Heteronuclear Overhauser Effect Measurements in Surfactant Systems. 1. The Direct Estimation of the Distance between Water and the Micellar Surface

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Abstract: Heteronuclear Overhauser effect (HOE) NMR experiments have been applied to micellized surfactant in water. These experiments include a variant of the HOESY two-dimensional experiment (perturbation of proton and observation of carbon-13) which shows a correlation between water protons and the carboxylate ^{13}C of sodium alkanoates. Nonselective one-dimensional experiments, concerning essentially aliphatic carbons, are discussed with regard to cross-relaxation terms between proton and carbon-13 and within the proton spin system. A new selective one-dimensional experiment allows quantification of cross-relaxation between water protons and the carboxylate ^{13}C. From these data, an average distance of 2.8 Å between water and the micellar surface is found to be nearly constant for the three systems investigated (sodium octanoate at 2 M and 1 M concentrations and sodium decanoate at 1 M concentration).

Introduction

The HOESY experiment (heteronuclear Overhauser effect spectroscopy) is the counterpart in the heteronuclear case of the widely used NOESY experiment. In the first dimension, a group of nuclides of the same isotopic species (generally protons) is perturbed by means of frequency labeling, and after a mixing time, responses arising from another nucleus (generally carbon-13) are observed in the second dimension. Cross-peaks in the 2D map are indicative of cross-relaxation between two well-identified nuclei of different isotopic nature; this reflects the existence of a non-negligible dipolar interaction modulated by molecular motions. The method was proposed seven years ago simultaneously by Rinaldi[1] on the one hand and Yu and Levy[2] on the other hand. When applied to *intramolecular* interactions, it does not furnish much more information than conventional spectroscopic methods, and the method is of lower sensitivity than the conventional correlation spectroscopy based on heteronuclear couplings since the major responses arise from directly bonded nuclei. However, it becomes more interesting, for instance, in the case of nuclei which are not directly bonded to protons. Surprisingly enough, the method has been used little for the detection of *intermolecular* dipolar interactions: by observing phosphorus-31, Yu and Levy[2] demonstrated that the terminal phosphorus of adenosine triphosphate is the most accessible to water; by observing lithium-6, Bauer and Schleyer[3] determined stereospecific lithiation; and, quite recently, by observing carbon-13, Seba and Ancian[4] were able to characterize hydration of pyridone derivatives.

We report here on a study of micellized surfactants using variants of the HOESY sequence. In addition to a slight modification of the 2D basic sequence, these variants include both nonselective and selective heteronuclear Overhauser effect experiments. The latter have been devised to obtain quantitative spectroscopic data and, hopefully, quantitative molecular information. As discussed later, the nonselective 1D experiment can be tentatively used for determining the proton–carbon cross-relaxation terms in the aliphatic chain. The selective experiment should provide information about bound water and about the nature of hydration. The systems that we have investigated are sodium alkanoates primarily because their polar head possesses a carbon that is not bonded to a proton. We shall therefore be looking for a nuclear Overhauser effect between any kind of proton and the carbon-13 of the carboxylate group; in other words, we want to determine the dipolar cross-relaxation terms with protons of the surfactant molecule but also, and this is actually our goal, with the water protons. For sensitivity reasons, we had to limit ourselves to only two surfactants which can be dissolved in water at relatively high concentrations (1 or 2 M): sodium octanoate and sodium decanoate.

Two-Dimensional HOESY Experiments

We have found it useful to slightly modify the conventional[5] HOESY sequence (middle of Figure 1) by inserting a saturation procedure applied to carbon-13 magnetization prior to the mixing interval (Figure 1). This saturation sequence is made up of two long pulses (2 ms and 1 ms, respectively) applied along the two directions of the rotating frame, following the suggestion of Bax and co-workers.[6] This has two advantages: (i) the state of carbon magnetization is perfectly defined at the beginning of the mixing time (magnetization is zero), and (ii) since time averaging is generally needed, the experiment can be repeated according to the proton relaxation times, which are usually much shorter than those of carbons. Furthermore, the 180° phase alternation of the second proton pulse along with the alternation of the acquisition sign has the effect of canceling any carbon-13 magnetization which would recover by relaxation during the mixing time. As a consequence, pure NOE spectra are obtained. Other conventional phase cycling for eliminating quadrature detection artifacts in t_2 or pulse imperfection effects have been superimposed. Finally, the resulting two-dimensional spectra can be obtained in the pure absorption mode because amplitude modulation is used in t_1; this positions the proton frequency at one extremity of the spectrum, which does not result in a serious penalty because of the relatively narrow frequency range of proton spectra. A typical result is shown in Figure 2. A long mixing time has been used (2 s) in order to enhance cross-peaks arising from weak cross-relaxation terms; this is effective, provided that the relevant protons have sufficiently long relaxation times. Other than correlations by cross-relaxation with protons directly bonded to the aliphatic carbons, two cross-peaks are observed at the carboxylate position. As expected, one arises from the neighboring CH_2 and the other is located, in ν_1, at the water resonance. This observation represents a direct visualization of bound water that is definitely ascertained by the cross-section shown in Figure 3. The two cross-peaks are seen to be of comparable intensity, indicating that water is close enough to the polar head. Because of the obviously different dynamical behavior of the water–polar head dipolar interaction on the one hand and the $(CH_2)_\alpha$–polar head dipolar interaction on the other hand (the former proceeds from extreme narrowing as will be seen below whereas the latter is subjected

