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ORIGINAL CONTRIBUTION

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Micellization of sodium dodecyl sulfonate and Triton X-100 in polyacrylamide water solution studied by ^{1}H NMR relaxation and two-dimensional nuclear overhauser enhancement spectroscopy

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Abstract Micellization of Triton X-100 (TX-100) and sodium dodecyl sulfonate (SDSN) in the presence of partially hydrolyzed polyacrylamide (PAAM) was studied by ^{1}H NMR spin–spin and spin–lattice relaxation. Relaxation experiment results show that TX-100 behaves differently from SDSN in micellization in the presence of PAAM. PAAM causes a decrease in the critical micellar concentration of SDSN, while it has no influence on the critical micellar concentration of TX-100. The lack of cross peaks between protons of PAAM and those of TX-100 and SDSN in the 2D nuclear Overhauser enhancement spectroscopy (NOESY) spectra confirms self-aggregation of TX-100 and SDSN in the presence of PAAM. The identity of each of the corresponding interproton distances of TX-100 with and without the addition of PAAM further confirms the formation of normal TX-100 micelles in the presence of PAAM. Besides, the distances between protons on the hydrophilic and hydrophobic chains in TX-100 micelles, calculated from the 2D NOESY spectra, are remarkably shorter than those for an extended hydrophilic poly(oxyethylene) chain. This implies that the hydrophilic chain is curled upon micellization.

Key words ^{1}H NMR relaxation · Two-dimensional nuclear Overhauser enhancement spectroscopy · Micellization · Triton X-100 · Sodium dodecyl sulfonate

Introduction

Mixtures of polymer and surfactant aqueous solutions find wide applications in various fields of industrial processes and biological systems, and are studied extensively by various methods, such as surface and interfacial tensions, viscosity, light scattering, conductivity, electrophoretic mobility, NMR, etc. [1–16]. Most of the studies focus on poly(ethylene oxide)–surfactant systems; however, polyacrylamide(PAAM)–surfactant aqueous solutions have considerable importance in enhanced oil recovery as pusher fluids to provide mobility control. The properties and hence the efficiency of these systems, should be greatly dependent on the interaction between the constituents, polymer and surfactant, in the solution: this problem has been studied even less. The aim of this work is to get detailed information about this important interaction at a molecular level by NMR relaxation and 2D nuclear Overhauser enhancement spectroscopy (NOESY).

Experimental

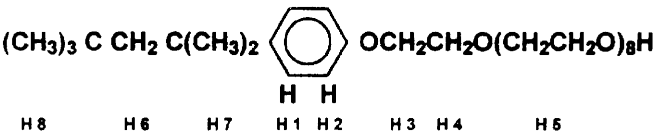
Sodium dodecyl sulfonate (SDSN) was of chemically pure grade from the Yongjia Fine Chemical Plant of China. Triton X-100 (TX-100) was a chemically pure reagent from the Nailai Company of Japan. D_2O was produced by the Beijing Chemical Factory of China. PAAM was a partially hydrolyzed product (27%) from the Sanjing Qingan Company of Japan, and had a molecular weight of 4×10^4 g. The concentrations of the solutions of surfactants are expressed in terms of their critical micellar concentrations (cmc). The cmcs of SDSN and TX-100 are 9.7 [17] and 0.30 [18] mM, respectively. The concentration of PAAM is expressed in terms of grams per liter of solution.

NMR measurements were performed on a Bruker ARX-500 spectrometer with a ^{1}H frequency of 500.13 MHz. Inversion recovery and CPMG pulse sequences were used to measure the spin–lattice (T_1) and spin–spin (T_2) relaxation times at 40 °C for SDSN solution and at 25 °C for TX-100. Sixteen accumulations were usually acquired, but for dilute solutions (0.5 cmc) the number of accumulations was increased to 256. D_2O (99.8%) was used as the solvent instead of water in order to weaken the water proton signal. The presaturation method was used to further suppress the proton signal of the solvent. 2D NOESY experiments were performed with the standard pulse programs of the ARX-500 with mixing times of 10, 50 and 500 ms and 16 accumulations at 25 °C for TX-100 systems without and with the addition of PAAM, and mixing times of 1200 and 900 ms for SDSN and SDSN–PAAM systems, respectively, at 40 °C.

