

# NMR Investigation of the Exchange Kinetics of Quaternary Ammonium Dimeric Surfactants C<sub>14</sub>-s-C<sub>14</sub>·2Br

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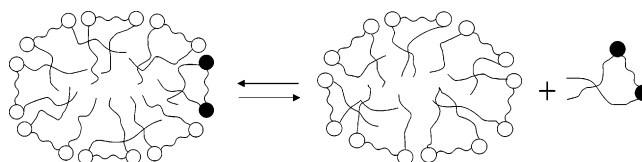
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The exchange kinetics of cationic gemini surfactants of the alkanediyl- $\alpha$ - $\omega$ -bis(tetradecyldimethylammonium bromide) type, with alkanediyl being 1,2-ethylene, 1,3-propylene, and 1,4-butylene, were investigated by <sup>1</sup>H NMR, 2D COSY, and 2D EXSY experiments. In contrast to the conventional surfactants, a second set of well-resolved resonance peaks appeared in the <sup>1</sup>H NMR spectra of these surfactants when their concentrations reached their critical concentrations. These two sets of resonance peaks originate from their monomers and micelles, which are proved by the correlation in the 2D COSY experiments and the cross polarization in the 2D NOESY spectra. Therefore, exchanges between monomers in the bulk solution and in the micelles or other aggregates of this series of surfactants occur slowly on the NMR time scale. The exchange rate constants were obtained by both NMR line shape analysis and 2D EXSY experiments, which are very consistent with each other. The exchange rate constants for the gemini surfactants were found to be orders of magnitude less than those for the conventional single surfactants, and for geminis 14-s-14, the shorter the spacer, the slower the exchange dynamic. It still has been found that the fast exchange between monomers in the bulk solution and in the micelles for gemini surfactant 12-2-12 at 25 °C occurs slowly at 5 °C on the NMR time scale.

## Introduction

The surfactant molecules dissolved in water cooperatively assemble into micelles when the concentration is above critical micellization concentration (cmc). Micelles are in dynamic equilibrium; rapid exchange occurs between surfactants in the micelles and in the surrounding bulk solution (Figure 1).<sup>1–9</sup> For single-chain surfactants and some gemini surfactants with short alkyl side chains, exchange between surfactant molecules in the micelles and in the bulk solutions is relatively fast. It requires fast techniques such as ultrasonic absorption,<sup>1,5,6</sup> pressure-jump, temperature-jump, and stopped-flow dilution techniques to trace the exchange process, including the relatively slower exchange for nonionic surfactants.<sup>2–5</sup> The exchange rate in this regime is too fast on the NMR time scale. Therefore, NMR spectra show averaged signals for the surfactant molecules in all possible states.<sup>2</sup> However, for some cationic gemini surfactants, exchange between monomers in the bulk solution and in the micelles or other aggregates occurs slowly on the NMR time scale; thus, NMR spectroscopy provides an efficient tool for studying micelle formation of this kind of surfactants and mixing of various surfactants.<sup>7</sup>

The unique ability to resolve and assign the separate signals due to nuclei in different chemical environments makes NMR especially powerful for kinetic studies.<sup>10</sup> It has been used to



**Figure 1.** Schematic representation of gemini surfactant exchange between micelles and the bulk phase.

investigate chemical exchange for many years. Many particular reports and reviews appeared.<sup>10–13</sup> Especially, an article<sup>10</sup> written by Charles L. Perrin and Tammy J. Dwyer chiefly discussed the application of two-dimensional NMR to the study of kinetics of chemical exchange, which will be helpful for realization of 2D EXSY. Besides, in another review, Alex D. Bain<sup>11</sup> stated, in detail, the variety of chemical exchange effects, kinetics and thermodynamic theory, and various NMR techniques for studying slow and fast exchange.

