Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Electrical Aspects of Adsorbing Colloid Flotation. XVIII. NMR Studies of Sodium Dodecyl Sulfate Sorbed on $Al(OD)_3$

William Abraham[a]; Thomas M. Harris[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Abraham, William , Harris, Thomas M. and Wilson, David J.(1984) 'Electrical Aspects of Adsorbing Colloid Flotation. XVIII. NMR Studies of Sodium Dodecyl Sulfate Sorbed on $Al(OD)_3$', Separation Science and Technology, 19: 6, 389 — 402
To link to this Article: DOI: 10.1080/01496398408060659
URL: http://dx.doi.org/10.1080/01496398408060659

SEPARATION SCIENCE AND TECHNOLOGY, 19(6 & 7), pp. 389-402, 1984

Electrical Aspects of Adsorbing Colloid Flotation. XVIII. NMR Studies of Sodium Dodecyl Sulfate Sorbed on $Al(OD)_3$

WILLIAM ABRAHAM, THOMAS M. HARRIS, and DAVID J. WILSON*

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Adsorption of dodecyl sulfate on $Al(OD)_3$ flocs has been studied by means of proton and ^{13}C-NMR. Spin-lattice relaxation times (T_1) of α-CH_2 and the unresolved methylene proton signals were measured in monomer, micellar, and adsorbed forms of the surfactant. These results, together with the spin-spin relaxation times (T_2) estimated from the line-widths of ^{13}C signals, indicate that dodecyl sulfate ions adsorbed on $Al(OD)_3$ flocs are more constrained in their motions than are micellar dodecyl sulfate ions, and that the binding to the floc is through the sulfate group.

INTRODUCTION

Nuclear magnetic resonance has been widely used for studying the binding of surfactants to various substrates. NMR techniques give information at the molecular level on the environments of the various nuclei and on the molecular dynamics of the system. One may hope to get insight from NMR data about (a) the extent of binding and the nature of the interactions involved in the binding of the surfactant to the substrate, (b) the segmental motion of the alkyl chain of the surfactant, and (c) the equilibrium between adsorbed and free surfactant species. Such information should prove useful in understanding the details of the process by which surfactant adsorption on precipitates, flocs, and mineral particles makes them hydrophobic and therefore separable by flotation methods.

*To whom correspondence should be addressed.

 0149-6395/84/1906-0389$3.50/0

Interaction of aliphatic sulfates and albumin has been studied by NMR (*1–3*). Oakes (*1*) studied the binding of dodecyl sulfate to bovine serum albumin by ^{1}H-NMR. Kragh-Hansen and Riisom (*3*) found that the motion of the dodecyl sulfate bound to unfolded albumin is more restricted than that in micelles from ^{13}C spin-lattice relaxation time (T_1) measurements. NMR has proved useful in studies of the binding of small molecules to macromolecules, substrate-enzyme binding (*4*), drug-receptor interactions (*5, 6*), and mutagen-DNA interactions (*7, 8*). Other more recent applications of NMR to such binding studies in biochemical systems have been reviewed by Jardetzky and Roberts (*9*). Barnet et al. (*10*) have used a new spin echo pulse sequence to determine the fraction of polymer bound at solid surfaces in aqueous and nonaqueous dispersions. Hydrogen bonding of surface-bonded amino groups in aminated silica gels was studied by measuring ^{13}C spin-lattice relaxation times (*11*). Proton NMR has provided valuable data that are sensitive to the motions of the adsorbed species (*12*). Adsorption of neopentane on graphite (*13*) and rutile (*14*) has been studied by means of ^{1}H-NMR and the reduced dimensionality of the adsorbate motions deduced from the NMR parameters. ^{13}C-NMR was used to investigate acetone adsorbed on silica gel surfaces (*15, 16*).

In the present study, adsorption of sodium dodecyl sulfate (SDS) on freshly prepared aluminum deuteroxide flocs was investigated by ^{1}H-NMR; some natural abundance ^{13}C spectra were also taken. Temperature and concentration dependences were studied. Also, three different concentrations of SDS in the absence of floc were studied—one below the critical micelle concentration (CMC), one slightly above the CMC, and the third far above the CMC. Because of the narrow range of chemical shifts in ^{1}H-NMR, our measurements of chemical shift values did not yield useful information. T_1 measurements, on the other hand, were found to be quite well suited for extracting information on the molecular dynamics of these systems.

