

## ARTICLE

# Interaction in Binary Mixtures of Gemini Surfactant G12-6-12 and CTAB by NMR

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The interaction between *N,N'*-bis(dimethyldodecyl)-1,6-hexanediammoniumdibromide (G12-6-12) and cetyltrimethylammonium bromide (CTAB) in D<sub>2</sub>O aqueous medium has been investigated by NMR at 298 K. The measured critical micelle concentration (cmc) of G12-6-12 and CTAB are about 0.773 and 0.668 mmol/L, respectively. The cmc\* (cmc of mixture) values are less than CMC\* (cmc of ideally mixed solution) in the mixed system, and the interaction parameter  $\beta_M < 0$  at different molar fractions  $\alpha$  of G12-6-12 in the mixed systems, but just when  $\alpha \leq 0.3$ , cmc\* values are much smaller than CMC\*, and  $\beta_M$  satisfies the relation of  $|\beta_M| > |\ln(\text{cmc}_1/\text{cmc}_2)|$  (cmc<sub>1</sub>: cmc of pure G12-6-12 and cmc<sub>2</sub>: cmc of pure CTAB). The results indicate that there exists synergism between G12-6-12 and CTAB, and they can form mixed micelles, which is further proven by 2D NOESY and self-diffusion coefficient *D* experiments. There are intermolecular cross peaks between G12-6-12 and CTAB in 2D NOESY, and the radius of micelles in mixed solution is bigger than that in G12-6-12 pure solution in *D* experiments, indicating there are mixed micelles. However, when  $\alpha > 0.3$ , we find that  $\text{cmc}^* \approx \text{CMC}^*$ ,  $\beta_M \approx 0$ , obviously, the two surfactants are almost ideal mixing fitting the pseudo-phase separation model and regular solution theory.

**Key words:** Interaction, Gemini surfactant, Cetyltrimethylammonium bromide, NMR

## I. INTRODUCTION

Gemini surfactants, consisting of two hydrophobic chains and two polar hydrophilic headgroups covalently linked by a spacer, have been attracting great attention for the special performance in the area of surfactant research. With their unique chemical structures, Gemini surfactants have been found to possess the properties which are superior to those of corresponding conventional surfactant [1–5] and hence have been widely used in many application fields, such as drug entrapment and release [6], the food industry [7], antibacterial and antifungal agents [8], oil recovery [9], *etc.*

The mixed solution of two or more surfactants has better performances than their respective pure solution, such as better wetting ability, lower surface tension and lower critical micelle concentration (cmc) and so forth [10]. The mixed surfactant systems often show synergistic behavior, and this will result in the reduction of the total amount of surfactant used in a particular application, which in turn reduces both production costs and environmental pollution [11]. Most of the inves-

tigations focused on the surface activity, micellar behavior and other properties in pure and mixed states in aqueous solutions through some macroscopic physicochemical properties [12–15]. And with the development of analytical instruments, the interaction, mixed micelle formation mechanism, interfacial property and other properties of the binary surfactant mixed systems were studied by conductivity, surface tension, fluorescence quenching technique and other methods [16–23]. In recent years, the pure and binary surfactant mixed system have been studied via NMR technology, which provides information at a molecular level [24–30]. However, most of them focus on the solution and interface properties of the mixed system consisting of two different types of surfactants, and there are few reports on the interaction between quaternary ammonium cationic Gemini surfactant and conventional cationic surfactant by NMR.

In the present work, we synthesized the cationic Gemini surfactant *N,N'*-bis(dimethyldodecyl)-1,6-hexanediammoniumdibromide (G12-6-12) and measured the cmc of G12-6-12 and Cetyltrimethylammonium bromide (CTAB) by NMR, and calculate the experimental cmc\* (cmc of mixture) and ideal CMC\* (cmc of ideally mixed solution) values. The interaction parameter  $\beta_M$  values were obtained within Rubingh's regular solution theory for mixed micelles. Combining 2D

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NOESY and self-diffusion coefficient  $D$  experiments with above results, we discussed the interaction of G12-6-12 and CTAB.

## II. MATERIALS AND METHODS

### A. Materials

CTAB was purchased from Shanghai Cheng Xin Chemical Ltd. with a purity of 99.0%, Gemini surfactant  $N, N'$ -bis (dimethyldodecyl)-1,6-hexanediammoniumdibromide (G12-6-12) was synthesized [31], and the structure was characterized by melting point, Fourier transformed infrared spectroscopy (FTIR), and  $^1\text{H}$  NMR. G12-6-12 or CTAB was used after three times recrystallizations with acetone.  $\text{Me}_3\text{Si}-(\text{CH}_3)\text{-SO}_3\text{Na}$  (DSS) is a spectrum pure reagent without any further purification.  $\text{D}_2\text{O}$  (99.9% deuterated) is a product of Cambridge Isotope Laboratories, Inc.

