

Mixed Micelles of Triton X-100 and Cetyl Trimethylammonium Bromide in Aqueous Solution Studied by ^1H NMR

H. Z. Yuan,[†] S. Zhao,[‡] G. Z. Cheng,[§] L. Zhang,[‡] X. J. Miao,[†] S. Z. Mao,[†] J. Y. Yu,[‡]
L. F. Shen,[†] and Y. R. Du^{*,†}

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, The Chinese Academy of Sciences, Wuhan 430071, P.R. China, Institute of Photochemistry, The Chinese Academy of Sciences, Beijing 100101, P.R. China, and Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China

Received: August 30, 2000; In Final Form: January 5, 2001

^1H NMR chemical shift, spin–lattice relaxation time, spin–spin relaxation time, and two-dimensional nuclear Overhauser enhancement (2D NOESY) measurements show that Triton X-100 (TX-100) molecules coaggregate with cetyl trimethylammonium bromide (CTAB) molecules in aqueous solutions. The concentration of TX-100 in the mixed solutions of this study is 3 mM, with varying molar ratios of CTAB/TX-100 (C/T) ranging from 0.5 to 2.9. The results give information about the structure of the mixed micelles. The α -methylene group of CTAB is in the near vicinity of the phenoxy ring of TX-100. The trimethyl group attached to the polar head of CTAB locates between the first oxyethylene group next to the phenoxy ring of TX-100, and the end methyl group of CTAB is close to those of TX-100. The closely packed (coiled) hydrophilic polyoxyethylene chains in the exterior part of the mixed micelles gradually extend with an increase in C/T in the mixed solution. CTAB and TX-100 molecules are uniformly mixed in the micelles in each mixed solution.

Introduction

The study of structures and properties of mixed micelles formed from different types of surfactants, especially nonionic–ionic, by various methods, including theoretical and experimental approaches, is a topic of intense research for various purposes^{1–18} because the properties of the mixed surfactants are often better than those attainable in their individual states. Although this synergetic behavior of mixed surfactant systems has been utilized for many years, precise knowledge of the arrangement of the different kinds of surfactant molecules in the co-aggregates is still little understood. Poly(ethylene glycol) alkyl ethers were used for the nonionic type of surfactant in most of the studies of mixed micelles reported.^{2–4,9,11,12} Only a few studies are concerned with Triton X-100 (TX-100) mixed micelles.^{1,7} Garamus has used TX-100 as the nonionic surfactant in the study of mixed surfactant systems (TX-100/1-bromo-4-tridecylpyridine) by small-angle neutron scattering (SANS) and found that mixed micelles with larger sizes were formed between the two types of surfactants; however, the relative arrangement of the molecules of the two surfactants in the mixed micelles was not dealt with.¹ We have chosen a binary mixed surfactant system consisting of two well-known surfactants, TX-100 as the nonionic surfactant and cetyl trimethylammonium bromide (CTAB) as the cationic surfactant. The structure and dynamic properties of their self-aggregated micelles have been thoroughly studied by various methods, including ^1H nuclear magnetic resonance measurements.^{19–23} The extension of our ^1H NMR relaxation and 2D NOESY studies of self-aggregation of these

surfactants^{22,23} to the investigation of their mixed aqueous systems gives informative results shown below.

Experimental Section

Cetyl trimethylammonium bromide is an analytical-grade reagent produced by Jining Institute of Chemical Engineering of China. TX-100 is a chemically pure reagent of Nacalai Tesque Inc., Kyoto, Japan. It is quality of certainty. D_2O is produced by Beijing Chemical Factory of China. They were used as received, without any further purification. All the ^1H NMR measurements were performed on a Bruker ARX-500 NMR spectrometer with a ^1H frequency of 500.13 MHz. Inversion recovery and CPMG pulse sequences were used for T_1 (spin–lattice) and T_2 (spin–spin) relaxation time measurements, respectively, at 25 °C. Sixteen accumulations were acquired generally. D_2O (99.5%) was used as solvent instead of water in order to weaken the water signal. Meanwhile, the presaturation method was used to further suppress the proton signal of the solvent. 2D NOESY experiments were performed with the standard three-pulse sequence.²⁴ A mixing time of 100 ms was chosen to avoid spin diffusion in these systems of slow motion.

