

## Mechanism of the Mixed Surfactant Micelle Formation

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This article provides a full description of the mixed micelle formation process at a molecular level. The mechanism of mixed micelle formation in binary surfactant aqueous solution systems, ionic/nonionic mixed systems (12-2-12/TX-100, 14-2-14/TX-100, and SDS/TX-100), and ionic/ionic mixed systems (12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB), in heavy water solutions was studied by <sup>1</sup>H NMR spectroscopy. The critical micellization concentrations of each individual component in the mixed surfactant solutions were gained by analyzing changes in chemical shift and intensities of resonance peaks. The chemical shift changes indicated that in the 12-2-12/TX-100 and SDS/TX-100 systems, micelles of TX-100 formed first, and then 12-2-12 or SDS molecules were fused in the micelles, respectively, which has been proved by 2D NOESY experiments. In contrast, 14-2-14 was the first component to form the micelles in the 14-2-14/TX-100 system. Although 12-2-12 and 14-2-14 are analogs and differ only in the length of the hydrophobic chain by two methylene groups, they showed different behaviors in the micellization processes in the mixture with TX-100. The observation suggests that in the binary surfactant system under current study, the component with lower cmc in the mixed solution aggregates first; then, the other one fuses, resulting in the mixed micelles as the total concentration increases. The same results were obtained for the ionic/ionic solutions, 12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB. The above results suggest that the two mixed surfactants do not aggregate synchronously. It obviously demonstrates that the so-called “cmc of the mixed surfactant solution” needs reconsideration.

### Introduction

Surfactant mixtures are commonly used in many practical applications. In addition to lower cost of purification than a single compound, the mixed surfactants are advantageous because of better performance.<sup>1,2</sup> This property can be explained by synergistic interactions generated between different types of surfactants.<sup>3,4</sup> Such synergetic effects are important for a wide range of surfactant-based phenomena such as foaming, emulsification, solubilization, and detergency.<sup>5</sup> Therefore, the investigation of aqueous mixtures of similar or different types of amphiphiles has attracted much attention.<sup>6–11</sup>

In the early 1950s, H. Lange<sup>12</sup> and K. Shinoda<sup>13</sup> studied the properties of mixed solutions of two homologous surfactants, respectively, by assuming ideal mixing in the micelles, a theoretical equation for the critical micellization concentration (cmc) was derived. However, in many practical surfactant applications, mixing of surfactants is nonideal. The degree of departure from ideal mixing can be modeled by employing the regular solution theory (RST) with an interaction parameter proposed by Rubingh.<sup>14</sup> Rosen and Hua<sup>15–17</sup> have extended Rubingh's treatment of mixed micelle formation to the adsorption of binary mixtures of surfactants, including anionic/cationic systems, and derived the conditions for synergetic effects in

the surface tension reduction efficiency, the surface tension reduction effectiveness, and mixed micelle formation.<sup>18,19</sup>

Interactions of surfactants in mixed solutions is highly complicated, especially mixing of different types of surfactants, which have attracted considerable interest over the past decade.<sup>5,20–24</sup> Although there have been many studies on micelles and the surface behavior of surfactant mixtures, most of them focus on the interaction parameters of mixed micelles by using Rubingh's equations.<sup>22–24</sup> To the best of our knowledge, the process and mechanism of the mixed surfactant micelle formation has been paid rare attention.

Gemini surfactants are a new class of dimer-like surfactants, consisting of two amphiphilic moieties connected at the level of the head groups by a spacer group of varied nature.<sup>25</sup> Having these unique chemical structures, gemini surfactants have been found to possess properties that are superior to those of conventional surfactants.<sup>26</sup> These include low cmc values and unusually high surface activity, better solubilization, and multiplicity of aggregation.<sup>27</sup> In view of their high cost, gemini surfactants are likely to be used in combination with conventional surfactants. Recently, several research papers have appeared in the literature regarding their mixing behavior with conventional surfactants.<sup>24,28–30</sup> There are still numerous questions that need to be addressed.

Among the experimental techniques available for studying the mixed systems of surfactants, nuclear magnetic resonance (NMR) spectroscopy has unique advantages of not only providing microscopic information at molecular and atomic levels but also offering the advantages of being able to observe indepen-

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dently the behavior of the surfactants in the mixture. In this work, an NMR approach is utilized to investigate the process and mechanism of the mixed surfactant micelle formation of six pairs of mixed surfactant solutions. Both cationic geminis 12-2-12 and 14-2-14 with nonionic surfactant Triton X-100 and with cationic surfactant TTAB, respectively, and anionic surfactant SDS mixed with Triton X-100 and with cationic surfactant CTAB were studied.

## Experimental Section

**Materials.** The quaternary ammonium dimeric surfactants, 12-2-12 (MW614.67) and 14-2-14 (MW670.77), have been synthesized by the Southwest Petroleum University. The sodium dodecyl sulfate (SDS, MW288.38) was the product of Alfa Aesar with a purity of 99%. Triton X-100 (TX-100, MW646.86) was the product of Nacalai Tesque. The *n*-tetradecyl trimethyl ammonium bromide (TTAB, MW336.39) was the product of TCI. The hexadecyl trimethyl ammonium bromide (CTAB, MW364.45) was the product of Acros Organics. D<sub>2</sub>O was the product of Acros with a purity of 99% and a deuteration of 99.8%, respectively. The above-mentioned reagents were used as received, without any further purification. D<sub>2</sub>O was used as solvent instead of water to weaken the water signal.

All three ionic/nonionic mixed solutions of 12-2-12/TX-100, 14-2-14/TX-100, and SDS/TX-100 were prepared in terms of the mole fraction of TX-100 in the mixed solutions ( $\alpha_{\text{TX-100}}$ ), respectively, equaling 0.1, 0.6, and 0.9 for 12-2-12/TX-100 mixed system, 0.1, 0.2, 0.3, 0.5, and 0.7 for SDS/TX-100 mixed system, and 0.3 for 14-2-14/TX-100 mixed system, with the total concentrations of all the mixed solutions changing regularly at each mole fraction. For the three ionic/ionic mixed solutions, the mole fraction of each surfactant was also kept constant, only the total concentrations of all mixed solutions changed regularly.

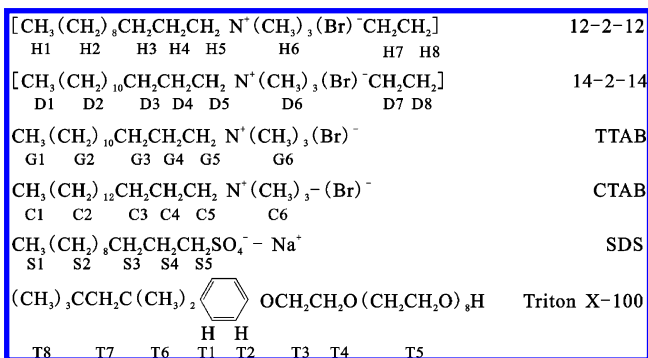
**Experiments.** NMR experiments were performed at 25 °C on Bruker AVANCE spectrometers with a proton frequency of 600.13 MHz (12-2-12/TX-100, 12-2-12/TTAB, and 14-2-14/TTAB mixed systems) and 500.13 MHz (SDS/TX-100 and SDS/CTAB mixed systems) and Varian INOVA spectrometer with a proton frequency of 500.13 MHz (14-2-14/TX-100 mixed system), respectively. TSP (Me<sub>3</sub>Si-CD<sub>2</sub>CD<sub>2</sub>-CO<sub>2</sub>Na) was used as the external reference. To ensure complete recovery of magnetization vector, a small pulse flip-angle 30° was used rather than 90° in the conventional single pulse sequence. Two-dimensional nuclear Overhauser enhancement (2D NOESY) experiments were performed with the standard three-pulse sequence, with a mixing time of 0.2 or 0.3 s. Thirty-two accumulations and  $t_2$  ( $F_2$  dimension)  $\times$   $t_1$  ( $F_1$  dimension) =  $2k \times 196$  sampling data points array. The data point array  $F_2$  ( $F_2$  dimension)  $\times$   $F_1$  ( $F_1$  dimension) = 2048  $\times$  512 was used in the Fourier transformation after the zero filling.

