\|4\rangle = 1/\sqrt{2}\{\|\alpha\alpha\beta\rangle - \|\alpha\beta\alpha\rangle\}$	$-{}^1\!/\!_2\omega_C$	$^1\!/\!_2$	0	−1
$\|5\rangle = \|\beta\alpha\alpha\rangle$	$-\omega_H + {}^1\!/\!_2\omega_C$	$-{}^1\!/\!_2$	1	1
$\|6\rangle = 1/\sqrt{2}\{\|\beta\alpha\beta\rangle + \|\beta\beta\alpha\rangle\}$	$+{}^1\!/\!_2\omega_C$	$-{}^1\!/\!_2$	0	1
$\|7\rangle = \|\beta\beta\beta\rangle$	$\omega_H + {}^1\!/\!_2\omega_C$	$-{}^1\!/\!_2$	−1	1
$\|8\rangle = 1/\sqrt{2}\{\|\beta\alpha\beta\rangle - \|\beta\beta\alpha\rangle\}$	${}^1\!/\!_2\omega_C$	$-{}^1\!/\!_2$	0	−1

[a] m_1, M_{23}, and P_{23} are the eigenvalues of $\hat{I}_z(1)$, $(\hat{I}_z(2) + \hat{I}_z(3))$, and $\hat{P}_{23}$, respectively. [b] Energy contributions due to the scalar coupling have been neglected.

Theory

The characteristic property of amphiphilic molecules is the formation of aggregates, of one type or another, when dispersed in water. When interpreting NMR data from such systems it is often essential to include this chemical information into one's model. Line-shape effects (T_2's) are very sensitive to the aggregate structure since it is affected by static interactions[24,25] (dipole-dipole or quadrupole) and slow (correlation time $\tau_c \gg 1/\omega_0$) aggregate motions.[2-4,26-28] T_1, on the other hand, is rather unaffected by changes in aggregate structure and/or phase transitions[29] since T_1 is determined by motions with $\tau_c \lesssim 1/\omega_0$. A consequence of the liquid-like internal behavior of micellar and liquid crystalline systems is that such fast motions are always present. One should note that these fast local motions do not give rise to local isotropy as demonstrated by the observation of dipole-dipole and quadrupole splittings in the liquid crystalline system.

It seems conceivable that micellar systems provide a case where aggregate motion contributes to T_1. Depending on the surfactant, the magnetic field, the nucleus studied, and the temperature, it is possible to find cases where the correlation time for micellar rotation τ_r is of the same order of magnitude as the inverse Larmor frequency.

The relaxation of a ^{13}C nucleus in a CH$_2$ group in an alkyl chain is dominated by the dipolar coupling to the directly bonded protons. We therefore choose to concentrate the treatment of the relaxation to explicitly include only the three spins of a ^{13}C^{1}H$_2$ group. However, the relaxation of the protons probably has important contributions from the coupling to the other protons in the chain. The effect of this coupling will be discussed below. The time-independent spin Hamiltonian for the ^{13}C^{1}H$_2$ group can be written (in angular frequency units, X approximation)

$$\hat{H}_0 = -\omega_C\hat{I}_z(1) - \omega_H\{\hat{I}_z(2) + \hat{I}_z(3)\} + 2\pi J_{HC}\hat{I}_z(1)\{\hat{I}_z(2) + \hat{I}_z(3)\} \quad (1)$$

where 1 denotes the carbon spin and 2 and 3 are the proton spins. Table I shows the eigenfunctions of $\hat{H}_0$ and their respective eigenvalues for the constants of motion, $\hat{H}_0$, $\hat{I}_z(1)$, $\hat{I}_z(2) + \hat{I}_z(3)$, and $\hat{P}_{23}$, where $\hat{P}_{23}$ is the permutation of spin 2 and 3. The Hamiltonian $\hat{H}_0$ gives rise to a triplet spectrum, but when measuring ^{13}C relaxation times one usually employs proton decoupling so that only a singlet is observed. The decoupling field can be regarded as causing rapid transitions between states with the same values of M_1 and P_{23} but different values of M_{23}, i.e., between states 1, 2, and 3 and between states 5, 6, and 7 (cf. Table I). (The coupling Hamiltonian is symmetric with respect to P_{23} and thus cannot affect the value of P_{23}.) From the relaxation point of view the effect of the decoupling is equivalent to a chemical exchange which is fast compared to the relevant relaxation times but slow compared to correlation times.