Results and discussion

Interaction of PAAM with TX-100

^{1}H spin–spin relaxation times of all the protons of TX-100 in 10, 5 and 0.5 cmc aqueous solutions with various amounts of PAAM added are listed in Table 1. H1-H8 stand for the corresponding proton signals as indicated by the following formula:



In a previous study we observed that the spin–spin relaxation time of the protons included in the surface layer of the micellar core is of the order of only several tens of microseconds [19]. Therefore, it is reasonable to evaluate the situation of the surfactant molecule by the ^{1}H spin–spin relaxation time. Table 1 shows that the T_2 of each of the protons of TX-100 in solutions at concentrations higher than its cmc are almost identical within the experimental error of 10–15% and are independent of whether PAAM was added or not. This suggests that TX-100 forms normal micelles in the presence of PAAM in solution. In a dilute solution of 0.5 cmc, the addition of 1 g/l PAAM did not have a significant influence on the spin–spin relaxation of the protons (H1, H2, H3) which participated in the formation of the micelles. By significant influence we mean that the T_2 decay curve of the surfactant in a 0.5 cmc solution of TX-100 with the addition of PAAM remains exponential as in the absence of PAAM, although the T_2 values are somewhat smaller than those in the absence of PAAM. This slight decrease in T_2 may be attributed to the increase in the viscosity of the solution due to the presence of the polymer PAAM. As has been shown in our previous study [20], the spin–spin relaxation decay of protons participating in the formation of the thin surface layer of the micellar core of TX-100 (H1-H4 and H6-H8) exhibits biexponential behavior. The T_2 value of the fast relaxing component is very small and is of the order of several tens of milliseconds. However, the spin–spin relaxation of these protons of TX-100 molecules in 0.5 cmc solution exhibits exponential behavior, it is in the individual molecular state, the motion of which is in the extreme narrowing condition. The addition of PAAM did not alter this character. This indicates that TX-100 molecules still move freely in this dilute solution in the presence of PAAM.

It is well known that 2D NOESY is an effective method to study the 3D structure of large molecules, such as proteins which have long τ_c. Cross signals in a NOESY spectrum rely on the cross relaxation of longitudinal magnetization during the mixing time. One can extract valuable information about internuclear distances from the intensity of the cross peaks with the aid of one known distance in the molecule [21]. Ellena et al. [22] have shown that the effect of spin diffusion within the proton-spin system should receive great attention in the analysis of the cross relaxation of this kind of slow-tumbling system. Therefore, the 2D NOESY experiments were performed with mixing times of 500, 50 and 10 ms for 10 cmc TX-100 aqueous solution, without and with 5 g/l PAAM added. The intensity ratios of the diagonal peak of H1 to the cross peak H1-H2 are 1.6, 7.0 and 33 for mixing times of 500, 50 and 10 ms, respectively. This shows that mixing times of 50 and 10 ms are short enough to restore the interdistance specificity. However, the signal-to-noise ratio in the experiment with a mixing time of 10 ms is rather poor. Contour plots of the spectra for a mixing time of 50 ms are shown in Fig. 1. The intensities of the

Table 1 ^{1}H spin–spin relaxation times (T_2/ms) of Triton X-100 in polyacrylamide (*PAAM*) aqueous solutions with varying concentrations of TX-100 ($Conc_T$) and PAAM ($Conc_P$)

$Conc_T$	10 cmc	10 cmc	10 cmc	10 cmc	5 cmc	5 cmc	5 cmc	0.5 cmc	0.5 cmc
$Conc_P$	–	0.1 g/1	1 g/1	5 g/1	–	1 g/1	5 g/1	–	1g/1
H1	69	72	71	69	72	79	81	861	533
H2	81	81	81	77	85	84	91	1073	702
H3	89	81	83	78	94	92	85	508	349
H4	149	120	142	151	166	225	127	524	601
H5	364	399	384	348	360	384	293	606	789
H6	50	52	51	–	55	46	47	383	433
H7	60	60	62	54	64	65	73	306	316
H8	148	147	145	137	156	156	170	601	606