Proton NMR experiments are easily carried out on these systems; spectra can be obtained even at low concentrations of surfactant in a relatively short period of time. One problem is that the recording of Fourier transform ^{1}H-NMR spectra in dilute solutions is hampered by the large residual solvent signal from HDO. This dynamic range problem has been overcome by several techniques (*17–20*).

EXPERIMENTAL

Aluminum deuteroxide slurries were prepared from a solution made by dissolving anhydrous $AlCl_3$ in D_2O. The pD of this solution was adjusted to

6 with 1.0 *M* NaOD solution. The desired quantity of SDS was added as a 40 g/L solution in hot D_2O, and the pD readjusted back to 6.0 by addition of 1.0 *M* D_2SO_4. The solution was stirred for 5 min and immediately transferred to 10-mm NMR tubes. The quantity of $AlCl_3$ was chosen to give a floc height in the NMR tubes of about 2.5 cm. (This was a concentration of Al in the samples of 2400 mg/L.) Much higher concentrations of Al did not give good spectra because of excessive solids in the samples and gelling, while lower concentrations gave too little floc in the region of the rf coil in the NMR probe.

The amount of SDS adsorbed was determined by analyzing the supernatant liquid for SDS by the Methylene Blue method we used earlier (*21, 22*).

Proton NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the pulsed F.T. mode at 89.55 MHz using a deuterium field frequency lock on the solvent D_2O and using 10 mm diameter sample tubes. For recording spectra, the standard WEFT $[180°\text{-}\tau(\text{HSP})\text{-}90°\text{-}T]_n$ pulse sequence was used, in which the free induction decay signal is accumulated after the 90° pulse. The interval τ is the time required for the proton signal from residual HDO to attain zero net longitudinal magnetization, during which the other proton resonances fully relax. (Although $\tau = T_1(\text{HDO}) \cdot \ln 2$ theoretically, the HDO signal did not vanish when this value of τ was used. Therefore, the value of τ was selected by trial and error for each run.) This differential relaxation is possible only when $\tau \geq 5T_1$ (sample resonances) (*17*) and when the difference between the T_1 values of the sample protons and the HDO protons is large. In the present system, typical T_1 values for sample protons are ≤ 1 s, while T_1 for the HDO signal is 15.5 s. The interval τ and the total pulse repetition time, $\tau + T_1$ are adjusted to minimize or eliminate the residual HDO solvent signal. A homogeneity spoiling pulse (HSP) was applied during a portion of the interval between the 180 and 90° pulses to eliminate the transverse magnetization before the 90° sampling pulse (*18*). A program was written to generate the above pulse sequence using the PG 200 pulse programmer. For measuring spin-lattice relaxation times T_1, this WEFT sequence was combined with the standard inversion recovery pulse sequence (*23*). Thus we used the pulse sequence $[180°\text{-}\tau\text{-}180°\text{-HSP-}t_n\text{-}90°\text{-}T]_N$, where $\tau \geq 5T_1$ (sample protons) is chosen to minimize the HDO signal, HSP is the homogeneity spoiling pulse, t_n is the variable pulse interval, T includes the data acquisition time and the delay before the next sequence, and N is the number of repetitions of the pulse sequence.

Some ^{13}C-NMR work was also carried out. Proton noise-decoupled natural abundance ^{13}C spectra were obtained on the JEOL FX-90 Q Fourier transform spectrometer operated at 22.5 MHz. Acetonitrile was used as an

internal reference to measure the ^{13}C chemical shifts. The spectral width was 5000 Hz.

