Colloid Polym Sci 276:1125–1130 (1998)
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ORIGINAL CONTRIBUTION

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Hydrocarbon chain packing in the micellar core of surfactants studied by ^{1}H NMR relaxation

Received: 10 March 1998
Accepted: 19 June 1998

Project supported by National Climbing Project (B) "The Fundamental Research of Alkali-Surfactant-Polymer Flooding for Enhanced Oil Recovery"

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Abstract ^{1}H NMR spin–lattice and spin–spin relaxation of different types (cationic cetyltrimethyl ammonium bromide, anionic sodium dodecyl sulfonate and nonionic Triton X-100) of surfactants in water solution were studied. Simulation of the decay curves of proton relaxation shows that the spin lattice relaxation of all the samples exhibits exponentially, while the spin–spin relaxation for several protons on the hydrophobic chains forming the micellar core is bi-exponential. The fast relaxing component is attributed to the part of the segments of the hydrophobic chain, situated near or on the surface of the micellar core, while the slower relaxing component is attributed to the rest part staying in the interior. The latter exchanges with the former in equilibrium. Thus, a part of each certain segment of the hydrophobic chain has an opportunity to stay in the surface layer of the micellar core and spend some time on the interface experiencing hydrophilic environment. Generally, the protons on the methylene carbon of the hydrophobic chain nearest to the polar head have more chance to spend time in the hydrophilic environment. However, it seems to be dependent on the chemical structure of the surfactant molecule. Large size of the polar group of CTAB shows steric hindrance on the packing of the hydrophobic chain. Quantitative results are given. The fact, that the fraction of slow relaxing protons on the hydrophilic ethylene oxide long chain of Triton X-100 dominates over that of fast relaxing protons, and that their T_2 values are larger than those of the protons on the hydrocarbon chain in the interior of the micellar core, suggests that the ethylene oxide chain does not participate in the formation of the micellar core.

Key words ^{1}H NMR spin–spin relaxation – micelle – Triton X-100 – sodium dodecyl sulfonate – cetyl trimethyl ammonium bromide – chain packing

Introduction

It is well known that surfactants are widely used as detergents, solubilizers and emulsifiers in scientific research and various industries. These surfactant molecules undergo self-association in water solutions forming aggregates, micelles, above a certain concentration, cmc (critical micellar concentration). The structure and dynamic property of the surfactant micelles play an important role in their use. It is accepted that the micelles consist of an interior core, in which the hydrophobic hydrocarbon chains are packed, and an exterior part, having the polar groups surrounding it. This allows the micelle to have contact with the water medium. Studies of aggregation of surfactants in water are numerous, both theoretical and experimental [1, 2], even by different NMR techniques since the seventies [3–18]. It was assumed that the hydrophobic chains embedded in the interior core move freely as if they were in the hydrocarbon liquid. However, this feature of micelles deserves further study. The aim of this study is to obtain a relatively quantitative description of the dynamic motion of the individual molecular segments of surfactants in water solutions by ^{1}H NMR spin–spin relaxation.

Experimental

Cetyl trimethyl ammonium bromide (CTAB) is analytical grade reagent produced by Jining Institute of Chemical Engineering of China, sodium dodecyl sulfonate (SDSN) is of chemically pure grade of Yongjia Fine Chemical Plant of China and Triton X-100 is the chemical pure reagent of Nailai Company of Japan. D_2O is produced by Beijing Chemical Factory of China. Concentration of the solutions are expressed by times of cmc of the surfactants. Cmc of SDSN, CTAB and Triton X-100 are 9.7 [19], 0.92 [20] and 0.30 [20] mM, respectively, T_1(spin–lattice) and T_2(spin–spin) NMR relaxation time measurements were performed on Bruker ARX-500 with a ^{1}H frequency of 500.13 MHz, using inversion recovery and CPMG pulse sequences, respectively, at 40 °C for SDSN solution and 25 °C for the other two surfactants. 16 accumulations were acquired generally, but for very dilute solutions number of accumulations was increased up to 256 · D_2O (99.5%) was used as solvent instead of water in order to weaken the water signal. Meanwhile, presaturation method was used to further suppress the proton signal of the solvent.