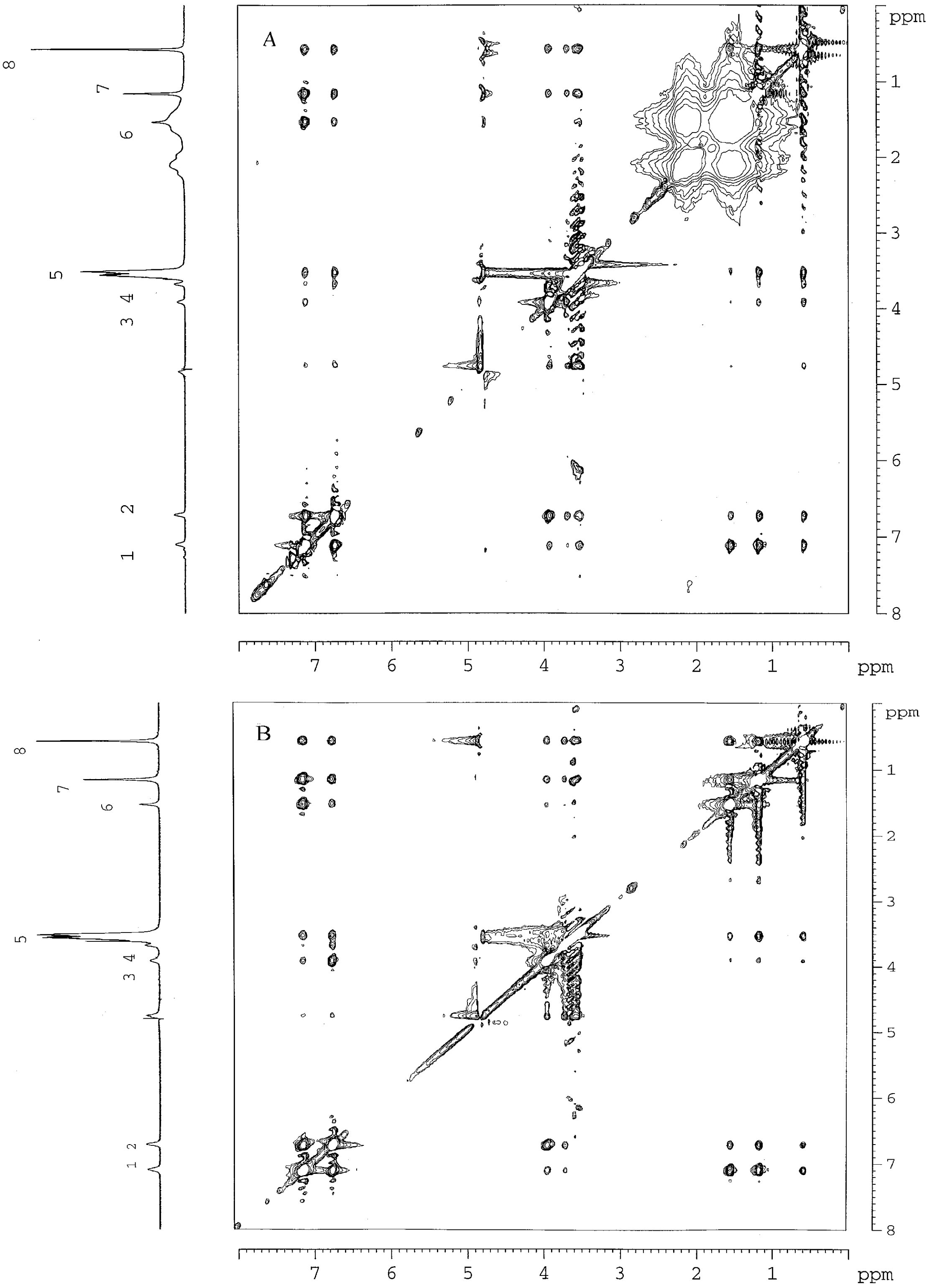


Fig. 1 Contour plot of 2D nuclear Overhauser enhancement spectroscopy (*NOESY*) spectra of Triton X-100 solution at a concentration of 10 cmc **A** with and **B** without the addition of polyacrylamide (*PAAM*) at a mixing time of 50 ms at 25 °C

cross peaks for mixing times of 500, 50 and 10 ms were measured. The distances between pairs of these protons were calculated from the measured intensities of the cross peaks. The following formula was used with the aid of the known distance H1-H2 in the molecule (2.4 Å) and the corresponding cross signal intensity

$$\sqrt[6]{\frac{I_{12}}{I_{mn}}} = \frac{r_{mn}}{r_{12}} \quad ,$$

where, I_{12} and I_{mn} are the intensities of the cross peak between H1 and H2 and that between the two nuclei of interest, respectively. r_{12} and r_{mn} are the corresponding internuclear distances. The internuclear distance values measured are listed in Table 2. It should be mentioned that the proton signals of the poly(oxyethylene) chain, H5, overlap greatly. The intensities of the cross peaks of H5 with other protons are due to contributions from the sum of the eight oxyethylene segments. The internuclear distances between H5 and the other protons listed in Table 2 are the average values of these eight oxyethylene segments. Nine methyl protons of the end methyl groups (H8) and six methyl protons of the dimethyl groups next to the phenoxy ring (H7) are also taken into account in the calculation of the internuclear distances from the intensities of the corresponding cross peaks.