RESULTS

The ^1H-NMR spectrum of SDS dissolved in D_2O shows a well-resolved triplet at 3.9 ppm downfield from tetramethylsilane (TMS) which is assigned to the α-CH_2 group. The CH_2 group β to the sulfate yields a multiplet at 1.56 ppm, and the terminal methyl shows up at 0.74 ppm. The rest of the methylene groups give a broad peak centered at 1.15 ppm. The chemical shifts for these groups in the monomer, micellar, and adsorbed forms are shown in Table 1. There are no significant changes in chemical shift values. The narrow range of ^1H chemical shifts generally, the absence of any hydrogen bonding of these protons, and the absence of aromatic rings which could cause changes in chemical shifts by changing ring current effects make this a not-surprising result.

The spin-lattice relaxation times T_1 for these samples are shown in Table 2. In some cases it was not possible to make these measurements on the terminal methyl and the α-methylene peaks. Table 3 shows the temperature dependence of T_1 for some of these samples.

Some representative proton spectra of SDS are shown in Fig. 1; these illustrate the very marked change in line shape which occurs when the surfactant is adsorbed on $Al(OD)_3$.

Figure 2 shows the natural abundance ^{13}C-NMR spectrum of a 6,000-mg/L solution of SDS after 10,000 scans. Spectral assignments have been made for dodecylsulfate by Kragh-Hansen and Riisom (*3*). They assigned the low-field resonance at 69.97 ppm to the carbon adjacent to the sulfate group.

TABLE 1
Proton Chemical Shifts of Free and Sorbed SDS at 22°C

Sample SDS concentration	Chemical shifts	
	α-CH_2	$(CH_2)_{10}$
5 m*M*	3.90	1.12
10 m*M*	3.88	1.13
100 m*M*	3.88	1.16
Floc + 70 m*M*	3.88	1.13
Floc + 59 m*M*	3.86	1.14
Floc + 47 m*M*	3.87	1.15
Floc + 23 m*M*	—	1.17
Floc + 12 m*M*	—	—

TABLE 2
T_1s of Free and Sorbed SDS at 22°C

Sample SDS concentration	% Adsorbed	T_1 (ms)	
		α-CH_2	$(-CH_2-)_{10}$
5 m*M*	—	906.9	679.7
10 m*M*	—	704.3	523.9
100 m*M*	—	650.1	380.0
Floc + 70 m*M*	39.4	420.5	364.7
		(394)	
Floc + 59 m*M*	45.6	381.1	316.1
Floc + 47 m*M*	50.0	—	267.7 (295.7)
Floc + 23 m*M*	92.7	—	270.2
Floc + 12 m*M*	>95	—	—

TABLE 3
Temperature Dependence of SDS T_1s

Sample SDS concentration	Temperature (°C)	T_1 (ms)	
		α-CH_2	$(-CH_2-)_{10}$
5 m*M*	22	906.9	679.7
	30	—	762
	40	1070	857
	50	—	916.1
	60	—	980.3
10 m*M*	22	704.3	523.9
	30	974.2	554
	40	780.3	715.7
	50	1312	913.8
	60	1888.2	1135.4
100 m*M*	22	650.1	380
	30	731.2	422.3
	40	734.4	512.7
	50	799	607.8
	60	865.3	711.9
Floc + 23 m*M*	22	—	270.2
	30	—	348.4
	60	—	371.5
	50	—	431.0
	60	—	484.2

