

# A Comprehensive Study on the Synthesis and Micellization of Disymmetric Gemini Imidazolium Surfactants

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Received: 7 January 2016 / Accepted: 26 April 2016  
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**Abstract** Two groups of disymmetric Gemini imidazolium surfactants,  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  ( $m = 10, 12, 14$ ) and  $[C_mC_4C_n\text{im}]\text{Br}_2$  ( $m + n = 24$ ,  $m = 12, 14, 16, 18$ ) surfactants, were synthesized and their structures were confirmed by  $^1\text{H}$  NMR and ESI-MS spectroscopy. Their adsorption at the air/water interface, thermodynamic parameters and aggregation behavior were explored by means of surface tension, electrical conductivity and steady-state fluorescence. A series of surface activity parameters, including cmc,  $\gamma_{\text{cmc}}$ ,  $\pi_{\text{cmc}}$ ,  $\text{p}C_{20}$ ,  $\text{cmc}/C_{20}$ ,  $\Gamma_{\text{max}}$  and  $A_{\text{min}}$ , were obtained from surface tension measurements. The results revealed that the overall hydrophobic chain length ( $N_c$ ) for  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  and the disymmetry ( $m/n$ ) for  $[C_mC_4C_n\text{im}]\text{Br}_2$  had a significant effect on the surface activity. The cmc values decreased with an increase of  $N_c$  or  $m/n$ . The thermodynamic parameters of micellization ( $\Delta G_m^\theta$ ,  $\Delta H_m^\theta$ ,  $\Delta S_m^\theta$ ) derived from the electrical conductivity indicated that the micellization process of  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  and  $[C_mC_4C_n\text{im}]\text{Br}_2$  was entropy-driven at different temperatures, but the contribution of  $\Delta H_m^\theta$  to  $\Delta G_m^\theta$  was enhanced by increasing  $N_c$  or  $m/n$ . The micropolarity and micellar aggregation number ( $N_{\text{agg}}$ ) were estimated by steady-state fluorescence measurements. The results showed that the surfactant with higher  $N_c$  or  $m/n$  can form larger micelles, due to a tighter micellar structure.

**Keywords** Disymmetric Gemini imidazolium surfactants · Synthesis · Surface activity · Thermodynamic parameters · Micropolarity · Aggregation number

## Introduction

Gemini surfactants, “dimers” of single-tailed surfactants linked at the level of, or very close to, the head groups by a spacer group, have gained much attention in the past few decades [1–4]. Compared to the conventional single-tailed surfactants, Gemini surfactants exhibit overwhelming superiority, such as lower critical micelle concentration (cmc), higher adsorption efficiency, better wetting, foaming and lime-soap dispersing properties, and unusual rheological and aggregation properties [5–7], which makes them widely useful in skin care, petrochemistry, medicine, life science, and construction of porous materials [8–13]. Considerable effort has been exercised to design and develop a library of Gemini surfactants with diverse structure and functionality. The most investigated Gemini surfactants are the dicationic quaternary ammonium compounds with the general structure  $[C_mH_{2m+1}(\text{CH}_3)_2\text{N}(\text{CH}_2)_s\text{N}(\text{CH}_3)_2C_nH_{2n+1}]\text{Br}_2$ , abbreviated as  $C_mC_sC_n\text{Br}_2$  ( $m = n$ ) [14, 15]. The effect of alkyl tail length and spacer group length on the surface properties and micellization process has been systematically studied. Heterocycles headgroup-based Gemini surfactants, such as pyrrolidinium, imidazolium and hexahydropyridine Gemini surfactants, have also attracted increasing interest, and different hydrophilic head groups have a significant effect on the surface adsorption and aggregation behavior of Gemini surfactants [16–21]. For example, Gemini imidazolium surfactants ( $[C_mC_sC_n\text{im}]\text{Br}_2$ ,  $m = n$ ), employing heterocyclic imidazole as the headgroup and methylene as

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the spacer group, demonstrate higher surface activity and lower cmc [22–24]. In addition, owing to the existence of imidazolium headgroup, as cationic micelle systems, they show a distinctly greater tendency to self-aggregation and thus are used as supramolecular templates in the preparation of functional materials [25]; as cationic reverse-micelle systems, they display greater solubilization ability compared with cationic Gemini ammonium surfactants [26]. They can form tighter membranes [27] and thus be applied widely in the field of biology due to the strong attraction between the imidazolium headgroup and aromatic rings through  $\pi$ – $\pi$  interaction [28].