The time dependence of the ^{13}C magnetization is, using the density operator formalism

$$\frac{d}{dt}\langle\hat{I}_z(1)\rangle = \mathrm{Tr}\left\{\frac{d\hat{\rho}}{dt}\hat{I}_z(1)\right\} = \sum_k \frac{d}{dt}\rho_{kk}I_z(1)_{kk} = \sum_k I_z(1)_{kk}R_{kknn}\rho_{nn} \quad (2)$$

where the last equality follows from the Wangsness-Bloch-Redfield theory.[30] Here ρ_{kk} is an element of the density matrix and R_{kknn} is an element of the relaxation supermatrix.

Since microscopic reversibility implies

$$R_{kkkk} = -\sum_{n \neq k} R_{kknn} \quad (3)$$

eq 2 can be rewritten as

$$d\langle I_z(1)\rangle/dt = \sum_{kn} I_z(1)_{kk}R_{kknn}(\rho_{kk} - \rho_{nn}) \quad (4)$$

through the decoupling $\rho_{11} = \rho_{22} = \rho_{33}$ and $\rho_{55} = \rho_{66} = \rho_{77}$, which reduces the number of independent terms in eq 4. In the following we assume that the transitions between the triplet and singlet states (i.e., the relaxation of P_{23}) are rapid relative to the ^{13}C T_1 relaxation. In that case $\rho_{11} = \rho_{44}$ and $\rho_{55} = \rho_{88}$ and

$$\frac{1}{T_1} = \frac{1}{4}\sum_{k=1}^{4}\sum_{n=5}^{8} R_{kknn}$$

If this assumption does not apply the ^{13}C M_z magnetization decays as two or more exponentials, where the major component is due to the relaxation between states (1,2,3) and (5,6,7).

The interpretation of the T_1 data has now been reduced to the problem of calculating the elements R_{kknn}. In a multispin system so-called cross correlation effects[31,34] play an important role. In a micellar system one can make use of the structural knowledge of the system to set up a model that takes care of the cross correlation effects due to the aggregate motion. This is done by assuming that the time-dependent Hamiltonian $\hat{H}(t)$ describing the dipolar interaction can be written as a sum

$$\hat{H}(t) = \hat{H}_f(t) + \hat{H}_s(t) \quad (5)$$

where the component $\hat{H}_f(t)$ has correlation times characteristic of the fast local motion and $\hat{H}_s(t)$ is time dependent due to a slower aggregate motion. It is required that $\hat{H}_f(t)$ averaged over the local motion is zero. The decomposition of the Hamiltonian as in eq 5 has previously been made in the interpretation of proton,[34,35] deuteron,[27] nitrogen,[4] phosphorus,[28] and ionic quadrupolar nuclei[36] NMR data of amphiphile-water systems. When the fast local motion occurs in an environment that has on average a threefold or higher symmetry the expression for $\hat{H}_s(t)$ is[37]

$$\hat{H}_s(t) = -\frac{\sqrt{6}\mu_0\hbar}{4\pi}\sum_q\sum_{i>j}\gamma_i\gamma_j r_{ij}^{-3} \times \overline{D_{00}^{(2)}(\Omega_{MD}^{ij})}\,D_{0q}^{(2)}(\Omega_{DL}(t))\hat{A}_q^{(2)}(ij) \quad (6)$$

The sum is over the different nuclei i and j and the different components q of a second-order spherical tensor. $D_{0q}^{(2)}(\Omega)$ is a Wigner rotation matrix element.[38] γ is the magnetogyric

Table II. Calculated (from Equation 7) Values of $1/T_1{}^s$ (s^{-1}) for Octanoate Micelles at Three Different Magnetic Field Strengths

carbon[a]	S[b]	$T_1{}^{-1}$ at 6.3 T	T^{-1} at 2.34 T	$T_1{}^{-1}$ at 1.40 T
C_2	0.26	1.14	2.07	2.43
$C_{3,4}$[c]	0.18	0.54	0.99	1.16
C_5	0.17	0.48	0.88	1.03
C_6	0.15	0.38	0.69	0.81
C_7	0.11	0.20	0.37	0.43
C_8	0.05	0.04	0.08	0.09