### B. Experiments

IR spectrum was recorded as a thin film on KBr pellet on FTIR (Spectrum one, Perkin-Elmer Optoelectronics Inc., USA). The melting point of G12-6-12 was measured at WRS-2A digital melting point instrument, Shanghai Shen Guang Instrument Co., Ltd.

All the mixed solutions were prepared in terms of different molar fractions of G12-6-12 ( $\alpha$ ) in the G12-6-12/CTAB mixed solution,  $\alpha=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8,$  and  $1.0,$  respectively, and the concentration ranged from  $0.01$  mmol/L to  $8$  mmol/L. The dilute solutions were stored for two weeks in the sample tube before the NMR experiments. In addition,  $1$  mmol/L DSS solution was prepared as the external standard.

All the NMR experiments were operated on a UNITY Varian INOVA-600 spectrometer with a proton frequency of  $599.78$  MHz at  $298$  K. For assuring complete recovery of magnetization vector, a small pulse flip-angle  $30^\circ$  was used rather than  $90^\circ$  in the standard single pulse sequence. The bipolar gradient longitudinal eddy-current delay (LED-BPP) sequence [32] was used to measure the self-diffusion coefficient  $D$ , with  $gt_1=3.5$  ms,  $del=0.1$  s. Two dimensional nuclear overhauser enhancement (2D NOESY) experiments were performed with standard three-pulse sequences with a mixing time of  $600$  ms, and  $t_2 \times t_1=2048 \times 512$  sampling data points array. The data point array  $F_2 \times F_1=2048 \times 512$  was used in the Fourier transformation after zero filling.  $\text{D}_2\text{O}$  was used as a solvent instead of water in order to weaken the water signal.

## III. THEORETICAL BACKGROUND

The molecular aggregation state would change with the concentration of the surfactant in aqueous solution.

For surfactants of fast exchange between the monomers and micelles in the bulk solution, the observed chemical shift  $\delta_{\text{obs}}$  of the resonance peak can be expressed as the weighted mean of chemical shifts of the monomers  $\delta_{\text{mon}}$  and micelles  $\delta_{\text{mic}}$  at concentrations above their cmc according to the pseudo-phase transition model [33] by the following equation:

$$\delta_{\text{obs}} = \frac{c_{\text{mon}}}{c_t} \delta_{\text{mon}} + \frac{c_{\text{mic}}}{c_t} \delta_{\text{mic}} \quad (1)$$

where  $c_{\text{mon}}$  and  $c_{\text{mic}}$  are the concentrations of monomers and micelles, respectively. The total concentration  $c_t$  is equal to  $c_{\text{mon}}$  and  $c_{\text{mic}}$ , namely,  $c_t=c_{\text{mon}}+c_{\text{mic}}$ .

The surfactants exist in the form of monomers at concentrations below their cmc, so that

$$c_t = c_{\text{mon}}, \quad \delta_{\text{obs}} = \delta_{\text{mon}} \quad (2)$$

Above their cmc, it is supposed that the free monomer concentration remains unchanged and equals to cmc, namely,  $c_{\text{mon}}=\text{cmc}$ , so Eq.(1) can be rewritten as

$$\delta_{\text{obs}} = \frac{\text{cmc}}{c_t} (\delta_{\text{mon}} - \delta_{\text{mic}}) + \delta_{\text{mic}} \quad (3)$$

According to Eq.(2) and Eq.(3), by plotting  $\delta_{\text{obs}}$  as a function of the reciprocal of the total concentration ( $1/c_t$ ) at concentrations above and below the cmc, two straight lines should form, and the intersection point is  $1/\text{cmc}$ . Thus the cmc of surfactant can be obtained easily.

Self-diffusion coefficients  $D$  could quantify the size of surfactant molecules in aqueous solutions, which reflects state of the molecules [34]. The relation between  $D$  and the micellar hydrodynamic radius,  $R_h$ , is expressed by the Stokes-Einstein equation [35],

$$D = \frac{kT}{6\pi\eta R_h} \quad (4)$$

where  $\eta$  represents the viscosity of the solution, which approximately equals that of  $\text{D}_2\text{O}$ . It is reasonable to say that the bigger the micellar radius is, the smaller the micellar  $D$  is.