## Results and Discussion

Chemical structures and proton numbering of 12-2-12, 14-2-14, TTAB, CTAB, SDS, and TX-100 are shown in Scheme 1.

**1. Ionic/Nonionic Mixed Solutions. 1.1. 12-2-12/TX-100 Mixed System.** The selected regions of <sup>1</sup>H NMR spectra of 12-2-12/TX-100 at various total concentrations with  $\alpha_{\text{TX-100}}$  remaining constant of 0.6 in D<sub>2</sub>O at 25 °C are shown in Figure 1. It is evident that there are almost no changes in chemical shifts and line shapes in the <sup>1</sup>H NMR spectra until the total concentration is up to 0.25 mM. This indicates that the molecules of TX-100 and 12-2-12 in the solution remain in the monomeric states at the lower concentrations. At the total concentration above

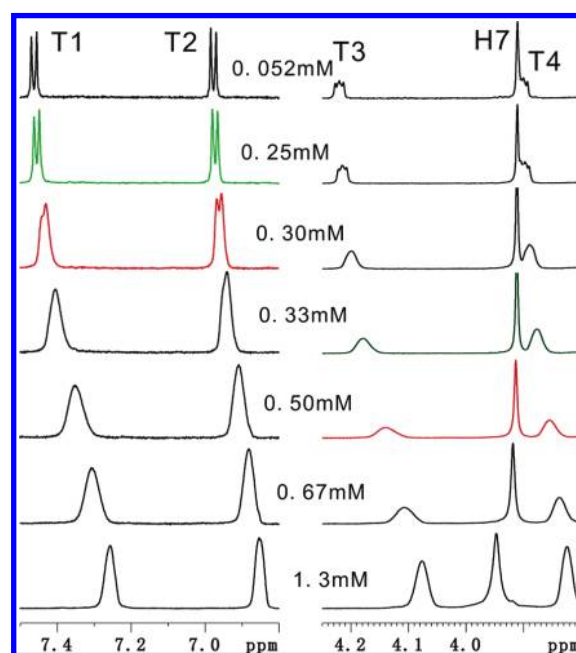
## SCHEME 1: Chemical Structures and Proton Numbering of 12-2-12, 14-2-14, TTAB, CTAB, SDS, and TX-100



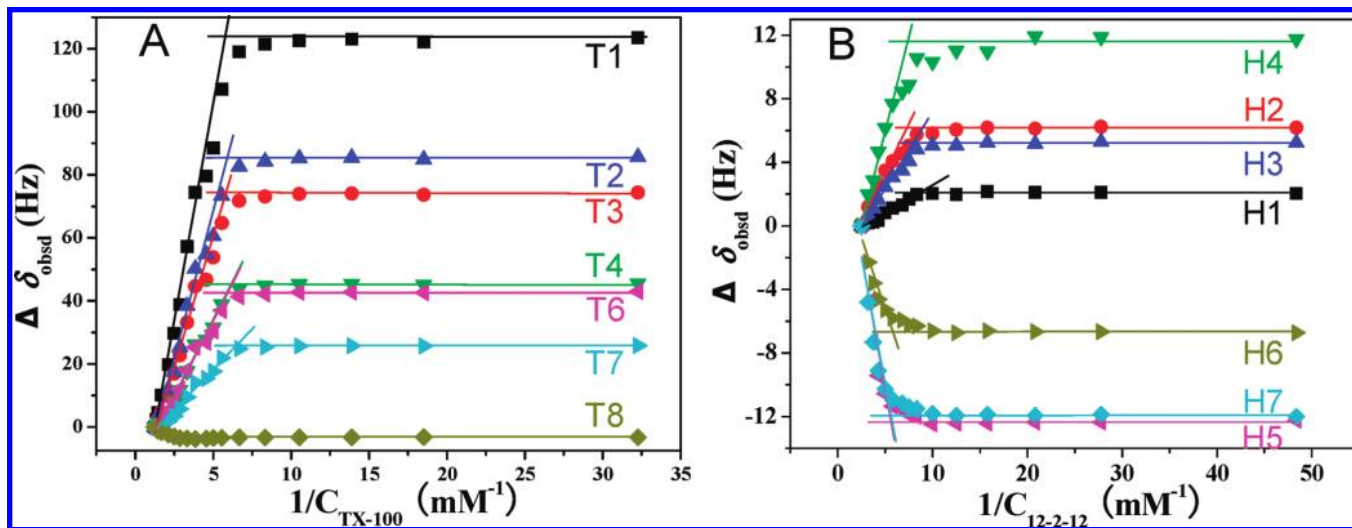
0.25 mM, the resonances of TX-100 were moved toward high-field and broaden in a similar manner as that in pure TX-100 solutions.<sup>31</sup> This indicates that the molecules of TX-100 in mixed solutions begin to aggregate and form micelles. In contrast with TX-100, the peak widths and positions of 12-2-12 remain unchanged until the total concentration reaches 0.50 mM, and the peaks begin broadening and moving to low-field instead of high-field as that of TX-100.

This may be understood as the molecules of 12-2-12 started to aggregate at the concentration above 0.50 mM. In summary, micelles of TX-100 formed first in 12-2-12/TX-100 mixed solutions at the concentration between 0.25 and 0.30 mM; then, as the total concentration increased to ~0.50 mM, micelles of 12-2-12 were formed.

In individual surfactant solutions, for surfactant undergoing fast exchange between the monomers and micelles in the bulk solution, the observed chemical shift ( $\delta_{\text{obsd}}$ ) of the resonance peak can be expressed as the weighted mean of chemical shifts of the micelles ( $\delta_{\text{mic}}$ ) and monomers ( $\delta_{\text{mon}}$ ) at concentrations above their cmc's<sup>31</sup>



**Figure 1.** Selected regions of <sup>1</sup>H NMR spectra of 12-2-12/TX-100 system at various concentrations as labeled in D<sub>2</sub>O at 25 °C with  $\alpha_{\text{TX-100}}$  remaining constant at 0.6.



**Figure 2.** Variations of  $\delta_{\text{obsd}}$  of certain protons of (A) TX-100 and (B) 12-2-12 in 12-2-12/TX-100 mixed solutions as a function of reciprocals of their individual concentrations in  $\text{D}_2\text{O}$  at 25 °C for  $\alpha_{\text{TX-100}} = 0.6$ . The points of intersection of two lines indicate the cmc's.

**TABLE 1: cmc Values of 12-2-12 ( $\text{cmc}_{12-2-12}^*$ ), TX-100 ( $\text{cmc}_{\text{TX-100}}^*$ ), and  $\alpha_{\text{TX-100}}^*$  ( $\alpha_{\text{TX-100}}^* = \text{cmc}_{\text{TX-100}}^*/[\text{cmc}_{\text{TX-100}}^* + \text{cmc}_{12-2-12}^*]$ ) at Different Molar Fractions in 12-2-12/TX-100 mixed Solutions<sup>a</sup>**

$\alpha_{\text{TX-100}}$	$\text{cmc}_{\text{TX-100}}^*$ (mM)	$\text{cmc}_{12-2-12}^*$ (mM)	$\alpha_{\text{TX-100}}^*$
0		0.86 <sup>32</sup>	
0.1	$0.059 \pm 0.0026$ ( $0.59 \pm 0.023$ )	$0.75 \pm 0.028$ ( $0.83 \pm 0.031$ )	0.073
0.6	$0.17 \pm 0.0075$ ( $0.28 \pm 0.012$ )	$0.15 \pm 0.024$ ( $0.37 \pm 0.059$ )	0.53
0.9	$0.24 \pm 0.010$ ( $0.27 \pm 0.011$ )	$0.030 \pm 0.0023$ ( $0.30 \pm 0.021$ )	0.89
1	0.30 <sup>33</sup>		

<sup>a</sup> Values in brackets are the total concentrations, and the errors calculated by STDEV function come from the analysis of multiple resonances for a single sample.