The dissymmetric Gemini surfactants consist of two different hydrophobic chains or two different hydrophilic head groups, connected by a rigid or flexible spacer group. Owing to more controlled molecular structures, these surfactants have many peculiar properties, such as the enhanced contribution of enthalpy to the Gibbs free energy [29], higher efficiency of reducing surface tension and greater ability to the formation of micelles caused by the dissymmetric Gemini surfactants with ionic–nonionic head groups [30], counterions-free systems constructed by the dissymmetric Gemini surfactants containing cationic–anionic head groups [31], and various morphologies of aggregates formed by the dissymmetric Gemini surfactants making use of their different length alkyl chains [32, 33]. Currently, the synthesis and properties of the dissymmetric ammonium Gemini surfactants ( $C_mC_nC_nBr_2$ ,  $m \neq n$ ) [34, 35] and the dissymmetric pyrrolidinium Gemini surfactants ( $C_mC_nC_nPB$ ,  $m \neq n$ ) have been researched in detail [36]. Their results indicate the dissymmetric degree of the hydrophobic chains have a strong influence on the physicochemical properties of the surfactants. However, no works have focused on preparing and exploring the dissymmetric Gemini imidazolium surfactants ( $[C_mC_nC_n\text{-im}]\text{Br}_2$ ,  $m \neq n$ ). The motivation of the present work is to further study the effect of dissymmetric degree on the physicochemical properties of these surfactants and build up the structure–property relationships of them. Therefore, a series of dissymmetric Gemini imidazolium surfactants with a four-methylene spacer group were synthesized and characterized by  $^1\text{H}$  NMR and ESI–MS spectroscopy (Scheme 1). The investigated surfactants can be divided into two groups: the dissymmetric  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  ( $m = 10, 12, 14$ ) surfactants with 14 carbon atoms in one hydrocarbon chain, and the dissymmetric  $[C_mC_4C_n\text{im}]\text{Br}_2$  ( $m + n = 24$ ,  $m = 12, 14, 16, 18$ ) surfactants with the same total carbon number of 24 in the two hydrophobic chains. Their surface activity, aggregation number and thermodynamic properties of micellization were obtained by means of surface tension, steady-state fluorescence and electrical conductivity measurements. Therefore, the effect of dissymmetry of the hydrophobic chains on the surface

activity and micellization process can be discussed comparatively and systematically.

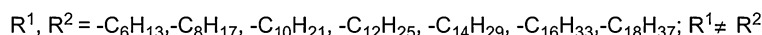
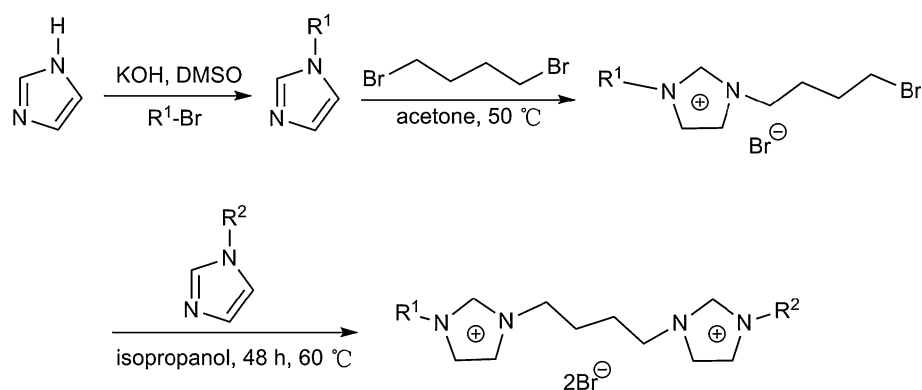
## Experimental Section

### Materials

Imidazole, potassium hydroxide, dimethyl sulfoxide (DMSO), chloroform, anhydrous magnesium sulfate, ethyl acetate, acetone, hexane, methanol, and isopropanol were purchased from Chengdu Kelong Reagent. Alkyl bromide ( $C_nH_{2n+1}Br$ ,  $n = 6, 8, 10, 12, 14, 16$  and  $18$ ), 1, 4-dibromobutane, and pyrene (99 %) were purchased from Aladdin Reagent. Benzophenone (C.P.) was purchased from Sinopharm Reagent. Ultrapure water was utilized for preparing all the surfactant solutions.