The non-ideality of the mixed system can be expressed by an interaction parameter,  $\beta_M$ , which was given by the regular solution theory (RST) [36] proposed by Rubingh *et al.* and can be calculated with the following equations,

$$\frac{(x_M)^2 \ln \left( \frac{\text{cmc}^* \alpha}{\text{cmc}_1 x_M} \right)}{(1-x_M)^2 \ln \left[ \frac{\text{cmc}^* (1-\alpha)}{\text{cmc}_2 (1-x_M)} \right]} = 1 \quad (5)$$

$$\beta_M = \frac{\ln \left( \frac{\text{cmc}^* \alpha}{\text{cmc}_1 x_M} \right)}{(1-x_M)^2} \quad (6)$$

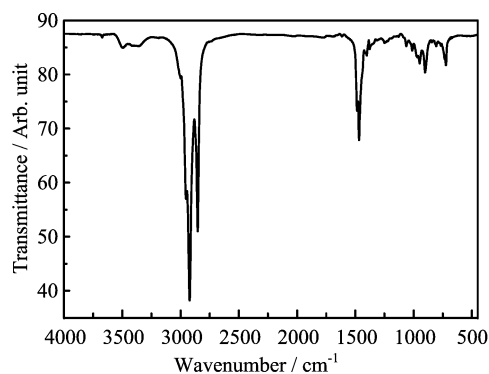


FIG. 1 IR spectrum of G12-6-12.

where  $x_M$  is the molar fraction of G12-6-12 in mixed micelles when the total concentration of mixed solution is equal to  $\text{cmc}^*$ ,  $\beta_M$  is the interaction parameter which is a measure for the extent of interaction between the surfactants.  $\beta_M=0$ , indicates no interactions between two surfactants,  $\beta_M>0$  or  $\beta_M<0$  represent repulsive or attractive interactions. The conditions for synergism or antagonism for two surfactants have been shown mathematically as: for synergism,  $\beta_M<0$  and  $|\beta_M|>|\ln(\text{cmc}_1/\text{cmc}_2)|$ ; for antagonism,  $\beta_M>0$  and  $|\beta_M|>|\ln(\text{cmc}_1/\text{cmc}_2)|$  [37].

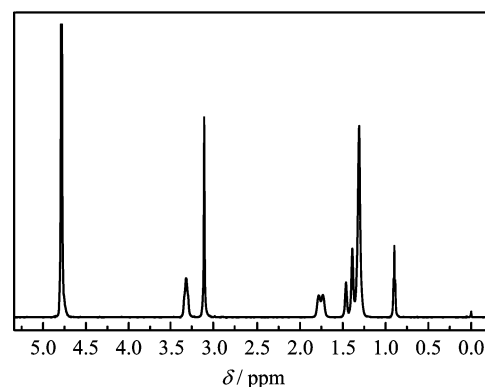
## IV. RESULTS AND DISCUSSION

### A. Structure characterization of G12-6-12

We synthesized the Gemini surfactant G12-6-12, and the structure was characterized by melting point, FTIR and  $^1\text{H}$  NMR. IR and  $^1\text{H}$  NMR spectra are shown in Fig.1 and Fig.2, respectively. The main characteristic peaks of G12-6-12 in IR spectrum are N-CH<sub>3</sub> and long carbon chain. Figure 1 shows significant bands at 2952, 2922, and 2852  $\text{cm}^{-1}$ , revealing the high strength absorption bands from the C-H stretching vibrations, and 1484, 1468, 1402, 1377, and 722  $\text{cm}^{-1}$  are C-H bending vibration in plane. And peaks in the 1062–901  $\text{cm}^{-1}$  region shows the C-N stretching vibrations. From Fig.2, we can see peaks  $\delta$  0.898 (t, 6H, CH<sub>3</sub>), 1.308 (m, 28H, (CH<sub>2</sub>)<sub>7</sub>), 1.389 (m, 8H, (CH<sub>2</sub>)<sub>2</sub>), 1.462 (m, 4H, CH<sub>2</sub>), 1.782 (m, 4H, CH<sub>2</sub>), 1.733 (m, 4H, CH<sub>2</sub>), 3.119 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 3.332 (t, 8H, CH<sub>2</sub>). The chemical shifts, peak splitting, integral values are consistent with the structure of G12-6-12. Furthermore, the measured melting point of G12-6-12 is 227.4–227.9 °C, the melting range is rather short, which gives further evidence of the high purity G12-6-12.

### B. Proton numbering and assignments

The chemical structures and the proton numbering of G12-6-12 and CTAB are shown in Fig.3.  $^1\text{H}$  NMR

FIG. 2  $^1\text{H}$  NMR spectrum of G12-6-12.TABLE I The chemical shifts of  $^1\text{H}$  NMR of pure G12-6-12 and CTAB, [G12-6-12]=5 mmol/L, [CTAB]=5 mmol/L.