It has been shown that the critical micellar concentration (cmc) of a cationic gemini surfactant, 14-2-14, was not detected when using dynamic surface tension. It reflects a very slow adsorption of the surfactant due to its slow kinetics of micellization.<sup>14</sup> Ivan Huc and Reiko Oda<sup>7</sup> reported the slow exchange on the NMR time scale between monomeric and aggregated amphiphiles for this gemini surfactant, 14-2-14, and its lifetimes of monomeric and aggregated species obtained through line shape analysis of the broadened signals. C. Groth et al.<sup>3</sup> and Zana Raoul's group<sup>4</sup> investigated the exchange kinetics of geminis 12-s-12 by the stopped-flow technique combined with pulse-field-gradient spin-echo nuclear magnetic resonance measurements and pressure-jump relaxation techniques, respec-

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tively. However, for geminis 14-3-14 and 14-4-14, which have the same side alkyl chains but different spacer group lengths than gemini surfactant 14-2-14, the chemical exchange behavior between the surfactant monomers in aggregates and that in the surrounding solution has not been reported yet. Furthermore, the dependence of the exchange behavior and the exchange rate constants on the length of the spacer in the cationic gemini surfactants 14-s-14 are unknown. Accordingly, in this paper, the chemical exchange for geminis 14-s-14 ( $s = 2, 3$ , and  $4$ ) was investigated using NMR methods. <sup>1</sup>H NMR spectra provide intuitionist evidence of chemical exchange from the variation in line shape with concentration, and 2D COSY and 2D NOESY confirm the existence of slow exchange further. The exchange rate constants have been obtained using the classic line shape analysis and 2D exchange spectroscopy.

## Experimental Section

**Materials.** The quaternary ammonium dimeric surfactants, 12-2-12 and 14-s-14 ( $s = 2, 3$ , and  $4$ ), have been synthesized by the Southwest Petroleum University, who offered us the cmc value for 14-s-14 measured by surface tension. It was  $1.60 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ . D<sub>2</sub>O (99.8%) is the product of Beijing Chemical Factory of China. The above-mentioned reagents were used as received, without any further purification. D<sub>2</sub>O was used as the solvent instead of water in order to weaken the water signal.

**NMR Experiments.** All of the NMR measurements were performed on a Varian INOVA-500 NMR spectrometer with a <sup>1</sup>H frequency of 500.13 MHz at 25 °C. 2D <sup>1</sup>H, <sup>1</sup>H COSY spectra were carried out using the pulse programs supplied with the apparatus. Two-dimensional nuclear Overhauser enhancement (2D NOESY) experiments were performed with the standard three-pulse sequence. In order to get more and strong cross peaks and, at the same time, to avoid the effect of spin diffusion, 100 ms of mixing time was chosen. Thirty-two accumulations and  $t_2$  ( $F_2$  dimension)  $\times$   $t_1$  ( $F_1$  dimension) =  $2000 \times 256$  sampling data points array were used. 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. 2D EXSY experiments were processed with the same pulse sequence as that of 2D NOESY, but as an especially powerful method to study exchange kinetics, it is different from 2D NOESY. Several 2D EXSY experiments with varied mixing times were performed for choosing the optimum mixing time ( $t_{m,\text{opt}}$ ). The experimental parameters and the processing of experimental data are similar to those of 2D NOESY, as listed above. The assignments of signals were completed according to <sup>1</sup>H NMR, 2D COSY, and 2D NOESY.

**Line Shape Analysis Method.** An estimate of the characteristic time of exchange,  $\tau$ , can be very simply obtained from line shape analysis of a sample at a concentration which is twice the cmc.<sup>7</sup> At this concentration, the exchange characteristic lifetimes of monomeric and aggregated species are both equal to  $\tau$ , whose value is then given by

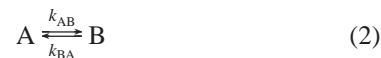
$$1/\tau = \pi \Delta \nu \quad (1)$$

where  $\Delta \nu$  is the line width difference between the monomer signal at twice the cmc (broadened by the exchange) and below the cmc (no exchange), as obtained from a least-square analysis of the spectra. The  $\tau$  values can be measured as long as separate signals are observed, which requires  $1/\tau < |\nu_m - \nu_a|$ , where  $\nu_m$  and  $\nu_a$  are the monomer and the aggregate signal frequencies.<sup>7</sup>

**2D Exchange Spectroscopy.** The general technique for the investigation of magnetic or chemical exchange processes in

liquids and solids, 2D EXSY, was proposed and demonstrated completely by Ernst and co-workers.<sup>15,16</sup>