### Synthesis of *N*-Alkyl Imidazole

A mixture of imidazole (30 mmol, 2.04 g), potassium hydroxide (30 mmol, 1.68 g) and dimethyl sulfoxide (10 mL) was stirred for 2 h at room temperature. After that, alkyl bromide (25.0 mmol of 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, or 1-bromooctadecane) was dropped in slowly and the mixture was stirred for an additional 4 h. Upon completion, water (30 mL) was added to the resulting mixture followed by extraction with chloroform ( $5 \times 30$  mL). The combined organic layer was dried over anhydrous magnesium sulfate and the filtrate was concentrated under reduced pressure. The residue was subjected to flash chromatography with ethyl acetate as eluent to give *N*-alkyl imidazole. The respective yields of *N*-hexyl imidazole, *N*-octyl imidazole, *N*-decyl imidazole, *N*-dodecyl imidazole, *N*-tetradecyl imidazole, *N*-hexadecyl imidazole and *N*-octadecyl imidazole are 84.6, 82.3, 81.2, 80.5, 80.4, 79.8 and 79.6 %.  $^1\text{H}$  NMR (Bruker Avance III 500, 500 MHz,  $\text{CDCl}_3$ ) *N*-hexyl imidazole:  $\delta$  7.42 (s,  $-\text{NCHN}-$ ), 7.01 (s,  $-\text{NCHCHN}-$ ), 6.87 (s,  $-\text{NCHCHN}-$ ), 3.88 (t,  $-\text{NCH}_2-$ ), 1.73 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.25–1.27 (m,  $-\text{NCH}_2\text{CH}_2(\text{CH}_2)_3-$ ), 0.85 (t,  $-\text{CH}_2\text{CH}_3$ ). *N*-octyl imidazole:  $\delta$  7.44 (s,  $-\text{NCHN}-$ ), 7.03 (s,  $-\text{NCHCHN}-$ ), 6.88 (s,  $-\text{NCHCHN}-$ ), 3.90 (t,  $-\text{NCH}_2-$ ), 1.75 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.24–1.27 (m,  $-\text{NCH}_2\text{CH}_2(\text{CH}_2)_5-$ ), 0.85 (t,  $-\text{CH}_2\text{CH}_3$ ). *N*-decyl imidazole:  $\delta$  7.41 (s,  $-\text{NCHN}-$ ), 6.99 (s,  $-\text{NCHCHN}-$ ), 6.86 (s,  $-\text{NCHCHN}-$ ), 3.88 (t,  $-\text{NCH}_2-$ ), 1.74 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.21–1.25 (m,  $-\text{NCH}_2\text{CH}_2(\text{CH}_2)_7-$ ), 0.85 (t,  $-\text{CH}_2\text{CH}_3$ ). *N*-dodecyl imidazole:  $\delta$  7.44 (s,  $-\text{NCHN}-$ ), 7.03 (s,  $-\text{NCHCHN}-$ ), 6.88 (s,  $-\text{NCHCHN}-$ ), 3.90 (t,  $-\text{NCH}_2-$ ), 1.75 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.23–1.27 (m,  $-\text{NCH}_2\text{CH}_2(\text{CH}_2)_9-$ ), 0.88 (t,  $-\text{CH}_2\text{CH}_3$ ). *N*-tetradecyl imidazole:  $\delta$  7.43 (s,  $-\text{NCHN}-$ ), 7.01 (s,  $-\text{NCHCHN}-$ ), 6.88 (s,

**Scheme 1** Synthesis route of the disymmetric Gemini imidazolium surfactants

–NCHCHN–), 3.89 (t, –NCH<sub>2</sub>–), 1.75 (m, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.22–1.26 (m, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>–), 0.85 (t, –CH<sub>2</sub>CH<sub>3</sub>); *N*-hexadecyl imidazole:  $\delta$  7.45 (s, –NCHN–), 7.05 (s, –NCHCHN–), 6.90 (s, –NCHCHN–), 3.91 (t, –NCH<sub>2</sub>–), 1.76 (m, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.25–1.32 (m, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>13</sub>–), 0.87 (t, –CH<sub>2</sub>CH<sub>3</sub>); *N*-octadecyl imidazole:  $\delta$  7.44 (s, –NCHN–), 7.04 (s, –NCHCHN–), 6.89 (s, –NCHCHN–), 3.91 (t, –NCH<sub>2</sub>–), 1.76 (m, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.21–1.30 (m, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>–), 0.87 (t, –CH<sub>2</sub>CH<sub>3</sub>).