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(1) Rinaldi, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 5167–5168.

(2) (a) Yu, C.; Levy, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 6994–6995. (b) Yu, C.; Levy, G. C. *J. Am. Chem. Soc.* **1984**, *106*, 6533–6537.

(3) Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827–833.

(4) Seba, H.; Ancian, B. *J. Chem. Soc., Chem. Commun.* **1990**, 996–997.

(5) Köver, K. B.; Batta, G. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 223–266 and references therein.

(6) See for instance: Néry, H.; Söderman, O.; Canet, D.; Walderhaug, H.; Lindman, B. *J. Phys. Chem.* **1986**, *90*, 5802–5808.

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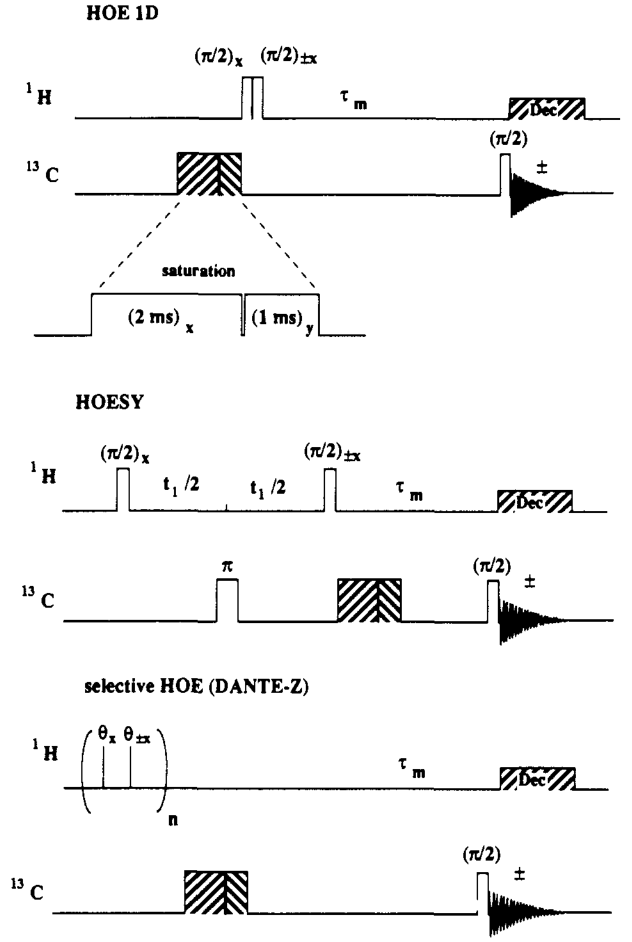

Figure 1. Pulse sequences employed in this work. Top: the one-dimensional version of the conventional 2D HOESY experiment (middle). Bottom: one-dimensional HOE experiment with the selective inversion of a proton resonance. In all cases, a saturation procedure has been applied to carbon magnetization to ensure well-defined initial conditions prior to the mixing time τ_m.

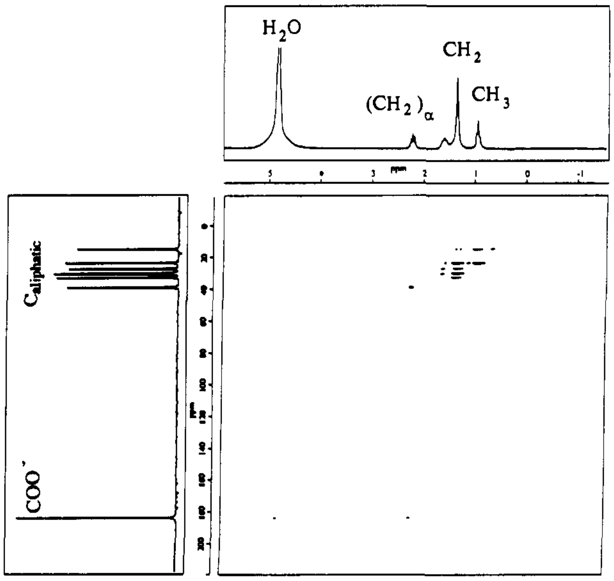

Figure 2. A typical HOESY 2D map of sodium octanoate (2 M) micellar solution (horizontal scale, proton; vertical scale, carbon-13), showing correlations between aliphatic carbons and directly bonded protons. Two cross-peaks are seen at the carboxylate level: one arises from the proton of the CH_2 neighboring group and the other from water protons.

