

J	flux of the solute through the membrane, eq 1, mol $m^{-2} s^{-1}$	$\Lambda(x,a)$	local hydraulic permeability, eq 3, $m^4 N^{-1} s^{-1}$
J_v	volume flux through the membrane, eq 2, $m s^{-1}$	$\Lambda_1(x)$	concentration-independent part of $\Lambda(x,a)$, eq 21 and 33, $m^4 N^{-1} s^{-1}$
$k(x)$	local partition coefficient in the membrane, eq 5	$\Lambda_2(x)$	coefficient of inverse proportionality of $\Lambda(x,a)$ with the concentration, eq 21 and 33, $mol m N^{-1} s^{-1}$
L_p	filtration coefficient or hydraulic permeability, eq 1 and 32, $m^3 N^{-1} s^{-1}$	$\lambda(x)$	integral defined by eq 8, $s m^{-1}$
L_p^0	filtration coefficient corrected for concentration effects at small J_v , eq 33, $m^3 N^{-1} s^{-1}$	ξ	space coordinate in transport direction, m
l	membrane thickness, m	σ	reflection coefficient in eq 1 and 2
P	pressure, $N m^{-2}$	$\sigma(x)$	local reflection coefficient in the membrane, eq 3
R	universal gas constant, $N m mol^{-1} K^{-1}$	$\langle \sigma \rangle$	average reflection coefficient, eq 25
$R(J_v)$	solute retention in a reverse-osmosis experiment, eq 42	ϕ_p	pore volume fraction of the membrane
T	absolute temperature, K	ω	solute permeability of the membrane in eq 1, $m s^{-1}$
x	space coordinate in transport direction, m	$\omega(x)$	partial solute permeability, eq 22, $m s^{-1}$
α	dimensionless quantity determined by the structure of the membrane, defined by eq 30		
β	dimensionless quantity, defined by eq 34		
γ	dimensionless quantity, defined by eq 35		
Δc	difference between the concentrations on both sides of the membrane, eq 1, $mol m^{-3}$		
ΔP	difference between the pressures on both sides of the membrane, eq 2, $N m^{-2}$		
ϵ_j	position at which a discontinuity occurs in the membrane parameters, eq 38, m		

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Supplementary Material Available: Appendix A, providing a derivation of eq 3 and 4, and Appendix B, comparing results at low Péclet values with those of Kedem and Katchalsky for multilayer membranes (7 pages). Ordering information is given on any current masthead page.

Hydration of Ionic Surfactant Micelles from Water Oxygen-17 Magnetic Relaxation

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Water oxygen-17 relaxation rates have been measured for aqueous solutions of micelles composed of ionic surfactants of varying alkyl chain length, head group, and counterion. The concentration of surfactant and salt was also varied. From these measurements, supplemented with relaxation data for short-chain molecules and with quadrupolar splittings from anisotropic mesophases, we derive structural and dynamic information about the molecular details of the water-micelle interaction. Water molecules at the micelle surface reorient anisotropically, typically 2–3 times slower than in pure water. The average lifetime for water molecules associated with sodium dodecyl sulfate micelles is 6–37 ns. The water-hydrocarbon contact in the micellar solutions is equivalent to less than two fully exposed methylene groups per amphiphile. Small head groups and small counterions produce the largest effects on the ^{17}O relaxation rate, as expected from geometrical and electrostatic considerations.

Introduction

There are few systems in which the solute-solvent interaction has more dramatic consequences than in aqueous surfactant solutions. A characteristic feature of these systems is the cooperative self-association of surfactant, i.e., amphiphilic molecules composed of a polar, often charged, part and a relatively large nonpolar part, to form large aggregates, known as micelles. Aggregation typically occurs only above a well-defined surfactant concentration (cmc). Several recent reviews¹⁻⁴ provide extensive accounts of the phenomenon of surfactant association.

The overwhelming majority of experimental and theoretical studies have confirmed the classical picture of

micelles, proposed originally by Hartley.⁵ According to this picture, the micellar aggregate consists of a liquidlike hydrocarbon core, with the charged head groups residing at the surface in contact with the surrounding aqueous medium. Although there has been some controversy⁶⁻⁸ about the degree of water penetration into the hydrocarbon core, it seems that no unequivocal evidence of substantial water penetration exists. On the other hand, some water-hydrocarbon contact inevitably exists since most head groups are simply too small to completely cover the curved aggregate surface. Another factor which leads to water-hydrocarbon contact is the so-called "dynamic roughness" of the micelle surface. Thus, Aniansson⁹ es-