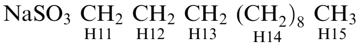
Table 2 Interproton distances (Å) of TX-100 in micelles without and with the addition of 5 g/l PAAM calculated from 2D nuclear Overhauser enhancement spectroscopy spectra at mixing times of 500, 50 and 10 ms. r_{500}, r_{50} and r_{10} are the interproton distances of TX-100 at mixing times of 500, 50 and 10 ms, respectively. r_{P500}, r_{P50} and r_{P10} are the corresponding interproton distances of TX-100 with the addition of PAAM

	r_{500}	r_{P500}	r_{50}	r_{P50}	r_{10}	r_{P10}
H1-H2	2.4	2.4	2.4	2.4	2.4	2.4
H1-H3	3.2	3.2	4.5	–	–	–
H1-H4	3.9	3.9	–	–	–	–
H1-H5	5.1	5.0	7.4	6.9	–	4.3
H1-H6	2.9	2.8	2.9	2.8	3.0	3.0
H1-H7	3.3	3.2	3.2	3.2	3.3	3.3
H1-H8	4.1	3.9	4.8	4.4	5.0	5.2
H2-H3	2.8	2.8	3.0	2.9	3.0	3.0
H2-H4	3.5	3.1	4.0	–	–	–
H2-H5	4.9	4.8	6.3	6.2	7.9	3.9
H2-H6	3.1	3.1	4.1	4.7	–	–
H2-H7	3.5	3.4	4.3	4.2	4.7	4.6
H2-H8	4.0	3.9	5.1	4.5	5.2	4.3
H3-H4	3.0	3.0	2.6	3.0	2.9	2.3
H3-H5	5.0	5.0	–	5.7	–	3.8
H3-H6	4.1	4.1	–	–	–	4.2
H3-H7	4.4	4.4	5.5	–	–	4.5
H3-H8	4.6	4.6	6.4	5.1	5.3	4.7
H4-H5	3.9	3.9	5.3	8.4	–	5.1
H4-H6	4.7	4.7	–	–	–	–
H4-H7	4.7	4.7	5.9	–	–	4.8
H4-H8	4.7	4.7	5.5	–	–	3.8
H5-H6	5.6	5.7	7.8	5.7	–	5.7
H5-H7	5.8	5.8	6.8	6.6	7.3	7.2
H5-H8	5.7	5.7	7.2	6.6	7.3	–
H6-H7	3.4	3.4	3.2	2.7	3.2	2.6
H6-H8	4.1	4.1	3.7	3.9	4.3	–
H7-H8	4.4	4.4	4.3	4.2	4.4	3.9

The two cross peaks of protons at 2.44 and 1.72 ppm are from the interaction between protons of the methylene and methine groups of the main chain of PAAM. It is obvious that no cross peaks can be found between protons (2.44 and 1.72 ppm) of PAAM and the protons of TX-100 in the solution. This suggests that there are hardly any protons of PAAM in the proximity of any protons of TX-100 (at least 5 Å apart). Such large interproton distances would not show any significant interactions between the protons of the polymer and those of TX-100; however, cross peaks between pairs of protons on the hydrophobic chain of the TX-100 molecule (H1-H6, H1-H7, H1-H8, H6-H7, H6-H8 and H7-H8) are strong enough to be detected. This implies that the hydrophobic interaction between PAAM and the hydrophobic part of the TX-100 molecule is far weaker than that among the hydrophobic chains of TX-100 molecules themselves. The interproton distances measured from the 2D NOESY spectrum show that they are almost identical with each other within experimental error for the same mixing time experiment no matter whether PAAM is added to the TX-100 solution or not, although the data scatter a little for different mixing times. This provides evidence TX-100 forms normal, but not mixed, micelles irrespective of whether PAAM is present in the medium or not. Good agreement is found with the results of the relaxation measurements given above. It is worth noting that the interproton distances between the hydrophobic group and the hydrophilic chain of these micelles (4.8–7.8 Å) are remarkably shorter than those for an extended hydrophillic oxyethylene long chain (14–22 Å). This implies that the chain contracts and is curled upon micellization. The detailed investigation is beyond the scope of this discussion and will be published elsewhere.