### Synthesis of 1-(4-Bromobutyl)-3-Alkylimidazolium Bromide

1,4-dibromobutane (36.0 mmol, 7.70 g) was dissolved in dry acetone (50 mL) and the obtained *N*-alkyl imidazole (9.0 mmol of *N*-hexyl imidazole, *N*-octyl imidazole, *N*-decyl imidazole, or *N*-dodecyl imidazole) was added gradually. The reaction mixture was refluxed at 50 °C under nitrogen atmosphere and the reaction was monitored by TLC analysis. After the reaction finished, the solvent was removed under reduced pressure, and subsequently the un-reacted 1, 4-dibromobutane was washed thoroughly with hexane. The collected viscous liquid was purified by silica column chromatography with mixtures of acetone/methanol (10:1, by vol) as eluent to afford 1-(4-bromobutyl)-3-alkylimidazolium bromide. The yields of 1-(4-bromobutyl)-3-hexylimidazolium bromide, 1-(4-bromobutyl)-3-octylimidazolium bromide, 1-(4-bromobutyl)-3-decylimidazolium bromide and 1-(4-bromobutyl)-3-dodecylimidazolium bromide are 72.5, 74.1, 76.8 and 80.3 %, respectively. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 1-(4-bromobutyl)-3-hexylimidazolium bromide:  $\delta$  10.32 (s, –NCHN–), 7.68 (s, –NCHCHN–), 7.45 (s, –NCHCHN–), 4.43 (t, –N<sup>+</sup>–CH<sub>2</sub>–), 4.25 (t, –NCH<sub>2</sub>–), 3.41 (t, –CH<sub>2</sub>Br), 2.01–2.09 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.79–1.94 (m, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>–), 1.21 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–), 0.79 (t, –CH<sub>2</sub>CH<sub>3</sub>); 1-(4-bromobutyl)-3-octylimidazolium bromide:  $\delta$

10.39 (s, –NCHN–), 7.63 (s, –NCHCHN–), 7.40 (s, –NCHCHN–), 4.47 (t, –N<sup>+</sup>–CH<sub>2</sub>–), 4.28 (t, –NCH<sub>2</sub>–), 3.45 (t, –CH<sub>2</sub>Br), 2.06–2.14 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.90 (m, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>–), 1.24 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>–), 0.82 (t, –CH<sub>2</sub>CH<sub>3</sub>); 1-(4-bromobutyl)-3-decylimidazolium bromide:  $\delta$  10.31 (s, –NCHN–), 7.70 (s, –NCHCHN–), 7.46 (s, –NCHCHN–), 4.45 (t, –N<sup>+</sup>–CH<sub>2</sub>–), 4.29 (t, –NCH<sub>2</sub>–), 3.43 (t, –CH<sub>2</sub>Br), 2.08 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.92 (m, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>–), 1.26 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>–), 0.85 (t, –CH<sub>2</sub>CH<sub>3</sub>); 1-(4-bromobutyl)-3-dodecylimidazolium bromide:  $\delta$  10.49 (s, –NCHN–), 7.62 (s, –NCHCHN–), 7.40 (s, –NCHCHN–), 4.48 (t, –N<sup>+</sup>–CH<sub>2</sub>–), 4.28 (t, –NCH<sub>2</sub>–), 3.45 (t, –CH<sub>2</sub>Br), 2.11 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.91 (m, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>–), 1.17–1.33 (m, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>–), 0.84 (t, –CH<sub>2</sub>CH<sub>3</sub>).