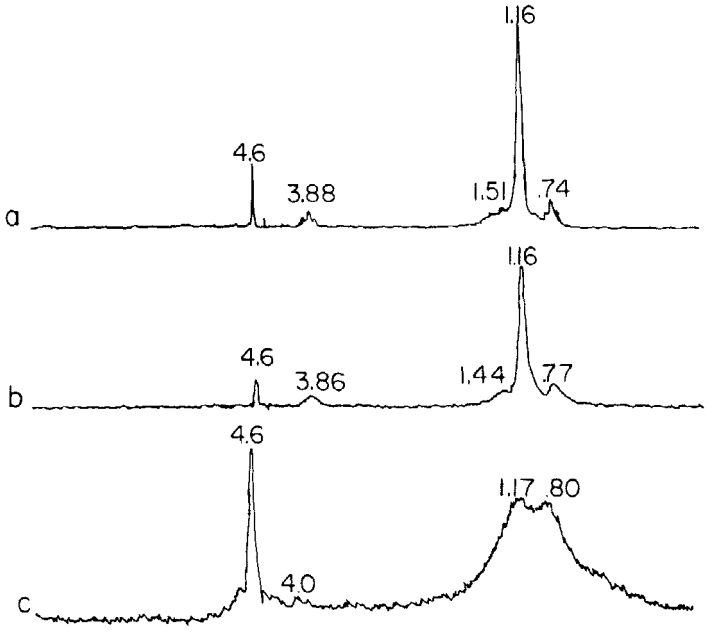

FIG. 1. Proton spectra of $Al(OD)_3$ floc and sodium dodecylsulfate. (a) No $Al(OD)_3$, 70 m*M* SDS. (b) 2.40 g Al/L; 70 m*M* SDS, of which 39.4% is adsorbed. (c) 2.40 g Al/L; 23 m*M* SDS, of which 93% is adsorbed.

Other assignments are as shown in Fig. 2. Figure 3 shows natural abundance ^{13}C spectra for three different samples, each containing 2,400 mg of Al/L as $Al(OD)_3$ floc: (a) contained 13,500 mg/L of dodecyl sulfate, (b) contained 10,000 mg/L of dodecyl sulfate, and (c) contained 6,750 mg/L of dodecyl sulfate.

DISCUSSION

Proton Chemical Shifts and Linewidths

As the surfactant goes from monomer to micellar to adsorbed form, we do not find any significant changes in chemical shifts in the proton spectrum of SDS. The narrow range of proton shifts, and the absence of hydrogen bonding of these protons or ring currents in the dodecyl sulfate ion, practically guarantee that any changes in chemical shift would be quite small.

Also, the expected small value of the anisotropy of the magnetic susceptibility tensor of $Al(OD)_3$ (which is diamagnetic) should result in a negligible contribution to the change in chemical shifts for surfactant molecules on adsorption. So we neither expect nor see any appreciable changes in chemical shifts on adsorption. The broadening of the lines on adsorption of the surfactant is sufficient to obscure any changes in chemical shift which may be taking place. The broadening of the peaks gives us some qualitative information about the changes in conditions seen by the surfactant ions. The fact that the peak corresponding to each group (α-CH_2, β-CH_2, terminal methyl) is unsplit cannot be interpreted in terms of a rate of exchange between sorbed and free surfactant ions, since the changes in the chemical shifts on adsorption are negligible.

The concentration values of SDS and $Al(OD)_3$ chosen were such that the fraction of surfactant adsorbed varied from 40% to over 95% of the added surfactant. In all the spectra the α-CH_2 peak shows the effect of adsorption most markedly. The α-methylene peak of free surfactant is a resolved triplet. For samples in which the fraction of surfactant adsorbed in less than 70%, this peak appears as an unresolved broad peak at about 3.9 ppm. For samples in which more than 70% of the surfactant is adsorbed, the α-methylene peak is broadened to the point where it can no longer be detected. Signal broadening due simply to the presence of the floc particles is very small, as seen from the HDO signal at 4.6 ppm, which is broadened only slightly compared to the SDS signals.

The other surfactant signals which occur as resolved peaks are also broadened by adsorption of the surfactant, but to a lesser extent than is the α-CH_2 peak. This can be explained qualitatively in terms of the freedom of

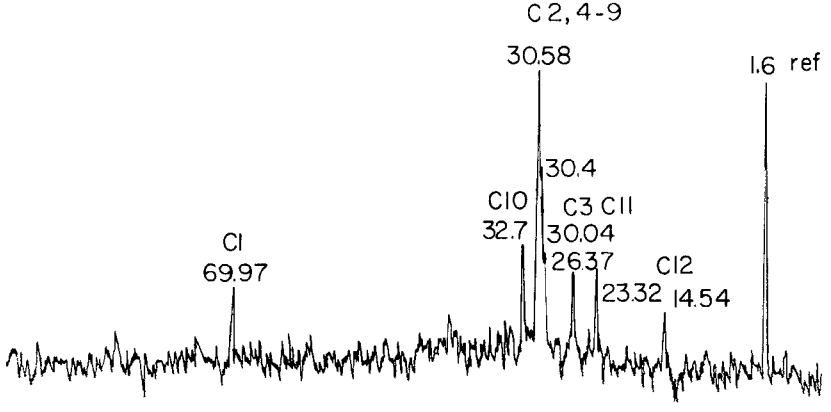

FIG. 2. Natural abundance ^{13}C-NMR spectrum of 6.00 g/L SDS in D_2O.