Results

Table 1 gives the ^1H chemical shifts of TX-100 (3 mmol/L), CTAB (9 mmol/L), and their mixtures of various molar ratios CTAB/TX-100 (C/T = 0.5, 1.6, 2.3, and 2.9) at a constant concentration of 3 mmol/L for TX-100 in D_2O solutions. C–N, C-1 to C-5, and T-1 to T-8 stand for the corresponding proton signals, as indicated by the formula shown in Figure 1. The chosen concentration ranges of CTAB and TX-100 are above the critical micellar concentrations (cmc) of the two surfactants to ascertain that micelles are formed. For clarity, variation of

* Corresponding author. Fax: 86-27-87885291. E-mail: lfshen@wipm.whcnc.ac.cn.

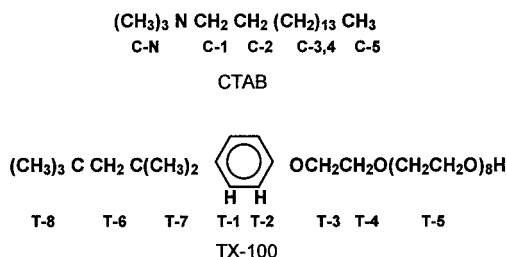
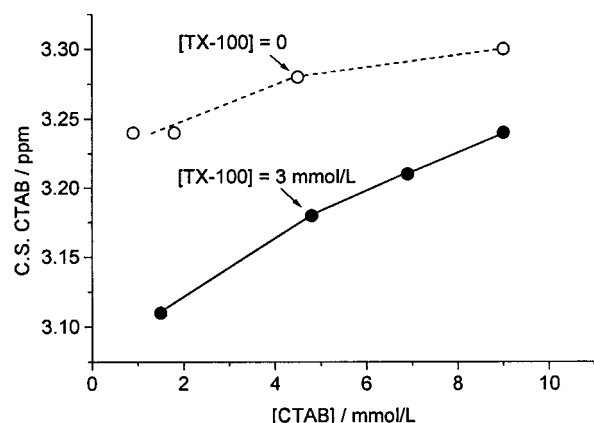
[†] Wuhan Institute of Physics and Mathematics.

[‡] Institute of Photochemistry.

[§] Wuhan University.

TABLE 1: ^1H Chemical Shifts (ppm) of Mixed TX-100 (T) and CTAB (C) Aqueous Systems at a Concentration of TX-100 of 3 mmol/L with Various Molar Ratios of C/T^a

C/T	0:1	0.5: 1	1.2:1	1.6:1	2.3:1	2.9:1	1:0
C-N	—	2.97	2.98	3.01	2.95	3.03	3.04
C-1	—	3.11	3.16	3.18	3.21	3.24	3.30
C-2	—	1.56	1.58	1.60	1.61	1.62	1.69
C-3	—	1.19	1.20	1.22	1.23	1.24	1.28
C-4	—	1.15	1.18	1.19	1.19	1.20	1.20
C-5	—	0.80	0.79	0.79	0.78	0.78	0.78
T-1	7.10	7.10	7.14	7.15	7.17	7.18	—
T-2	6.72	6.72	6.73	6.75	6.76	6.77	—
T-3	3.93	3.93	3.95	3.98	3.99	4.00	—
T-4	3.68	3.69	3.70	3.72	3.73	3.74	—
T-5	3.58	3.60	3.60	3.60	3.60	3.60	—
T-6	1.54	1.56	1.58	1.60	1.61	1.62	—
T-7	1.17	1.19	1.18	1.19	1.19	1.20	—
T-8	0.59	0.60	0.60	0.63	0.64	0.64	—

^a Concentration of CTAB in the system C/T = 1:0 is 9 mmol/L.**Figure 1.** Formulas and proton numbering of Triton X-100 and cetyl trimethylammonium bromide molecules.**Figure 2.** Variation in the chemical shift of C-1 with the concentration of CTAB in the presence and absence of TX-100.