### Synthesis of the Disymmetric Gemini Imidazolium Surfactants

An amount of 5.0 mmol of the obtained 1-(4-bromobutyl)-3-alkylimidazolium bromide (in which the alkyl were hexyl, octyl, decyl, or dodecyl, respectively) was dissolved in isopropanol (20 mL), followed by addition of 7.5 mmol of *N*-alkyl imidazole (in which the alkyl were octadecyl, hexadecyl, tetradecyl, or tetradecyl, correspondingly). The mixture was stirred at 60 °C for 48 h under nitrogen atmosphere. After removal of isopropanol, the residue was washed with ethyl acetate, purified three times by recrystallization in acetone and then dried under vacuum for 48 h, to yield the disymmetric Gemini imidazolium surfactants as white powders. The respective yields of [C<sub>18</sub>C<sub>4</sub>C<sub>6</sub>im]Br<sub>2</sub>, [C<sub>16</sub>C<sub>4</sub>C<sub>8</sub>im]Br<sub>2</sub>, [C<sub>14</sub>C<sub>4</sub>C<sub>10</sub>im]Br<sub>2</sub> and [C<sub>14</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub> are 85.5, 87.3, 88.2 and 89.0 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Take [C<sub>14</sub>C<sub>4</sub>C<sub>10</sub>im]Br<sub>2</sub> as an example:  $\delta$  10.27 (s, 2H, –NCHN–), 7.96 (s, 2H, –NCHCHN–), 7.15 (s, 2H, –NCHCHN–), 4.58 (t, 4H, –N<sup>+</sup>–CH<sub>2</sub>–), 4.24 (t, 4H, –NCH<sub>2</sub>–), 2.22 (m, 4H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.90 (m, 4H,

–NCH<sub>2</sub>CH<sub>2</sub>–), 1.19–1.37 (m, 36H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–), 0.87 (t, 6H, –CH<sub>2</sub>CH<sub>3</sub>); MS (Finnigan TSQ Quantum ultra AM, ESI) [M–2Br]<sup>2+</sup>: 264.32. [C<sub>14</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub>: δ 10.31 (s, 2H, –NCHN–), 7.98 (s, 2H, –NCHCHN–), 7.15 (s, 2H, –NCHCHN–), 4.58 (t, 4H, –N<sup>+</sup>–CH<sub>2</sub>–), 4.24 (t, 4H, –NCH<sub>2</sub>–), 2.23 (m, 4H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.89 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.21–1.36 (m, 40H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–), 0.87 (t, 6H, –CH<sub>2</sub>CH<sub>3</sub>); MS (ESI) [M–2Br]<sup>2+</sup>: 278.30.

### Synthesis of the Symmetric Gemini Imidazolium Surfactants ([C<sub>m</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub>, *m* = 12, 14)

A mixture of 10 mmol of *N*-dodecyl imidazole or *N*-tetradecyl imidazole, 1,4-dibromobutane (4 mmol, 0.856 g) and isopropanol (20 mL) was stirred for 48 h at 60 °C under nitrogen atmosphere. After removal of isopropanol, the residue was washed with ethyl acetate, further purified four times by recrystallization in acetone and then dried under vacuum for 48 h. [C<sub>12</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub> and [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub> as the white powder were gained. The respective yields of [C<sub>12</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub> and [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub> are 92.4 % and 93.3 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) [C<sub>12</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub>: δ 10.19 (s, 2H, –NCHN–), 8.05 (s, 2H, –NCHCHN–), 7.21 (s, 2H, –NCHCHN–), 4.58 (t, 4H, –N<sup>+</sup>–CH<sub>2</sub>–), 4.24 (t, 4H, –NCH<sub>2</sub>–), 2.19 (m, 4H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.88 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.20–1.35 (m, 36H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>–), 0.86 (t, 6H, –CH<sub>2</sub>CH<sub>3</sub>); MS (ESI) [M–2Br]<sup>2+</sup>: 264.27. [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub>: δ 10.30 (s, 2H, –NCHN–), 7.99 (s, 2H, –NCHCHN–), 7.16 (s, 2H, –NCHCHN–), 4.58 (t, 4H, –N<sup>+</sup>–CH<sub>2</sub>–), 4.24 (t, 4H, –NCH<sub>2</sub>–), 2.22 (m, 4H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>–), 1.89 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 1.20–1.37 (m, 44H, –N<sup>+</sup>–CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>–), 0.87 (t, 6H, –CH<sub>2</sub>CH<sub>3</sub>); MS (ESI) [M–2Br]<sup>2+</sup>: 292.32.