Results and discussion

It is well known that surfactants either ionic or nonionic form micelles in water solution at concentrations above a certain value, cmc (critical micellar concentration). The structure and dynamic motion of these micelles received much attention. Efforts have been made to elucidate this aggregation state, by various methods as stated above, including ^{1}H, ^{13}C, ^{15}N, ^{14}N and ^{2}H NMR spin lattice relaxation methods [11–14]. Since a nucleus of spin-1/2 in a liquid will experience a fluctuating field, due to the magnetic moments of nuclei in other molecules as they execute Brownian motion, the general requirement of spin lattice relaxation is a magnetic dipole–dipole interaction fluctuating at the resonance frequency. This interaction may be modulated by molecular tumbling (affect the intermolecular and intramolecular interactions) or by translational diffusion (intermolecular interactions). Tumbling motion of surfactant molecules comprised micelles is restricted therefore translational diffusion between the segments of the long hydrophobic chain is dominant. However, spin lattice relaxation is most efficient to local frequency motions, while proton spin–spin relaxation is sensitive to the slower translational diffusion of the long molecular chain, thus provides information about motions in a wide range of frequencies. The dependence of this intermolecular interaction upon the distance d between two nuclei is known to be proportional to d^{-3}, and it is also related to the motion of molecular chains. The smaller the distance between protons, i.e. the higher the density of protons, the stronger the interaction of the proton–proton dipolar coupling, the slower the motion of the molecular chains and, thus the smaller the T_2 value. Therefore, T_2 value of protons can be a measure of the distribution of protons in the space. The shorter the T_2, the closer or denser the identical protons. A knowledge of the T_2 of different segments on the hydrophobic chain will help to construct a picture of chain packing in the micellar core.

In a previous paper we have measured proton T_1 and T_2 of surfactants in water solution at a wide range of concentrations from lower to higher than cmc and have shown that T_2/T_1 value of Triton X-100 in dilute solutions is about unity, while in solutions with concentrations above cmc, all of T_2/T_1 of the protons of the hydrophobic chains in the micellar interior are smaller than 0.5 [21]. This value is even smaller than 2/3, which corresponds to T_1 minimum of the $\log T_1/\log \tau_c$ curve (dependence of T_1 on the correlation time for relaxation by isotropic random magnetic fields). Such circumstances generally occur for macromolecules in solutions [22]. This shows that the motion of these hydrocarbon chains is in the regime far away from the extreme narrowing condition of liquid hydrocarbon.

Further examination of the raw data of spin–spin relaxation by simulation of the decay curves shows that most of them exhibit bi-exponential behavior for solutions at concentrations higher than cmc, although spin–spin relaxation of these protons behaves exponentially in dilute solutions where aggregation of the surfactant molecules does not occur. Figure 1A and B shows typical simulations for phenyl proton of Triton X-100 in water solution at two different concentrations of 5 times and 0.5 times cmc, respectively. Dotted lines stand for exponential decay simulation. Solid line stands for bi-exponential simulation according to the following equation:

$$M(t) = M(0)[W_f \times \exp(-t/T_{2f}) + W_s \times \exp(-t/T_{2s})] ,$$

where $W_f + W_s = 1$, they stand for the fractions (weighting factors) of fast and slow relaxing protons, respectively,