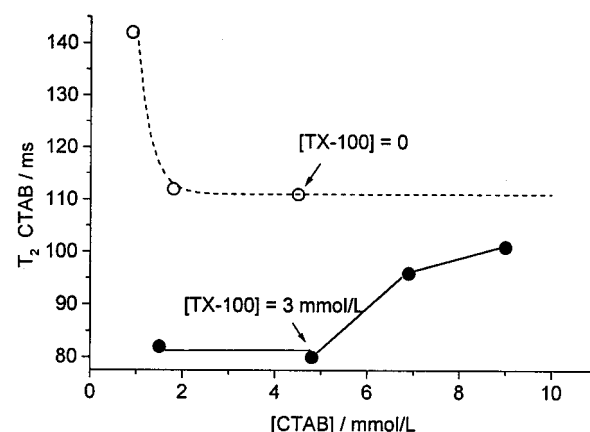
the chemical shift of C-1 with the concentration of CTAB in the presence and absence of TX-100 is shown in Figure 2. ^1H spin lattice, spin-spin relaxation times (T_1 , T_2) and their ratios (T_R) are listed in Tables 2 and 3, respectively. Figure 3 shows the variation of the T_2 of C-1 with the concentration of CTAB in the presence and absence of TX-100. The variations of chemical shift and the T_2 of T-1 are shown in Figure 4. Figure 5 gives the 2D NOESY contour plots of three mixed surfactant systems (C/T = 0.5, 1.2, and 1.6), which give an insight into the interaction between TX-100 and CTAB. A section (from 0.4 to 1.0 ppm) of Figure 5A is expanded (Figure 6) to show the cross-peaks between T-8 (0.6 ppm) and C-5 (0.8 ppm). Interproton distances were calculated.²⁵ There are altogether eight resolvable resonance peaks in the TX-100 ^1H spectrum. They represent eight kinds of chemically equivalent groups of spins, namely, $(\text{CH}_3)_3$ -(T-8), CH_2 -(T-6), $(\text{CH}_3)_2$ -(T-7), the *ortho*-(T-2) and *meta*-(T-1) protons on the phenoxy ring, OCH_2 -(T-3), CH_2O -(T-4), and $(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$ -(T-5). Chemi-

TABLE 2: Spin-Lattice Relaxation Times, T_1 (ms), of Mixed TX-100 (T) and CTAB (C) Aqueous Systems at a Concentration of TX-100 of 3 mmol/L with Various Molar Ratios of C/T^a

C/T	0:1	0.5: 1	1.6:1	2.3:1	2.9:1	1:0
C-N	—	600	620	575	511	694
C-1	—	627	678	658	581	699
C-5	—	537	1066	1072	920	1300
T-1	588	421	649	659	623	—
T-2	722	824	876	882	858	—
T-3	484	486	486	490	470	—
T-4	470	509	574	523	501	—
T-5	565	545	585	600	560	—
T-8	315	341	360	361	349	—

^a Concentration of CTAB in the system C/T = 1:0 is 9 mmol/L.**TABLE 3:** ^1H Spin-Spin Relaxation Times, T_2 (ms), and T_R (T_2/T_1) of Mixed TX-100 (T) and CTAB (C) Aqueous Systems at a Concentration of TX-100 at 3 mmol/L with Various Molar Ratios of C/T^a

C/T	0:1		0.5: 1		1.6:1		2.3:1		2.9:1		1:0	
	T_2	T_R	T_2	T_R	T_2	T_R	T_2	T_R	T_2	T_R	T_2	T_R
C-N	—	—	308	.51	332	.54	326	.57	323	.63	349	.50
C-1	—	—	82	.13	80	.12	96	.15	101	.17	105	.15
C-5	—	—	381	.71	440	.41	445	.42	456	.51	561	.43
T-1	47	.08	157	.25	195	.30	212	.32	215	.35	—	—
T-2	70	.10	176	.21	232	.26	254	.29	261	.30	—	—
T-3	45	.09	130	.27	152	.31	162	.33	158	.34	—	—
T-4	66	.14	164	.32	178	.31	195	.37	184	.37	—	—
T-5	318	.56	340	.62	448	.77	382	.64	378	.68	—	—
T-8	130	.41	219	.64	241	.67	248	.69	250	.72	—	—