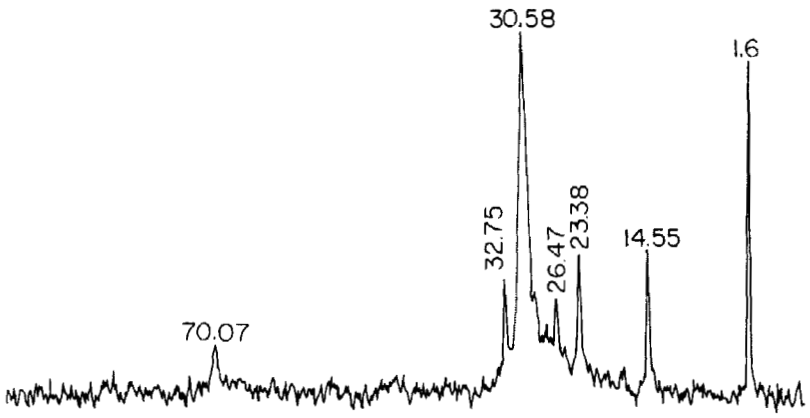

FIG. 3a. Natural abundance ^{13}C spectra of $Al(OD)_3$ floc and SDS in D_2O: 2.40 g Al/L, 13.50 g SDS/L.

motion of the various segments of the alkyl chain. The surfactant ions are presumably bound to positively charged sites on the floc by coulombic attraction of the surfactant sulfate groups. If the dipole–dipole relaxation process is the dominant relaxation mechanism (generally the case for protons), an increase in rotational correlation time τ_r will result in broader lines (*24*). τ_r will be larger for those nuclei in functional groups that are directly attached to the floc surface, and it will be smaller for protons farther

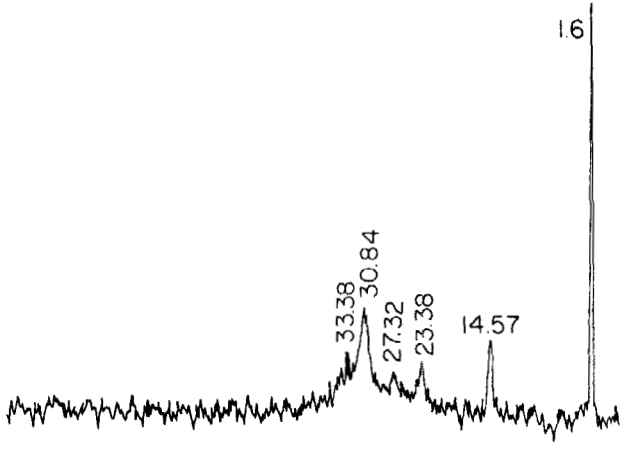

FIG. 3b. Natural abundance ^{13}C spectra of $Al(OD)_3$ floc and SDS in D_2O: 2.40 g Al/L, 10.00 g SDS/L.

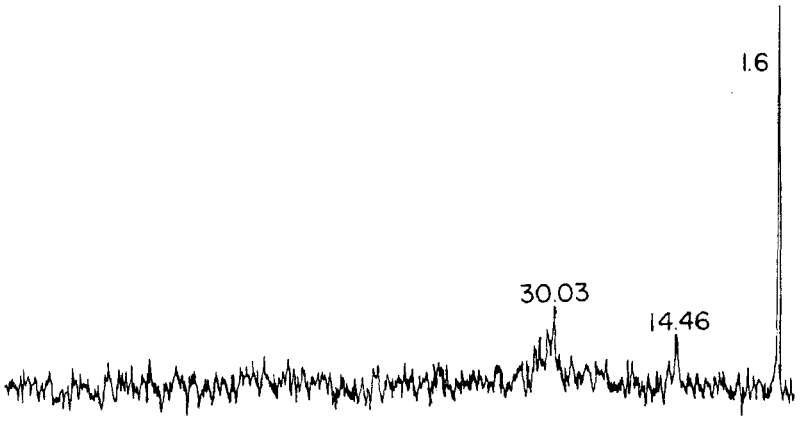

FIG. 3c. Natural abundance ^{13}C spectra of $Al(OD)_3$ floc and SDS in D_2O: 2.40 g Al/L, 6.75 g SDS/L.