$$\delta_{\text{obsd}} = (C_{\text{mon}}/C_T)\delta_{\text{mon}} + (C_{\text{mic}}/C_T)\delta_{\text{mic}} \quad (1)$$

where  $C_{\text{mon}}$  and  $C_{\text{mic}}$  are the concentrations of monomers and micelles, respectively, and  $C_T (= C_{\text{mon}} + C_{\text{mic}})$  is the total concentration. According to the pseudophase transition model, at the concentration below cmc, only monomers are present in the solution, and the observed chemical shift equals to the value of monomer, whereas at the concentration above the cmc, the concentration of the monomers remains unchanged and equals to cmc. This can be expressed mathematically by eq 2.

$$\begin{cases} \delta_{\text{obsd}} = \delta_{\text{mon}} & (C_T < \text{cmc}) \\ \delta_{\text{obsd}} = (\delta_{\text{mon}} - \delta_{\text{mic}})\text{cmc}/C_T + \delta_{\text{mic}} & (C_T > \text{cmc}) \end{cases} \quad (2)$$

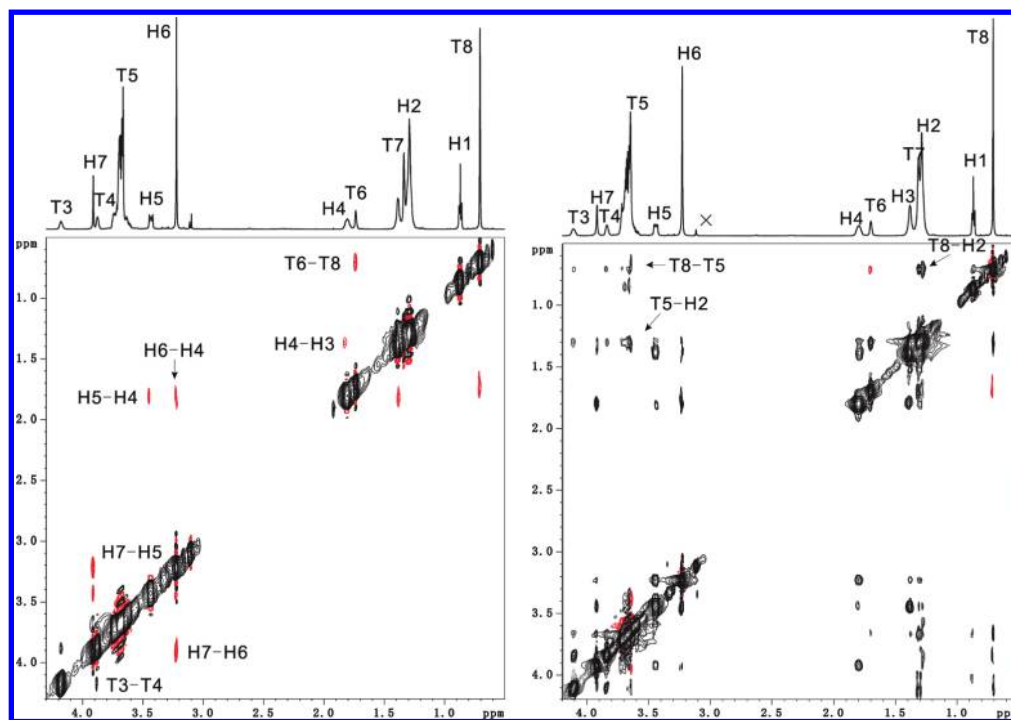
By plotting  $\delta_{\text{obsd}}$  as a function of the inversion of the total concentration ( $1/C_T$ ), one gets two straight lines. The slopes of the two lines are 0 and  $(\delta_{\text{mon}} - \delta_{\text{mic}})\text{cmc}$  before and after cmc, respectively, and the intersection of the two lines is the cmc. Figure 2 shows the typical results for the 12-2-12/TX-100 system with  $\alpha_{\text{TX-100}} = 0.6$ , where the left and right y axes are chemical shifts of certain protons of TX-100 and 12-2-12, respectively, and the x axis is the reciprocal of the concentration of TX-100 or 12-2-12. From the Figure, it is possible to derive the cmc values of 0.17 mM for TX-100 and 0.15 mM for 12-2-12, corresponding to the total concentration of 0.28 and 0.37 mM, respectively. The cmc values of 12-2-12 and TX-100 for the mixed solutions ( $\alpha_{\text{TX-100}} = 0.1, 0.6$ , and  $0.9$ ) were obtained in a similar way and listed in Table 1. From Table 1, it can be found that for  $\alpha_{\text{TX-100}} = 0.1, 0.6$ , and  $0.9$ , micelles of TX-100 always formed first in 12-2-12/TX-100 mixed solutions; then,

as the total concentrations increase, 12-2-12 molecules begin to show aggregation behavior.

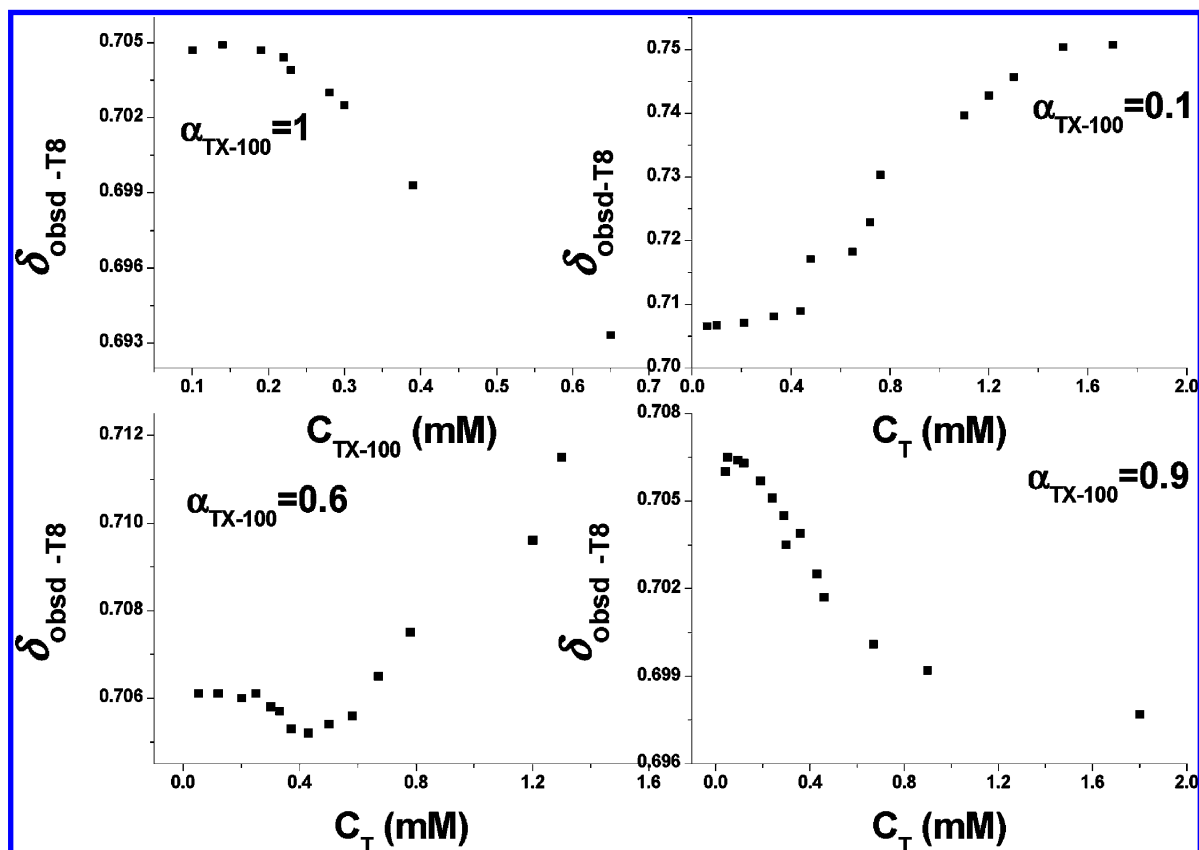
From Table 1, one still finds that for mixed solutions with starting mole fraction of  $\alpha_{\text{TX-100}} = 0.1, 0.6$ , and  $0.9$ , the mole fraction  $\alpha_{\text{TX-100}}^*$  ( $\text{cmc}_{\text{TX-100}}^*/[\text{cmc}_{\text{TX-100}}^* + \text{cmc}_{12-2-12}^*]$ ) in the solution at equilibrium, after mixed micelles formed, equals  $\alpha_{\text{TX-100}}$ . It suggests that the mole fraction of TX-100 in the mixed micelles equals that in the starting mixed solution.