to micellar slow motions), this result is essentially qualitative, and other experiments are really needed to arrive at a quantitative conclusion. These experiments must be one-dimensional since quantitativeness is hardly expected from two-dimensional measurements, which should be repeated anyway for different mixing times. Due to the duration of a single experiment (1 or 2 days), this cannot be seriously considered.

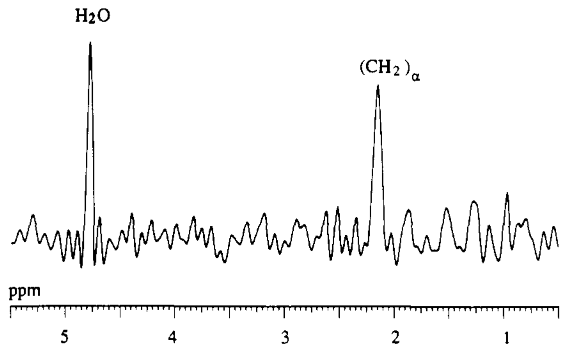

Figure 3. Cross-section of Figure 2 showing the dipolar interactions undergone by the carboxylate carbon.

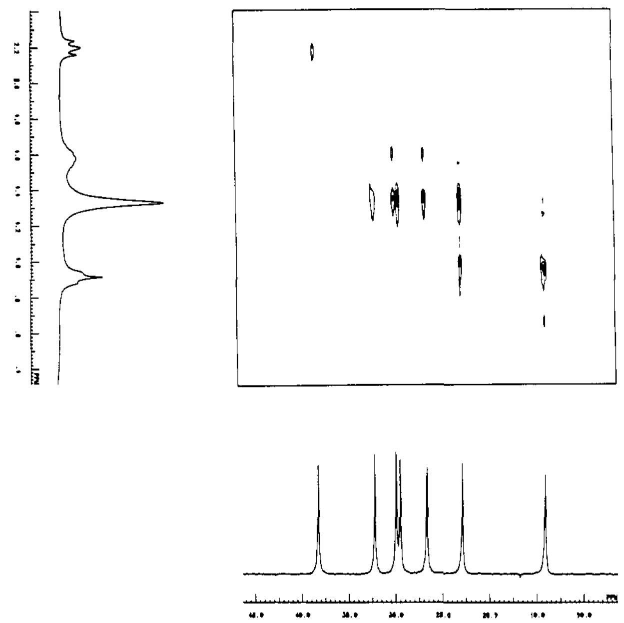

Figure 4. An expansion of the aliphatic region of the 2D map shown in Figure 2.

In passing, Figure 4 shows an expansion of the aliphatic part of the two-dimensional diagram. In several instances, two cross-peaks appear at the location of a given carbon. They may be due either to cross-relaxation with a nonbonded proton or to cross-relaxation among the proton spin system itself, or from the fact that the proton system is not first order. This aspect certainly deserves further investigation and will be the subject of a future study.

HOE One-Dimensional Experiment

The pulse sequence is sketched at the top of Figure 1. Regarding the initial state (at the beginning of the mixing time) and the cancellation of the carbon magnetization which would reconstruct through its own longitudinal relaxation, one gains the same benefits as in the 2D experiment. Therefore, by varying the mixing time, one obtains 1D spectra which purely reflect the heteronuclear NOE buildup. Simply, correlations with the different protons are missing; that is to say that all cross-relaxation terms affecting a given carbon contribute. Because of the dependency on interatomic distances, it can be safely assumed that nonbonded protons do not contribute, as far as aliphatic carbons are concerned. Of course, regarding the carboxylate group, contributions both from water and from the CH_2 in the α position add up (this will be dealt with in the next section). Figure 5 exhibits this global NOE buildup. One can notice that the $(CH_2)_\alpha$ signal decreases (left-most signal in the aliphatic region) while