away from the ionic head of the surfactant because of their greater freedom of motion.

One point of interest is the fairly abrupt change in the line shape of the large methylene peak at about 1.15 ppm. When the fraction of surfactant adsorbed is about 90% (Fig. 1c), this peak broadens very markedly and exhibits maxima at 1.17 and 0.80 ppm. When the fraction of surfactant adsorbed is greater than 95%, we find no signal from any of the surfactant protons at all at room temperature while at temperatures above 60°C faint signals appear at 1.53 and 1.15 ppm.

Proton Spin-Lattice Relaxation Times

At room temperature, as one increases the surfactant concentration from 5 m*M* (below the CMC) to 10 m*M* (somewhat above the CMC) to 100 m*M* (far above the CMC), the T_1 of the large methylene peak was found to decrease, in accordance with earlier results (*25, 26*). This is due to increased restriction of molecular motions in the surfactant as it goes from monomer to micellar form. At sufficiently high concentrations (100 m*M*), T_1 becomes still smaller, possibly due to the appearance of new micellar forms (large rodlike micelles, for example) instead of globular micelles. Formation of such rod-shaped micelles had been detected by NMR earlier (*27, 28*). As the temperature is increased, T_1 increases in all three solutions, as shown in Table 3. This is presumed to be due to the decrease in rotational correlation time τ_r as random thermal energies increase (*29*). We note, however, that the

difference in T_1 between monomer and micellar forms of surfactant decreases at higher temperatures. This may be due to a loosening of micellar structure at the higher temperatures, or to an increase in the exchange rate between monomer and micellar surfactant, or to partial breakdown of micellar structures as the temperature is increased. Room temperature T_1s for samples in which the surfactant is bound to the floc are markedly smaller than those of the unadsorbed surfactant, as shown in Table 2. And as the fraction of bound surfactant increases, T_1 decreases, a reflection of the decreased average motional freedom of the surfactant ions.

The difference in T_1s between the sample containing 100 mM SDS only and samples in which 39 or 45% of the surfactant is adsorbed on floc is larger for the α-CH_2 peak than it is for the other methylene peaks. This is in agreement with our picture of the adsorbed surfactant as bound to the floc surface by its ionic head, which would more severely restrict the motion of the α-CH_2 group than it would the motions of the other methlyenes. This would not be the case for surfactant ions in micelles in which the ionic heads are not bound to a solid surface. Also, comparison of the T_1s for the other protons indicates that the adsorbed surfactant ions are more restricted in their motions than are those in the micellar environment.

The T_1 data for the sample in which more than 90% of the surfactant is adsorbed at room temperature (Table 3) show an increase in T_1 with increasing temperature, presumably due to an increasing exchange rate with free surfactant, a shift toward monomer in the free monomer $\rightleftharpoons$ adsorbed surfactant equilibrium, and an increase in the extent of molecular motions.

Another possible reason for the drastic reduction in the T_1 for the α-CH_2 protons on adsorption is the presence of trace amounts of paramagnetic ions, probably mainly Fe, which could be coprecipitated in the $Al(OD)_3$ flocs. This would have relatively little effect on the other methylenes, which are farther away from the solid. The line broadening and hence the reduction in T_1 due to the heterogeneous nature of the floc-loaded samples appears to be of minor importance. The data in Table 4 show that partially displacing the surfactant from the floc by increasing the pD results in very substantial increases in the T_1s of all the methylene protons. This would not occur if the line broadening was simply due to the heterogeneous nature of the samples containing floc.