The Krafft temperatures of [C<sub>m</sub>C<sub>4</sub>C<sub>n</sub>im]Br<sub>2</sub> (*m* + *n* = 24, *m* = 12, 14, 16, 18) were all lower than 15 °C. For [C<sub>14</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub> and [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub>, their solubility was not better than those of [C<sub>m</sub>C<sub>4</sub>C<sub>n</sub>im]Br<sub>2</sub> (*m* + *n* = 24, *m* = 12, 14, 16, 18), but when their concentration was not higher than 2 mmol/L, they can still remain as a clear aqueous solution at 15 °C. Therefore, in our experimental range of the prepared surfactant concentration, all the experiments can be performed at or above 15 °C.

### Equilibrium Surface Tension Measurements

The equilibrium surface tension was estimated by using the pendant drop method, performed on an optical contact angle measuring instrument (OCA 40; Beijing Eastern Dataphy Instruments). All measurements were taken at 25.0 ± 0.1 °C and the surfactant solutions were kept still for 30 min in order to achieve the system equilibrium.

### Electrical Conductivity Measurements

The electrical conductivity of surfactant solutions at five different temperatures was obtained by a conductivity analyzer (DDS-11A; Shanghai Leici TRONY Instrument). The measurements were repeated three times for each temperature and each temperature was controlled with a precision of ±0.1 °C.

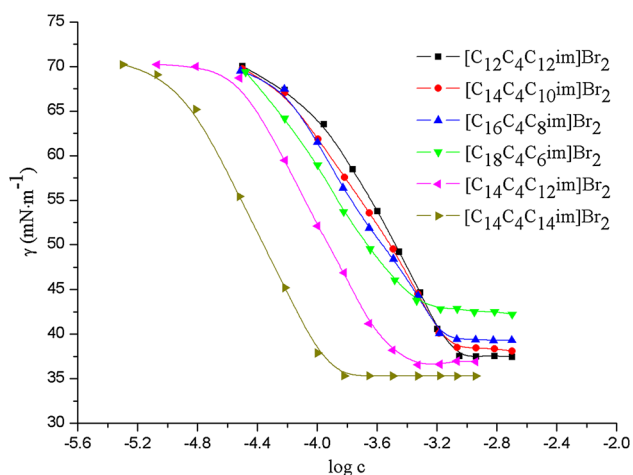
### Steady-State Fluorescence Measurements

Fluorescence spectra were recorded on a FluoroMax-4 spectrofluorometer with a 1-cm<sup>2</sup> quartz cuvette. Pyrene was used as the fluorescence probe and benzophenone as the quencher. The concentration of pyrene was kept at 1.0 × 10<sup>−6</sup> mol L<sup>−1</sup>. The excitation wavelength was fixed at 335 nm and the emission spectra range was selected from 350 to 500 nm. The slit widths of excitation and emission were set at 8 and 2 nm, respectively.

## Results and Discussion

### Adsorption at Air/Water Interface

The adsorption at air/water interface for Gemini imidazolium surfactants, including [C<sub>12</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub>, [C<sub>14</sub>C<sub>4</sub>C<sub>10</sub>im]Br<sub>2</sub>, [C<sub>16</sub>C<sub>4</sub>C<sub>8</sub>im]Br<sub>2</sub>, [C<sub>18</sub>C<sub>4</sub>C<sub>6</sub>im]Br<sub>2</sub>, [C<sub>14</sub>C<sub>4</sub>C<sub>12</sub>im]Br<sub>2</sub> and [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub>, was evaluated by the equilibrium surface tension as a function of surfactant concentration (Fig. 1). The surface tension gradually decreased with the increase of surfactant concentration and then reached a plateau. The concentration of the clear



**Fig. 1** Plots of surface tension vs. log *c* at 25 °C for the disymmetric Gemini imidazolium surfactants in aqueous solution. The error of surface tension value is ±0.2 mN/m