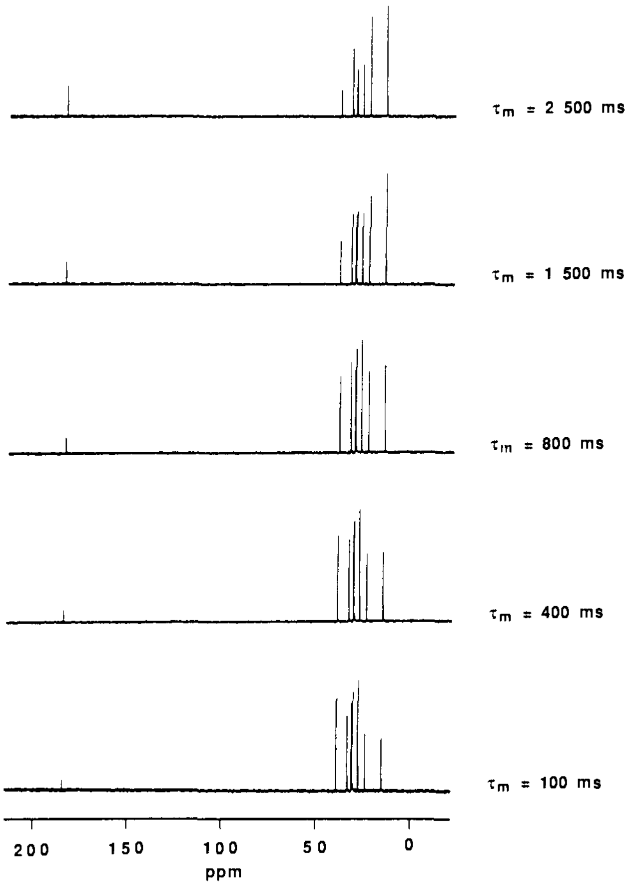

Figure 5. ^{13}C heteronuclear Overhauser effect buildup in a 2 M sodium octanoate micellar solution as obtained from the sequence sketched at the top of Figure 1; experiments performed at 75 MHz.

the carboxylate signal as well as the methyl signal still grows. Two examples of the evolution of the cross-relaxation induced magnetization are shown in Figure 6 where the experimental data are presented along theoretical curves which have been calculated with parameters extracted from a fit according to the simple Solomon equations. The agreement is excellent. However, as shown in Figure 7, the cross-relaxation term extracted from this fit may differ from the one derived from classical NOE determinations (performed, for instance, by the well-known gated decoupling method), which rest on the measurement of the equilibrium magnetization and of the steady-state magnetization under continuous proton irradiation. A striking feature is the equalization of apparent cross-relaxation terms (σ) up to C_5, which is accompanied by a similar equalization of the proton longitudinal relaxation (the latter can also be fitted in the calculations employing Solomon equations; see below). It is well-known that, in these organized systems, the mobility increases along the chain causing continuous evolution of relaxation parameters.[6] This discrepancy does not arise from experimental uncertainties (the accuracy in the determination of σ in all cases is better than 5%) but, rather, can be qualitatively explained as follows: Solomon equations imply a two-spin (or a two-magnetization) system (here the carbon-13 and the directly bonded protons). It turns out that protons are prone to interact with other protons of the alkyl chain, again by dipolar cross-relaxation (this is the well-known phenomenon of spin diffusion, which manifests itself in homonuclear NOESY experiments performed on large molecules[7]). Whenever the proton–proton cross-relaxation terms are large, spin diffusion becomes efficient and tends to unify all relaxation parameters; as a consequence the present results which concern *heteronuclear* cross-relaxation may be strongly altered by spin diffusion among the proton spin system. A last observation which corroborates this explanation is as follows: due to an enhanced mobility at the extremity of the alkyl chain (the last two carbons of the chain), the proton–proton cross-relaxation is much less efficient, and as a matter of fact, the proton–carbon cross-relaxation term extracted