For a system with two sites A and B, they may relax independently with relaxation rates  $R_{1A}$  and  $R_{1B}$ , which are the spin-lattice relaxation rates of nuclei in sites A and B, respectively. It is supposed to be a pure exchange system. A pseudo-first-order chemical exchange process is assumed, and  $k_{AB}$  is the rate constant for exchange from site A to site B



The dynamic process during the mixing time ( $t_m$ ) can be expressed by differential equation

$$\frac{d}{dt} \mathbf{M} = \mathbf{L} \cdot \mathbf{M} \quad (3)$$

where

$$\mathbf{M} = \begin{pmatrix} M_A \\ M_B \end{pmatrix} \quad (4a)$$

and

$$\mathbf{L} = \begin{pmatrix} -(k_{AB} + R_{1A}) & k_{BA} \\ k_{AB} & -(k_{BA} + R_{1B}) \end{pmatrix} \quad (4b)$$

Here,  $\mathbf{L}$  is dynamical matrix,  $k$  is exchange rate constant, and  $R_1$  is the spin-lattice relaxation rate.

If the amplitude matrix  $\mathbf{A}$  is defined as follows

$$\mathbf{A} = \mathbf{M}(t_m) \mathbf{M}_0^{-1} \quad (5)$$

$$\mathbf{M}_0 = \begin{pmatrix} I_{A0} & 0 \\ 0 & I_{B0} \end{pmatrix} \quad (6)$$

$$\mathbf{M}(t_m) = \begin{pmatrix} I_{AA} & I_{AB} \\ I_{BA} & I_{BB} \end{pmatrix} \quad (7)$$

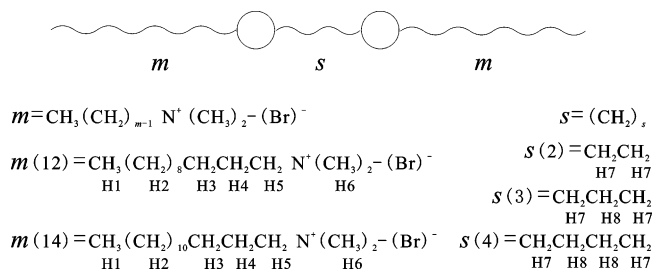
The dynamical matrix  $\mathbf{L}$  can be achieved based on the well-known formula

$$\mathbf{L} t_m = \ln \mathbf{A} \quad (8)$$

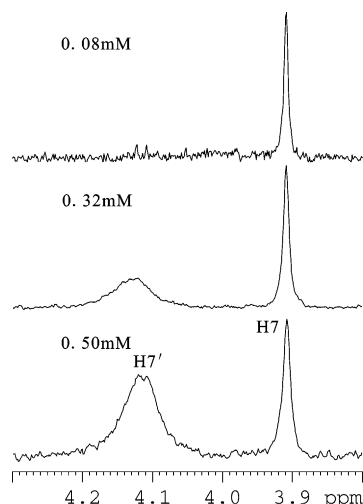
Matrices  $\mathbf{M}_0$  and  $\mathbf{M}(t_m)$  can be obtained by integrating the experimental NMR peaks, the elements of matrix  $\mathbf{M}_0$  being the intensities of diagonal peaks from the 2D EXSY spectrum at the mixing time of 0 ms, and can also be gained directly from the integrals of <sup>1</sup>H NMR corresponding peaks. The elements of matrix  $\mathbf{M}(t_m)$  are the intensities of diagonal peaks and cross peaks from the 2D EXSY spectrum at the mixing time of  $t_m$  ms. Since the integral in the NMR spectrum is relative, it is necessary to normalize the values of the elements of matrices  $\mathbf{M}_0$  and  $\mathbf{M}(t_m)$ . Generally, the values of the elements of matrix  $\mathbf{M}_0$  are normalized to 100, and those of matrix  $\mathbf{M}$  are normalized to  $100 \exp(-\bar{R} t_m)$ ;  $\bar{R}$  is the average of the spin-lattice relaxation rates of the nucleus involved in the exchange.