[a] Numbering of the carbon atoms starts from the polar head. [b] From ref 43. [c] Not resolved in the ^{2}H spectra.

ratio and μ_0 is the permeability of vacuum. The eulerian angles Ω_{MD} and Ω_{DL} specify coordinate transformations from the local symmetry director system to a molecular one and from a laboratory to the director system, respectively. $\hat{A}_q{}^{(2)}$ are irreducible spin operators.[37] The corresponding explicit expression for $\hat{H}_f(t)$ can be found in ref 37. One can note that, since $[\hat{H}_s,\hat{P}_{23}] = 0$, $\hat{H}_s(t)$ will not couple states with different parity with respect to P_{23}.

From the different nature of the local and the aggregate motions it is reasonable to assume that these motions are uncorrelated, i.e.

$$\overline{\hat{H}_s(t)\hat{H}_f(t+\tau)} = 0$$

for all τ. In that case, the two types of motion give independent contributions to the R matrix elements and $R_{kknn} = R^f{}_{kknn} + R^s{}_{kknn}$. The part R^f is due to the presumably complex alkyl chain motion within the micelle and the effects of this motion will not be further analyzed. Instead, $R^f{}_{kknn}$ will be treated as a parameter in the following. However, for the micelle itself much more structural information is available and it is a straightforward task to calculate the elements $R^s{}_{kknn}$ using the Hamiltonian in eq 6. The final expression for the contribution to T_1 from the slow aggregate motion is then

$$\frac{1}{T_1{}^s} = \left[\frac{\mu_0\hbar\gamma_C\gamma_H S}{4\pi r_{CH}{}^3}\right]^2 \frac{1}{5}\left\{\frac{3\tau_a}{1+\omega_C{}^2\tau_a{}^2} + \frac{\tau_a}{1+(\omega_H-\omega_C)^2\tau_a{}^2} + \frac{6\tau_a}{1+(\omega_H+\omega_C)^2\tau_a{}^2}\right\} \quad (7)$$

Since the C–H distance is known, the only unknown parameters in eq 7 are the correlation time τ_a and the local anisotropy $\overline{D_{00}(\Omega_{MD}{}^{CH})} = S$. From an assumed radius r_M of the micelle, τ_a can be calculated using the Stokes–Einstein relation

$$\tau_r = 4\pi r_M{}^3\eta/(3kT) \quad (8a)$$

$$\tau_D = r_L{}^2/(6D) \quad (8b)$$

$$1/\tau_a = 1/\tau_r + 1/\tau_D \quad (8c)$$

Here η is the viscosity of the medium (not the solution) and D is the monomer translational diffusion in the micelle. Both the micelle rotation, eq 8a, and the monomer diffusion, eq 8b, contribute to the effective correlation time τ_a as in eq 8c. For the lateral diffusion process the radius has been chosen as the micellar radius since the rate-limiting step in this process is expected to be due to the diffusion of the polar head group. The factor $\overline{D_{00}(\Omega_{MD}{}^{CH})}$ is analogous to the order parameters measured in the lyotropic liquid crystalline phases that surfactants form at higher concentrations.[39] Spectroscopic[34,35,40] and thermodynamic[41] observations strongly indicate that the local molecular packing is only slightly influenced by phase changes.[2b] It is then a reasonable assumption that $\overline{D_{00}{}^{(2)}(\Omega_{MD}{}^{CH})} = S$ can be obtained from measurements in the liquid crystalline state.