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timates an average protrusion of about 1.5 methylene groups in a sodium dodecyl sulfate micelle. A further important characteristic of ionic micellar solutions is the inhomogeneous distribution of counterions, with 40–80 % of the counterions confined to a region extending a few tenths of a nanometer out from the micelle surface.⁴

In theoretical models of micellar solutions, the aqueous phase is usually treated as a continuous dielectric medium. It is clear, however, that a detailed understanding of these systems will require explicit recognition of the molecular nature of the medium. Thus we would like to quantify the strength and range of the water–micelle interaction as well as its dynamic consequences. Quantities related to the amount of interacting water, e.g., “hydration numbers”, have been obtained mainly from transport properties, e.g., intrinsic viscosity,^{10–13} micellar sedimentation and diffusion coefficients,¹¹ and water self-diffusion coefficients,^{14–16} and also from molar volumes.¹⁷ The dynamic behavior, on the other hand, has been probed by various relaxation techniques: magnetic,^{18,19} dielectric^{20,21} or ultrasonic.²²

The main conclusion from the viscosity and diffusion studies of solutions of ionic micelles is that the deduced “hydration numbers” of 4–10 water molecules per surfactant molecule, corresponding to the amount of water moving with the micelle as a kinetic entity, can be fully accounted for by the hydration of the charged head groups and of the associated counterions.²³ This conclusion is in qualitative agreement with the water proton chemical shift and longitudinal relaxation studies of Clifford and Pethica¹⁸ and of Walker,¹⁹ which indicate a reduced water–hydrocarbon contact upon micellization.

As regards the dynamics of the associated water, e.g., reorientational rate and anisotropy and average residence time, considerable uncertainty remains. Due mainly to the influence of hydrocarbon protons on the water proton relaxation behavior, it has not been possible to extract dynamic information from proton relaxation rates.^{18,19} The most detailed studies of the microdynamics of water in micellar solutions are the dielectric relaxation measurements from the Göttingen group.^{20,21} As compared to magnetic relaxation, the dielectric relaxation technique has the advantage of accessibility to frequencies in the gigahertz range. However, the theoretical understanding of dielectric relaxation in terms of molecular parameters is at present rather limited. To interpret dielectric relaxation data one is thus forced to use continuum models involving many adjustable parameters and based on several simplifying assumptions. Nevertheless, the main conclusion from these studies,^{20,21} that the “hydration water” reorients

less than an order of magnitude slower than pure water, is probably indisputable, because of the well-characterized dispersion in the gigahertz range. Finally, mention should be made of a recent ultrasonic relaxation study²² in which a relaxation process below 2 MHz was detected at high surfactant concentrations. The authors suggest that water exchange between the hydration and bulk regions is the underlying process, however, no quantitative analysis was attempted.

In the present contribution we report water ¹⁷O relaxation rates for a variety of ionic surfactant solutions above the cmc, and also for a few nonassociated molecules. After a brief exposé of the relevant relaxation theory, which involves a “two-step model” with explicit reference to the anisotropy in the “bound” water reorientation, we present and interpret the relaxation data in five sections. The first section deals with the extent of water–hydrocarbon contact in micelles and the second with the effect on the ¹⁷O relaxation of alkyl chain length. In the third section we exploit the well-established growth of sodium dodecyl sulfate micelles upon salt addition to estimate the average residence time for water molecules at the micelle surface. Next we consider the analogous case of the sphere-to-rod transition for hexadecyltrimethylammonium bromide micelles and, finally, we discuss the effect of head group and counterion on the hydration.

Experimental Section

Chemicals. The surfactants were obtained from the following sources: acetic acid (Merck, Suprapur), propionic acid (BDH, min 99%), octanoic, dodecanoic, tetradecanoic, and hexadecanoic acids (BDH, specially pure), sodium dodecyl sulfate (BDH, specially purified for biochemical work), hexadecyltrimethylammonium bromide (BDH and Merck).

The potassium salts were prepared by neutralization with KOH, and then freeze dried and recrystallized from absolute ethanol. The molar masses were checked by titration with perchloric acid in glacial acetic acid. The sodium and cesium salts were prepared by neutralization with NaOH (EKA) or CsOH (Ventron). Added NaCl was from Merck (Suprapur).

Hexadecyltrimethylammonium chloride was prepared by transferring the bromide salt to the hydroxide form on a Dowex 21 K ion exchanger (BDH). The hydroxide was immediately neutralized with HCl to pH 4–5, whereafter the solution was lyophilized and the chloride salt recrystallized from acetone.