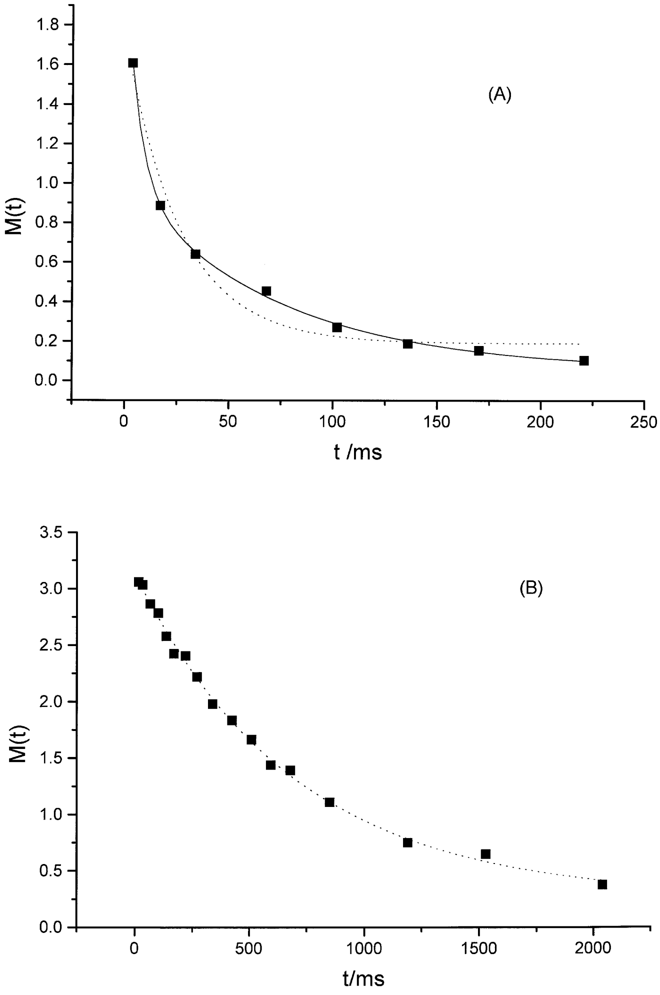

Fig. 1 Simulation of ^1H spin–spin relaxation process for proton on the phenoxy ring of Triton X-100 in solution at concentration of 5 times cmc (A) and 0.5 times cmc (B). Points are experimentally measured, solid line is the curve calculated by bi-exponential simulation, dotted lines are those calculated by exponential simulation

and T_{2f} and T_{2s} are the corresponding spin–spin relaxation times. It is obvious that the dotted curve (exponential decay) does not fit the experimental points for solution at concentration higher than cmc, but the solid bi-exponential curve fits well. Figure 1B shows that exponential simulation of the same proton at concentration of 0.5 cmc fits well the experimental data. This is because the Triton X-100 molecules are in the mono-molecular state at concentration below cmc. Simulation results are listed in Table 1 for anionic SDSN at concentrations higher and lower than cmc, in Table 2 for cationic CTAB and in Table 3 for non-ionic triton X-100.

Sodium dodecyl sulfonate

It is obvious from Table 1 that T_2 of protons on the α- and β-carbon atoms to the SO_3^- group in SDSN consists of two components, one of several (3–6) ms and the other of hundreds of ms. It is worth noting that the short T_2 component has a very high weighting factor of more than 98% and the long one is almost negligible. However, as the methylene protons go further along towards the hydrophobic end the T_2 value of the fast relaxing component becomes longer and its weighting factor smaller. For example, the T_2 value of the fast relaxing component increases from several (3–6) ms for protons at α- and β-positions to several tens of ms for protons on the γ-carbon, the corresponding weighting factor decreased to about 25%. The extreme weakening of the bi-exponential behavior of the T_2 relaxation occurs with the methyl protons on the end of the hydrocarbon chain, which exhibits exponential decay. Since T_2 value can be a measure of the distance between identical protons, i.e. the density of protons in the space, we can assign the fast relaxing component to the dense state and slower relaxing one to the relatively loose state. Hydrocarbon chains constrained in the micellar core

Table 1 ^1H spin–spin relaxation parameters of sodium dodecyl sulfonate at various concentrations

Concentration[a] [cmc]	Relaxation parameters	Chemical formula of SDSN					
		SO_3^-	$-CH_2$	$-CH_2$	$-CH_2$	$-(CH_2)_8$	$-CH_3$
10	T_{2f} (ms)		5	4	51	129	–
	W_f (%)		99	98	22	3	–
	T_{2s} (ms)		176	374	413	451	751
	W_s (%)		1	2	78	97	100
5	T_{2f} (ms)		3	4	28	275	–
	W_f (%)		97	98	28	22	–
	T_{2s} (ms)		27	403	404	493	735
	W_s (%)		3	2	72	78	100
0.2	T_2 (ms)		159	626	826	1040	1300

[a] Concentration in terms of times of critical micellar concentration. T_{2f}, T_{2s}, W_f and W_s are fast and slow relaxation times and their weighting factors, respectively.