^a Concentration of CTAB in the system C/T=1:0 is 9 mmol/L.**Figure 3.** Variation in the T_2 of C-1 with the concentration of CTAB in the presence and absence of TX-100

cal shifts of protons in $(\text{CH}_2\text{CH}_2\text{O})_8$ (labeled as a single group T-5) are very close, as indicated by the broad signals in the spectra of Figure 5. This results in the difficulty of determination of the interproton distances between each individual proton pairs in the groups of chemically equivalent protons directly from the intensities of the cross-peak of the 2D NOESY spectrum. However, the average distance between groups of spins can be obtained from their cross-peak intensities.^{26,27} Therefore, the interproton distances calculated are actually the geometrically average distances between groups having chemically equivalent protons. Although these calculated internuclear distances are not precise, they can characterize the conformation of the system we are studying. It should be mentioned that the proton signals of the polyoxyethylene chain, T-5, overlap seriously. The intensities of cross-peaks of T-5 with other protons are the contribution of the sum of the eight oxyethylene groups. The internuclear distances between T-5 and other protons are the

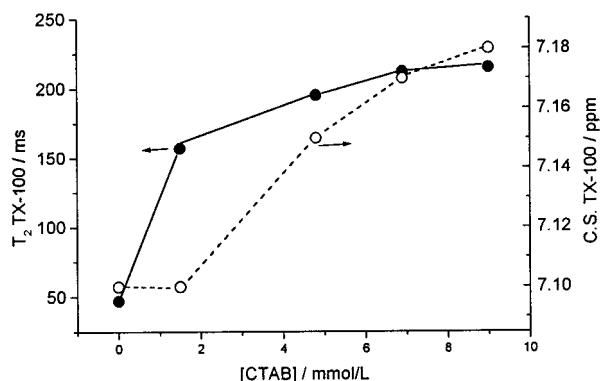


Figure 4. Variation in the chemical shift and T_2 of T-1 with the concentration of CTAB.

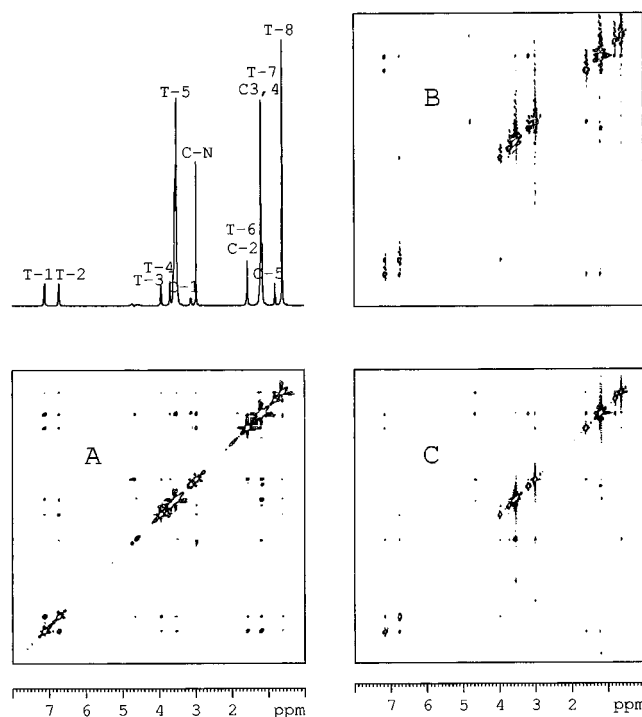


Figure 5. Contour plots of 2D NOESY measurements of TX-100/CTAB mixed aqueous solutions, with C/T = 0.5 (A), 1.2 (B), and 1.6 (C). The mixing time is 100 ms.

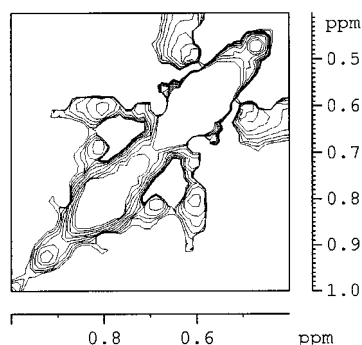


Figure 6. Section (0.4–1.0 ppm) of the contour plot in the 2D NOESY experiment of TX-100/CTAB mixed solution with C/T = 0.5:1, showing the cross-peaks between T-8 (0.80 ppm) and C-5 (0.6 ppm).

average values of the eight oxyethylene groups. Nine methyl protons of the end methyl groups (T-8) and the nine protons of the trimethyl group of CTAB are also taken into account in calculating the internuclear distances from the intensities of the corresponding cross-peaks. Interproton distances calculated from