Calculated ^{13}C T_1 Values of Sodium Octanoate Micelles. As an application of the theory presented above we have chosen to study the micelles formed by sodium octanoate. For this surfactant the critical micelle concentration (cmc) is rather high (~0.40 M). Therefore it is feasible to study the amphiphile both in its monomeric aqueous form and aggregated into micelles. Furthermore, the physical chemistry of the system has been extensively studied.[42] Finally, the alkyl deuterium splittings in the hexagonal phase formed at higher concentrations have also been reported.[43]

The aggregation numbers (10–25) reported[44] for the octanoate micelles are roughly consistent with what one would predict for a spherical micelle. Let the radius be that of a fully extended chain. For $C_7H_{15}COO^-$ this corresponds to r_M = 13.5 Å and eq 8a gives a rotational correlation time $\tau_r = 2.5 \times 10^{-9}$ s. A molecular motion competing with the micellar rotation is the monomer diffusion along the curved micellar surface. Equation 8b applies for this case. The diffusion coefficient for sodium octanoate has been measured in the lamellar phase[45] to $D = 2 \times 10^{-10}$ m^2 s^{-1}. The correlation time τ_D for this motion is 1.5×10^{-9} s. The combined effects, eq 8c, of the two motions then give an aggregate correlation time $\tau_a = 9.5 \times 10^{-10}$ s. One can note that, for typical magnetic field strengths, $\omega\tau_a$ approaches unity and one might expect a field dependence of the relaxation times. In Table II $T_1{}^s$ is evaluated from eq 7 for three different magnetic field strengths. The value of τ_a is chosen as 9.5×10^{-10} s and S for the different carbons is obtained as $2S_{CD}$ measured in the hexagonal phase.[43] The factor 2 arises since in the latter phase one has a diffusional motion around the rods reducing the order parameter to one-half of that valid locally. In Table II one can see that the contributions from the slow motion are substantial particularly for carbons near the polar head, and $T_1{}^s$'s are in fact of the same order of magnitude as those previously observed in micellar systems.[12,15,16] Furthermore, there is a clear field dependence and it is thus possible to obtain a further test of the theory by measuring the T_1's at different magnetic field strengths.

Experimental Section

The measurements at 15 MHz (1.40 T) were performed on a JEOL FX 60 spectrometer and the ones at 25 MHz (2.34 T) on a Varian XL 100 spectrometer, both working in the Fourier transform mode. The T_1 values were measured by means of the fast inversion recovery (FIRFT) method. Even though this fast method was used, more than 50 h of accumulation was needed for the lowest amphiphile concentrations used. The final T_1 values were calculated by making a three-parameter fit of the FIRFT data to the equation

$$I = I_0(1 - A_e{}^{-\tau/T_1}) \quad (9)$$

where I_0 and I are the intensities of the NMR signal at equilibrium and for a delay time of τ, respectively. A is the parameter that has the value 2 in the normal inversion recovery experiment.

To make sure that the two spectrometers give the same T_1 in the limit of extreme narrowing, two samples of glycerol, one 75% w/w and one 50% w/w glycerol in D_2O, were used. The T_1's were 0.3 and 1.3 s and there was no difference between the two spectrometers. The temperature was 28 °C throughout. Samples were prepared as described elsewhere.[46]

Experimental Results

Within the phase separation model, the ^{13}C T_1 above the cmc is

$$(1/T_1)_{obsd} = (1/T_1)_m - \mathrm{cmc}\{(1/T_1)_m - (1/T_1)_f\}/C_t \quad (10)$$

where the subscripts m and f stand for micellar and free amphiphile, respectively. By plotting $(1/T_1)_{obsd}$ vs. the inverse total concentration C_t one expects to obtain two lines intersecting at the cmc. Such a plot is presented in Figure 1. The