^{13}C Chemical Shift Data

The most obvious effect of the addition of $Al(OD)_3$ flocs on the ^{13}C-NMR spectra of SDS solutions is the broadening of the spectral lines. Comparison of Figs. 2 and 3a reveals that the different carbon resonances are affected to

TABLE 4
pD Dependence of SDS T_1s[a]

pD	% Adsorbed	T_1(ms)	
		α-CH_2	$(-CH_2-)_{10}$
6.0	40	346.3	308.6
7.5	29	356.8	358.0
8.5	19	394.3	376.4

[a]The amount of floc present in all these samples was 2400 mg/L. $T = 22°C$. Error involved in these T_1 measurements is roughly 15%.

different extents. The α-carbon peak is broadened the most, the terminal methyl carbon peak is broadened the least, and the peak of the acetonitrile standard at 1.7 ppm is affected to a negligible extent. Such selective broadening rules out the possibility that the peak broadening is caused by the heterogeneity of the floc-containing samples. The broadening of the SDS ^{13}C peaks by adsorption of the SDS on $Al(OD)_3$ indicates decreases in the spin–spin relaxation times T_2. Peak widths have been measured and T_2s estimated from these; the values of $\Delta\nu_{1/2}$ and T_2 for these lines are given in Tables 5 and 6. We note that the signal-to-noise ratios in these natural abundance ^{13}C spectra are not very favorable, and that those results should be regarded as qualitative only. The T_2 values in Table 6 are not true spin–spin relaxation times, since the line widths contain a contribution from the magnetic field inhomogeneity.

TABLE 5
^{13}C Spectra, Half-Widths of Lines for Sorbed and Free SDS[a]

	$\Delta\nu_{1/2}$ in Hz	
	Dodecyl sulfate (from Fig. 2)	Dodecyl sulfate + $Al(OD)_3$ floc (from Fig. 3a)
C1	4.92	11.95
C3	3.51	9.84
C4–9	16.16	28.11
C10	3.51	7.03
C11	5.62	9.13
C12	5.62	7.73
Reference peak	3.51	4.92

[a] $T_2 = \dfrac{1}{\pi^* \Delta\nu_{1/2}}$.

TABLE 6
^{13}C Spectra, T_2s of Lines for Sorbed and Free SDS

	DS alone		DS + $Al(OD)_3$ floc	
	$\Delta\nu_{1/2}$	T_2 (ms)	$\Delta\nu_{1/2}$	T_2
C1	4.92	64.7	11.95	26.6
C3	3.51	90.7	9.84	32.3
C4–9	16.16	19.7	28.11	11.3
C10	3.51	90.7	7.03	45.3
C11	5.62	56.6	9.13	34.9
C12	5.62	56.6	7.73	41.2
Reference peak	3.51	90.7	4.92	64.7

One interesting feature of the spectra of sorbed and free surfactant is seen by comparing Figs. 2 and 3a. Note the relative heights of the different peaks as compared to that of the terminal methyl carbon. The peak heights from carbons 1 and 3 appear to decrease relative to carbons 11 and 12 when adsorption takes place, an indication of broadening. Those carbons which are closer to the bound sulfate group are more restricted in their motion, and therefore the ^{13}C shielding tensor for them is expected to be somewhat anisotropic with respect to the magnetic field, thus reducing the intensities of the corresponding lines. It is this anisotropy which obliterates high resolution signals in the solid state. Our sorbed surfactants are not so rigidly held, so the effect is not so severe as it is in solids, and it is also felt most strongly by those carbons closest to the firmly anchored sulfate group. We note that the ^{13}C resonance of the β-carbon is overlapped by those from carbons 4 through 9.

When the fraction of surfactant adsorbed increases to 67%, the line broadening becomes greater, to the point that the peak from the α-carbon disappears. The broadening of the terminal methyl peak seen in Fig. 3b (as compared to Figs. 2 and 3a) reflects a greater contribution to the line from bound surfactant and indicates that the motion of even the terminal carbon atom is noticeably constrained. As the concentration of SDS is decreased still further, and the fraction of adsorbed molecules increases up to greater than 90%, the signals broaden to the point where the spectrum is barely visible even after 20,000 scans. We note, however, that the terminal methyl group's line (at 14.46 ppm) is one of the last features visible, presumably due to its being more mobile than the carbons closer to the binding site.