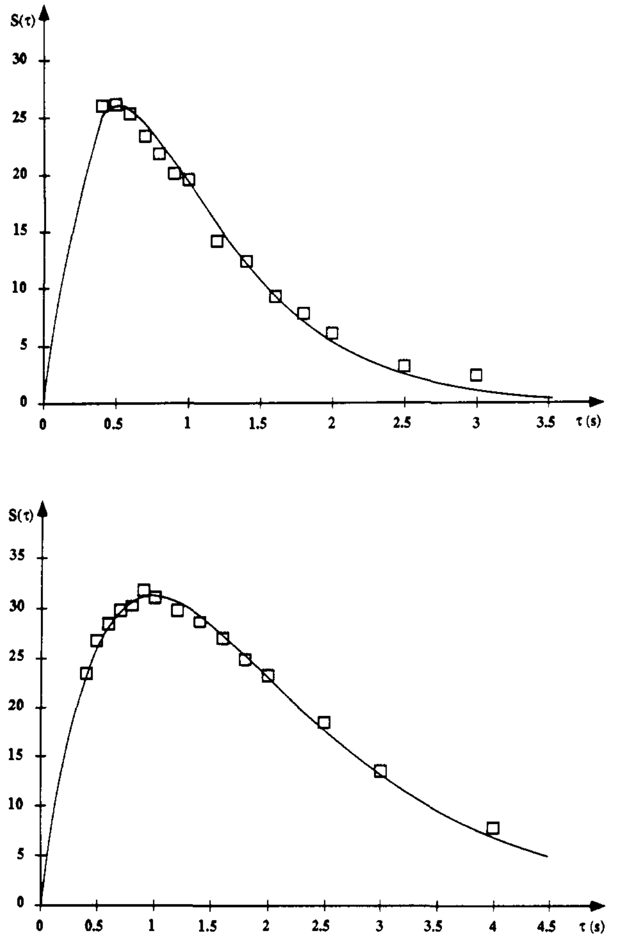

Figure 6. Experimental data points (squares) extracted from spectra such as those shown in Figure 5 along with theoretical curves (see text). Top: $(CH_2)_\alpha$. Bottom: penultimate carbon of the alkyl chain; experiments performed at 50 MHz. The vertical scale is such that 100 corresponds to the equilibrium magnetization.

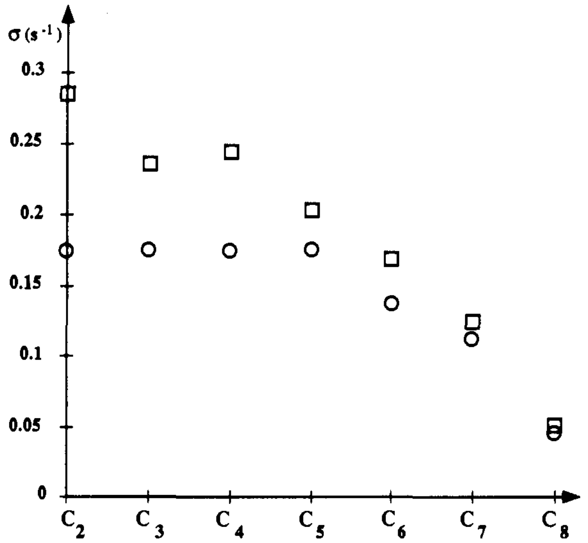

Figure 7. Apparent cross-relaxation terms derived from experimental data arising from the sequence at the top of Figure 1 (circles) as compared to those arising from classical measurements (squares); experiments performed at 50 MHz. Horizontal scale: carbon number in the aliphatic chain of sodium octanoate (numbering from the surfactant polar head).

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[7] Wüthrich, K. *NMR of proteins and nucleic acids*; Wiley: New York, 1986.

Table I. Data Relative to the Three Systems Investigated Here: Sodium Octanoate/Water at 2 M and 1 M Concentrations and Sodium Decanoate/Water at 1 M Concentration[a]

	$T_1(COO^-)$ (s)	$T_1(H_2O)$ (s)	$T_1(H_2{}^{17}O)$ (ms)	τ_c (ps)	σ_{CH} (s^{-1})	r (Å)	D_m/D_w	r_b (Å)
octanoate 2 M	12.15	1.66	1.6	4.6–6.5	1.26×10^{-4}	2.93–3.11	0.45	2.66–2.81
octanoate 1 M	17.8	1.85	4.3	2.8–3.95	0.44×10^{-4}	3.22–3.41	0.62	2.74–2.90
decanoate 1 M	10.4	1.83	4.3	2.8–3.95	0.40×10^{-4}	3.27–3.47	0.64	2.76–2.92

[a] The longitudinal relaxation times T_1, the cross-relaxation term σ_{CH}, and the ratio of water self-diffusion coefficients D_m/D_w have been determined experimentally. The correlation time τ_c and the distances r and r_b (both related to the approach of the surfactant polar head by water) have been calculated as indicated in the text.

from HOE measurements comes very close to the one obtained by the classical method. Owing to the fact that we have been dealing with rather long mixing times, these conclusions do not, however, preclude the possibility of accurately measuring proton–carbon cross-relaxation terms from the initial behavior of the evolution curves.[8]