G12-6-12	$\delta/\text{ppm}$	CTAB	$\delta/\text{ppm}$
G1	0.903	C1	0.881
G2	1.313	C2	1.299
G3	1.395	C3	1.380
G4	1.737	C4	1.788
G5/G7	3.342	C5	3.158
G6	3.133	C6	3.390
G8	1.787		
G9	1.471		

spectra of G12-6-12, CTAB and G12-6-12/CTAB mixed system are shown in Fig.4. The chemical shifts of the  $^1\text{H}$  NMR of G12-6-12 and CTAB are listed in Table I. Taking account of the signal to noise ratio (S/N) and proton peaks overlap in the G12-6-12/CTAB mixed system in Fig.4, we would primarily focus on the related information of the protons numbered G6 and C6.

### C. cmc of G12-6-12 and CTAB

According to Eq.(2) and Eq.(3), the  $\delta_{\text{obs}}$  of G1, G6, C1, and C6 are plotted as a function of  $1/c_t$ , as shown in Fig.5. It is evident that  $\delta_{\text{obs}}$  of G12-6-12 and CTAB remain unchanged at relatively lower concentrations, then a rapid increase occurs with the concentration, and forms a clear intersection, the cmc could be calculated from the intersection.  $\text{cmc}_1$  and  $\text{cmc}_2$  are the cmc of pure G12-6-12 and CTAB, then the cmc obtained via G6, G1, C6, and C1 was  $\text{cmc}_{1,G6}=0.773$  mmol/L,  $\text{cmc}_{1,G1}=0.781$  mmol/L,  $\text{cmc}_{2,C6}=0.668$  mmol/L, and  $\text{cmc}_{2,C1}=0.659$  mmol/L, respectively, which were in good agreement with the results in Refs.[38, 39]. Meanwhile we found that  $\text{cmc}_{1,G6}\approx\text{cmc}_{1,G1}$  and  $\text{cmc}_{2,G6}\approx\text{cmc}_{2,G1}$ , therefore we could choose either G6 or G1 and C6 or C1 protons as the object of study. For the sake of convenience, we

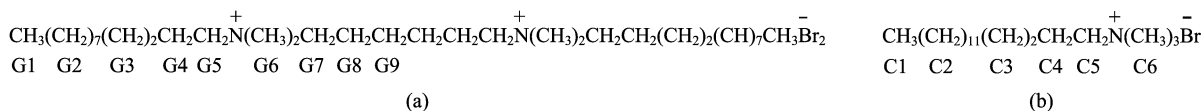


FIG. 3 Chemical structures and proton numbering of (a) G12-6-12 and (b) CTAB.

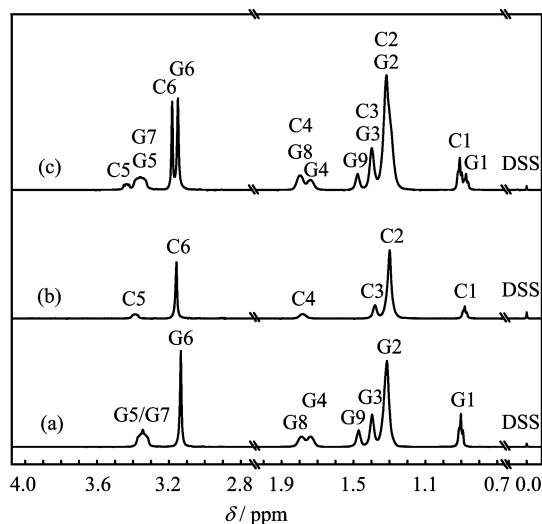


FIG. 4  $^1\text{H}$  NMR spectra and proton assignments of (a) G12-6-12, (b) CTAB, and (c) G12-6-12/CTAB mixed system,  $[\text{G12-6-12}] = 5 \text{ mmol/L}$  and  $[\text{CTAB}] = 5 \text{ mmol/L}$ .

mainly selected G6 and C6 protons to discuss the interaction and mixed micelle formation in G12-6-12/CTAB system.

Figure 6 presents the changes in chemical shifts, and peak shapes of G12-6-12 with the concentration. When  $[\text{G12-6-12}] < 0.8 \text{ mmol/L}$ , there are almost no changes in all the  $^1\text{H}$  NMR spectra, which reveals that, the G12-6-12 molecules keep in the monomeric states in the solution. At  $[\text{G12-6-12}] > 0.8 \text{ mmol/L}$ , the resonance peaks of G12-6-12 begin to move towards lower fields sharply, and the peak shapes change from wide to narrow, because the G12-6-12 monomers start to self-aggregate and form micelles. Therefore, the cmc of G12-6-12 should be about  $0.8 \text{ mmol/L}$ , this result is consistent with that in Fig.5(a). Moreover, we can also observe that the resonance peak of G6 proton in hydrophilic head groups move towards lower fields much more obviously than that of hydrophobic chains, that is, the chemical environment of the hydrophilic head groups changes more significantly with the concentration increasing. The results also indicate that the hydrophilic head groups of G12-6-12 arrange at the micelle surface and become closer to each other, while there are small variations of the density of hydrophobic chains in the micelle core.