TABLE 4: Interproton Distances (\AA) of TX-100 Molecules and Those between TX-100 and CTAB Molecules in Mixed Aqueous Systems at a Concentration of TX-100 of 3 mmol/L with Various Molar Ratios of C/T^a

C/T	HYP	0:1 (m)	0.5:1	1.2:1	1.6:1	0:1 (d)
T-1–T-2	2.4	2.4	2.4	2.4	2.4	2.4
T-1–T-3	5.3	4.5	4.7	—	—	—
T-1–T-4	6.9	5.2	—	—	—	—
T-1–T-5	19	7.4	6.6	—	—	—
T-1–T-8	4.9	4.8	6.5	—	—	—
T-2–T-3	3.4	3.0	3.0	2.9	3.1	3.2
T-2–T-4	4.7	4.2	—	—	—	—
T-2–T-5	16.8	6.4	6.4	—	—	—
T-2–T-8	6.3	5.1	6.3	—	—	—
T-3–T-4	2.8	2.9	2.9	2.9	3.1	2.8
T-3–T-5	14.8	4.8	—	—	—	—
T-3–T-8	7.6	6.4	6.6	—	—	—
T-4–T-5	13.7	5.3	3.9	—	—	—
T-4–T-8	9.3	5.5	—	—	—	—
T-5–T-8	21.1	7.2	9.7	—	—	—
T-3–C–N	—	—	5.3	—	—	—
T-4–C–N	—	—	5.2	—	—	—
T-8–C-5	—	—	5.2	—	—	—

^a HYP: interproton distances of TX-100 in the single molecular state calculated by using Hyperchem molecular graphics package. 0:1 (m)²³: micellar solution of TX-100 at a concentration of 3 mmol/L. 0:1 (d)²³: dilute TX-100 solution at a concentration of 0.15 mmol/L.

the 2D NOESY spectra of TX-100–CTAB mixed surfactant systems are listed in Table 4. The theoretically simulated values calculated by the HYPERCHEM molecular graphics package for a TX-100 molecule being put in water with the hydrophilic polyoxyethylene chain extended and the experimentally measured values of TX-100 micelles and single molecular TX-100 in solution below its cmc are also listed in Table 4 for comparison.

Discussion

We can deduce the relative arrangement of the molecules of the two types of surfactants if we carefully examine the variation of ^1H chemical shifts of the resonance peaks of the two surfactants due to mixing. Table 1 shows that the resonance peaks, C-1, C-2, C-3, and C-4, shift upfield as C/T decreases, i.e., as the fraction of TX-100 increases. The degree of upfield shift is the highest for the proton resonance of the methylene group nearest to the polar head, C-1. The further the methylene group is from the polar head, the weaker the tendency of the upfield shift of the proton resonance peak will be. It is evident from Figure 2 that the chemical shifts of CTAB for all the concentrations decrease in the presence of TX-100. The smaller the C/T (the larger the fraction of TX-100) is, the more intense the decrease in chemical shift will be. This upfield shift of the CTAB protons after mixing with TX-100 is evidence of the ring current effect of the aromatic phenyl group of TX-100. However, the chemical shift of the nine protons of the trimethyl groups attached to the nitrogen atom, C–N, is significantly less influenced (almost constant within experimental error, as shown in Table 1). Since the observed chemical shift is the weighted average of the monomer and micellar molecules, this shows that there is very slight variation of the weighting factor of monomers in these mixed surfactant solutions. Thus, the remarkable variation of the chemical shift of C-1 and C-2 should originate from the interaction between the aromatic ring of TX-100 and the methylene groups nearest to the polar head of CTAB. This ring current effect of the phenoxyl group of TX-100 has also been observed by the decrease in the chemical shift of T-1 by 0.26 ppm after the self-aggregation of TX-100.²⁸

This decrease is because the phenoxy rings get close to each other during micellization and each phenoxy proton experiences the aromatic ring current effect of the phenoxy rings of other TX-100 molecules being in the near vicinity. The downfield shift of the hydrophobic protons (T-1, T-2 and T-8) of TX-100 micelles in the presence of CTAB (Figure 4) is the reverse process, dilution of TX-100. The almost unchanged chemical shift of T-5 (polyoxyethylene protons in the exterior of the hydrophobic micellar core) shows that the change of cmc in the mixed surfactant system is very slight. The larger the fraction of CTAB is, the more intense the downfield shift will be. Consequently, we can come to the conclusion that the α -methylene group of CTAB molecule is located in the near vicinity of the phenoxy ring of TX-100. The hydrophobic chains of TX-100 and CTAB, having the end methyl groups pointed to the center of the hydrophobic core of the mixed micelles, are uniformly mixed in the packed hydrophobic mixed micellar core.