Aqueous surfactant solutions were made from doubly distilled (quartz apparatus) water, enriched to about 1% in ¹⁷O by addition of 10 atom % H₂¹⁷O (Biogenzia Lemanina). The solution pH was adjusted, with KOH, NaOH, or HCl, sufficiently far from neutral (cf. Table I) for the proton exchange broadening^{30,61} to be negligible.

Relaxation Measurements. Oxygen-17 magnetic relaxation rates were measured at 13.56 MHz on a modified Varian XL-100-15 Fourier transform spectrometer and at 34.56 MHz on a home-built Fourier transform spectrometer with a 6-T wide-bore magnet from Oxford Instrument Co.

Longitudinal relaxation rates were measured by inversion recovery (π – τ – $\pi/2$ pulse sequences). Each R_1 value is the result of a least-squares fit to the magnetization vs. delay time for eight different τ values. Transverse relaxation rates were obtained from the line width ($\Delta\nu_{1/2}$) at half-amplitude of the absorption curve according to $R_2 = \pi\Delta\nu_{1/2}$. The contribution to the line width from magnetic field inhomogeneity was eliminated by measuring at 3–6 concentrations and taking the slope $\partial R_2/\partial m$, or by sub-

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tracting the relaxation rate for a sample of pure water (pH 2.7) measured at the same temperature.

Two to four independent measurements of R_1 as well as of R_2 were performed on each sample. In those cases where no significant difference between R_1 and R_2 (or the corresponding slopes) was observed, the reported values are averages over all R_1 and R_2 data. The quantity $n(R_B - R_F)$, reported in Table I, was obtained according to eq 2 as explained in a footnote to the table. The experiments were carried out at a probe temperature of 27.4 °C, which was kept constant to within ± 0.2 °C by the passage of dry thermostated air.

Results and Discussion

General Considerations. In aqueous surfactant solutions the ^{17}O nuclei are distributed over several motional states with different intrinsic relaxation rates but with negligible chemical shift differences. If the exchange of water molecules between these states is fast compared to the intrinsic relaxation rates (see below), then the total relaxation rate may be decomposed^{24,25} according to eq 1, where the sum runs over all states and P_i is the fractional population in state i .

$$R = \sum_i P_i R_i \quad (1)$$

For aqueous surfactant solutions above the cmc, it is reasonable to consider three states: water "bound" to micelles, water "bound" to monomeric (nonmicellized) amphiphiles, and "free" water. Furthermore, we will adopt the phase separation model,¹⁻⁴ according to which the monomer concentration remains constant above the cmc. For a fast exchange three-state model, the excess relaxation rate is thus given by eq 2. In eq 2, m is the total am-

$$R_{\text{ex}} = R - R_F = \frac{n_{\text{mon}} m}{55.5} (R_{\text{mon}} - R_F) \quad m < m_{\text{cmc}} \quad (2a)$$

$$R_{\text{ex}} = R - R_F = \frac{n_{\text{mon}} m_{\text{cmc}}}{55.5} (R_{\text{mon}} - R_F) + \frac{n_{\text{mic}} (m - m_{\text{cmc}})}{55.5} (R_{\text{mic}} - R_F) \quad m > m_{\text{cmc}} \quad (2b)$$

phiphile molality, n is the number of motionally perturbed water molecules per amphiphile, and the subscripts F, mon, and mic refer to "free" water and water "bound" to monomeric or micellized amphiphiles, respectively. For the variation of the excess relaxation rate with the total amphiphile molality we find

$$\partial R_{\text{ex}} / \partial m = \frac{n}{55.5} (R_B - R_F) \quad (3)$$

where n and R_B refer to monomeric or micellized amphiphiles depending on whether m is lower or higher than m_{cmc} .

It is well-known¹⁻⁴ that the phase separation model is not strictly valid, in particular, the monomer concentration decreases above the cmc.^{16,62} For the present purposes, however, eq 2 and 3 are excellent approximations. This is so because, with one exception, our data refer to concentrations that are so much larger than the cmc (Table I) that any variation in the small contribution to the ^{17}O relaxation rate from monomeric amphiphiles must necessarily be small. The exception is octanoate, which has a relatively high cmc. The data of Puyal¹⁶ for sodium octanoate show, however, that the effect of decreasing

monomer concentration is merely 2%, which is less than the standard deviation in $\partial R_{\text{ex}} / \partial m$.