Interaction between PAAM and SDSN

^{1}H spin–spin relaxation times (T_2) and spin–lattice relaxation times (T_1) were measured for SDSN at concentrations of 5, 2 and 0.5 cmc without and with the addition of various amounts of PAAM. T_2 and the ratio T_2/T_1 values of all of the proton signals of SDSN are listed in Tables 3 and 4, respectively. H11-H15 stand for the corresponding proton signals as indicated by the following formula:



$$\mathrm{NaSO_3}\,\underset{\mathrm{H11}}{\mathrm{CH_2}}\,\underset{\mathrm{H12}}{\mathrm{CH_2}}\,\underset{\mathrm{H13}}{\mathrm{CH_2}}\,\underset{\mathrm{H14}}{(\mathrm{CH_2})_8}\,\underset{\mathrm{H15}}{\mathrm{CH_3}}$$

The T_2 values of the protons in micelles of SDSN (5 and 2 cmc solution) do not seem to be influenced significantly within experimental error by the addition of PAAM; however, in dilute solution (0.5 cmc), the T_2

Table 3 ^{1}H T_2 relaxation times (ms) of sodium dodecyl sulfonate (*SDSN*) in PAAM aqueous solutions with varying concentrations of SDSN (*Conc*$_s$) and PAAM

Conc$_s$	5 cmc	5 cmc	5 cmc	2 cmc	2 cmc	2 cmc	0.5 cmc	0.5 cmc	0.5 cmc
Conc$_P$	–	1 g/l	5 g/l	–	1 g/l	5 g/l	–	1 g/l	5 g/l
H11	77	42	89	77	88	34	115	82	47
H12	375	405	183	369	210	183	621	412	97
H13	505	879	158	521	559	530	862	644	852
H14	620	1174	518	597	637	613	1017	491	1184
H15	915	1840	868	765	1011	989	1578	814	1711

Table 4 ^{1}H T_2/spin–lattice relaxation times of SDSN in PAAM aqueous solutions

Conc$_s$	5 cmc	5 cmc	5 cmc	2 cmc	2 cmc	2 cmc	0.5 cmc	0.5 cmc	0.5 cmc
Conc$_P$	–	1 g/l	5 g/l	–	1 g/l	5 g/l	–	1 g/l	5 g/l
H11	0.05	0.02	0.05	0.05	0.07	0.02	0.04	0.06	0.02
H12	0.20	0.50	0.20	0.26	0.22	0.23	0.42	0.42	0.16
H13	0.46	0.82	0.18	0.43	0.63	0.59	0.47	0.54	0.89
H14	0.43	0.69	0.50	0.39	0.57	0.52	0.60	0.49	0.71
H15	0.28	0.45	0.48	0.23	0.48	0.44	0.41	0.46	0.56

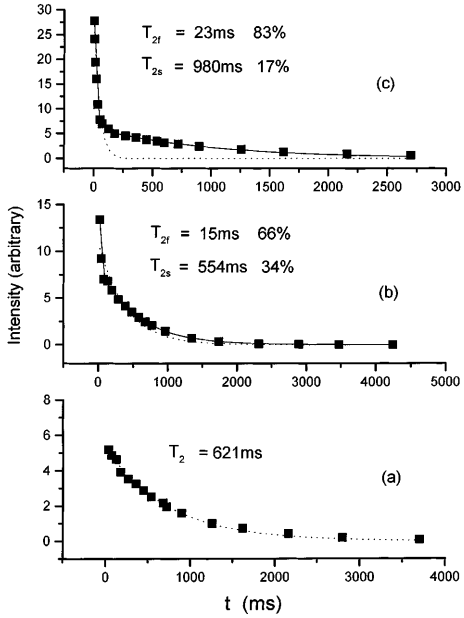


Fig. 2 Simulation curves of H12 spin–spin relaxation decay of a sodium dodecyl sulfonate (*SDSN*) solution at a concentration of 0.5 cmc with various amounts of PAAM added: **A** without, **B** 1 g/l PAAM **C** 5 g/l PAAM