From eq 8, it is obvious that in order to evaluate the exchange rate constant, it is necessary to derive the dynamic matrix  $\mathbf{L}$  from the amplitude matrix  $\mathbf{A}$ . It is an alternative to directly diagonalizing the matrix  $\mathbf{A}$ .<sup>17</sup> Generally, it is simpler to expand  $\ln \mathbf{A}$  into a Taylor series<sup>18</sup>

$$\mathbf{L} t_m = \ln \mathbf{A} = (\mathbf{A} - \mathbf{I}) - \frac{1}{2} (\mathbf{A} - \mathbf{I})^2 + \frac{1}{3} (\mathbf{A} - \mathbf{I})^3 \dots \quad (9)$$



**Figure 2.** Chemical structures and proton labeling of gemini surfactants 12(*m*)-2(*s*)-12(*m*) and 14(*m*)-*s*-14(*m*) molecules, *s* = 2, 3, and 4.



**Figure 3.** A selected region of the  $^1\text{H}$  NMR spectra of 14-2-14 at various concentrations in  $\text{D}_2\text{O}$  at 25  $^\circ\text{C}$ .

However, there is a precondition for the Taylor's expansion of  $\ln \mathbf{A}$ , which is that the eigenvalues of the amplitude matrix  $\mathbf{A}$  not exceed 1, which assures that the Taylor series of eq 9 converges well enough. Nevertheless, by mathematical study of NMR two-dimensional chemical exchange spectroscopy (2D EXSY), it has been found that the eigenvalues of the amplitude matrix  $\mathbf{A}$  are always real, positive, and do not exceed 1.<sup>18</sup>

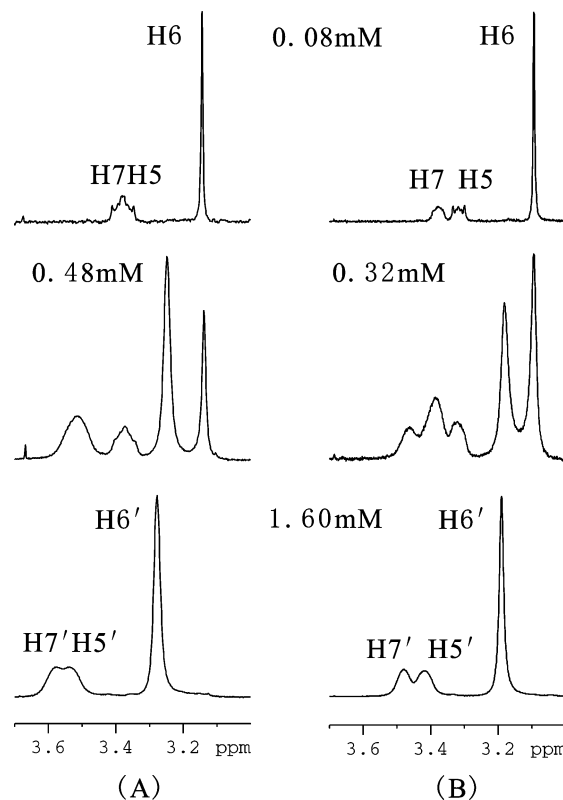
Actually, according to the investigation,<sup>10,19</sup> it is very important to choose the optimum mixing time. The determination of  $t_{\text{m, opt}}$  is gained by processing several 2D EXSY experiments with various mixing times. For a two-site system, the optimum mixing time can be shown as follows

$$t_{\text{m, opt}} \approx (R_1 + k_{\text{AB}} + k_{\text{BA}})^{-1} \quad (10)$$