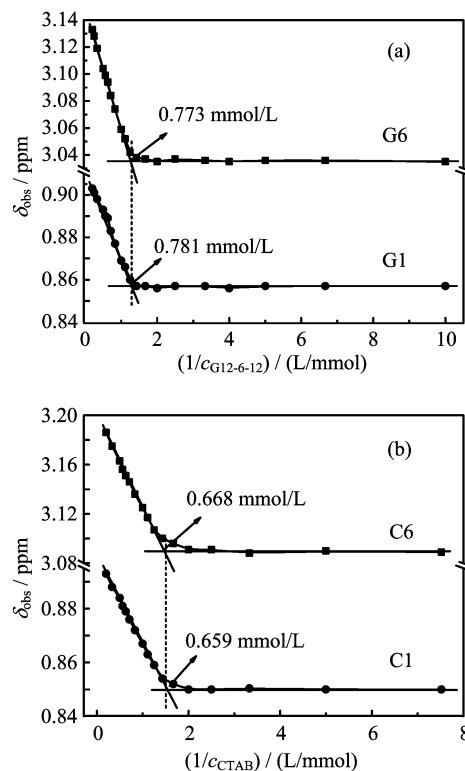


FIG. 5 Variation of chemical shifts of (a) G12-6-12 and (b) CTAB *vs.* reciprocals of their concentration in  $\text{D}_2\text{O}$ .

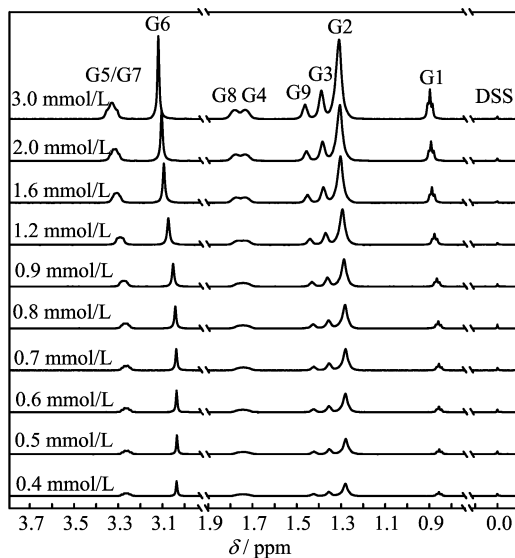
#### D. Interaction between G12-6-12 and CTAB

The cmc of surfactant solution could be determined by many methods, such as surface tension, conductivity, NMR and other methods [38], but only NMR method can determine the cmc of each component in the mixed surfactant system [28, 33, 39, 40]. In accordance with Eq.(3), we can make approximations for the mixture of surfactant solution system [40].

Figure 7 shows the curves of the chemical shifts of G6 or C6 versus the reciprocals of G12-6-12 or CTAB concentration in G12-6-12/CTAB system with  $\alpha_{\text{G12-6-12}} = 0.5$ . The variation tendency of the chemical shifts appears inflection points, corresponding cmc is  $\text{cmc}_1^* = 0.416 \text{ mmol/L}$ ,  $\text{cmc}_2^* = 0.292 \text{ mmol/L}$  (\* stands for cmc in mixed solution state) and we found that  $\text{cmc}_1^* < \text{cmc}_1 = 0.773 \text{ mmol/L}$ ,  $\text{cmc}_2^* < \text{cmc}_2 = 0.668 \text{ mmol/L}$ . That is, cmc of either G12-6-12 or CTAB is less than that of the corresponding pure solution. Thus the mixture of the two surfactants can reduce the cmc of solution and improve the surface ac-

TABLE II The experimental and ideal cmc, and  $\beta_M$  of the mixed systems at different  $\alpha$ .

$\alpha$	$\text{cmc}_1^*/(\text{mmol/L})$	$\text{cmc}_2^*/(\text{mmol/L})$	$\text{cmc}^*/(\text{mmol/L})$	$\text{CMC}^*/(\text{mmol/L})$	$x_M$	$\beta_M$
0.0		0.668	0.668	0.668		
0.1	0.083	0.516	0.599	0.677	0.167	-1.107
0.2	0.152	0.452	0.604	0.687	0.243	-0.770
0.3	0.198	0.446	0.644	0.696	0.301	-0.381
0.4	0.372	0.319	0.691	0.706	0.371	-0.093
0.5	0.416	0.292	0.708	0.717	0.464	-0.046
0.6	0.508	0.212	0.720	0.727	0.563	-0.031
0.8	0.637	0.104	0.741	0.749	0.769	-0.052
1.0	0.773		0.773	0.773		