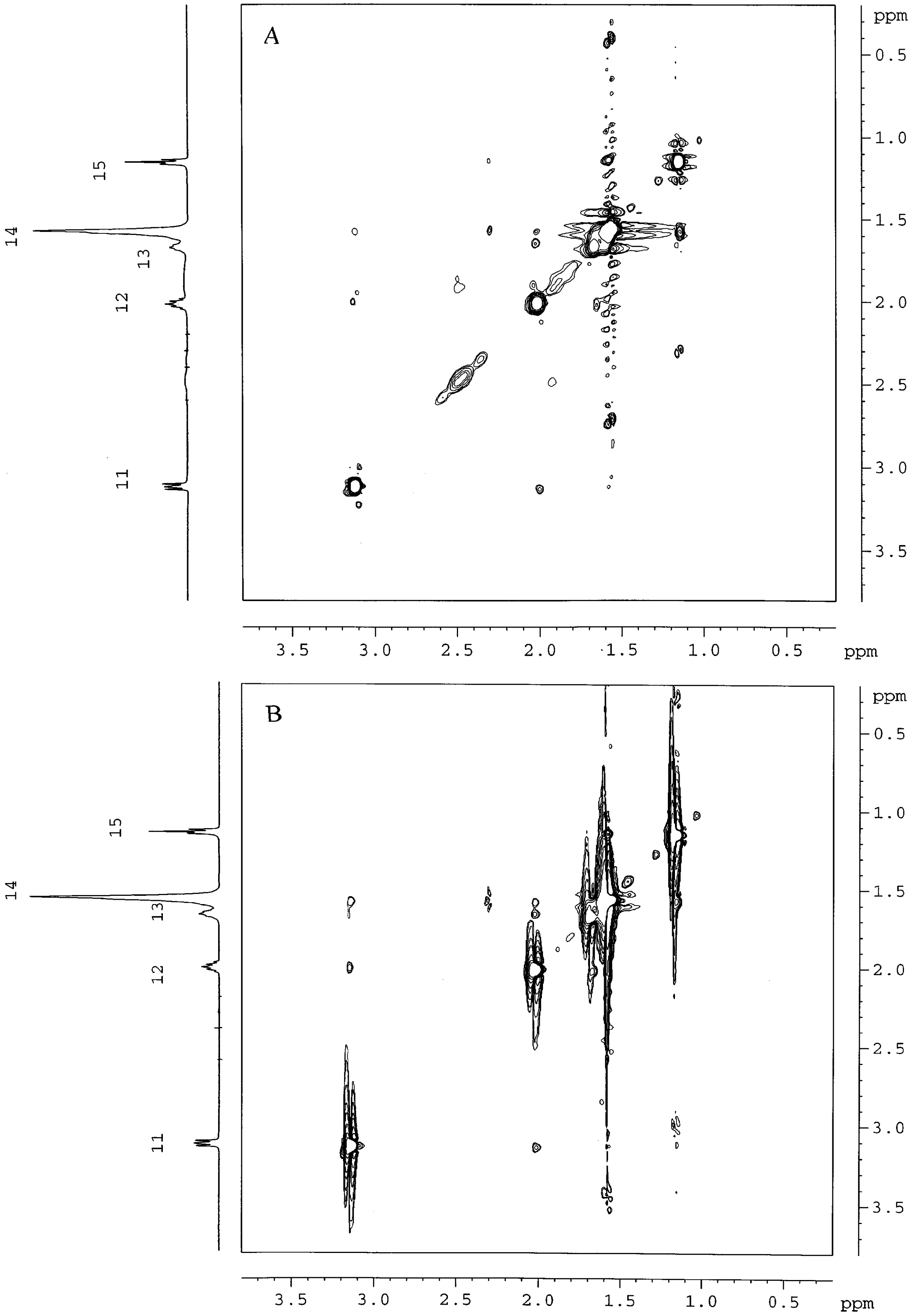
Table 5 Behavior of the T_2 relaxation decay in the SDSN dilute solution (0.5 cmc) with and without the addition of PAAM (g/l)