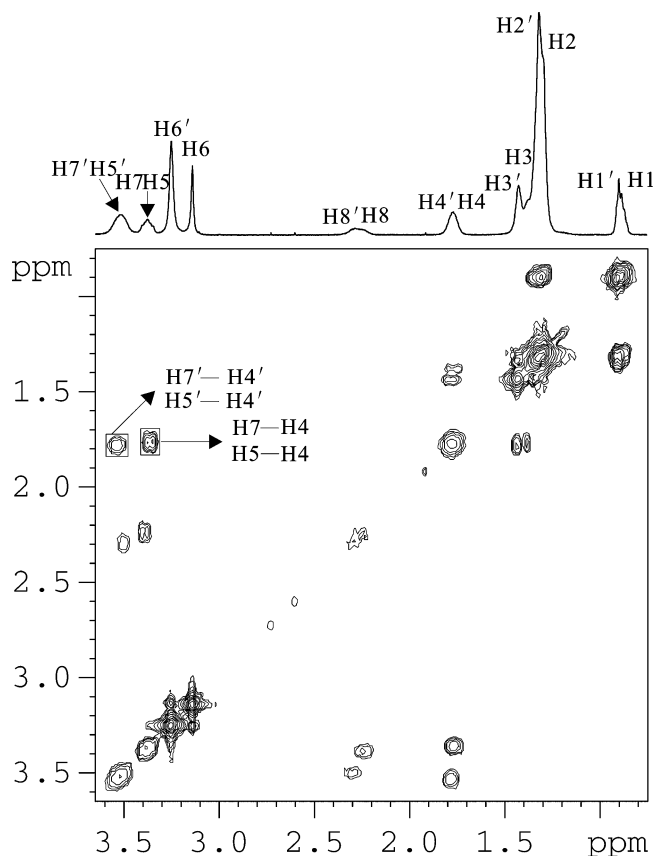
After obtaining the optimum mixing times,  $t_{\text{m, opt}}$ , the exchange rate constants  $k_{\text{AB}}$  and  $k_{\text{BA}}$  of the three exchange systems investigated at the individual optimum mixing time were obtained.

## Results and Discussion

**Slow Exchange on the NMR Time Scale.** Chemical structures and proton labeling of gemini surfactants 12(*m*)-2(*s*)-12(*m*) and 14(*m*)-*s*-14(*m*) molecules, *s* = 2, 3, and 4, are shown in Figure 2. A series of selected regions of the  $^1\text{H}$  NMR spectra of the 14-*s*-14 geminis at various concentrations in  $\text{D}_2\text{O}$  at 25  $^\circ\text{C}$  are shown in Figures 3 and 4. A number of additional broadened peaks, denoted as proton labels with primes (H1'–H8'), appeared in the  $^1\text{H}$  NMR spectra when the concentrations of the surfactant reached their critical micellization concentrations. The intensities of these broadened peaks increased with the increase in surfactant concentration.

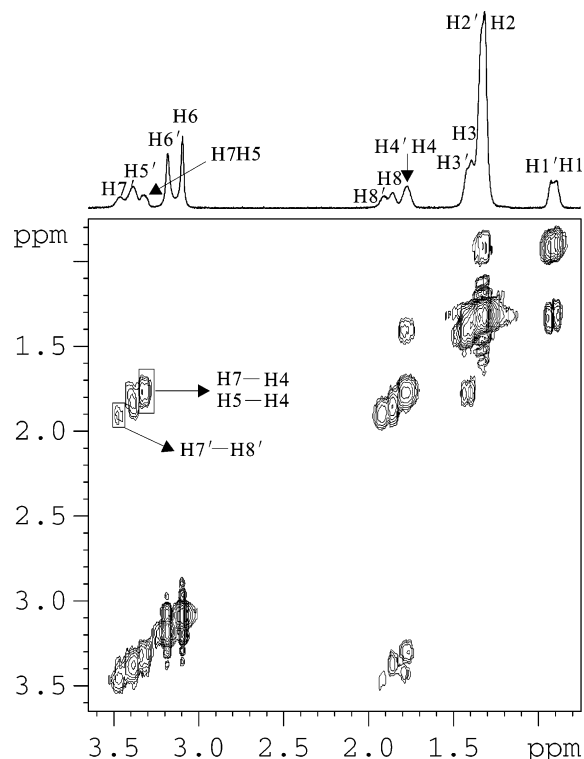


**Figure 4.** Selected regions of the  $^1\text{H}$  NMR spectra of 14-3-14 (A) and 14-4-14 (B) at various concentrations in  $\text{D}_2\text{O}$  at 25  $^\circ\text{C}$ .