Equation 3 contains two unknowns: n and R_B . (R_F is taken to be equal to the relaxation rate for pure water, which was determined to be $129.7 \pm 2 \text{ s}^{-1}$ at 27.4 °C.) The quantity n is a measure of the number of water molecules, per amphiphile molecule, whose reorientational motion is significantly perturbed. The interpretation of the intrinsic relaxation rate R_B for these n water molecules depends on the model chosen to describe the molecular motions. The simplest model considers the "bound" water molecules to reorient isotropically with a rotational correlation time τ_{cB} , in which case R_B is given²⁶ by eq 4. The water ^{17}O

$$R_B = \frac{12\pi^2}{125} \chi^2 (1 + \eta^2/3) \tau_{\text{cB}} \quad (4)$$

quadrupole coupling constant $\chi = 6.67 \text{ MHz}$,^{27,28} and is virtually independent of the molecular environment. The asymmetry parameter for the electric field gradient is taken to be the same as in ice:²⁹ $\eta = 0.93$.

As will be clear from the following, the isotropic reorientation model, underlying eq 4, cannot satisfactorily explain all our data. This model has also been found inadequate in connection with recent ^{17}O studies^{28,30} of aqueous solutions of macromolecules. In a more realistic model one has to recognize that the water-micelle interaction inevitably induces some anisotropy in the reorientation of the interacting water molecules. This local anisotropic reorientation can only partially average the quadrupolar interaction,^{27,31} the remaining part being averaged out by a slower motion, e.g., exchange of water molecules with the bulk or reorientation of the entire micelle. We will now assume that (1) the fast and slow motions occur independently and on different time scales, (2) there is local threefold symmetry around the normal to the micelle surface, and (3) the anisotropy is small. It can then be shown^{27,31} that R_B can be decomposed into one contribution from the fast (f) motion and another contribution from the slow (s) motion, as in eq 5.

$$R_B = \frac{12\pi^2}{125} \chi^2 [(1 + \eta^2/3 - A^2) \tau_{\text{cB}}^f + A^2 \tau_{\text{cB}}^s] \quad (5)$$

The residual anisotropy A , the magnitude of which is confined to the range $[0,1]$, is determined by the asymmetry parameter η and by the orientational probability distribution for the "bound" water molecules with respect to the normal to the micelle surface.²⁷ For completely isotropic reorientation, $A = 0$ and eq 5 reduces to eq 4. From eq 5, which is valid only for $A^2 \ll 1$, it is seen that for the slow motion to contribute significantly to the relaxation rate, it must be slower than the fast motion by a factor of the order of $1/A^2$. If both micelle reorientation (correlation time τ_{rB}) and water exchange (average lifetime τ_{tB}) contribute to the slow motion, then this may be characterized by an effective correlation time²⁵ according to eq 6.

$$\frac{1}{\tau_{\text{cB}}^s} = \frac{1}{\tau_{\text{rB}}} + \frac{1}{\tau_{\text{tB}}} \quad (6)$$

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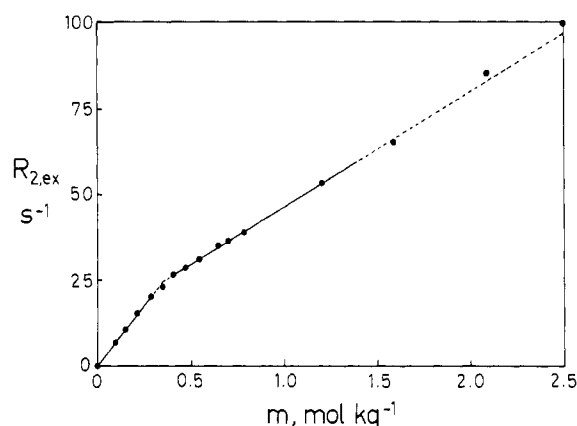


Figure 1. Water ^{17}O transverse excess relaxation rate vs. molality of potassium octanoate at 27.7 °C and 13.56 MHz. The lines were obtained by least-squares fits to the data points connected by solid lines.

If the slow motion is not fast compared to the inverse angular resonance frequency $1/\omega_0$, then the longitudinal and transverse relaxation rates become unequal. In eq 4 and 5, τ_{CB} and τ_{CB}^s , respectively, should then be multiplied by^{32,33}

$$\frac{0.2}{1 + (\omega_0\tau_{\text{CB}})^2} + \frac{0.8}{1 + (2\omega_0\tau_{\text{CB}}^s)^2} \quad (7a)$$

for the longitudinal relaxation rate, and by

$$0.3 + \frac{0.5}{1 + (\omega_0\tau_{\text{CB}})^2} + \frac{0.2}{1 + (2\omega_0\tau_{\text{CB}}^s)^2} \quad (7b)$$

for the transverse relaxation rate.