Table 2 ^{1}H spin–spin relaxation parameters of cetyl trimethyl ammonium bromide at various concentrations

Concentration[a] [cmc]	Relaxation parameters	Chemical formula of CTAB $(CH_3)_3$–N^+	–CH_2	–CH_2	–CH_2	–$(CH_2)_{12}$	–CH_3
10	T_2 (ms)	309	–	–	–	–	–
	T_{2f} (ms)	–	36	153	145	159	–
	W_f (%)	–	89	100	84	69	–
	T_{2s} (ms)	–	142	–	255	317	467
	W_f (%)	–	11	–	16	31	100
5	T_2	278	–	–	–	–	–
	T_{2f} (ms)	–	51	162	128	125	–
	W_f (%)	–	62	100	64	35	–
	T_{2s} (ms)	–	142	–	217	259	490
	W_s (%)	–	38	–	36	65	100
0.2	T_2 (ms)	361	297	349	323	453	643

[a] Concentration in terms of times of critical micellar concentration. T_{2f}, T_{2s}, W_f and W_s are fast and slow relaxation times and their weighting factors, respectively.

Table 3 ^{1}H spin–spin relaxation parameters of triton X-100 at various concentrations

Concentration[a] [cmc]	Relaxation parameters	Chemical formula of Triton X-100 HO CH_2CH_2	$(OCH_2CH_2)_8$	OCH_2	CH_2O			$C(CH_3)_2$	CH_2	$C(CH_3)_3$
10	T_{2f} (ms)	11	11	8	9	11	10	9	9	10
	W_f (%)	21	24	50	56	57	55	65	69	35
	T_{2s} (ms)	345	314	59	60	95	117	76	58	157
	W_s (%)	79	76	50	44	43	45	35	31	65
	T_2/T_1	0.6	0.5	0.1	0.1	0.1	0.1	0.1	0.1	0.4
5	T_{2f} (ms)	11	11	10	9	7	10	9	8	7
	W_f (%)	18	24	52	57	54	52	62	67	37
	T_{2s} (ms)	384	313	92	101	73	112	82	69	191
	W_s (%)	82	76	48	43	46	48	38	33	63
	T_2/T_1	0.5	0.5	0.2	0.1	0.1	0.1	0.2	0.1	–
0.2	T_2 (ms)	649	–	545	538	973	1128	317	362	585
	T_2/T_1	1.0	–	1.0	1.1	–	1.1	0.8	1.0	1.1

[a] Concentration in terms of times of critical micellar concentration. T_{2f}, T_{2s}, W_f and W_s are fast and slow relaxation times and their weighting factors, respectively. T_2/T_1 was calculated by using T_2 values given by the spectrometer (single exponential decay).

have considerable freedom of movement and undergo conformational and orientational changes. Accordingly, W_f represents the probability for the methylene protons to form a dense surface layer on the micellar core protecting the penetration of water into the hydrophobic interior and W_s for methylene protons to stay in the interior of the micellar core. A relatively quantitative picture of chain packing in the micellar core can be obtained. Forming the micelle almost all (more than 98%) of the α- and β-methylene groups stay in the surface layer of the micellar core. They spend almost all of the time in a hydrophilic environment. The further the methylene group goes away from the SO_3^- group the less its probability to stay in the interface. The methyl group at the end of the hydrocarbon chain has no opportunity to spend time in the hydrophilic environment, although its motion is in the regime for macromolecular solutions far away from the extreme narrowing condition for liquid hydrocarbon.

Cetyl trimethyl ammonium bromide

Similar but considerably different picture was obtained for cationic CTAB. For the α-methylene protons to the N^+ polar head the T_2 decay curve exhibits bi-exponentiality with a T_2 value of 36 ms and a weighting factor of 89% for the fast relaxing component. They are considerably longer and smaller, respectively, than those of the fast relaxing component in the case of SDSN. The decay curve of β- methylene protons is almost exponential with a T_2 value of 153 ms, somewhat the same as that of the slow relaxing component of the α- methylene protons (142 ms), but the same as that of the fast relaxing protons of the γ-methylene protons (145 ms). These intermediate β-methylene protons should be considered as relaxing fast in comparison with the case of SDSN, where almost all (99–98%) of the protons attached to the two carbon atoms nearest to the polar head relax fast. Similarly, the