Selective HOE Experiments

Our primary goal was to detect dipolar interactions between water protons and the carboxylate carbon. Fortunately, concerning the water protons, one does not have to worry about possible spin diffusion. The only problem is thus to devise a good selective excitation scheme for obtaining, in the one-dimensional mode, the equivalent of the water row in the two-dimensional diagram. This amounts also to transforming the nonselective $(\pi/2)_x(\pi/2)_{\pm x}$ pulses of the HOE 1D experiment into selective pulses. This can be done in a very simple way by using a DANTE pulse train whose phases alternate in every other experiment (Figure 1, bottom). When phases are identical for the whole train, water magnetization is effectively inverted; when phases are alternating, nothing happens to the water magnetization. The interest of this sequence lies in a very good excitation profile, since it is actually the *z* magnetization which is involved. As a matter of fact, this procedure corresponds to the recently proposed DANTE-Z technique[9] which yields a M_z profile almost free from oscillations in contrast with M_x and M_y profiles. Consequently, this method ensures not only perfect selectivity but also efficient inversion. A typical result of selective NOE buildup is shown in Figure 8.

In the case of the selective HOE experiment involving water, the Solomon equations which are recalled below (H refers to a water proton and C to the carbon-13 of the carboxylate group) strictly apply with, however, some special features.

$$\frac{dI_z{}^H}{dt} = -R_1{}^H(I_z{}^H - I_{eq}{}^H) - \sigma_{CH}(I_z{}^C - I_{eq}{}^C)$$

$$\frac{dI_z{}^C}{dt} = -R_1{}^C(I_z{}^C - I_{eq}{}^C) - \sigma_{CH}(I_z{}^H - I_{eq}{}^H) \qquad (1)$$

σ_{CH} is the cross-relaxation term between *one* water proton and the carboxylate carbon. As a consequence, $I_z{}^H$ or $I_{eq}{}^H$ represents the proton magnetization which is involved in the NOE-transfer process. Likewise, the specific proton relaxation rate $R_1{}^H$ may be unknown since only the global relaxation rate of water in the micellar solution can be determined via an independent measurement. Considering the actual experiment and its phase cycling, it is simple to derive the evolution of carbon magnetization as a function of the parameters involved in Solomon equations. We obtain

$$I_z{}^C(\tau_m)/I_{eq}{}^C = (I_{eq}{}^H/I_{eq}{}^C)(\sigma/X)(e^{\lambda_1\tau_m} - e^{\lambda_2\tau_m}) \qquad (2)$$

where

$$\lambda_{1,2} = -R_+/2 \pm X/2$$

$$X = \sqrt{R_-{}^2 + 4\sigma_{CH}{}^2}$$

with

$$R_\pm = R_1{}^C \pm R_1{}^H$$

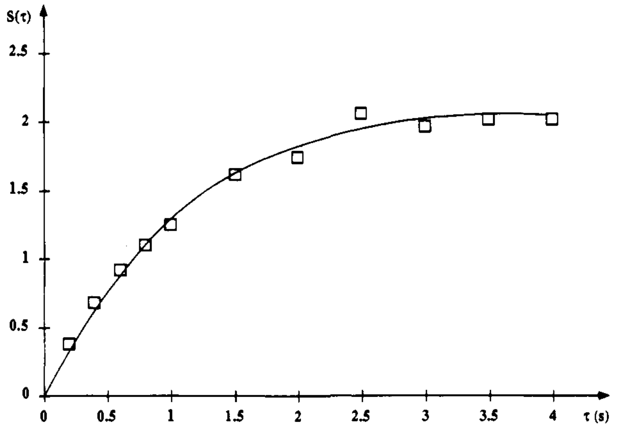

Figure 8. Experimental amplitudes (squares) of the carboxylate peak of sodium octanoate (2 M micellar solution) as a function of the mixing time τ_m upon selective inversion of the water resonance (pulse sequence of the bottom of Figure 1). The vertical scale is such that 100 corresponds to the equilibrium magnetization. The continuous curve is obtained from eq 2 with the fitted cross-relaxation rate (see text).

The relative simplicity of this equation stems from the fact that initial conditions at the beginning of the mixing period are perfectly defined.

$$I_z{}^C(0) = 0 \qquad \text{and} \qquad I_z{}^H(0) = -I_{eq}{}^H$$

Although not explicitly predicted by the above equations, it turns out that, in practice, σ_{CH} and $I_{eq}{}^H$ cannot be separated. Only their product is accessible. As shown by simulations, an interesting feature of the carbon magnetization evolution is its sensitivity to the proton specific relaxation rate $R_1{}^H$. This will be explored in the following section.