The relaxation times of surfactants in aqueous solutions above their cmc's are dependent on their concentrations. The observed relaxation times are weighted average values of those of micelles (restricted motion with short relaxation times) and monomers (free motion in the extreme narrowing condition with long relaxation times). We have shown²⁸ that the spin-spin relaxation times of CTAB protons in aqueous solution above its cmc decrease exponentially with an increase in the CTAB concentration, as shown in Figure 3. This is because the contribution of the monomer becomes less and less important with the increase in the total concentration of the surfactant (the weighting factor of the monomer decreases). Consequently, relaxation times should always decrease with an increase in the total concentration of the surfactant above its cmc, no matter how high is the cmc. In other words, both an increase and a decrease in cmc result in a decrease in relaxation times with an increase in the total concentration of the surfactant. However, this is not the case for the mixed surfactant solution studied. Spin-spin relaxation times of C-1 to C-5 increase with an increase in the concentration of CTAB (above its cmc) when TX-100 is present at a concentration of 3 mmol/L. Figure 3 shows remarkable difference in the tendency of variation of the T_2 of C-1 when TX-100 is present or absent. The T_2 values of C-1 in the mixed surfactant systems are lower than those in CTAB self-aggregated micelles. It is obvious that the shortening of the T_2 of C-1 becomes more and more intense with the decrease in C/T. It could only be attributed to the interaction between CTAB and TX-100 molecules. It is not reasonable to discuss the effect on C-2, C-3, and C-4 because after mixing, C-2 overlaps with T-6. C-3 and C-4 overlap with T-7 as well after mixing (Table 1). However, the shortening of the T_2 of C-5 is significant for the C/T = 0.5 mixed system.

Turning to the T_2 of TX-100 resonance peaks of these systems (Table 3), we find that the T_2 of T-1, T-2, and T-8 (protons forming the hydrophobic core of TX-100 micelles) become longer as C/T increases, although the concentration of TX-100 kept constant. We will not discuss the T_2 of the overlapped resonance peaks (T-6 and T-7). As mentioned above, the change of the weighting factor of TX-100 monomers is slight in this mixed surfactant solution. So the variation of the T_2 values of the hydrophobic protons (T-1, T-2 and T-8) of TX-100 with the concentration of CTAB at constant concentration of TX-100 shows significant interaction between the hydrophobic chains of the two surfactants in the mixed micellar cores. The TX-100 molecules are less closely packed in the mixed micelles than in its self-aggregated ones, but the inverse was observed

for the CTAB molecules. Spin-lattice relaxation measurements, especially T_R , the T_2/T_1 ratio, (Table 3) support the results of T_2 measurements. The T_1 values of the TX-100 protons become longer as the fraction of added CTAB increases. The spin-spin relaxation times of the hydrophilic protons (T-3, T-4 and T-5) increase with an increase in C/T to a less extent. This increase may be attributed to the change of conformation of the polyoxyethylene chains. They gradually extend with the increase in C/T to leave space for the trimethyl groups attached to the polar heads of CTAB which are not involved in the hydrophobic micellar core. The increase in the interproton distances between T-5 and the hydrophobic protons shown in the 2D NOESY maps in Figure 5 strongly supports this conformational change.