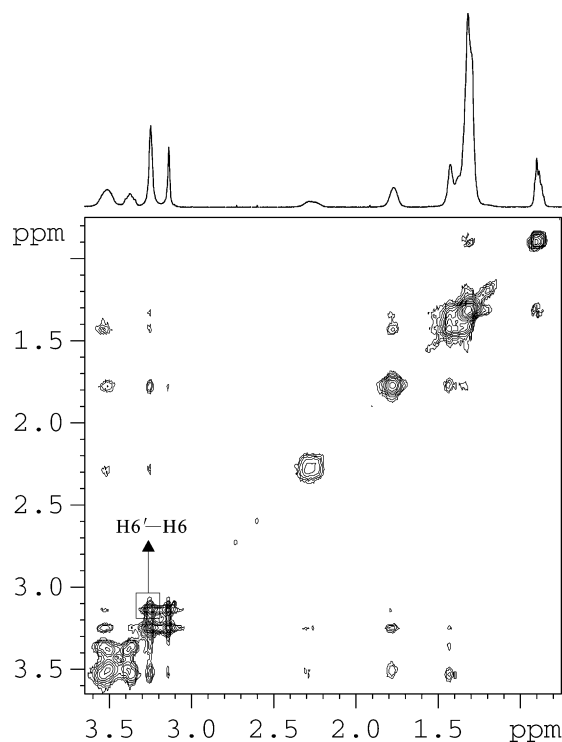


**Figure 5.** 2D  $^1\text{H}$ ,  $^1\text{H}$  COSY spectrum of 14-3-14 in  $\text{D}_2\text{O}$  at a concentration of 0.48 mM at 25  $^\circ\text{C}$ .

2D COSY spectra shown in Figures 5 and 6 show correlations between the narrow proton peaks (H7 and H5, H7 and H8, etc.), which indicates that they are the protons of monomers in the



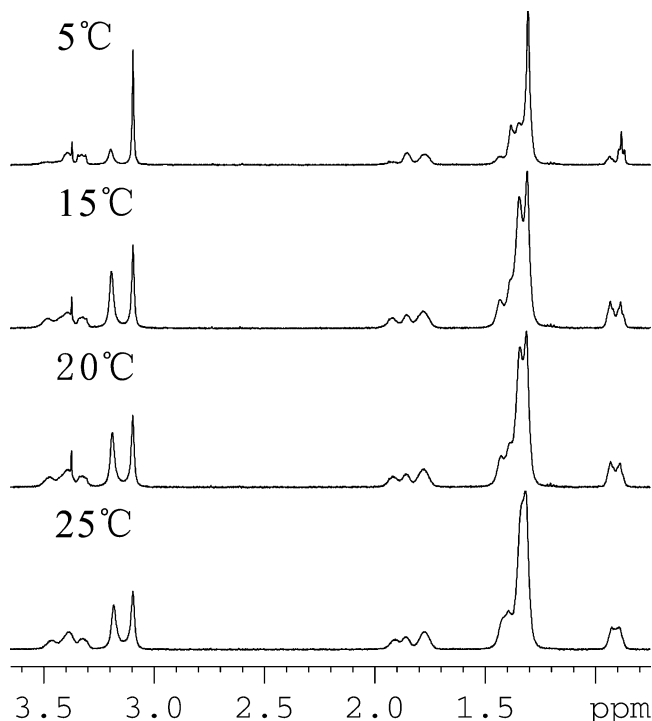
**Figure 6.** 2D  $^1\text{H}$ , $^1\text{H}$  COSY spectrum of 14-4-14 in  $\text{D}_2\text{O}$  at a concentration of 0.32 mM at 25  $^\circ\text{C}$ .



**Figure 7.** 2D NOESY spectrum of 14-3-14 in  $\text{D}_2\text{O}$  at a concentration of 0.48 mM with a mixing time of 100 ms at 25  $^\circ\text{C}$ .

bulk solution. It is interesting that the broadened peaks also form a correlated intramolecular network, without any couplings with the narrow peaks. It suggests that this is an individual network of intramolecular protons.

However, the 2D NOESY spectrum of 14-3-14 in  $\text{D}_2\text{O}$  at a concentration of 0.48 mM with a mixing time of 100 ms at 25  $^\circ\text{C}$ , shown in Figure 7, gives information about the cross polarization transfer between the two sets of protons, H6 with



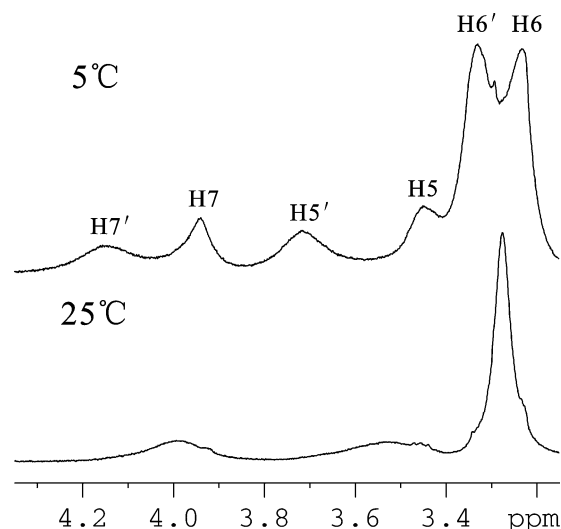
**Figure 8.**  $^1\text{H}$  NMR spectra of 14-4-14 at a concentration of 0.32 mM at various temperatures.

