CHEMISTRY LETTERS, pp. 599-602, 1977. Published by the Chemical Society of Japan

^{1}H-NMR STUDY OF AEROSOL OT IN SOLUTION

Masaharu UENO, Hiroshi KISHIMOTO, and Yoshimasa KYOGOKU*
Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuho-ku, Nagoya 467
* Institute for Protein Research, Osaka University, Suita, Osaka 565

The solution states of Aerosol OT were studied by ^{1}H-NMR measurements. In water two hydrocarbon chains of Aerosol OT molecules in monomeric state aggregate with each other with hydrophobic interactions as in micellar state.

Aerosol OT(sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethane-sulfonate, Fig.1) is one of the typical anionic surfactants and it dissolves both in aqueous and organic solvents.$^{1)}$ It has a bulky hydrocarbon part containing two main chains and side chains and offers an interesting subject from a conformational point of view. NMR studies have been reported on surfactant solutions$^{2)}$, but only a few reports refer to conformation or environment differences between solvents.$^{3)}$ In this paper the solution states of Aerosol OT in aqueous and organic solvents were studied by means of ^{1}H-NMR measurements and compared with each other.

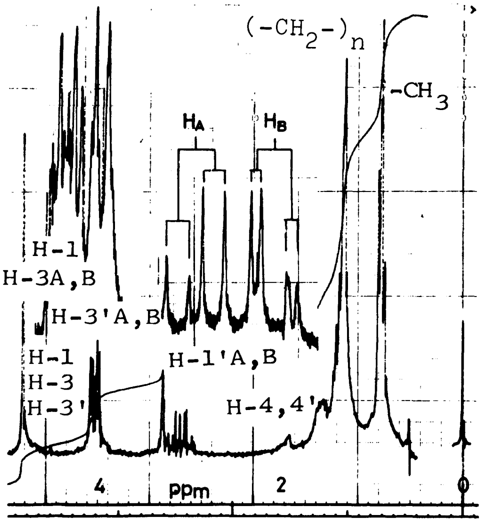


Fig. 2. The 220-MHz proton magnetic resonance spectra of Aerosol OT in the methanol-d$_4$ solution at 25^{o}C.

(1) ^{1}H-NMR spectra: The ^{1}H-NMR spectra were recorded on a Varian HR-220 spectrometer and JEOL PFT-100 pulse Fourier transform NMR spectrometer. In Fig. 2, the 220-MHz NMR spectra of Aerosol OT in methanol-d$_4$ were shown and assigned on the basis of relative signal areas, spin-spin decoupling experiments and general considerations of electron shielding.

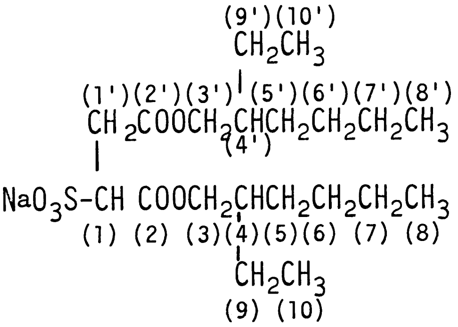


Fig. 1. Chemical structure of Aerosol OT

(2) Chemical shift: chemical shifts were measured

Table I. Chemical Shifts (in ppm Relative to TMS) of the Proton Magnetic Resonance Spectra of Aerosol OT.

	CD_3OD	$CDCl_3$	D_2O*	D_2O**
H-1	4.05	4.40	0.33	4.10
H-1'A	3.14	3.25	-0.60	3.17
H-1'B	2.99	3.16	-0.71	3.06
H-3A,B	4.05	4.14	0.33	4.10
H-3'A,B	3.97	4.01	0.25	4.02
H-4,4'	1.52	1.55	-2.23	1.54
$(-CH_2-)_n$	1.28	1.26	-2.50	1.27
$-CH_3$	0.88	0.89	-2.89	0.88

* In ppm relative to dioxane.

** Values correlated to make the values of CH_3 group in D_2O coincide with that in CD_3OD.

Table II, Micelle Formation Shifts (in Hz at 100 MHz) of Aerosol OT in $CDCl_3$ and D_2O.