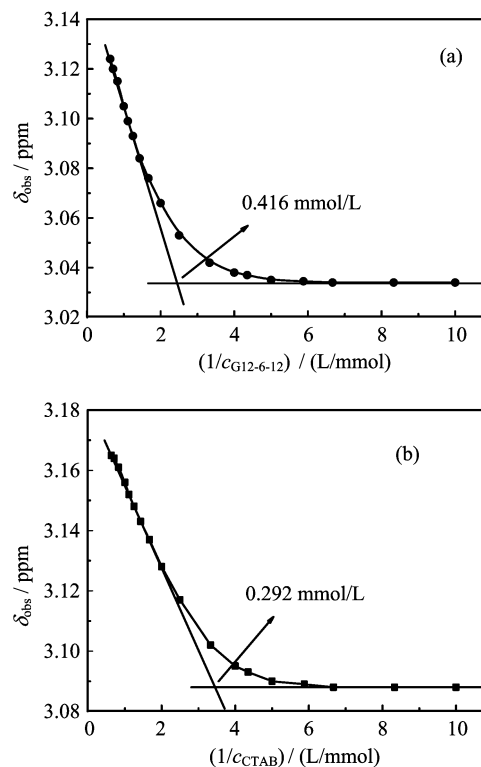
FIG. 6  $^1\text{H}$  NMR spectra of G12-6-12 at various concentrations with the DSS external standard.

tive properties.

Similarly, the cmc of G12-6-12 ( $\text{cmc}_1^*$ ) and CTAB ( $\text{cmc}_2^*$ ) in the mixed system at other different molar fractions could be obtained as shown Table II, and the sum of  $\text{cmc}_1^*$  and  $\text{cmc}_2^*$  is equal to the critical micellar concentration of the mixture ( $\text{cmc}^*$ ), namely,  $\text{cmc}^* = \text{cmc}_1^* + \text{cmc}_2^*$  [41, 42].  $\text{CMC}^*$  is the cmc of the ideal mixing state according to the pseudo-phase separation model and it can be calculated by the following formula [43],

$$\frac{1}{\text{CMC}^*} = \frac{\alpha}{\text{cmc}_1} + \frac{1-\alpha}{\text{cmc}_2} \quad (7)$$

where  $\text{cmc}_1$  and  $\text{cmc}_2$  are the cmc of pure G12-6-12 and CTAB, respectively. The pseudo-phase separation model assumes that the mixed micelle can be treated as a separate phase; there is a dynamic equilibrium between surfactant monomers and micelles in the solution. The  $\text{CMC}^*$  values of G12-6-12/CTAB mixed system at different  $\alpha$  are recorded in Table II. According to Eq.(5)

FIG. 7 Variation of chemical shifts of (a) G6 proton and (b) C6 proton vs. reciprocals of their concentration in G12-6-12/CTAB mixed solution with  $\alpha_{\text{G12-6-12}}=0.5$ .

and Eq.(6),  $x_M$  and  $\beta_M$  are calculated and also listed in Table II.

In Table II, at different  $\alpha$ , we found that  $\text{cmc}_1^* < \text{cmc}_1 = 0.773$  mmol/L,  $\text{cmc}_2^* < \text{cmc}_2 = 0.668$  mmol/L. When  $\alpha > 0.3$ ,  $0.668$  mmol/L  $< \text{cmc}^* < 0.773$  mmol/L; when  $\alpha \leq 0.3$ ,  $\text{cmc}^* < \text{cmc}_2 = 0.668$  mmol/L and  $\text{cmc}^* < \text{cmc}_1 = 0.773$  mmol/L, these results show that there may be two different molecular aggregation states and the dividing point is  $\alpha=0.3$ . We further found that when  $\alpha \leq 0.3$ ,  $\text{cmc}^*$  values are much smaller than  $\text{CMC}^*$ ,  $\beta_M$  satisfies the condition that  $|\beta_M| > |\ln(\text{cmc}_1/\text{cmc}_2)| = 0.146$ , indicating that G12-6-12/CTAB mixed system is non-ideal solution, and there