Extent of Water-Hydrocarbon Contact. The variation of the water ^{17}O excess relaxation rate ($R_1 = R_2$) with concentration of potassium octanoate is shown in Figure 1. There are two linear regions interrupted by a well-defined change of slope at 0.350 mol kg⁻¹, which we identify as the cmc. (Literature cmc values³⁴⁻³⁹ fall in the range 0.35–0.45 mol kg⁻¹.) The reduction in the quantity $n(R_B - R_F)$, obtained from the slopes according to eq 3, from 3.90×10^3 below the cmc to 1.86×10^3 above the cmc (Table I), indicates a substantial reduction of the water-hydrocarbon contact upon micellization. (As noted above, the effect of decreasing monomer concentration above the cmc is negligible.)

In order to quantify this conclusion, we performed measurements on solutions of two short-chain potassium alkanoates. From the data in Table I it is seen that octanoate micelles produce virtually the same effect on the water ^{17}O relaxation as does propionate. We can thus infer that the water-hydrocarbon contact in potassium octanoate micelles corresponds to at most two fully exposed methylene groups per amphiphile. This must be taken as an upper limit since, as discussed above (eq 5), there may be a contribution from slow motions to the relaxation rate for the micellar solution. On the other hand, a much smaller hydrocarbon exposure is unlikely on purely geometrical grounds. Thus, in a molecular model with an aggregation number⁴⁰ of 11 only about half of the "surface

TABLE I: Water ^{17}O Relaxation Data for Aqueous Surfactant Solutions at 27.4 ± 0.2 °C

surfactant ^a	cmc, ^b mol kg ⁻¹	m, mol kg ⁻¹	pH	$10^{-3} n \cdot$ $(R_B - R_F),^c$ s ⁻¹
CH ₃ CO ₂ K		0.49	12.0	1.38 ± 0.05
CH ₃ CH ₂ CO ₂ K		0.56	12.2	1.84 ± 0.05
C ₇ CO ₂ K	0.35	0.10–0.32	12.1	3.90 ± 0.14
C ₇ CO ₂ K	0.35	0.45–1.00	12.1	1.86 ± 0.04
C ₁₁ CO ₂ Na	0.023	0.42	11.8	2.93 ± 0.20
C ₁₁ CO ₂ K	0.024	0.44	10.5	1.99 ± 0.20
C ₁₁ CO ₂ Cs	0.025	0.45	12.3	2.18 ± 0.20
C ₁₃ CO ₂ K	0.006	0.10–0.50	12.0	2.19 ± 0.09
C ₁₅ CO ₂ K	0.002	0.10–0.55	12.0	2.09 ± 0.06
				(R_1)
				2.48 ± 0.18
				(R_2)
C ₁₂ OSO ₃ Na	0.008	0.10–0.90	10.9	1.77 ± 0.05
C ₁₂ OSO ₃ Na	0.001	0.10 + 0.38 m NaCl	10.9	3.88 ± 0.30
C ₁₂ OSO ₃ Na	<0.001	0.10 + 0.72 m NaCl	10.9	4.42 ± 0.50
(CH ₃) ₄ NBr		1.0–3.7	1–2	1.18^d
(C ₄ H ₉) ₄ NBr		0.6–2.4	1–2	8.06^d
C ₁₆ N(CH ₃) ₃ Cl	0.001	0.18	3.6	2.99 ± 0.30
C ₁₆ N(CH ₃) ₃ Br	0.001	0.18	3.4	1.88 ± 0.30
C ₁₆ N(CH ₃) ₃ Br	0.001	0.57	3.4	2.19 ± 0.10

^a C_n denotes the normal alkyl chain CH₃(CH₂)_{n-1}.
^b From ref 34, except for C₇CO₂K, the cmc of which is taken from Figure 1. ^c With one exception, we found no significant difference between R_1 and R_2 and no significant frequency dependence between 13.56 and 34.56 MHz. The exception is C₁₁CO₂K, for which $R_1 \neq R_2$ at 34.56 MHz. The quantity $n(R_B - R_F)$ was obtained, according to eq 2, from least-squares fits to 5–12 data points (each derived from 2–4 measurements) in the indicated concentration range (± 1 standard deviation), or from measurements at a single concentration (\pm estimated uncertainty). The data for the dodecanoates have been corrected for the monomer contribution (5–10 %), using $n(R_{\text{mon}} - R_F) = 5.5 \times 10^3$ (extrapolated from the monomer data). ^d From ref 41.

area" is occupied by carboxylate groups.