It has been concluded that in 12-2-12/TX-100 mixed systems, there are micelles of TX-100 formed first; then, molecules of 12-2-12 were fused in the micelles. However, it cannot be judged from  $^1\text{H}$  NMR spectra what kind of micelles formed (single pure micelles or mixed micelles composed of two components). 2D NOESY experiments give abundant information about the space relationship of surfactant molecules in the micelles and can be applied to estimate the kind of micelles. Therefore, 2D NOESY spectra were recorded for certain samples of 12-2-12/TX-100 mixed solutions of  $\alpha_{\text{TX-100}} = 0.6$ , whose concentrations are lower and higher than the cmc's of TX-100 and of 12-2-12, viz.  $C_T = 0.23, 0.33$ , and  $0.50$  mM, with a mixing time of  $0.2$  s, except whose concentration equals  $0.23$  mM with a mixing time of  $0.3$  s.

When the total concentration of the 12-2-12/TX-100 mixed solution is  $0.23$  mM, there are few cross peaks in 2D NOESY spectra, which come from intramolecular proton interactions of molecules of 12-2-12 and TX-100. This suggests that there are not any micelles formed in the solutions. Moreover, owing to low concentration, the rotational correlation time of the molecules is short, and the cross and diagonal peaks in the 2D NOESY spectrum have opposite signs, commonly called negative cross peaks. When the total concentration increases to  $0.33$  mM (Figure 3, left), there are more cross peaks, and most of



**Figure 3.** 2D NOESY spectra of 12-2-12/TX-100 mixed solutions of 0.33 mM (left) and 0.50 mM (right), with a mixing time of 0.2 s for  $\alpha_{\text{TX-100}} = 0.6$  (sign of cross peaks is the same as that of diagonal peaks, black; otherwise, red).

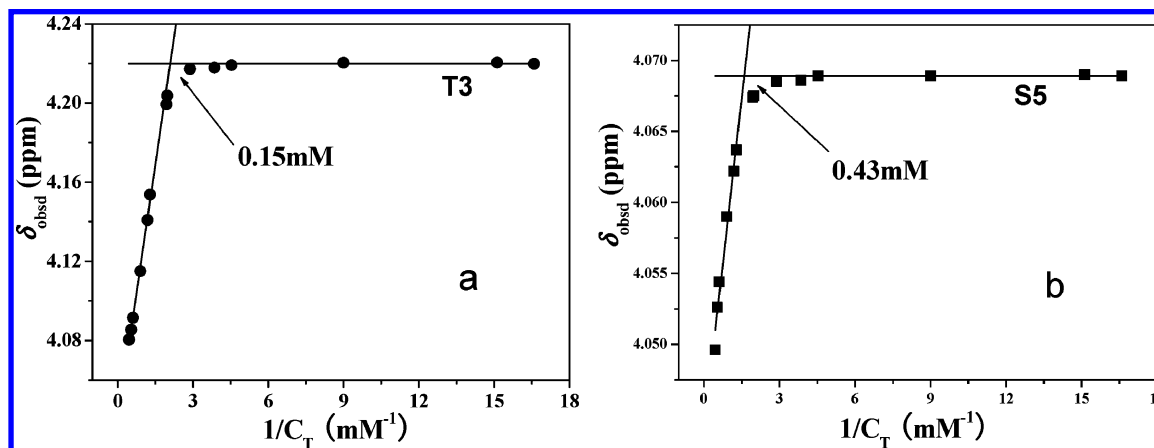


**Figure 4.** Variations of  $\delta_{\text{obsd}}$  for T8 (TX-100) in 12-2-12/TX-100 mixed solutions at different molar fractions as a function of total concentrations in  $\text{D}_2\text{O}$  at 25 °C.

the cross peaks from protons of TX-100 have the same sign with diagonal peaks, called positive cross peaks, because of the long correlation time resulting from higher concentration. Moreover, cross peaks appeared that did not show up when the total concentration was 0.23 mM. This suggested that there are

micelles of TX-100 formed. Furthermore, the sign of cross peaks from protons of 12-2-12 is still negative, and there are no correlation peaks between protons of 12-2-12 and TX-100. Consequently, at  $C_T = 0.33$  mM, the single micelles of TX-100 are formed, and they are not mixed with 12-2-12.



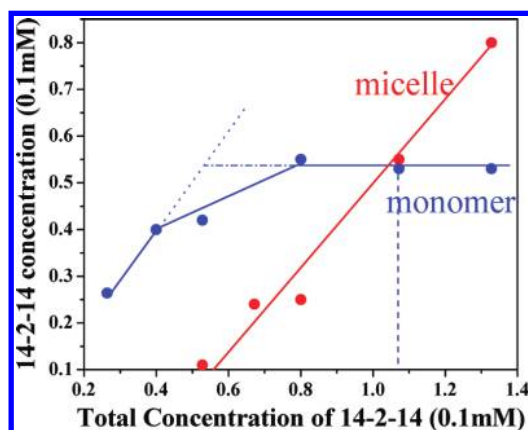


**Figure 5.** Variations of  $\delta_{\text{obsd}}$  of T3 (TX-100) and S5 (SDS) in SDS/TX-100 mixed solutions as a function of reciprocals of concentrations in  $\text{D}_2\text{O}$  at 25 °C for  $\alpha_{\text{TX-100}} = 0.3$ . The points of intersection of two lines indicate the cmc's.

**TABLE 2: cmc Values of SDS ( $\text{cmc}_{\text{SDS}}^*$ ), TX-100 ( $\text{cmc}_{\text{TX-100}}^*$ ), and  $\alpha_{\text{TX-100}}^*$  ( $\alpha_{\text{TX-100}}^* = \text{cmc}_{\text{TX-100}}^* / [\text{cmc}_{\text{TX-100}}^* + \text{cmc}_{\text{SDS}}^*]$ ) at Different Molar Fractions in SDS/TX-100 Mixed Solutions<sup>a</sup>**

$\alpha_{\text{TX-100}}$	$\text{cmc}_{\text{TX-100}}^*$ (mM)	$\text{cmc}_{\text{SDS}}^*$ (mM)	$\alpha_{\text{TX-100}}^*$
0		8.4 <sup>35</sup>	
0.1	$0.11 \pm 0.0057$ ( $1.1 \pm 0.058$ )	$1.1 \pm 0.0069$ ( $1.2 \pm 0.0075$ )	0.091
0.2	$0.12 \pm 0.0028$ ( $0.60 \pm 0.014$ )	$0.65 \pm 0.0036$ ( $0.81 \pm 0.0043$ )	0.16
0.3	$0.15 \pm 0.0031$ ( $0.50 \pm 0.010$ )	$0.43 \pm 0.030$ ( $0.61 \pm 0.042$ )	0.26
0.5	$0.18 \pm 0.0027$ ( $0.36 \pm 0.0055$ )	$0.19 \pm 0.0048$ ( $0.38 \pm 0.0094$ )	0.49
0.7	$0.20 \pm 0.0016$ ( $0.29 \pm 0.0023$ )	$0.10 \pm 0.0035$ ( $0.33 \pm 0.011$ )	0.67
1	0.30		

<sup>a</sup> Values in brackets are the total concentrations, and the errors calculated by STDEV function come from the analysis of multiple resonances for a single sample.



**Figure 6.** Variations of molar concentrations of monomers and micelles of 14-2-14 in 14-2-14/TX-100 mixed solutions as a function of reciprocals of concentrations of 14-2-14 in  $\text{D}_2\text{O}$  at 25 °C for  $\alpha_{\text{TX-100}} = 0.3$ .