γ-methylene protons have T_2 value of 128–145 ms and weighting factors of 64–84% for the fast relaxing component and 217–255 ms and 36–16% for the slow relaxing component, respectively. W_s (the fraction of slow relaxing protons) increases as the methylene groups go further towards the end of the hydrocarbon chain. Finally, the methyl protons at the end of the chain relax exponentially with a T_2 value of 467–490 ms, which is shorter than that of the methyl protons (643 ms) at concentrations lower than cmc (mono-molecular state). The three methyl groups attached to N^+ relax exponentially with a T_2 value slightly shorter than that in the mono-molecular state.

The above results suggest that the three methyl groups attached to the N^+ are situated in the exterior of the micellar core. Part of the α-, all of the β- and a considerable part of the γ-methylene groups have the probability of staying in the surface layer of the micellar core. The other methylene groups further from the polar head have less opportunity to spend time in the hydrophilic environment. The difference in chain packing between CTAB and SDSN is that only a part of the α-methylene protons (weighting factor less than 90%), but one hundred percent of β-methylene protons stay in the interface. Besides, the density of protons in the surface layer of the micellar core is lower ($T_2 = 36$ and 153 ms for the fast relaxing component of the α- and β-methylene protons) than that in the case of SDSN ($T_2 = 5$ and 4 ms, respectively). This can probably be attributed to the steric hindrance produced by the three methyl groups attached to the polar head and may be the reason for easy transformation of micelle shapes of tetra-alkyl ammonium salts.

Triton X-100

Simulation of the ^{1}H spin–spin relaxation decay curve for non-ionic surfactant Triton X-100 gave interesting information about the dynamic structure of its micelles. In contrast to the case of SDSN and CTAB, spin–spin relaxation of all of the protons exhibit bi-exponential behavior with a short T_2 value of about 10 ms for all protons in the molecule at concentrations higher than cmc. However, the weighting factor of the fast relaxing component and the T_2 value of the slower relaxing component differ for protons at different positions on the molecular chain. The fast relaxing component of the di-methyl protons (with T_2 value of 9 ms) and the methylene protons (with T_2 value of 9 ms) nearest to the phenoxy ring has the highest weighting factors of 65 and 69%, respectively. The fast relaxing component of the *meta*- and *ortho*-protons on the phenoxy ring and the protons on the first ethoxy group right next to the phenyl ring have slightly lower weighting factors of 55, 57, 56 and 50%, respectively. In contrast to the case of SDSN and CTAB the trimethyl protons at the end of the hyrdophobic chain relax bi-exponentially, with a weighting factor of the fast relaxing component ($T_2 = 10$ ms) of 35–37%, i.e. a part of the end methyl group has the probability to spend time in the hydrophilic environment. This might be due to the less flexibility of the branched hydrophobic chain making the packing of the chain difficult to form a thin rigid layer on the surface of the micellar core. The farther the ethoxy protons from the phenoxy ring, the lower the weighting factor of the fast relaxing component. It decreases to 24% for protons at the intermediate positions, and finally, to 18% for the end ethoxy methylene protons.

The highest weighting factor of the fast relaxing component occurs for the protons of the dimethyl group next to the phenoxy ring and the methylene group of the hydrophobic chain. This suggests that these groups are the main constituents of the rigid interfacial layer. The bi-exponential behavior of the protons on the phenoxy ring and on the first ethylene oxide group next to the phenoxy ring shows that about 50% of each of these groups participates in the formation of the rigid micellar surface. Rest of the corresponding parts stay in the hydrophilic environment as a thick intermediate region allowing the coexistence of water with the first ethylene oxide and the phenoxy group. If we compare the relaxation behavior between protons on different parts of the molecule, we could see that T_{2s} values of the protons on the ethylene oxide chain (314–384 ms) are remarkably greater than those of the protons on the hydrophobic chain. They are slightly smaller than those of the protons on the same ethylene oxide chain in the mono-molecular state (524–649 ms). This suggests that the hydrophilic ethylene oxide chains stay in the exterior of the micellar core, moving freely in the solution. The small part of these ethylene oxide groups (20%) relaxing fast may be those entangled segments, as in the case of polymer solutions where flexible molecular chains are so squeezed [23].