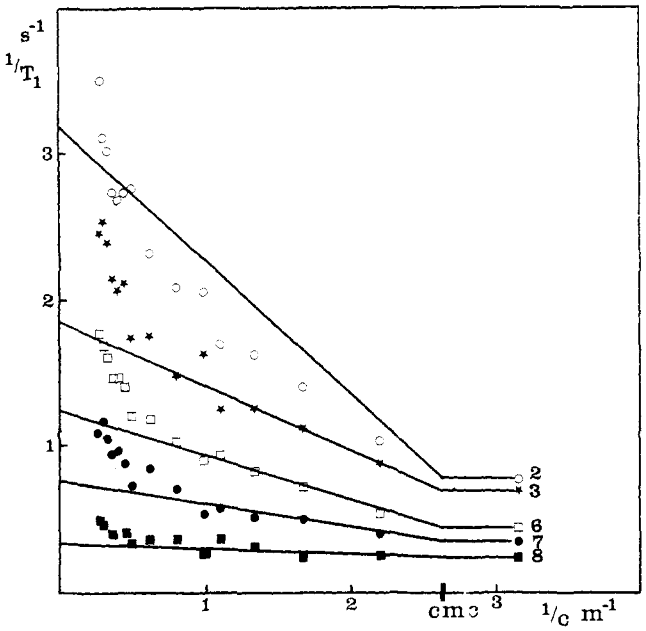

Figure 1. The inverse ^{13}C longitudinal relaxation time measured at 1.40 T plotted against the inverse sodium octanoate concentration. The lines drawn show the theoretical prediction of eq 7 and 11. The carbons are numbered with the polar head group as one and consequently the methyl carbon as number eight.

experimental points in the range 0.5–1 *m* correspond reasonably well to straight lines but at higher concentrations deviations from linearity are evident showing that structural changes affecting the ^{13}C relaxation times occur. Included in Figure 1 are the theoretical predictions based on the phase separation model (eq 10), the values in Table II for the contribution of the slow motion and the assumption, in the absence of a detailed description, that the fast motion contributes to T_1 to the same extent as in the monomeric aqueous state, i.e.

$$(1/T_1)_{\mathrm{calcd}} = (1/T_1)_{\mathrm{mon}} + p_{\mathrm{mic}}(1/T_1{}^{\mathrm{s}}) \qquad (11)$$

where p_{mic} is the relative amount of micellized amphiphile.

The unexpectedly good agreement between the theoretical estimates and the experimental values indicates that in fact the slow motion gives substantial contributions to T_1. A more critical test of this assertion is obtained by measuring T_1 at different magnetic field strengths. Figures 2a,b show a comparison between T_1 values measured at 2.34 and 1.40 T. It is seen that the relaxation rates measured at the lower magnetic field strength are systematically larger than those at the higher field. The uncertainty of T_1 in each particular point is substantial compared to the field dependence so we have chosen to compare the experimental field dependence with the theoretical predictions by drawing a smooth line through the values determined at 1.40 T and to convert this line to one valid for 2.34 T. Here again the agreement is gratifying.

Discussion

The fact that the ^{13}C T_1 values of sodium octanoate micellar solutions are magnetic field dependent shows that motions with correlation times of the order of 10^{-9} s contribute to the spin-lattice relaxation. From the structural knowledge of the system the most probable source of the long correlation time is the motion of the micelle. This motion can consist of either the rotation of the aggregate as a single entity or the diffusion of the amphiphile along the micellar surface. The actual calculation showed that both motions are approximately equally effective. The correlation time estimated from the field dependence of T_1 shows reasonable agreement with the τ_a calculated from structural data.