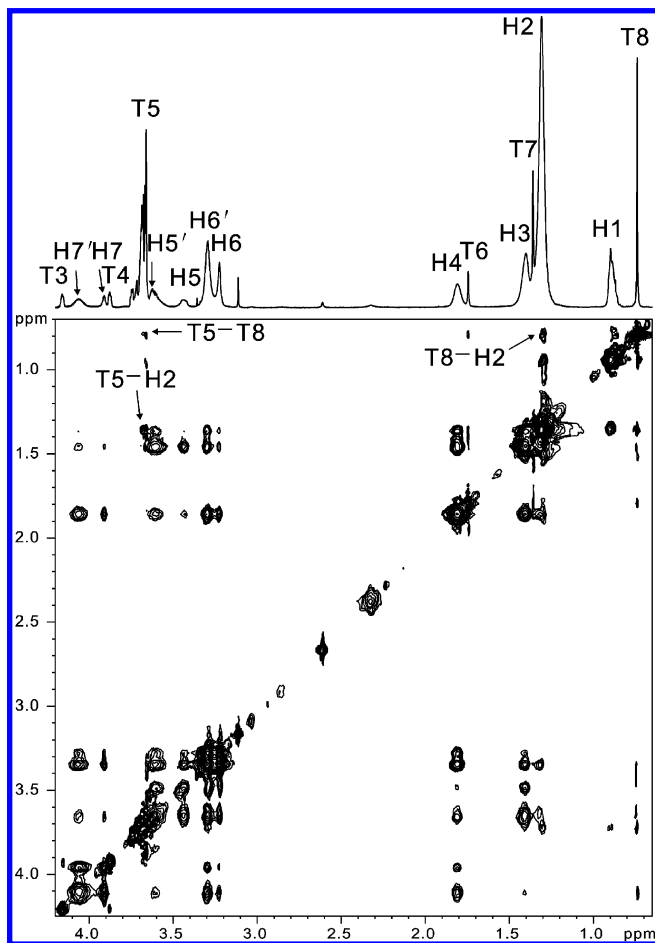
At  $C_T = 0.50$  mM, obvious cross peaks resulting from intermolecules interaction of TX-100 can be observed in their 2D NOESY spectrum (Figure 3, right), such as T2-T5, T1-T5, and so on. Also, the sign of most of the cross peaks for 12-2-12 changed to positive. Interestingly, the distinct cross-peaks between protons of 12-2-12 and TX-100 (T5-H2, T8-H2) can be found; it is a powerful evidence of mixed micelles formation. This suggests that when the concentration comes up to the cmc of 12-2-12 in mixed solutions, molecules of 12-2-12 joined in the micelles of TX-100 already formed, viz. mixed micelles of 12-2-12 and TX-100 are formed.

Carefully examining  $^1\text{H}$  NMR spectra of 12-2-12/TX-100 mixed systems, one finds that the variation of chemical shift for proton T8 ( $\delta_{\text{T8}}$ ) of TX-100 in mixed solution is different

and more complicated than those of TX-100 in its pure solution. Chemical shifts  $\delta_{\text{obsd}}$  (ppm) for T8 protons of mixed solutions of 12-2-12/TX-100 at different molar fractions and different total concentrations in  $\text{D}_2\text{O}$  at 25 °C are shown in Figure 4. In pure solutions of TX-100, for  $\alpha_{\text{TX-100}} = 1.0$ ,  $\delta_{\text{T8}}$  moves monotonously to a higher field as the concentration increases. Contrarily, with  $\alpha_{\text{TX-100}} = 0.1$ ,  $\delta_{\text{T8}}$  moves to a lower field with the increase in total concentration. This indicates that T8 in 12-2-12/TX-100 mixed micelles is located in a lower field than that in pure TX-100 micelles, which probably resulted from the interactions of molecules among 12-2-12 and TX-100. That is why  $\delta_{\text{T8}}$  in mixed solutions is higher than those in pure solutions, when molecules of TX-100 are in the monomeric state.

For  $\alpha_{\text{TX-100}} = 0.6$ , variations of  $\delta_{\text{T8}}$  are relatively more complicated. When the total concentration is 0.30 mM, lower than  $\text{cmc}_{12-2-12}$  in the mixed solution,  $\delta_{\text{T8}}$  moves to a higher field. This shows that micelles of individual TX-100 molecules are formed. When  $C_T$  equals 0.43 mM (higher than  $\text{cmc}_{12-2-12}$  in mixed solution,  $\text{cmc}_{12-2-12}^*$ ),  $\delta_{\text{T8}}$  begins to shift to a lower field. As we have discussed,  $\delta_{\text{T8}}$  in 12-2-12/TX-100 mixed micelles is located in a lower field than that in pure TX-100 micelles. This indicates that there are mixed micelles of 12-2-12 and TX-100 formed at this concentration, which is in agreement with the conclusion derived from 2D NOESY spectra. For  $\alpha_{\text{TX-100}} = 0.9$ ,  $\delta_{\text{T8}}$  moves to a higher field as the total concentration increases on the whole; when  $C_T$  is equal or higher than  $\text{cmc}_{12-2-12}^*$ ,  $\delta_{\text{T8}}$  begins to shift to lower field slightly, this also indicates that mixed micelles of 12-2-12 and TX-100 are formed at this concentration.

**1.2. SDS/TX-100 Mixed System.** The 12-2-12/TX-100 system is a mixed system of cationic and nonionic surfactants. Will the same conclusion be deduced from a mixed system of anionic and nonionic surfactant? Therefore, we investigated the SDS/

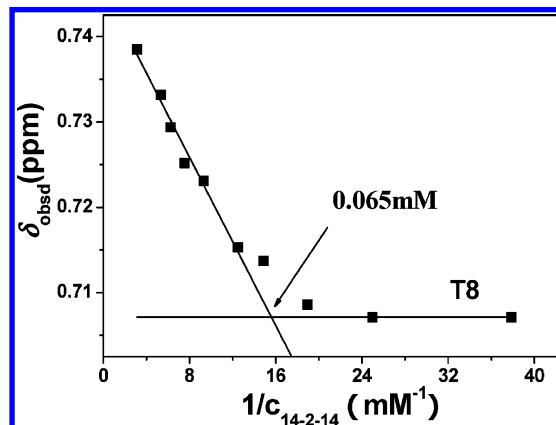


**Figure 7.** 2D NOESY spectrum of 14-2-14/TX-100 mixed solutions of 0.21 mM with a mixing time of 0.3 s for  $\alpha_{\text{TX-100}} = 0.3$ .

TX-100 mixed system by  $^1\text{H}$  NMR experiments for  $\alpha_{\text{TX-100}} = 0.1, 0.2, 0.3, 0.5$ , and  $0.7$ . Exchange between micelles and monomers for surfactant SDS and TX-100 is fast on the NMR time scale, which is similar to the 12-2-12/TX-100 mixed system discussed above. The cmc values of SDS and TX-100 in this mixed system can also be obtained by fitting variations of observed chemical shifts as a function of reciprocals of concentrations.

Variations of  $\delta_{\text{obsd}}$  of T3 (TX-100) and S5 (SDS) in SDS/TX-100 mixed solutions as a function of reciprocals of concentrations in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$  for  $\alpha_{\text{TX-100}} = 0.3$  are shown in Figure 5. The cmc values obtained for TX-100 and SDS in mixed solutions are  $0.15$  ( $\text{cmc}_{\text{TX-100}}^*$ ) and  $0.43$  mM ( $\text{cmc}_{\text{SDS}}^*$ ), respectively. In the same way, the cmc values of SDS and TX-100 in mixed solutions for various molar fraction of TX-100 were obtained (Table 2). It also can be found that for various molar fraction of TX-100, micelles of TX-100 formed first in SDS/TX-100 mixed solutions the same as 12-2-12/TX-100 mixed systems; then, as the total concentrations increase, SDS molecules start to show aggregation behavior. Besides, the cross peaks between the protons of SDS and those of TX-100 in the 2D NOESY spectrum have been reported by Wang et al.,<sup>34</sup> which is direct evidence of the mixed micelle formation. The results show that for  $\alpha_{\text{TX-100}} = 0.1, 0.2, 0.3, 0.5$ , and  $0.7$  systems,  $\alpha_{\text{TX-100}}^*$  ( $\text{cmc}_{\text{TX-100}}^*/[\text{cmc}_{\text{TX-100}}^* + \text{cmc}_{\text{SDS}}^*]$ ) also equals  $\alpha_{\text{TX-100}}$ .