Selective NOE between Water and the Surfactant Polar Head: Results and Discussion

With reference to eq 2 and to the previous section, it can be seen that the evolution of carbon magnetization as a function of the mixing time depends on the two specific relaxation rates $R_1{}^C$ and $R_1{}^H$ and on the quantity $(I_{eq}{}^H/I_{eq}{}^C)\sigma_{CH}$. $R_1{}^C$ is easily determined from an independent measurement, whereas $R_1{}^H$ and $(I_{eq}{}^H/I_{eq}{}^C)\sigma_{CH}$ can be fitted from experimental data and eq 2. It turned out that, in all cases, the fitted value of $R_1{}^H$ was close to the value found for water in the micellar solution as obtained from an independent measurement at the proton frequency. It can therefore be concluded that the *whole water magnetization* is responsible for the NOE transfer. This ascertains rapid exchange between free and bound water, a concept which is widely recognized. From the known concentrations of both components (surfactant and water) and from the ratio of gyromagnetic ratios, it is then a simple matter to calculate $I_{eq}{}^H/I_{eq}{}^C$ and to derive the cross-relaxation term σ_{CH} (between one water proton and the carboxylate carbon). $R_1{}^H$ in eq 1 having been recognized as simply the relaxation rate of water in the micellar solution, σ_{CH} becomes finally the only quantity to be fitted from the experimental selective NOE data. Results are gathered in Table I; again an accuracy better than 5% is obtained. The values found for this cross-relaxation term remain to be interpreted, possibly in terms of distance. As is well-known, σ_{CH} can be expressed as the product of a geometrical term and a dynamical term.[10] In the limit of

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[8] Elbayed, K.; Canet, D.; Brondeau, J. *Mol. Phys.* **1989**, *68*, 295–314 and references therein.

[9] Boudot, D.; Canet, D.; Brondeau, J.; Boubel, J. C. *J. Magn. Reson.* **1989**, *83*, 428–439.

extreme narrowing, an effective correlation time τ_c stands for the dynamical term with the condition $4\pi^2\nu^2\tau_c^2 \ll 1$ (ν: measurement frequency), so that we can express σ_{CH} as

$$\sigma_{CH} = (1/2)(\gamma_H\gamma_C\hbar)^2\tau_c/r^6 \qquad (3)$$

where r is the carbon–proton distance.

From experiments performed at two different frequencies (50 and 75.5 MHz) which yield very similar results, it can be safely assumed that extreme narrowing effectively prevails. The next step, which is to evaluate τ_c, necessitates some assumptions. Formula 3 implies that the dipolar CH interaction is modulated solely by rotational motions. As a consequence, the significance of r is of "dynamical" or "average" nature since water is expected to translate rapidly within the micellar solution. Having adopted this view, we can reasonably assume that the rotational dynamics of the vector joining water to the surfactant polar head is similar to the dynamics of water itself. This assumption is further supported by the fact that water relaxation times fall in the extreme narrowing range,[11,12] just like the cross-relaxation terms investigated here, whereas surfactant relaxation parameters are strongly frequency dependent.[6] Owing to the crudeness of this model, it would be illusory to go into details of reorientation of bound water.[12] It can furthermore be pointed out that, because of the exponent 6 affecting r, a misevaluation of τ_c by a factor of 2 would entail a change in r only by about 10%. We shall therefore rely on an effective τ_c derived from relaxation of water in the micellar solution in a self-consistent manner since we are dealing with the whole water magnetization. The best choice is oxygen-17 relaxation, which is known to be exclusively intramolecular and to reliably represent rotational motion.[12] An effective τ_c can be deduced from the longitudinal ^{17}O relaxation time, which originates exclusively from the quadrupolar mechanism. From the well-known expressions of quadrupolar relaxation in the extreme narrowing range,[10] we arrive at the practical formula

$$(\tau_c)_{ps} = \frac{1056}{(\chi_{MHz})^2(T_1)_{ms}} \qquad (4)$$

where χ is the quadrupolar coupling constant. No unique value for χ can be considered; following Lankhorst et al.,[13] it can be reasonably thought to lie in the range 7.8–9.3 MHz. Calculations have been performed with these two limiting values, and r can then be deduced from eq 3 through the practical formula

$$r_{Å} = 0.51[(\tau_c)_{ps}/\sigma_{(s^{-1})}]^{1/6} \qquad (5)$$

From Table I, r is seen to lie in the range 3–3.5 Å; this is a first approach leading to a sort of "dynamical distance" between water and the micelle surface. However, such a distance is certainly hardly meaningful since it originates from all the water molecules present in the micellar solution. More sound results would be obtained by resorting to the concept of bound and free water in rapid exchange. σ_{CH} of eq 3 can then be expressed as