H6', H5, H7 with H5', H7', and so forth. It suggests the interaction between these two individual sets of protons. Combined with the fact that the intensities of the broadened peaks increase with the increase in concentration of the surfactant, one can assign the broadened peaks to the protons of the monomers involved in the micelles, the motion of which is relatively restricted. They are exchanging with the protons of the monomers in the bulk solution. The appearance of these two correlated sets of resonance peaks in the spectra implies that the exchange between the monomers in the bulk solution and those involved in the micelles are slow on the NMR time scale at 25  $^\circ\text{C}$ . At the same time, cross polarization transfer between the two sets of all protons of the molecules indicate that it is the exchange between the molecules not the protons in the bulk solution and the micelles.

Comparing the spectra in Figures 3 and 4, one finds that the broadened peaks become more overlapped as the spacer length is increased. It shows that the proton peaks become broader with the increase in spacer length, implying that the exchange rate becomes faster. To confirm this phenomenon, a series of  $^1\text{H}$  NMR spectra of 14-4-14 at a concentration of 0.32 mM have been traced at various temperatures below 25  $^\circ\text{C}$  down to 5  $^\circ\text{C}$ , as shown in Figure 8. Lowering the temperature resulted in improving the resolution of the free and aggregated peaks. At 15  $^\circ\text{C}$ , the two sets of peaks were well resolved. However, the aggregated, broadened peaks disappeared at 5  $^\circ\text{C}$ . This seems to be attributed to the poor solubility of the surfactant below its Krafft temperature, where no micelles could be formed. Any report about the Krafft temperature of 14-4-14 has not come out yet, but those of 12-4-12 and 16-4-16 are known, which are 10.6 and 33.6  $^\circ\text{C}$ , respectively,<sup>20</sup> and the  $T_k$  of 14-4-14 seems to be between them.

$^1\text{H}$  NMR spectra of 12-2-12 at a concentration of 1.80 mM (cmc = 0.95 mM<sup>7</sup>) at temperatures of 5 and 25  $^\circ\text{C}$  are shown in Figure 9. There is one set of relatively broad signals appearing in the  $^1\text{H}$  NMR spectrum at a temperature of 25  $^\circ\text{C}$ . However, at 5  $^\circ\text{C}$ , it was found that the broad signals changed into two sets of well-resolved peaks corresponding to the monomers in





**Figure 9.**  $^1\text{H}$  NMR spectra of 12-2-12 at a concentration of 1.80 mM at various temperatures.

**TABLE 1: The Exchange Rate Constants in  $\text{D}_2\text{O}$  at a Concentration of 0.32 mM for Gemini Surfactants 14-*s*-14 (*s* = 2, 3, and 4) at 25 °C**

surfactant	concentration mM	50% line width Hz	exchange rate constant $\text{s}^{-1}$
14-2-14	0.08	2.84	2.89
	0.32	3.76	
14-3-14	0.08	3.00	7.63
	0.32	5.43	
14-4-14	0.08	3.41	25.62
	0.32	11.57	

the bulk solution and in the micelles just like the geminis 14-*s*-14, which suggests that the fast exchange between monomers in the bulk solution and in the micelles for gemini surfactant 12-2-12 at 25 °C occurs slowly at 5 °C on the NMR time scale. The slow exchange phenomenon for 16-2-16 ( $T_k = 45\text{ °C}^{20}$ ) may be observed on the NMR time scale at a temperature near the Krafft temperature.