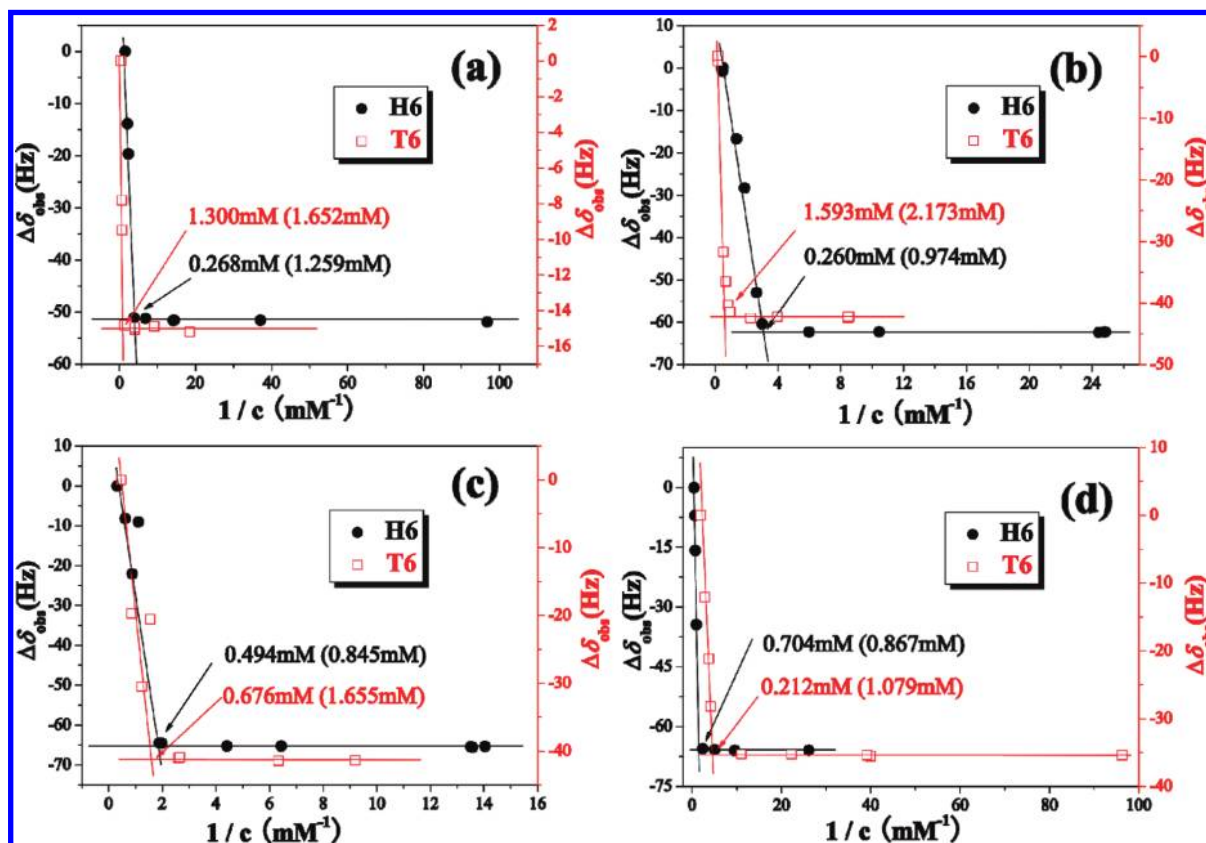
**1.3. 14-2-14/TX-100 Mixed System.** Variation in the  $^1\text{H}$  chemical shift is widely used to deduce the cmc of surfactants in solution on the basis that the exchange between monomers



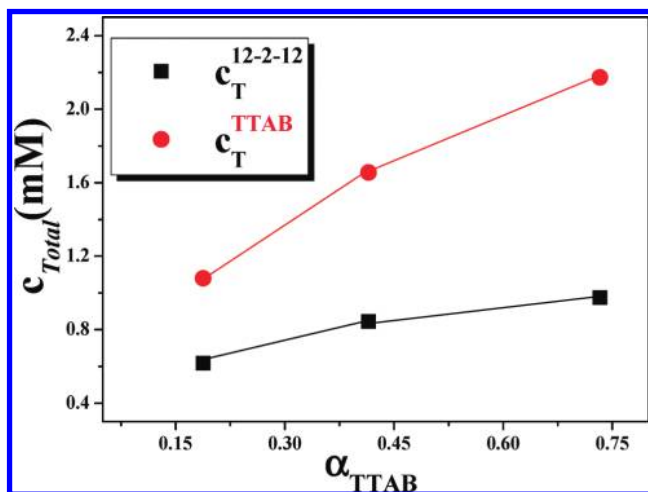
**Figure 8.** Variations of  $\delta_{\text{obsd}}$  of T8 (TX-100) in 14-2-14/TX-100 mixed solutions as a function of reciprocals of concentrations of 14-2-14 in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$  for  $\alpha_{\text{TX-100}} = 0.3$ . The points of intersection of two lines indicate the cmc's.

in the micelles and those in the bulk is fast on the NMR time scale. However, the appearance of a second broad resonance peak in the spectrum is direct evidence of the aggregation of the surfactant molecules. Huc and Oda<sup>32</sup> showed that a second peak appeared in the  $^1\text{H}$  spectrum of 14-2-14 surfactant at a concentration that is twice its cmc, and the integral of the second peak is equal to that of the monomer. This suggests the possibility of obtaining the cmc of a surfactant that has slow exchange on the NMR time scale. So, we chose the 14-2-14/TX-100 mixed system to obtain some deeper insight into the mechanism of mixed micelle formation through the direct evidence of the aggregation behavior. The molar fraction of TX-100 was chosen to be 0.3, not others, because the exchange gets faster as the molar fraction of TX-100 increases; when  $\alpha_{\text{TX-100}}$  is higher than 0.5, the slow exchange for 14-2-14 becomes fast exchange on the NMR time scale.<sup>36,37</sup>

Similar to 12-2-12/TX-100 and SDS/TX-100 systems,  $^1\text{H}$  NMR spectra of 14-2-14/TX-100 mixed system for  $\alpha_{\text{TX-100}} = 0.3$  at various total concentrations were acquired. The molar concentration of micelles and monomers of 14-2-14 in mixed solutions were obtained by integrating their resonance peaks, respectively, as shown in Figure 6. It can be found that starting from  $0.026$  mM 14-2-14 in the solution, the concentration of the 14-2-14 monomer increases monotonously with the increase in the concentration of the solution, suggesting that the 14-2-14 molecules remain in the monomer state. When the concentration of 14-2-14 is almost  $0.055$  mM, a second set of well-resolved resonance peaks appeared in the  $^1\text{H}$  NMR spectra, corresponding to the resonance peaks of 14-2-14 micelles, which are at lower fields from the proton resonance peaks of the corresponding monomers. Then, when the concentration of 14-2-14 is almost  $0.11$  mM, the molar concentration of monomers equals that of micelles, and thus the cmc value of 14-2-14 ( $\text{cmc}_{14-2-14}^*$ ) in mixed solutions is  $0.055$  mM. When the concentration is higher than  $\text{cmc}_{14-2-14}^*$ , with the further increase in total concentration, the molar concentration of monomers of 14-2-14 remains unchanged (in the initial stages of micelles formed, it departs a little from the cmc value, which maybe resulted from the formation of premicelles),<sup>38</sup> whereas the content of the micelles increases. That is to say, the increased 14-2-14 molecules in the solution associate, forming aggregates. Moreover, the aggregates of 14-2-14 at this concentration range should be single and pure micelles because the chemical shift of the resonance peaks for TX-100 does not show any changes at this interval. It is evident from Figure 7 that cross peaks



**Figure 9.** Variations of  $\delta_{\text{obsd}}$  of T6 (TTAB) and H6 (12-2-12) in 12-2-12/TTAB mixed solutions as a function of reciprocals of their individual concentrations in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$  for  $\alpha_{\text{TTAB}}$  = (a) 0.79, (b) 0.73, (c) 0.42, and (d) 0.19, respectively. The points of intersection of two lines indicate the cmc's, and the values in brackets are the total concentrations.