	D_2O	$CDCl_3$
H-1	3.4	-8
H-1'A,B	3.1	-4
H-3A,B	3.4	-4
H-3'A,B	6.2	-4
$(-CH_2-)_n$	1.1	0
$-CH_3$	-2.0	0

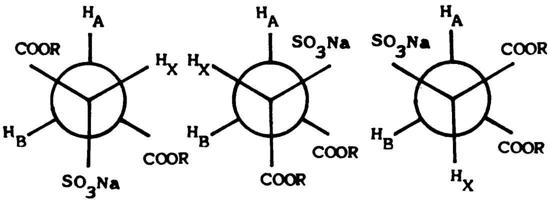
relative to the internal standard, i.e. TMS in organic solvents or dioxane in aqueous solvent and collected in Table I. The concentrations of Aerosol OT were 0.1 M in methanol and chloroform and 0.023 M in water. At these concentrations, a large part of Aerosol OT exists in a micellar state in chloroform and water with a very small amount of monomers in equilibrium,4,2-d) and all of Aerosol OT exist in a monomeric state in methanol.5) As shown in Table I, the lower field shift of methine proton H-1 in chloroform than in other solvents can be presumably attributed to the association of Aerosol OT with the polar head group. The chemical shifts were different between in a micellar state and in a monomeric state. Monomer and micellar chemical shifts were obtained as the extrapolated intercepts in plots of observed chemical shift vs. solute concentration and its reciprocal, respectively. We define the micelle formation shift as the difference of above values. In Table II, the micelle formation shifts were given with the sign given in the direction of high-field shift. In chloroform, low-field shifts were observed at micelle formation and the shift value was larger as the corresponding proton is located near the polar group, which can be presumably attributed to the aspect that the association of molecules by polar groups provides the more polar environment near the polar head. On the contrary, in water, high-field shifts for all plotons except for the methyl protons were observed. The micelle formation in water, generally, provides nonpolar environment around the molecules. A large micelle-formation shift of methylene protons H-3' can be presumably attributed to the following cause: In the monomeric state, the protons H-3' exist in polar environment with the exposure to the solvent and the hydration of carbonyl group near the protons H-3', while in the micellar state, the protons and carbonyl group exist in nonpolar environment in the micellar core.

(3) Spin-spin coupling constants: The values of the geminal and vicinal coupling constants, J_{AB}, J_{AX} and J_{BX} in the $CH-CH_2COOR$ (see in Fig. 3) fragment in methanol , chlo-

Table III. Geminal and Vicinal Coupling Constants of H-1' and H-1 (in Hz).

	J_{AB}	J_{AX}	J_{BX}
CD_3OD	17.2	12.2	3.8
CD_3Cl_3	18.6	8.9	6.1
D_2O	17.3	13.3	3.6

A and B correspond to two protons of methylene (H-1'), X methine proton (H-1).



(1) (2) (3)

Fig. 3. Rotational isomers about the C-C bond in the $CH-CH_2$ COOR fragment.

roform and water, were given in Table III. In methanol and water, the analysis of the values of J_{AX} and J_{BX} suggests that H_A, which is tentatively postulated to be in a lower field of H_A and H_B, is in a trans position with H_X, and H_B in a gauche position, i.e. the conformation of (3) in Fig. 3 is maintained. In this case, the hydrocarbon chains are in a gauche position with each other. On the other hand, in chloroform, the values of J_{AX} and J_{BX} indicate that they are the average values by the rapid exchange of conformations. If it is assumed that rotamers (1), (2) and (3) in Fig. 3 represent the minimum-energy staggered conformations for rotation about the C-C bond in the $CH-CH_2COOR$ fragment, the fractional populations $P_{(1)}$, $P_{(2)}$ and $P_{(3)}$ can be calculated from Eq. (1), (2) and (3), by measuring the average vicinal coupling constants, J_{AX} and J_{BX}.

$$J_{AX} = P_{(1)}J^{(1)}_{AX} + P_{(2)}J^{(2)}_{AX} + P_{(3)}J^{(3)}_{AX} \qquad (1)$$

$$J_{BX} = P_{(1)}J^{(1)}_{BX} + P_{(2)}J^{(2)}_{BX} + P_{(3)}J^{(3)}_{BX} \qquad (2)$$

$$P_{(1)} + P_{(2)} + P_{(3)} = 1 \qquad (3)$$

where $J^{(1)}_{AX}$, $J^{(2)}_{AX}$, --- and $J^{(3)}_{BX}$ are the values of the vicinal coupling constants in individual rotamers and these values were calculated from Eq. (4) with the mean coefficients adopted by Abraham$^{6)}$ and Tori et al.$^{7)}$.