$$\sigma_{CH} = p\sigma_b + (1 - p)\sigma_f \qquad (6)$$

where p is the proportion of bound water, σ_b and σ_f representing cross-relaxation terms in the bound and free states, respectively. Because of the dependence of σ upon $1/r^6$, σ_f is obviously very small and eq 6 reduces to

$$\sigma_{CH} = p\sigma_b \qquad (7)$$

from which an average distance between water in the first hydration layer and the micellar surface can be deduced. Let r_b represent this quantity, which is related to r of eq 5 by

$$r_b = p^{1/6}r \qquad (8)$$

The next step is to evaluate p. This can be accomplished by measuring the self-diffusion coefficient of water in the micellar solution, D_m, which permits one to estimate p according to[16]

$$p = 1 - \frac{D_m}{D_w} \qquad (9)$$

where D_w is the self-diffusion coefficient of pure water. It can be noticed that eq 9 is valid as long as the diffusion constant of bulk water is assumed to be significantly larger than the diffusion constant of water bound to the micelle. This assumption is widely used; would it not be exactly verified, little change in the results is expected because of the exponent $^1/_6$ affecting p in eq 8. D_m/D_w is given in Table I for the three systems investigated, together with the values of r_b derived from eqs 8 and 9. In contrast with the so-called "dynamical distance", r_b is seen, in a more consistent way, to be almost constant for the three systems investigated here, namely, around 2.8 Å. To the best of our knowledge, it is the first time that this distance has been estimated. Owing to the above discussions about the effect of the different parameters involved in its determination (τ_c and p), this estimated value is thought to be significant. Of course, the extension of these measurements at lower surfactant concentrations would be of interest. For sensitivity reasons, this would require ^{13}C-enriched carboxylate groups. Such a study is under way.

Experimental Section

Surfactants are of commercial provenance (Aldrich Chemical Co.). Twice-distilled water, with a small amount of D_2O for field-frequency stabilization, was employed. Concentrations of these three components were carefully determined since they are used in the calculation of I_{eq}^H/I_{eq}^C.

NMR measurements were carried out with either a Bruker MSL 300 instrument (carbon-13 frequency: 75.5 MHz) or a highly modified[13] Bruker WP 200 instrument (carbon-13 frequency: 50 MHz). HOESY two-dimensional experiments involve 128 incremented values of t_1, with 256 scans for each experiment and a recycle time of 6 s. The dimension of the final pure absorption 2D map is 1K × 1K. Again, 256 scans and a recycle time of 6 s were used for the nonselective HOE 1D experiments.

Selective HOE experiments were carried out with a recycle time of 10 s and 2048 scans. The DANTE sequence was adjusted with the proton channel to make sure that the water signal is perfectly inverted while the $(CH_2)_\alpha$ signal is unaffected. Typically, the DANTE-Z train includes ca. 20 pulses of 2-μs duraction. For these latter experiments, the carboxylate signal amplitude was refined by a nonlinear least-squares fit applied to the free induction decay.[15] Only the amplitude was allowed to vary, the other parameters (frequency, phase, and line width) being fixed at the values of a reference spectrum. The latter is necessary for determining I_{eq}^C and is obtained with a recycle time ensuring a complete return to thermal equilibrium and with the decoupler on only during acquisition.

Self-diffusion coefficients were obtained according to a method previously published,[17] using a radio-frequency field gradient of 2 G/cm.

Acknowledgment. It is a pleasure to thank Professor B. Ancian, whose work (ref 4) has stimulated the present research. We are grateful to F. Montigny for his help in data processing and to B. Diter for technical assistance.

Registry No. Water, 7732-18-5; sodium octanoate, 1984-06-1; sodium decanoate, 1002-62-6.

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(10) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, 1961; Chapter 8.

(11) Belmajdoub, A.; Boubel, J. C.; Canet, D. *J. Phys. Chem.* **1989**, *93*, 4844–4847.

(12) Halle, B.; Carlström, G. *J. Phys. Chem.* **1981**, *85*, 2142–2147.

(13) Lankhorst, D.; Schriever, J.; Leyte, J. C. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 215–221.

(14) Retournard, A.; Brondeau, J.; Diter, B.; Canet, D. *Rev. Sci. Instrum.* **1990**, *61*, 69–76.

(15) Montigny, F.; Brondeau, J.; Canet, D. *Chem. Phys. Lett.* **1990**, *170*, 175–180.

(16) Nilsson, G.; Lindman, B. *J. Phys. Chem.* **1983**, *87*, 4756–4761.

(17) Canet, D.; Diter, B.; Belmajdoub, A.; Brondeau, J.; Boubel, J. C.; Elbayed, K. *J. Magn. Reson.* **1989**, *81*, 1–12.