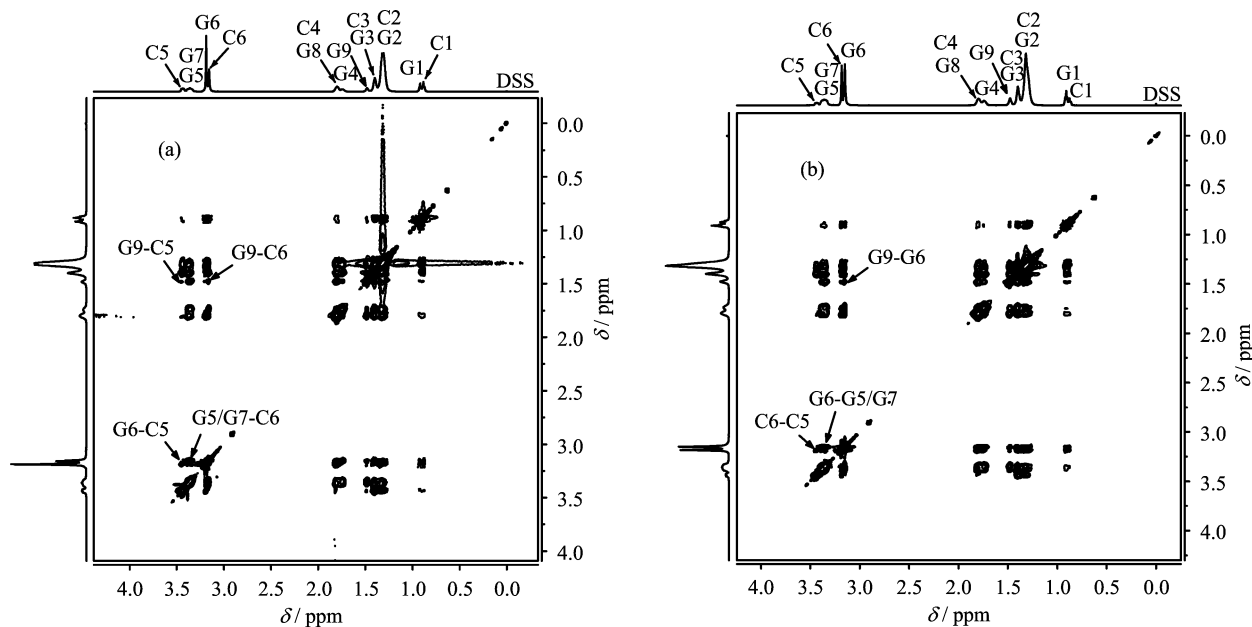


FIG. 8 Contour plots of the 2D NOESY spectra of G12-6-12/CTAB mixed system with a mixing time of 600 ms with (a)  $\alpha=0.3$ ,  $[G12-6-12]=3.0$  mmol/L,  $[CTAB]=7.0$  mmol/L; (b)  $\alpha=0.5$ ,  $[G12-6-12]=5.0$  mmol/L,  $[CTAB]=5.0$  mmol/L.

is synergism between G12-6-12 and CTAB molecules, but  $|\beta_M| < 3$ , indicating that the interaction between them is very weak [44]. When  $\alpha > 0.3$ ,  $cmc \approx CMC^*$  and  $\beta_M \approx 0$ , showing that they are almost ideal mixing. Thus it can be seen that just when  $\alpha \leq 0.3$ , there exists synergism between G12-6-12 and CTAB, thereinto, when  $\alpha=0.1$ , the synergism between G12-6-12 and CTAB is the strongest.

### E. The formation of mixed micelle

The formation of mixed micelle could be also confirmed by 2D NOESY and self-diffusion coefficient experiments. The 2D NOESY spectra for G12-6-12/CTAB mixed systems are shown in Fig.8 with  $\alpha=0.3$  and  $\alpha=0.5$ .

When  $\alpha=0.3$ ,  $[G12-6-12]=3.0$  mmol/L, and  $[CTAB]=7.0$  mmol/L, in Fig.8(a), except cross-peaks between protons on adjacent carbon atoms, there are intermolecular cross peaks between G12-6-12 and CTAB, G6-C5, G5/G7-C6, G9-C5, and G9-C6, which are marked with four arrows. The appearance of these cross peaks indicates that the distances between G5, G6, G7, G9 protons of G12-6-12 and C5, C6 protons of CTAB, respectively, are less than 5 Å [34], that is, hydrophilic groups of G12-6-12 and CTAB are very close in the mixed micelles. The results indicate that there is attractive interaction between G12-6-12 and CTAB and give direct evidence about the formation of mixed micelles.