The conclusion that the water-hydrocarbon contact corresponds to less than two fully exposed methylene groups holds also for micelles composed of the longer-chain alkanoates. A longer chain results in a slightly enhanced relaxation rate (Table I), which, however, is due to an increasing contribution from slow motions. This point is discussed in the following section.

The water-hydrocarbon contact in hexadecyltrimethylammonium bromide micelles may be estimated with the aid of ^{17}O relaxation rates for short-chain tetraalkylammonium bromides reported by Fister and Hertz⁴¹ (included in Table I). A comparison with the micelle data shows that an upper limit of two fully exposed methylene groups is reasonable also for hexadecyltrimethylammonium bromide micelles.

Effect of Alkyl Chain Length. The effect of alkyl chain length, i.e., of micelle size, on the water ^{17}O relaxation rate was investigated for potassium alkanoates with 8, 12, 14, and 16 carbon atoms. The data in Table I reveal a monotonic increase in relaxation rate with increasing chain length. From geometrical considerations, it is clear that the area per head group (at a surface which passes through the head groups) must decrease as the micelle grows ra-

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dially.⁴² (This effect, which is quite small, is a consequence of the assumption of a constant area per surfactant molecule at the surface of the hydrocarbon core.) One would thus expect the relaxation rate to decrease somewhat with increasing chain length, contrary to our observations. We therefore conclude that the effect of decreasing water-hydrocarbon contact is overcompensated by a contribution from slow motions according to eq 5. If micelle reorientation contributes to $\tau_{\text{CB}}^{\text{S}}$ (cf. eq 6), this slow contribution should increase with the chain length. This follows from the fact that a longer alkyl chain leads to a larger micelle per se and also increases the aggregation number. (According to the Debye-Stokes-Einstein relation, the rotational correlation time τ_{RB} , appearing in eq 6, is proportional to the cube of the micelle radius.)

For hexadecanoate micelles we observed a significant difference between the longitudinal and transverse relaxation rates at a resonance frequency of 34.56 MHz (Table I). This enables us to estimate the slow correlation time $\tau_{\text{CB}}^{\text{S}}$, if we assume that the fast contribution to the relaxation rates is the same as for acetate. (As noted above, the water-hydrocarbon contact should be smaller for hexadecanoate micelles than for octanoate micelles.) Inserting data from Table I into eq 3, 5, and 7 we thus find $\tau_{\text{CB}}^{\text{S}} = 3$ ns. This figure agrees well with the observed maximum in the longitudinal relaxation rate vs. chain length (Table I), although this maximum is barely significant by itself. From eq 7a one can thus infer that R_1 should exhibit a maximum at $\omega_0\tau_{\text{CB}}^{\text{S}} = 0.6158$, which, at a resonance frequency of 34.56 MHz, corresponds to $\tau_{\text{CB}}^{\text{S}} = 2.8$ ns.

With this estimate for $\tau_{\text{CB}}^{\text{S}}$, it can be shown that the isotropic motion model, i.e., eq 4, is physically unreasonable. Thus $n(R_{\text{B}} - R_{\text{F}}) = 2.09 \times 10^3 \text{ s}^{-1}$ and $\tau_{\text{CB}}^{\text{S}} = 3$ ns for hexadecanoate micelles yield, with eq 4 and 7a, the completely absurd result: $n = 0.03$. This clearly demonstrates that it is necessary to take into account explicitly the consequences of the anisotropy in the "bound" water reorientation, as we have done in eq 5.

NaDS Micelles at High NaCl Concentration. From several light-scattering studies⁴³⁻⁴⁶ it has been inferred that sodium dodecyl sulfate (NaDS) micelles, at high NaCl concentrations, grow laterally to form large rod-shaped aggregates exceeding 50 nm in length. If the slow correlation time $\tau_{\text{CB}}^{\text{S}}$, entering in eq 5, were determined solely by aggregate reorientation, then one would expect that NaCl addition to NaDS micelle solutions should increase the transverse ^{17}O relaxation rate by orders of magnitude or even lead to quadrupolar splittings. As can be seen from Table I, this is not the case; the relaxation rate is enhanced by merely a factor of 2.5. This observation implies that $\tau_{\text{CB}}^{\text{S}}$ is controlled, to a large extent, by a more rapid motion, which we identify as exchange of water molecules between the "free" and "bound" states. On the basis of this interpretation, we will now proceed to estimate the average residence time τ_{IB} for water molecules associated with the micelle surface.