$$J_{vic} = 14.3 \cos^2\phi \ (90^\circ \le \phi \le 180^\circ) \text{ or } 12.4 \cos^2\phi \ (0^\circ \le \phi \le 90^\circ) \qquad (4)$$

Solving simultaneously Eq. (1), (2) and (3), we get $P_{(1)} = 0.3$, $P_{(2)} = 0.2$ and $P_{(3)} = 0.5$. Then it is clear that in chloroform the hydrocarbon chains in the gauche positions (2), (3) and in the trans position (1) rapidly exchange in conformation with each other with the populations calculated above. But in these discussions was tacitly postulated the assignment of H_A and H_B, which was necessary to distinguish between rotamers (1) and (3). The experimental assignment of H_A and H_B can be made with difficulty by the selective deuteration. However, the above postulation can be considered to be valid by the consideration of following aspects. (I) In the micellar state in water, where hydrocarbon chains exist in the micellar core, it is not possible from a sterically hindered view point that two hydrocarbon chains are kept in a trans position with each other. (II) From a ^{13}C-NMR measurement of Aerosol OT, it was found that in micellar state in water the influence of shift reagent on carbonyl carbons C-2 and 2' are almost the same in quantity with each other.$^{8)}$ This observation could not be accounted for by the conformation (1) but (3).

The concentration dependence of the vicinal coupling constants, J_{AX} and J_{BX}, in water were given in Table IV. The difference of the values by about 1 Hz between the measurements at 100 MHz and 220 MHz could be attributed to the error due to the overlap of the signals at 100 MHz. As shown in Table IV, the values of J_{AX} or J_{BX} above c.m.c. (2.5×10^{-3} M) and below c.m.c. are almost the same. From this observation it was concluded that in monomeric state H_A and H_X are almost kept in trans position with each other and H_B and H_X in a gauche position. This conclusion suggests that the hydrocarbon chains are in a gauche position and then supports the presumption, i.e. the agglomeration of two hydrocarbon chains, based on the analysis of the heat capacity difference accompanying micelle formation,$^{4)}$ which is very interesting from the view-point of the intra-molecular association with hydrophobic interactions.

Table IV. Concentration Dependence of Vicinal Coupling Constants of H-1 and H-1' (in Hz).

J_{AX}	J_{BX}	concentration $\times 10^3$ (mol l^{-1})
12.3 (13.3)	4.7 (3.6)	23
12.4	4.6	12
12.6	5.5	4
11.6	5.9	2.3
12.1	5.7	2.2
12.1	5.7	2.0

( ) : The values obtained from the 220-MHz NMR measurements.

The others: From the 100-MHz NMR measurement.

References

1) H. Kishimoto and M. Ueno, Yakugaku Zasshi, 94, 1408 (1974).

2) a) H. Inoue and T. Nakagawa, J. Phys. Chem., 70, 1108 (1966); b) J. Clifford and B.A. Pethica, Ttans. Faraday Soc., 61, 182 (1965); c) F. Podo, A. Ray, and G. Némethy, J. Am. Chem. Soc., 95, 6164 (1973); d) M. Ueno, H. Kishimoto, and Y. Kyogoku, Bull. Chem. Soc. Jpn., 49, 1776 (1976). e) References cited there in.

3) O. A. ElSeoud, E. J. Fendler, J. H. Fendler, and R. T. Medary, J. Phys. Chem., 77, 1876 (1973).

4) Y. Sato, M. Ueno, and H. Kishimoto, Yakugaku Zasshi, 95, 1286 (1975).

5) A. Kitahara, T. Kobayashi, and T. Tachibana, J. Phys. Chem., 66 363 (1962).

6) R. J. Abraham, Mol. Phys., 5, 513 (1962).

7) K. Tori, K. Kuriyama, and E. Kondo, Tetrahedron Letters, 1963, 1485.

8) M. Ueno, H. Kishimoto, and Y. Kyogoku, J. Colloid Sci., submitted for publication.

(Received January 27, 1977)