In the absence of ^{13}C-enriched surfactants, it is not possible to make any quantitative measurements of T_1s due to the prohibitively large amount of instrument time required to measure T_1s at these low ^{13}C concentrations.

CONCLUSIONS

Proton and ^{13}C-NMR data indicate that dodecyl sulfate ions adsorbed on $Al(OD)_3$ flocs are more constrained in their motions than are micellar dodecyl sulfate ions, and that motional constraints decrease as one moves away from the ionic head of the surfactant species. This supports the model in which the ionic head of the surfactant is bound to a site on the floc.

Acknowledgment

This work was supported by a grant from the National Science Foundation.

REFERENCES

1. J. Oakes, *Eur. J. Biochem., 36,* 553 (1973).
2. N. Muller and R. J. Mead, *Biochemistry, 12,* 3831 (1973).
3. U. Kragh-Hansen and T. Riisom, *Eur. J. Biochem., 70,* 15 (1976).
4. D. P. Hollis, *Biochemistry, 6,* 2080 (1967).
5. J. J. Fischer and O. Jardetzky, *J. Am. Chem. Soc., 87,* 3237 (1965).
6. O. Jardetzky, *Mol. Pharmacol., 1,* 214 (1965).
7. D. J. Blears and S. S. Danyluk, *Biopolymers, 5,* 535 (1967).
8. B. H. Arison and K. Hoogsteen, *Biochemistry, 9,* 3976 (1970).
9. O. Jardetzky and G. C. K. Roberts, *NMR in Molecular Biology*, Academic, New York, 1981.
10. K. G. Barnet, T. Cosgrove, B. Vincent, and D. S. Lissons, *Macromolecules, 14,* 1018 (1981).
11. S. Shinoda and Y. Saito, *J. Colloid Interface Sci., 89,* 293 (1982).
12. J. Tabony, *Prog. Nucl. Magn. Reson. Spectrosc., 14,* 1 (1980).
13. J. Tabony and J. W. White, *Mol. Phys., 40,* 1209 (1980).
14. J. Tabony and S. J. Roser, *Ibid., 44,* 329 (1981).
15. T. Bernstein, D. Michel, and N. Pfeifer, *J. Colloid Interface Sci., 84,* 310 (1981).
16. V. Y. Borovkov, A. V. Zaiko, and V. B. Kazarsky, *J. Catal., 75,* 219 (1982).
17. S. L. Palt and B. D. Sykes, *J. Chem. Phys., 56,* 3182 (1971).
18. F. W. Benz, J. Feeney, and J. C. K. Roberts, *J. Magn. Reson., 8,* 114 (1972).
19. A. G. Redfield and R. K. Gupta, *J. Chem. Phys., 54,* 1148 (1971).
20. T. Inubushi and E. D. Becker, *J. Magn. Reson., 51,* 128 (1983).
21. M. C. Rand et al. (eds.), *Standard Methods for the Examination of Water and Wastewater*, 14th ed., American Public Health Association, 1976, p. 600.
22. J. E. Kiefer, P. C. Sundareswaran, and D. J. Wilson, *Sep. Sci. Technol., 17,* 561 (1982).
23. R. Freeman and H. D. W. Hill, *J. Chem. Phys., 54,* 301 (1971).
24. A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, London, 1961.

25. E. J. Staples and G. J. Tiddy, *J. Chem. Soc., Faraday Trans., 1,* 2530 (1979).
26. N. Nery and D. Canet, *J. Colloid Interface Sci., 77,* 174 (1980).
27. E. Williams, B. Sears, A. Allerhand, and E. H. Cordes, *J. Am. Chem. Soc., 95,* 4871 (1975).
28. K. Kalyanasundaram, M. Gratzel, and J. K. Thomas, *Ibid., 97,* 3915 (1975).
29. N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev., 73,* 679 (1948).

Received by editor February 27, 1984