**Table 1** Surface activity of the disymmetric Gemini imidazolium surfactants at 25 °C

Surfactant	<i>m/n</i>	cmc (mmol/L)			$\gamma_{\text{cmc}}$ (mN/m)	$\pi_{\text{cmc}}$ (mN/m)	$\text{p}C_{20}$	cmc/ $C_{20}$	$\Gamma_{\text{max}}$ ( $\mu\text{mol}/\text{m}^2$ )	$A_{\text{min}}$ ( $\text{nm}^2$ )	$N_{\text{agg}}$
		Surface tension	Electrical conductivity	Steady-state fluorescence							
[C <sub>12</sub> C <sub>4</sub> C <sub>12</sub> im]Br <sub>2</sub>	1	0.73	0.738	0.73	37.50	34.47	3.54	2.50	1.76	0.94	16
[C <sub>14</sub> C <sub>4</sub> C <sub>10</sub> im]Br <sub>2</sub>	1.4	0.69	0.717	0.70	38.34	33.63	3.59	2.68	1.56	1.06	18
[C <sub>16</sub> C <sub>4</sub> C <sub>8</sub> im]Br <sub>2</sub>	2	0.63	0.649	0.64	39.36	32.61	3.65	2.81	1.49	1.11	21
[C <sub>18</sub> C <sub>4</sub> C <sub>6</sub> im]Br <sub>2</sub>	3	0.50	0.565	0.55	42.59	29.38	3.76	2.88	1.29	1.29	27
[C <sub>14</sub> C <sub>4</sub> C <sub>12</sub> im]Br <sub>2</sub>	1.17	0.26	0.316	0.29	36.77	35.20	4.02	2.72	1.88	0.88	20
[C <sub>14</sub> C <sub>4</sub> C <sub>14</sub> im]Br <sub>2</sub>	1	0.12	0.132	0.13	35.31	36.66	4.42	3.16	1.96	0.85	22

breakpoint in the  $\gamma$ -log  $c$  curves corresponded to the critical micelle concentration (cmc), indicating the formation of micelles, and the surface tension at the cmc was defined as  $\gamma_{\text{cmc}}$ . In addition, the absence of a minimum near the breakpoint suggested a low concentration of surface chemical impurities for the investigated Gemini surfactants [20]. In this work, the classic Gibbs adsorption theory was used to study the surface properties of the disymmetric Gemini imidazolium surfactants.

The maximum surface excess concentration,  $\Gamma_{\text{max}}$ , and the minimum average area occupied by a single surfactant molecule at the air/water interface,  $A_{\text{min}}$ , can be estimated according to the Gibbs adsorption equation [37]:

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \times \frac{d\gamma}{d\log c} \quad (1)$$

$$A_{\text{min}} = \frac{10^{24}}{N_A \Gamma_{\text{max}}} \quad (2)$$

where  $\Gamma_{\text{max}}$  is in  $\mu\text{mol}/\text{m}^2$ ,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature in Kelvin,  $\gamma$  is the surface tension in  $\text{mN m}^{-1}$ ,  $c$  is the surfactant concentration and  $(d\gamma/d\log c)$  is the slope of the linear part in the  $\gamma$ -log  $c$  curves where the surfactant concentration is below the cmc. In aqueous solutions of the investigated Gemini imidazolium surfactants,  $n$  is taken as 3, considering one dimeric ion and two counterions in the surfactant molecule [38].  $N_A$  is Avogadro's number and  $A_{\text{min}}$  is in  $\text{nm}^2/\text{molecule}$ .

The adsorption efficiency at the air–water interface,  $\text{p}C_{20}$ , and the surface pressure at cmc,  $\pi_{\text{cmc}}$ , are obtained from Eqs. (3, 4):