**The Exchange Rate Constant.** The exchange rate constants (of the whole exchange process) of gemini 14-*s*-14, which are the reciprocal of the exchange characteristic times, were gained for the protons of *N*-methyl (H6) by line shape analysis of their  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  at concentrations of 0.08 and 0.32 mM at 25 °C and are listed in Table 1. 2D exchange spectroscopy experiments of 14-*s*-14 at a concentration of 0.32 mM in  $\text{D}_2\text{O}$  were performed with several mixing times at 25 °C. The corresponding exchange rate constants of *N*-methyl protons at different mixing times were gained by Taylor's expansion of  $\ln \mathbf{A}$ . It has been found that all of the eigenvalues of the amplitude matrix  $\mathbf{A}$  do not exceed 1, even at longer mixing times. Besides, the matrix diagonalization method for evaluating  $\ln \mathbf{A}$  has been tried. The results obtained by these two methods are in good accordance. After that, the optimum mixing times of the three gemini surfactants were evaluated. Then,  $k_{AB}$ , the rate constant of entry of surfactant molecules into micelles, and  $k_{BA}$ , the rate constant of the exit of micellized molecules from micelles, are listed in Table 2.

The results gained by line shape analysis and 2D EXSY, which are listed in Tables 1 and 2, are in good agreement. It shows that the exchange rate constants of this series of gemini surfactants are orders of magnitude less than those for the conventional single-chain surfactants (reciprocal of the exchange

**TABLE 2: The Exchange Rate Constants of  $k_{AB}$  and  $k_{BA}$  in  $\text{D}_2\text{O}$  at a Concentration of 0.32 mM for Gemini Surfactants 14-2-14, 14-3-14, and 14-4-14 at Different and the Optimal Mixing Times at 25 °C**

surfactant	mixing time ms	exchange rate constant/ $\text{s}^{-1}$		$t_{m,\text{opt}}$ ms
		$k_{AB}$	$k_{BA}$	
14-2-14	80	2.13	3.57	108
	<b>105</b>	<b>2.19</b>	<b>3.54</b>	<b>108</b>
	120	2.09	3.65	108
14-3-14	40	5.77	8.57	57
	<b>55</b>	<b>6.55</b>	<b>8.84</b>	<b>53</b>
14-4-14	80	6.58	8.50	54
	<b>15</b>	<b>29.70</b>	<b>40.44</b>	<b>14</b>
	20	28.17	37.62	14
	37	24.67	32.16	17

characteristic times of 1 ns–1 ms<sup>6</sup>). Moreover, the exchange rate constant decreases with decreasing of the spacer length in the series of 14-*s*-14. It means that the shorter the spacer length, the slower the chemical exchange. A possible explanation for this behavior is that for a gemini surfactant with a short spacer, steric hindrance between the two adjacent polar heads may force the gemini surfactant molecule to adopt a conformation where the two alkyl chains are in a trans position with respect to one another.<sup>3,4</sup> Then, the molecule enters and exits the micelle in a slow stepwise process involving one alkyl chain and then the other. Then, for longer spacers, the steric hindrance decreases along with the proportion of gemini surfactants in the trans conformation, allowing the two chains to enter and exit the micelle simultaneously and much more quickly. Furthermore, in our previous investigation,<sup>21</sup> it was proved that the shorter the spacer group, the denser the packing of the molecule in the micelle. Another possible reason for a decrease in the exchange rate constant as the spacer decreases is that the denser the packing of the molecule in the micelle, the harder the entry into or exit from the micelles of molecules.

## Conclusions

The use of 2D COSY and 2D NOESY confirms that the  $^1\text{H}$  NMR spectra of each of these series of gemini surfactant micellar solutions are composed of protons of two individual intramolecular networks, which are interacting with each other through cross polarization. The set of narrow peaks are for the protons of the free monomers in the bulk solution, and the broadened peaks are for those involved in the micelles with restricted motion. The appearance of these two sets of resonance peaks for each surfactant suggests that the chemical exchange between the free surfactant monomers in the solution and those involved in the micelles is slow on the NMR time scale at 25 °C. The fast exchange between monomers in the bulk solution and in the micelles or other aggregates for 12-2-12 at 25 °C occurs slowly at 5 °C on the NMR time scale. The exchange rate constants of these 14-*s*-14 surfactants obtained by line shape analysis and 2D EXSY experiments are remarkably less than those of the conventional single-chain surfactants. The length of the spacer determining the conformation of the micelle shows a significant effect on the exchange rate constants.

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