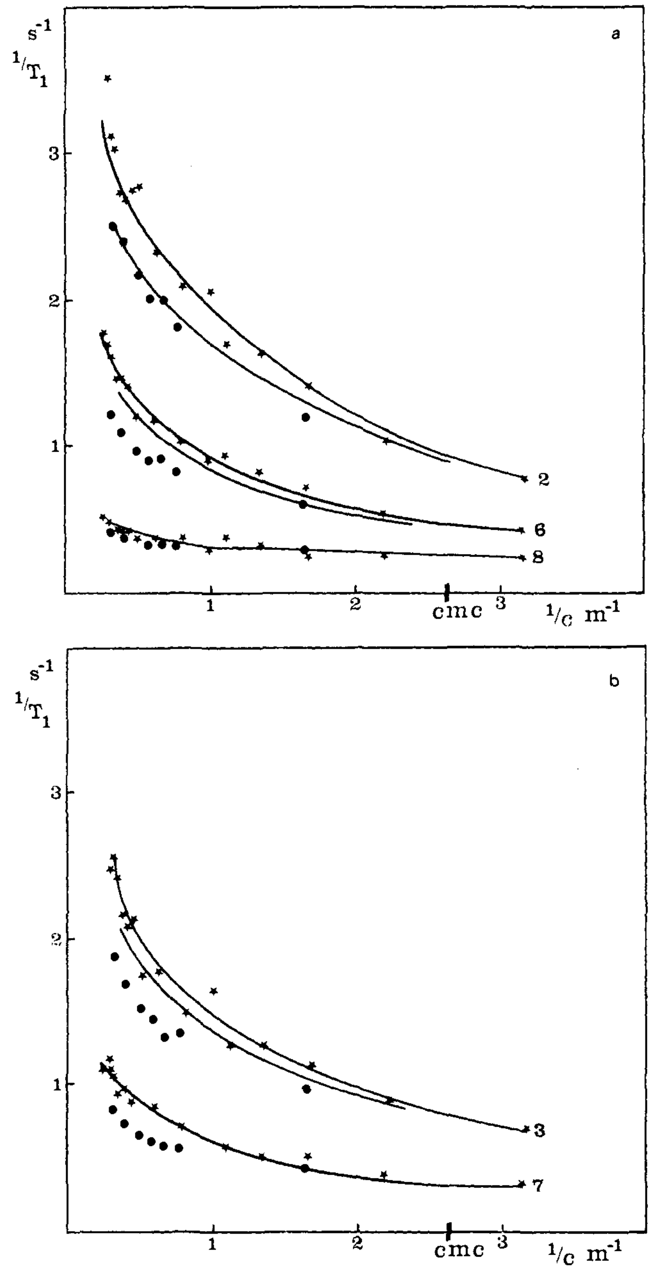

Figure 2. The inverse ^{13}C T_1 at two different magnetic field strengths plotted against the inverse sodium octanoate concentration: ★ corresponds to 15 MHz (1.4 T) while ● corresponds to 25 MHz (2.34 T). The lines for carbons 7 and 8 and the upper lines for carbons 2, 3, and 6 are visual fits to the experimental data at 15 MHz. The lower lines for carbons 2, 3, and 6 have been calculated from the upper lines to correspond to the data at 25 MHz (cf. Table II). The carbons are numbered as in Figure 1.

The agreement obtained between the observed T_1 and the quantitative estimates using order parameters determined for the hexagonal phase gives further support to the model proposed for the relaxation. We thus conclude that for octanoate micelles the overall motion of the aggregate is important for the T_1 relaxation of ^{13}C nuclei in the alkyl chain, in particular for nuclei close to the polar head group. It follows also that the intramicellar motion is even faster than previous interpretations of ^{13}C relaxation have suggested.

Owing to the structural similarity of different surfactant micelles it seems likely that the same mechanism also applies to other micellar systems. The relative importance of the overall motion decreases as the magnetic field strength is increased (cf. Table II) and when the size of the surfactant and, thus of the spherical micelle, is increased.

Since the T_1's in the octanoate system behave qualitatively in the same way as for other micellar systems studied[12,15,16] one might expect that the overall micellar motion is of importance also in these cases. For ω-phenylalkanoate soap micelles Menger and Jerkunica[21] recently found an anomalously high (3.6) ratio, R, $T_1(\text{ortho})/T_1(\text{para})$, for the phenyl ring carbons. The local order parameter S entering the expression for T_1^s in eq 7 is clearly smaller for the ortho than for the para carbon. The rotation of the phenyl ring only affects S_{ortho} while additional motions contribute to S_{ortho} and S_{para} to an equal extent. It seems to us that the most likely rationalization of the high R value observed by Menger and Jerkunica[21] is in a large difference in the local order parameters.

The nonlinearity of the concentration dependence of T_1^{-1} (Figure 1) shows that the phase separation model is only approximately valid and that structural changes occur in the micelles as the amphiphile concentration is changed. The latter is clear from a recent ^{13}C chemical shift study[47] and from the calorimetrically determined concentration dependence of the partial molal enthalpy of octanoate.[41] The structural change might consist of a slight increase in the aggregation number with a concomitant expulsion of water. From eq 7 it is seen that the T_1 values are sensitive to the value of the local order parameter and a marked change in S can change T_1 appreciably. At higher concentrations micelles often transform into rod-shaped aggregates[48] and this will of course affect the relaxation due to the slow motion. For a long cylinder the rotational diffusion will be too slow to contribute to T_1 while the monomer diffusion around the rod gives a correlation time $\tau_D = r^2(4D)$. Equation 7 remains valid if the right-hand side is multiplied by $3/4$. Thus the slow motion can be expected to give an important contribution to T_1 also for rod-like micelles and in normal hexagonal liquid crystalline phases.

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