**Figure 10.** Variations of the total concentration at the cmc of 12-2-12 ( $c_{\text{T}}^{12-2-12}$ ) and TTAB ( $c_{\text{T}}^{\text{TTAB}}$ ) in 12-2-12/TTAB mixed solutions as a function of mole fraction of TTAB ( $\alpha_{\text{TTAB}}$ ).

between protons of TX-100 (T5 and T8) and those of 14-2-14 (H2) merged. It suggests that after the micellization of the surfactant of lower cmc (14-2-14 in this case), when the total concentration reaches and exceeds the cmc of the surfactant with higher cmc (TX-100 in this case), the TX-100 molecules participate in the mixed micelles. This further supports the conclusion made for the 12-2-12/TX-100 mixed solution.

The cmc value of the fast exchanging TX-100 was also gained as before by the fitting chemical shift of resonance peaks of T8 as a function of reciprocals of concentrations (Figure 8), which is  $\sim 0.028$  mM ( $\text{cmc}_{\text{TX-100}}^*$ , corresponding to  $C_{14-2-14} = 0.065$  mM). This result indicates that when the concentration of 14-

2-14 in mixed solutions is 0.065 mM, the molecules of TX-100 aggregate into micelles. Further looking into variations of chemical shift for T8, one finds that when the concentration of TX-100 is equal or higher than  $\text{cmc}_{\text{TX-100}}^*$ ,  $\delta_{\text{T8}}$  begins to move to a lower field as the concentration increases. As we have discussed,  $\delta_{\text{T8}}$  moves monotonously to a higher field as the concentration increases in pure TX-100 micelles. This suggests that T8 in 14-2-14/TX-100 mixed micelles is located in a lower field than that in pure TX-100 micelles, similar to the 12-2-12/TX-100 system. The change in the  $\delta_{\text{T8}}$  is direct evidence that molecules of TX-100 join 14-2-14 molecules forming mixed micelles.

Moreover, the same as in 12-2-12/TX-100 and SDS/TX-100 systems, for  $\alpha_{\text{TX-100}} = 0.3$ ,  $\alpha_{\text{TX-100}}^* (\text{cmc}_{\text{TX-100}}^* / [\text{cmc}_{\text{TX-100}}^* + \text{cmc}_{14-2-14}^*]) = 0.34$ , which equals  $\alpha_{\text{TX-100}}$ , the mole fraction of the total concentration.

It should be noticed that for 12-2-12/TX-100, there are micelles of TX-100 formed first; then, 12-2-12 molecules join them. However, in 14-2-14/TX-100 mixed system ( $\alpha_{\text{TX-100}} = 0.3$ ), micelles of 14-2-14 formed first, and molecules of TX-100 join the micelles of 14-2-14. Although 14-2-14 and 12-2-12 are analogs, they differ only in the length of the hydrophobic chain by two methylene groups, but in their mixed systems with TX-100, micelles of TX-100 do not always form first. That is because the cmc value of TX-100 is lower than that of 12-2-12, whereas the cmc value of 14-2-14 is much lower than that of TX-100. From the three ionic-nonionic mixed systems, 12-2-12/TX-100, SDS/TX-100, and 14-2-14/TX-100, studied above, one can conclude that individual micelles of the component, which has a lower cmc than the other component in the mixed solution, form first. As the total concentration increases, the concentration of the other component with higher cmc reaches

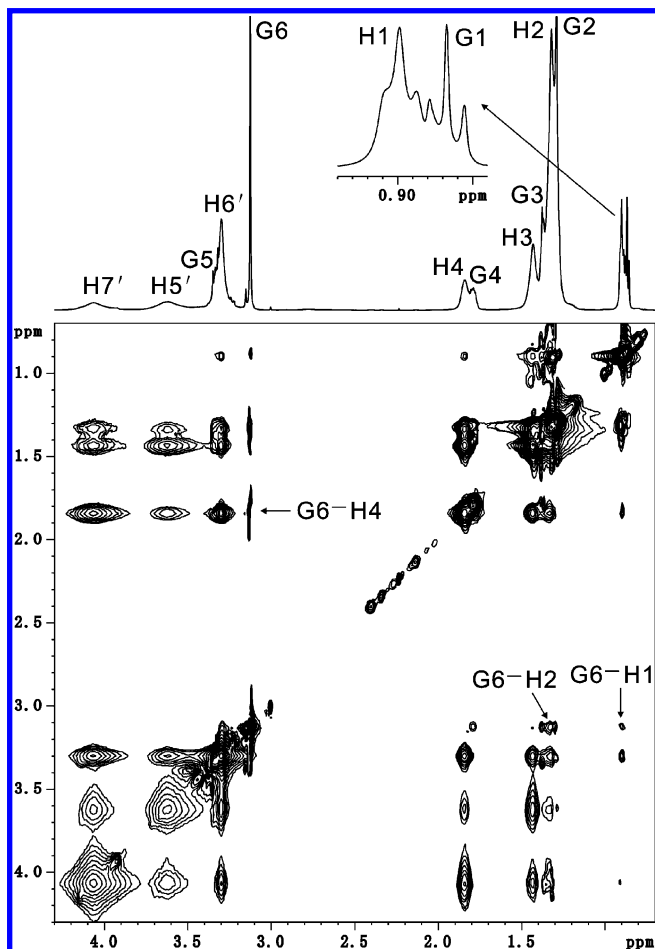


Figure 11. 2D NOESY spectrum of 12-2-12/TTAB mixed solution of 1.1 mM with a mixing time of 0.3 s for  $\alpha_{\text{TTAB}} = 0.42$ .

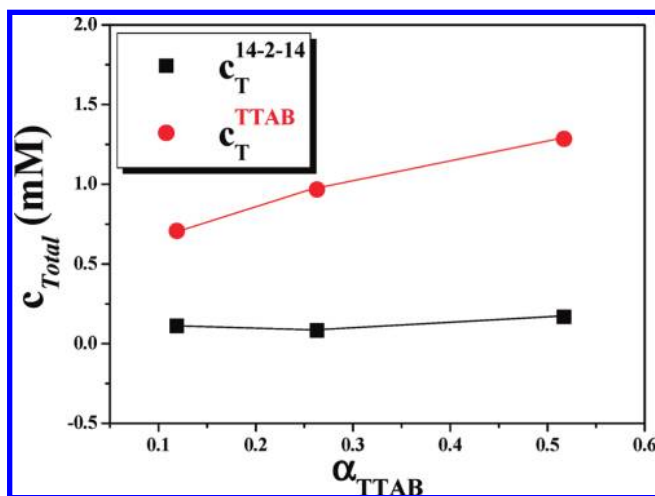


Figure 12. Variations of the total concentration at the cmc of 14-2-14 ( $c_{\text{T}}^{14-2-14}$ ) and TTAB ( $c_{\text{T}}^{\text{TTAB}}$ ) in 14-2-14/TTAB mixed solutions as a function of mole fraction of TTAB ( $\alpha_{\text{TTAB}}$ ).

its cmc in the mixed solution; then, its molecules join the already formed micelles of the component with lower cmc, forming mixed micelles.