Conclusion

In conclusion, information about the hydrophobic chain packing in the micellar core of surfactants in water solutions can be obtained by simulation of the spin–spin relaxation decay curve of the protons on each of the carbon atoms of the hydrophobic chain. For ionic surfactants such as SDSN and CTAB the first two methylene groups of the *n*-hydrocarbon long chain next to the polar head form a rigid thin layer situated on the surface of the micellar core which experiences the hydrophilic environment. Methylene groups farther from the polar head have remarkably less opportunity to spend time in this environment and for the extreme condition methyl group at the

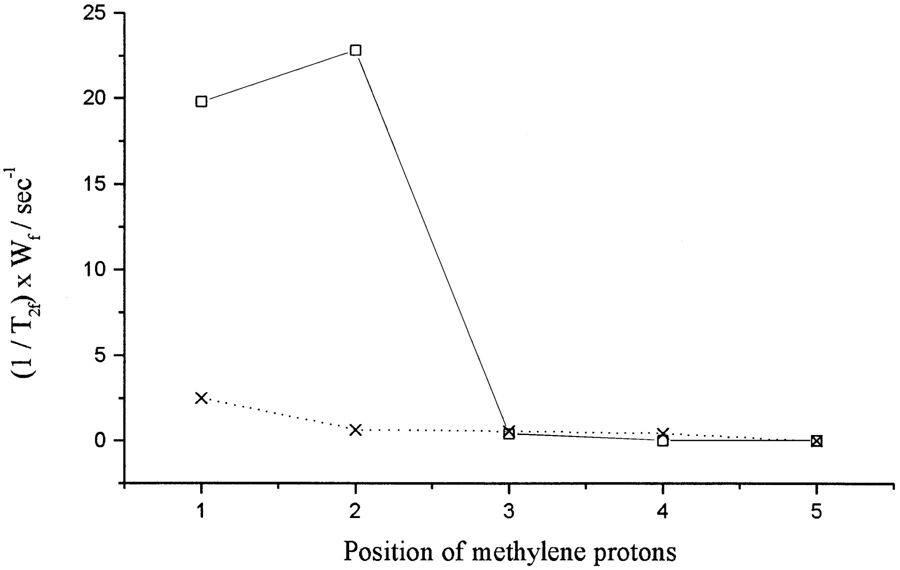

Fig. 2 Density of methylene protons at different carbon atoms of the hydrophobic chain (1) α-carbon atom to the polar group, (2) β-carbon atom to the polar group, (3) γ-carbon atom to the polar group, (4) intermediate carbon atoms between γ- and methyl carbons, (5) methyl carbon at the end of the hydrophobic chain. —□— SDSN curve. ---×--- CTAB curve

end of the hydrocarbon chain does not stay in the surface layer at all. The tightness of the surface layer of the micellar core is highly dependent on the shape and size of the polar head. The density of methylene protons in the surface layer of the micellar core of SDSN ($T_2 = 4$–5 ms) is higher than that of CTAB ($T_2 = 36$ ms) which has three methyl groups attached to the polar head. These methyl groups although staying in the exterior of the micellar core show steric hindrance effect on the packing of hydrocarbon chains on both the surface and the interior of the micellar core. This is clearly shown in Fig. 2 by plotting the density of methylene protons (expressed by the product of $1/T_{2f}$ with W_f) on different carbon atoms. The $1/T_{2f} \times W_f$ values of the γ-methylene protons for SDSN and CTAB coincide, whereas the corresponding values of α- and β-methylene protons show remarkable difference. For non-ionic surfactants such as Triton X-100 the first ethylene oxide next to the phenoxy ring is also involved in the micellar core. Together with the phenoxy ring the segments of the branched hydrophobic chain forms a relatively thick layer with hydrophilic character on the outer surface and hydrophobic character on the inner surface formed by the dimethyl and methylene groups. The less flexible character of the branched hydrophobic chain forced the trimethyl end group of the hydrophobic chain to spend some time in the surface layer of the micellar core. The long ethylene oxide hydrophilic chain executes free motion with some degree of entanglement as in the case of polymer solutions [23].

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