From the dimensions⁴³⁻⁴⁶ of the rod-shaped NaDS micelles and with the aid of Perrin's equations⁴⁷ we find an effective⁴⁸ rotational correlation time $\tau_{\text{RB}} \approx 2 \mu\text{s}$. Antici-

pating the result of the calculation, we assume that this is so much larger than the lifetime τ_{IB} that, according to eq 6, $\tau_{\text{CB}}^{\text{S}} = \tau_{\text{IB}}$. To proceed, we need an estimate of the residual anisotropy A , appearing in eq 5.

The local environment for water molecules interacting with the sulfate head groups is undoubtedly very nearly the same in the rod-shaped aggregates under discussion and in the hexagonal mesophase consisting of ordered rod-shaped aggregates. Since this latter system is anisotropic one obtains quadrupolar splittings in the water deuteron or ^{17}O spectra, from which the residual anisotropy can be extracted. Since the water ^{17}O residual anisotropy is simply twice that for water deuterons,^{27,49} we have not measured the ^{17}O splitting but have used literature data⁵⁰ for the deuteron splitting in the hexagonal phase of the D_2O -NaDS system. The observed splitting is 560 Hz for 21.6 mol of D_2O per mol of NaDS. Using the equation^{27,51} for the quadrupolar splitting in a powder sample and a deuteron quadrupole coupling constant²⁷ of 220 kHz, we find $|A| = 0.29/n$, where n is the water "coordination number". We have then multiplied by a factor of 2 to obtain the local anisotropy^{27,31} and by another factor of 2 to convert to the ^{17}O residual anisotropy, as noted above.

We can now substitute $\chi = 6.67 \text{ MHz}$, $\eta = 0.93$, and $|A| = 0.29/n$ into eq 5 for R_{B} , which on combination with the value $n(R_{\text{B}} - R_{\text{F}}) = (4.42 \pm 0.50) \times 10^3$, corresponding to the highest NaCl concentration in Table I, and the known value $R_{\text{F}} = 129.7 \text{ s}^{-1}$, yields an expression for the lifetime τ_{IB} as a function of n and $\tau_{\text{CB}}^{\text{F}}$. It seems reasonable to use a "coordination number" n in the range 6-9, in accordance with viscosity data.^{10,51} The fast correlation time $\tau_{\text{CB}}^{\text{F}}$ is certainly not shorter than 2.38 ps, which is the value for pure water at 27.4 °C. An upper limit is furnished by the relaxation rate for salt-free NaDS micelles (Table I), if we neglect the contribution from the slow motions in this case. It is found that values of n in the range 6-9 correspond to $\tau_{\text{CB}}^{\text{F}}$ values of 3.0 ± 0.5 times the pure water value. Finally, we go back to the expression for τ_{IB} , to find that values of n in the range 6-9 together with $\tau_{\text{CB}}^{\text{F}}$ values 1-3 times longer than for pure water correspond to lifetimes in the relatively narrow range 6-11 ns. Since this actually refers to an effective correlation time, in the sense of eq 7, the upper limit should be multiplied by 1/0.3. The final result is $6 < \tau_{\text{IB}} < 37$ ns.

The Sphere-to-Rod Transition for HTABr Micelles. In the absence of added salt, hexadecyltrimethylammonium bromide (HTABr) micelles undergo a change, at about 0.3 mol kg^{-1} , from an essentially spherical to a cylindrical shape. Upon further increase in concentration, the rodlike aggregates grow along the cylindrical axis. This transition gives rise to dramatic changes in physical properties such as reduced viscosity,¹² light scattering,¹² small angle X-ray scattering,⁵² transverse magnetic relaxation rates of ^{14}N (head groups)⁵³ and of ^{81}Br (counterions),⁵⁴ and anisotropy of the electrical conductivity in oriented solutions.⁵⁵ The increase in the water ^{17}O relaxation rate (Table I), however, is quite small, in fact barely significant. The explanation is most probably the same as in the case of NaDS, i.e., the residual anisotropy is averaged out, not by aggregate re-

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orientation, but by water exchange. (The effective rotational correlation time, as deduced in the ^{14}N relaxation study,⁵³ exceeds 340 ns.)

The approach used in the preceding section to estimate the water lifetime for NaDS micelles cannot, however, be used for HTABr micelles. The reason is that no independent information about the residual anisotropy is available. Thus no resolved deuteron splittings could be observed in a study⁵⁶ of the hexagonal phase of the D_2O -HTABr system, indicating a very small anisotropy. This is not surprising, considering that the methyl groups act to keep the water molecules at some distance from the charge. The small residual anisotropy for water associated with the trimethylammonium group is also consistent with the insignificant effect of the sphere-to-rod transition on the ^{17}O relaxation rate, as compared to the transition in NaDS.