It is well-known that NMR, especially 2D NOESY, is an effective method for studying the three-dimensional structure of macromolecules, such as proteins which have long motional correlation time of molecule.^{25,29} 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 NOESY cross-peaks with one known distance in the molecule.^{25,30} Kolehmainen³¹ reported intra- and intermolecular interactions between different kinds of molecules by 2D NOESY in aromatic solubilize-cholesterol systems. Fung et al.³² observed a conformational change of the alkyl chain upon the formation of micelles in the sodium *cis*-7-dodecane-1-yl sulfate system by 2D NOESY. So 2D NOESY experiments of the mixed systems in this study will give information about the interaction among the molecules of the two surfactants inside the mixed micelles. The discussion of the interaction of C-2, C-3, C-4, T-6, and T-7 with other protons in the mixed system is limited because of the overlap of these resonance peaks. Comparing the interproton distances of TX-100/CTAB mixed micelles with those of the TX-100 self-aggregated micelles we have reported,²³ we have noticed that the interproton distances between the protons of the next nearest groups of TX-100 molecules increase with the addition of CTAB (C/T = 0.5:1) in the solution, as shown in Table 4. These cross-peaks became undetectable when C/T increased to 1.2:1 and 1.6:1 (Figures 5A-5C and Table 4). This suggests that the intermolecular interactions among the TX-100 molecules in the micelles weaken by the mixing with CTAB. In these mixed systems the TX-100 molecules are separated as if they were in the single molecular state of dilute solution at a concentration below its cmc (0:1 (d) of Table 4). However, the fact that the ratio of ^1H spin-spin relaxation time to spin-lattice relaxation time, T_R (Table 3), of the protons of CTAB and TX-100 molecules in the mixed surfactant solutions is much less than unity indicates that these molecules are soft solidlike, i.e., in the aggregated state.

The interesting phenomenon is that the intensities of cross-peaks between the hydrophilic polyoxyethylene protons (T-5) and the remote hydrophobic protons (e.g., T-1, T-2, and T-8), observed for the self-aggregated TX-100 micelles,²³ gradually decrease with an increase in C/T in the 2D NOESY map of the mixed micelles. It suggests that the polyoxyethylene chains gradually extend with the increase in C/T to leave space for the three methyl groups attached to the nitrogen atom of the CTAB polar head because they are not involved in the hydrophobic micellar core. Meanwhile, the appearance of cross-peaks of C-N with T-3 and T-4 (Figure 5A) is direct evidence of the location of the three methyl groups attached to the nitrogen atom of CTAB, which is between the first oxyethylene groups next to the phenoxy rings of TX-100. The interproton

distances between C—N and T-3 and between C—N and T-4 are 5.3 and 5.2 Å, respectively (Table 4).

An Important fact should be noted that cross-peaks between the end methyl protons of TX-100 and the hydrophobic methyl protons of CTAB were observed in the mixed surfactant system (Figure 6). The interproton distance is 5.2 Å. This observation gives strong evidence of the interaction between CTAB and TX-100 molecules in the hydrophobic micellar cores. It also implies that the hydrophobic chains of CTAB are not extended in the mixed hydrophobic micellar core; otherwise, their end methyl groups will not be near to the end methyl groups of the short branched TX-100 hydrophobic chains. This is similar to the conformational change of the alkyl chain upon the formation of micelles in the sodium *cis*-7-dodecane-1-yl sulfate system shown by Fung et al.³² It should be emphasized that interaction of other proton pairs between TX-100 and CTAB could also exist; however, it is not reasonable to discuss their interactions from the 2D NOESY map because proton signals of T-6 and T-7 overlap seriously with C-2, C-3, and C-4.

In conclusion, mixed micelles are formed in mixed solutions of TX-100 and CTAB. They are uniformly mixed in the mixed micelles. Interactions both between the hydrophobic protons and between the hydrophilic protons of the two surfactants were observed. The α -methylene group of CTAB is near to the phenoxy ring of TX-100. The end methyl group of CTAB and those of TX-100 are in the near vicinity. The trimethyl groups attached to the polar heads of CTAB molecules are located between the first oxyethylene groups next to the phenoxy rings of TX-100 molecules. The fact that the closely packed hydrophilic polyoxyethylene chains of TX-100 outside the hydrophobic micellar core gradually extend with an increase in C/T, supports the steric-hindrance effect of the trimethyl groups of CTAB on the conformation of the polyoxyethylene chains of TX-100. Intermolecular interaction among TX-100 molecules gradually weakens in mixed micelles as C/T increases. However, intermolecular interactions between hydrophobic protons of TX-100 and those of CTAB are obvious.

Acknowledgment. Financial support by the National Key Basic Research Development Program "Fundamental Studies of the Extensively Enhanced Petroleum Recovery" (Grant G19990225) is gratefully acknowledged.