When  $\alpha=0.5$ ,  $[G12-6-12]=5.0$  mmol/L, and  $[CTAB]=5.0$  mmol/L, in Fig.8(b), there are just intramolecular cross peaks between G12-6-12 and CTAB, G9-G6,

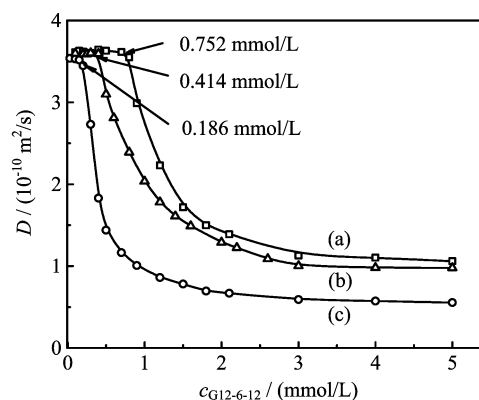


FIG. 9  $D$  of G12-6-12 *vs.* G12-6-12 concentration in (a) pure, (b) mixed solution with  $\alpha=0.5$ , and (c) mixed solution with  $\alpha=0.3$ .

C6-C5, and G6-G5/G7, because of the changes of the chemical environment of G6 and C6 protons in  $N-CH_3$ , which is different from the results of  $\alpha=0.3$ . The results show that they may self-aggregate freely, that is, there is no attractive interaction between them and they are almost ideal mixing.

Plots of self-diffusion coefficient  $D$  for G12-6-12 versus G12-6-12 concentration in pure G12-6-12 solution and G12-6-12/CTAB mixed solution with  $\alpha=0.3$  and  $\alpha=0.5$ , are shown in Fig.9.

From Fig.9, at relatively lower concentrations,  $D$  keeps unchanged whether in pure or in mixed solution,  $D_{\text{pure}} \approx D_{0.3} \approx D_{0.5}$ , showing that G12-6-12 remains in the monomeric states. With the G12-6-12 concentration increasing and reaching its  $cmc$ ,  $D$  starts falling,

and  $D_{0.3}$  decreases more rapidly than  $D_{\text{pure}}$  and  $D_{0.5}$ , and we can see that the cmc are about 0.752, 0.186, and 0.414 mmol/L, respectively, which is consistent with the data in Table II (0.773, 0.198, and 0.416 mmol/L). At a relatively higher concentration, it can be seen that  $D_{0.3} < D_{\text{pure}} \approx D_{0.5}$ . According to Eq.(4),  $D$  is inversely proportional to the micellar hydrodynamic radius ( $R_h$ ), consequently, the size of micelles in the mixed solution with  $\alpha=0.3$  is bigger than that in G12-6-12 pure solution and the mixed solution with  $\alpha=0.5$ , which further show that G12-6-12 and CTAB have formed the mixed micelles with  $\alpha=0.3$ . But  $D_{0.5} \approx D_{\text{pure}}$ , indicating that G12-6-12 and CTAB are ideal mixing in the studied concentration range. Thus the results are in good agreement with that obtained from the 2D NOESY experiment results. Similar experimental results were also obtained in the 2D NOESY and self-diffusion coefficient experiments of other mixed solutions with  $\alpha \leq 0.3$  and  $\alpha > 0.3$ , respectively, which are not shown here.

## V. CONCLUSION

We studied the mixed system of cationic surfactant G12-6-12 and CTAB by NMR and found an interesting phenomenon, that is, just when  $\alpha \leq 0.3$ , there exists synergism between G12-6-12 and CTAB; when  $\alpha > 0.3$ , there is almost no interaction. The conclusions are shown as follows: (i) The cmc of G12-6-12 and CTAB, measured by the variation of  $^1\text{H}$  NMR chemical shifts and peak shape, by self-diffusion coefficient, respectively, are consistent with each other. (ii) The cmc of both G12-6-12 and CTAB in the mixed system ( $\text{cmc}_1^*$  and  $\text{cmc}_2^*$ ) are lower than those of the corresponding pure G12-6-12 and CTAB, respectively. (iii) When  $\alpha \leq 0.3$ ,  $\text{cmc}^* < \text{CMC}^*$  and  $\beta_M < 0$ , it shows that the G12-6-12/CTAB mixed system is a non-ideal mixed system and synergism exists between G12-6-12 and CTAB, therinto, when  $\alpha=0.1$  the synergism is the strongest; when  $\alpha > 0.3$ ,  $\text{cmc}^* \approx \text{CMC}^*$ ,  $\beta_M \approx 0$ , indicating that they are almost ideal mixing. (iv) When  $\alpha \leq 0.3$ , there are intermolecular cross peaks between G12-6-12 and CTAB, G6-C5, G5/G7-C6, G9-C5, and G9-C6 in 2D NOESY, and the size of micelles in the mixed solution with  $\alpha \leq 0.3$  is bigger than that in G12-6-12 pure solution by self-diffusion coefficient experiments, which further shows that synergism exists between them. However when  $\alpha > 0.3$ , there are only G9-G6, C6-C5, and G6-G5/G7, and the size of micelles in the mixed solution with  $\alpha > 0.3$  is close to that in G12-6-12 pure solution by self-diffusion coefficient experiment results, which indicates that they are almost ideal mixing.

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