It should be pointed out here that the extremely large "hydration numbers" ($n = 60\text{--}70$) suggested for HTABr micelles by Ekwall et al.¹² receive no support from our data. They are probably an artifact arising from the electroviscous effect. In fact, the water-HTABr interaction appears to be very weak. Thus Mukerjee¹⁰ has estimated, from viscosity data, a hydration number of 4.1 ± 1.3 for tetradecyltrimethylammonium chloride micelles. And, as the data in Table I show, HTABr micelles produce a considerably smaller ^{17}O relaxation enhancement than do HTACl micelles.

Effect of Counterion and Head Group. The effect of the nature of the counterion on the water ^{17}O relaxation rate was investigated for dodecanoate micelles and for hexadecyltrimethylammonium micelles. In the former case we found (Table I) that sodium counterions are substantially more effective than either potassium or cesium ions in enhancing the ^{17}O relaxation rate. It is known⁵⁷ that all three counterions retain their primary hydration upon association to alkanolate micelles. Consequently, the origin of the difference must be that the smaller size of the sodium ions results in a stronger dynamical perturbation of the adjacent water molecules. (This effect on the ^{17}O relaxation is likely to dominate over the effects caused by the higher aggregation number and the more extensive counterion association for CsDS as compared to NaDS, recently reported⁶² by Frahm et al. Indeed, if these were the only counterion effects the ^{17}O relaxation rate would, contrary to observation, be largest for CsDS.) The difference in the ^{17}O relaxation enhancement between sodium and potassium dodecanoate micelles is about three times larger than the difference between NaCl and KCl in the absence of surfactant (unpublished data). The micelles thus have the effect of enhancing the difference in "hydration" between Na^+ and K^+ . This may be due to the fact that the proximity of a large hydrocarbon core with low relative permittivity acts to enhance all electrostatic interactions in the adjacent aqueous region.⁵⁸

It has not been conclusively demonstrated whether chloride and bromide ions retain their primary hydration upon association to alkyl trimethylammonium micelles.^{3,4} However, in view of the striking differences between HTACl and HTABr as regards micelle shape at high concentration,⁵⁹ it is plausible that associated Cl^- and Br^-

differ in hydration. The much larger effect of HTACl micelles, as compared to HTABr micelles (Table I), is thus probably due partly to the different ionic radii and partly to exclusion of some hydration water upon Br^- association.

To get an idea of the importance of the nature of the head group in determining the water ^{17}O relaxation rate, we may compare the data in Table I for NaDS (salt-free) and sodium dodecanoate micelles. It is seen that the carboxylate group produces a much larger effect than the sulfate group. This difference can be accounted for qualitatively on the basis of the smaller size of the COO^- group, relative to the OSO_3^- group. Consequently, there is more space available for water molecules to penetrate between the head groups in the alkanolate micelles.

Conclusions and Summary

The present study confirms our previous^{28,30} conclusion that water ^{17}O relaxation in aqueous solutions of macromolecules or large molecular aggregates cannot be satisfactorily explained by a simple two-state model in which each state is characterized by a single correlation time. Rather, one must introduce two correlation times to describe the stepwise averaging of the quadrupolar interaction in the "bound" state. The contributions from the fast and slow motions to the relaxation rate are often of comparable magnitude when the slow correlation time is in the nanosecond range. Micellar systems are ideally suited for application of the two-step model, because of their simple structure and because the weighting factor for the slow component, i.e., the square of the residual anisotropy, often can be obtained from quadrupolar splittings in the corresponding anisotropic mesophases.

The rate of local water reorientation at the micelle surface is typically 2–3 times slower than in pure water. This is also true for the hydration water of small solutes and agrees with results from dielectric relaxation studies.^{20,21,60} The residual anisotropy is averaged out mainly by micelle reorientation for small micelles and mainly by water exchange for large micelles. The average lifetime for water molecules associated with sodium dodecyl sulfate micelles is between 6 and 37 ns.

No long-range water-micelle interaction is indicated by our data. For potassium octanoate micelles, the ^{17}O relaxation enhancement corresponds to hydration of the carboxylate head groups, the potassium counterions, and a water-hydrocarbon contact equivalent to less than two fully exposed methylene groups. For longer-chain micelles the water-hydrocarbon contact is of similar magnitude. Small head groups permit more water to penetrate between themselves, as evidenced by the larger effect on the ^{17}O relaxation rate of micelles with carboxylate head groups as compared to those with sulfate head groups. The influence of counterions on the ^{17}O relaxation rate can be explained in terms of the ionic radii and a possible dehydration accompanying Br^- association to hexadecyltrimethylammonium micelles.

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