References and Notes

- (1) Garamus, V. M. *Langmuir* **1997**, *13*, 6388.
- (2) Shiloach, A.; Blankschtein, D. *Langmuir* **1999**, *14*, 7166.
- (3) Yamaguchi, S. *Langmuir* **1999**, *14*, 7183.
- (4) Yoshida, K.; Dubin, P. L. *Colloids Surf., A* **1999**, *147*, 161.
- (5) Morris, K. F.; Johnson, C. S. Jr. *J. Phys. Chem.* **1994**, *98*, 603.
- (6) Ghosh, S.; Moulik, S. P. *J. Colloid Interface. Sci.* **1998**, *208* (2), 357.
- (7) Moulik, S. P.; Ghosh, S. *J. Mol. Liq.* **1997**, *72*, 1.
- (8) Esaka, Y.; Tanaka, K.; Uno, B.; Goto, M.; Kano, A. *Anal. Chem.* **1997**, *69* (7), 1332.
- (9) Palous, J. L.; Turmine, M.; Latellier, P. *J. Phys. Chem. B* **1998**, *102* (30), 5886.
- (10) Brinkmann, U.; Neumann, E.; Robinson, B. H. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (9), 1281.
- (11) Nilson, P. G.; Lindman, B. *J. Phys. Chem.* **1984**, *88*, 5391.
- (12) Ganesh, K. N.; Mitra, P.; Balasubramanian, D. *J. Phys. Chem.* **1982**, *86*, 4291.
- (13) Zachariasse, K. A.; Van Phue, N.; Kozankiewicz, B. *J. Phys. Chem.* **1981**, *85*, 2676.
- (14) Miller, D. D.; Lenhart, W.; Antalek, B. J.; Williams, A. J.; Hewitt, J. M. *Langmuir* **1994**, *10*, 68.
- (15) Sierra, M. L.; Svenson, M. *Langmuir* **1999**, *15*, (7), 2301.
- (16) Dickinson, E.; Ritzoulis, C.; Povey, M. J. W. *J. Colloid Interface Sci.* **1999**, *212* (2), 466.
- (17) Corkill, J. M.; Goodman, J. F.; Tate, J. R. *Trans. Faraday Soc.* **1964**, *60*, 986.
- (18) Tokiwa, F.; Moriyama, N. *J. Colloid Interface Sci.* **1969**, *30*, 338.
- (19) Krovvidi, K. R.; Muscat, A.; Stroeve, P.; Ruckenstein, E. *J. Colloid Interface Sci.* **1984**, *100*, 497.
- (20) Brown, W.; Rynden, R.; Stam, J.; Alngen, M.; Svensk, G. *J. Phys. Chem.* **1989**, *93*, 2512.
- (21) Ribeiro, A. A.; Dennis, E. A. *J. Phys. Chem.* **1976**, *80*, 1746.
- (22) Zhao, S.; Yuan, H. Z.; Yu, J. Y.; Du, Y. R. *Colloid Polym. Sci.* **1998**, *276*, 1125.
- (23) Yuan, H. Z.; Cheng, G. Z.; Zhao, S.; Miao, X. J.; Yu, J. Y.; Shen, L. F.; Du, Y. R. *Langmuir* **2000**, *16* (7), 3030.
- (24) Ernst, R. R.; Bodenhausen, G.; Wokaun, A., *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: New York, 1987.
- (25) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.
- (26) Liu, H.; Thomas, P. D.; James, T. L. *J. Magn. Reson.*, **1992**, *98*, 163.
- (27) Wuthrich, K.; Billeter, M.; Braun, W. *J. Mol. Biol.*, **1983**, *169*, 949.
- (28) Yuan, H. Z.; Du, Y. R.; Zhao, S.; Yu, J. Y. *Sci. China, Ser. A* **1999**, *42* (3), 319.
- (29) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95.
- (30) Borgias, B. A.; Gochin, M.; Kerwood, D. J.; James, T. L. *Prog. NMR Spectrosc.* **1990**, *22*, 83.
- (31) Kolehmainen, E. *Magn. Reson. Chem.* **1988**, *26*, 760.
- (32) Zhao, J.; Fung, B. M. *J. Phys. Chem.* **1993**, *97*, 5185.