**2. Ionic/Ionic Mixed Solutions.** As is concluded above, for the three ionic/nonionic mixed systems studied above, 12-2-12/TX-100, SDS/TX-100, and 14-2-14/TX-100, individual micelles of the component, which has a lower cmc than the other component in the mixed solution, form first. As the total concentration increases, until the concentration of the other

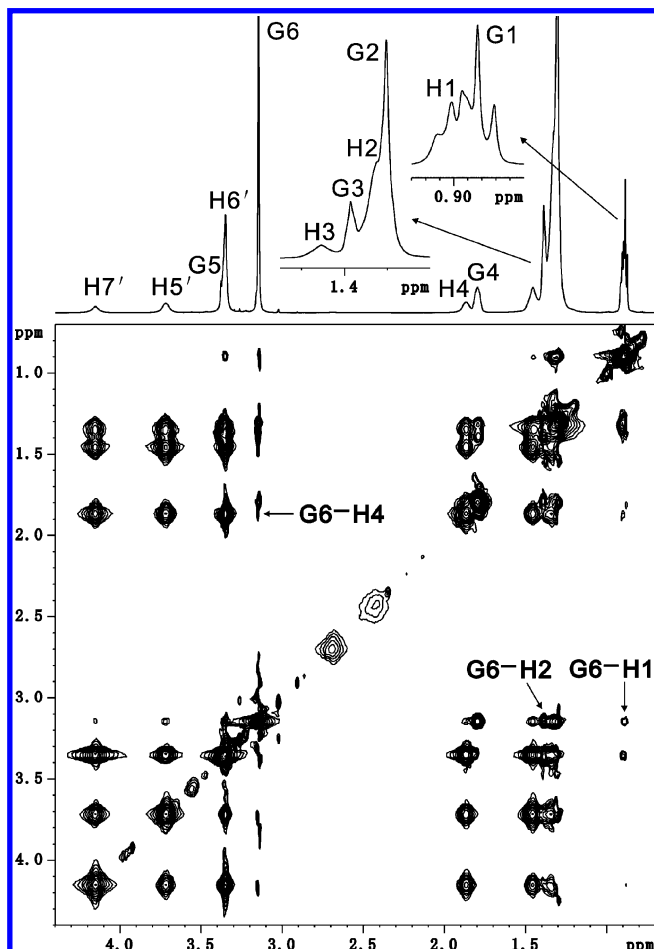


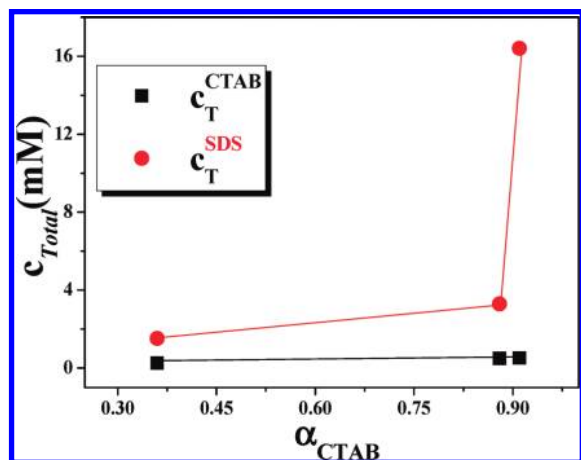
Figure 13. 2D NOESY spectrum of 14-2-14/TTAB mixed solution of 4.0 mM with a mixing time of 0.3 s for  $\alpha_{\text{TTAB}} = 0.75$ .

component with higher cmc reaches its cmc in the mixed solution, its molecules join the already formed micelles, forming mixed micelles. What about ionic/ionic mixed solutions? To answer this question completely, we studied three ionic/ionic mixed solutions, including cationic/cationic, 12-2-12/TTAB, 14-2-14/TTAB, and cationic/anionic, SDS/CTAB.

**2.1. 12-2-12/TTAB Mixed System.** As we all know, 12-2-12 ( $[\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3]_2(\text{CH}_2)_2 \cdot 2\text{Br}^-$ ) is a cationic quaternary ammonium gemini surfactant, and TTAB ( $\text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_3 \cdot \text{Br}^-$ ) is a cationic quaternary ammonium conventional surfactant. For their similarity in structure, they exhibit similar  $^1\text{H}$  NMR spectra, and most of their proton peaks overlap in the  $^1\text{H}$  NMR spectrum. Fortunately, the proton peaks of T6 (TTAB) can still be detected apart from the proton peaks of 12-2-12, and the proton peaks of H6 (12-2-12) can be detected, too. Similar to 12-2-12/TX-100, 14-2-14/TX-100, and SDS/TX-100 systems,  $^1\text{H}$  NMR spectra of 12-2-12/TTAB mixed systems, for  $\alpha_{\text{TTAB}} = 0.79, 0.73, 0.42, 0.19$ , at various total concentrations were acquired, respectively. Variations of  $\delta_{\text{obsd}}$  of T6 (TTAB) and H6 (12-2-12) in 12-2-12/TTAB mixed solutions as a function of reciprocals of their individual concentrations are shown in Figure 9. The cmc's of 12-2-12 and TTAB in mixed solutions were obtained and were the same as those for the above systems. The values of the total concentration when 12-2-12 ( $c_{\text{T}}^{12-2-12}$ ) or TTAB ( $c_{\text{T}}^{\text{TTAB}}$ ) started forming micelles are in the brackets.

The total concentrations at the cmc of 12-2-12 ( $c_{\text{T}}^{12-2-12}$ ) and TTAB ( $c_{\text{T}}^{\text{TTAB}}$ ) in 12-2-12/TTAB mixed solutions at different mole fractions of TTAB ( $\alpha_{\text{TTAB}}$ ) are depicted in Figure 10. It shows that the cmc's of the pair of mixed surfactants in the solution are different. Consequently, the one with lower cmc





**Figure 14.** Variations of the total concentration at the cmc of SDS ( $c_{\text{SDS}}^{\text{cmc}}$ ) and CTAB ( $c_{\text{CTAB}}^{\text{cmc}}$ ) in SDS/CTAB mixed solutions as a function of mole fraction of CTAB ( $\alpha_{\text{CTAB}}$ ).

in the mixed solution will aggregate first; then, the other will join the first micellized surfactant when its cmc is reached as the total concentration increases. The appearance of cross peaks between the protons of 12-2-12 and those of TTAB in the 2D NOESY spectrum of the mixed solution at the concentration higher than the cmc value of the surfactant with higher cmc (TTAB in this case) in the mixed solution, shown in Figure 11, shows that mixed micelles of the two cationic surfactants occurred. It definitely shows that the mechanism of mixed micellization is strictly dependent on the cmc of the pair of mixed surfactants but independent of the type of surfactant.

**2.2. 14-2-14/TTAB Mixed System.** 14-2-14 ( $[\text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_3]_2(\text{CH}_2)_2 \cdot 2\text{Br}^-$ ) is another cationic quaternary ammonium gemini surfactant. TTAB ( $\text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_3 \cdot \text{Br}^-$ ) is just a moiety of 14-2-14. Three 14-2-14/TTAB mixed solutions with different mole fraction of TTAB ( $\alpha_{\text{TTAB}}$ ) were investigated. The total concentrations at which 14-2-14 and TTAB begin to aggregate were detected, respectively. The results are shown in Figure 12. It further shows that although 14-2-14 and TTAB are very similar in chemical structure they still aggregate at different total concentrations of the mixed solution. The NOESY results (Figure 13) of the 14-2-14/TTAB mixed solution give the same conclusion as the 12-2-12/TTAB system.

**2.3. SDS/CTAB Mixed System.** It would be interesting to get some insight into the mixed micellization of the cationic/anionic surfactants, where electrostatic interaction may occur. Using the two well-known conventional surfactants, SDS and CTAB, as mixed surfactants at three different mole fractions, where precipitation does not occur, we also found that they aggregate at different total concentrations of the mixed solution, as depicted in Figure 14.

## Conclusions

Micellization of two different types of mixed surfactant systems, including three ionic/nonionic mixed solutions, 12-2-12/TX-100, SDS/TX-100, and 14-2-14/TX-100, and three ionic/ionic mixed solutions, 12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB, was investigated by  $^1\text{H}$  NMR and 2D NOESY experiments. The results show that for 12-2-12/TX-100 and SDS/TX-100 mixed systems, micelles of TX-100 (lower cmc value in the mixed solution) formed first, and then 12-2-12 and SDS join the micelles of TX-100, respectively, which was proved by 2D NOESY experiments. However, for 14-2-14/TX-100, micelles of 14-2-14 (with a much lower cmc value in the mixed solution than TX-100) formed first; then, TX-100 molecules join them. Although 14-2-14 and 12-2-12 are analogs, in their mixed systems with TX-100, micelles of TX-100 not

always formed first. The same results were obtained in the other three ionic/ionic mixed solutions, 12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB. 12-2-12, 14-2-14, CTAB form micelles first in 12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB mixed solutions, respectively. The above NMR study has fully described the mixed micelle formation at a molecular level. From the results of various mixed surfactant systems, one can conclude that neither pair of the mixed surfactants aggregates synchronously. It obviously demonstrates that the so-called "cmc of the mixed surfactant solution" needs reconsideration.

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