Conc$_P$	0		1		5	
	T_2 (ms)	%	T_2 (ms)	%	T_2 (ms)	%
H12	621	100	15 554	66 34	23 980	83 17
H13	862	100	158 721	48 52	17 924	40 60
H14	1017	100	491	100	16 1080	11 89
H15	1578	100	814	100	1711	100

value of H12 decreases from several hundreds of milliseconds (621 ms) for a solution without PAAM to several tens of milliseconds (97 ms) as the concentration of PAAM increases to 5 g/l. From Table 4 we can see the influence of PAAM addition on the T_2/T_1 value of H12 of SDSN in solution at a concentration of 0.5 cmc: it decreases from 0.42 for a solution without PAAM to 0.16 for a solution with 5 g/l PAAM added. This T_2/T_1 value of 0.16 is approximately the same as, and is even smaller than, that of SDSN micelles in solution at a concentration of 5 cmc (0.20). A T_2/T_1 value of about 0.1 for protons on the hydrophobic chain is characteristic for the formation of micelles as shown in our previous study [20]. This suggests that SDSN formed micelles at a concentration of 0.5 cmc in the presence of 5 g/l PAAM. In order to confirm this fact, spin–spin relaxation decay curves of H12-H15 for solutions of 0.5 cmc SDSN without and with 1 and 5 g/l PAAM were simulated. The simulated curves for H12 are shown in Fig. 2, where dotted lines represent exponential simulation and solid lines represent biexponential ones. It is obvious that in the 0.5 cmc solution, H12 of SDSN relaxes exponentially with a T_2 value of 621 ms which is typical for individual molecules in solution, as shown in Fig. 2A. The relaxation decay curve of this proton gradually becomes biexponential as the amount of PAAM added is increased, as shown in Fig. 2B and C. The T_2 decay curve becomes biexponential with the addition of 1 g/l PAAM. A fast relaxing component (T_2 = 15 ms) of 66% appeared. Finally, in the presence of 5 g/l PAAM, more than 80% of the H12 protons relax fast with a T_2 value of 23 ms. Simulation results of

▶

Fig. 3 Contour plot of the 2D NOESY spectra of a SDSN solution at a concentration of 5 cmc **A** with and **B** without the addition of 5 g/l PAAM at mixing times of 900 and 1200 ms, respectively, at 40 °C


A
15
14
13
12
11
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
B

H12-H15 are listed in Table 5. The biexponential behavior of the relaxation decay becomes less pronounced as the protons of the methylene groups go further from the polar group and the end methyl protons relax exponentially. This is characteristic for protons participating in the formation of SDSN micelles as shown in our previous publication [20].

In order to distinguish whether the SDSN micelles formed in the presence of PAAM are normal or mixed micelles, 2D NOESY experiments were performed for SDSN micelles (5 cmc solution) in the presence and absence of PAAM. Contour plots of these two spectra are shown in Fig. 3. Similar to the results for the TX-100 – PAAM system, Fig. 3A shows that there are no cross peaks of PAAM protons at 2.45 and 1.84 ppm with the five proton peaks of SDSN (H11-H15). This suggests the absence of interaction between PAAM and SDSN. Interproton distances calculated from the intensities of cross peaks in the 2D NOESY spectra of SDSN micelles with and without the addition of PAAM are identical within experimental error for each corresponding proton pair (Table 6); therefore, SDSN should form normal micelles in the presence of PAAM.

Consequently, simulation of the relaxation decay and 2D NOESY experiments for a SDSN solution of 0.5 cmc with and without addition of PAAM confirm the decrease in the cmc (self-aggregation) of SDSN caused by the presence of PAAM. This decrease can be attributed to the "salting out" effect of PAAM, because the addition of the partially hydrolyzed PAAM results in an increase in the number of negatively charged ions in solution. This may also be the reason for the formation of micelles of sodium dodecyl sulfate (SDS) in poly(*N*-isopropylacrylamide) microgel when the overall concentration of SDS is lower than its cmc as observed by Gao et al. [16].

Table 6 Interproton distances (Å) of SDSN micelles in water solution without and with the addition of PAAM calculated from 2D spectra with mixing times of 1200 and 900 ms, respectively

Conc$_S$	5	5
Conc$_p$ (g/l)	0	5
H11-H12	2.8	2.8
H11-H13	–	–
H11-H14	4.9	4.8
H11-H15	>5	>5
H12-H13	2.6	2.8
H12-H14	4.2	4.5
H12-H15	>5	>5
H13-H14	a	a
H13-H15	>5	>5
H14-H15	3.2	3.4

[a] Cross peaks of H13 with H14 are embedded in the big diagonal peak of H14

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