$$\text{p}C_{20} = -\log C_{20} \quad (3)$$

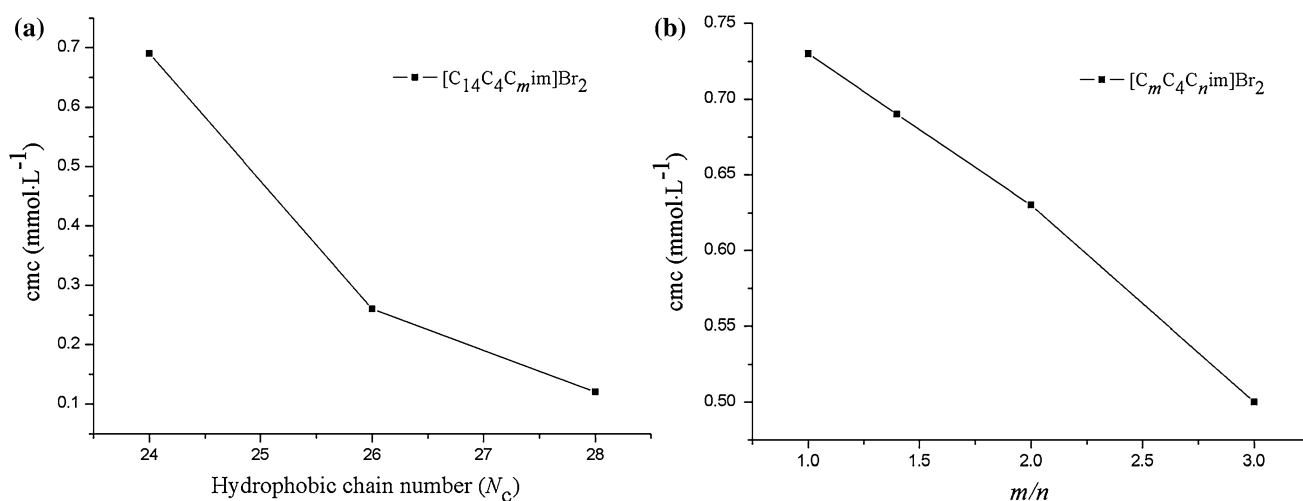
$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (4)$$

where  $C_{20}$  represents the surfactant concentration at which the surface tension of water is reduced by  $20 \text{ mN}\cdot\text{m}^{-1}$ . Generally, the larger the value of  $\text{p}C_{20}$ , the higher the adsorption efficiency of the surfactant.

$\gamma_0$  is the surface tension of water and  $\gamma_{\text{cmc}}$  is the surface tension of surfactant solution at the cmc. The larger the value of  $\pi_{\text{cmc}}$ , the higher the effectiveness of the surfactant to lower the surface tension of water. The value of  $\text{cmc}/C_{20}$  is related with the structural factors in the adsorption and micellization process. The surfactant with larger  $\text{cmc}/C_{20}$  value tends more to adsorb at the interface than to form micelles. Based on the  $\gamma$ -log  $c$  curves, the above-described physicochemical parameters for [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> and [C<sub>m</sub>C<sub>4</sub>C<sub>n</sub>im]Br<sub>2</sub>, such as cmc,  $\gamma_{\text{cmc}}$ ,  $\pi_{\text{cmc}}$ ,  $\text{p}C_{20}$ ,  $\text{cmc}/C_{20}$ ,  $\Gamma_{\text{max}}$  and  $A_{\text{min}}$ , are listed in Table 1.

From Fig. 2a, the values of cmc for the disymmetric [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> series decreased with the increasing total carbon number in two hydrocarbon chains regardless of the degree of disymmetry, implying that the longer overall hydrophobic chain length ( $N_c$ ), the higher the aggregation ability. The contribution of each additional methylene unit to the cmc values of [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> was higher than that of classic single-tailed surfactant homologues [C<sub>n</sub> mim]Br [39, 40]. It can be noticed that the  $\gamma_{\text{cmc}}$  values of [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> decreased with the increasing  $N_c$ , indicating that [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub> possessed higher surface activity, which could also be found from the changes of  $\pi_{\text{cmc}}$  and  $\text{p}C_{20}$  values. For the disymmetric [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> series, the changes of cmc,  $\gamma_{\text{cmc}}$ ,  $\pi_{\text{cmc}}$  and  $\text{p}C_{20}$  values with  $N_c$  were similar to those of the disymmetric Gemini pyrrolidinium surfactants (C<sub>m</sub>C<sub>3</sub>C<sub>14</sub>-PB,  $m = 10, 12, 14$ ) [36]. The  $\text{cmc}/C_{20}$  values increased with the increase of  $N_c$ , which suggested that, in comparison with micellization process, the adsorption at the air/water interface for [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> with longer hydrophobic chains was much easier. However, the  $A_{\text{min}}$  values of [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> decreased with the increasing  $N_c$ , meaning that [C<sub>14</sub>C<sub>4</sub>C<sub>14</sub>im]Br<sub>2</sub> had a higher packing density. The hydrophobic interactions were strengthened with the increasing  $N_c$ , which could promote the surfactant molecules to pack much more densely, and consequently the  $A_{\text{min}}$  values will decrease. This result was different from C<sub>m</sub>C<sub>3</sub>C<sub>14</sub>PB, and the possible reason was





**Fig. 2** Effect of the overall hydrophobic chain length (a) and the disymmetry (b) on cmc

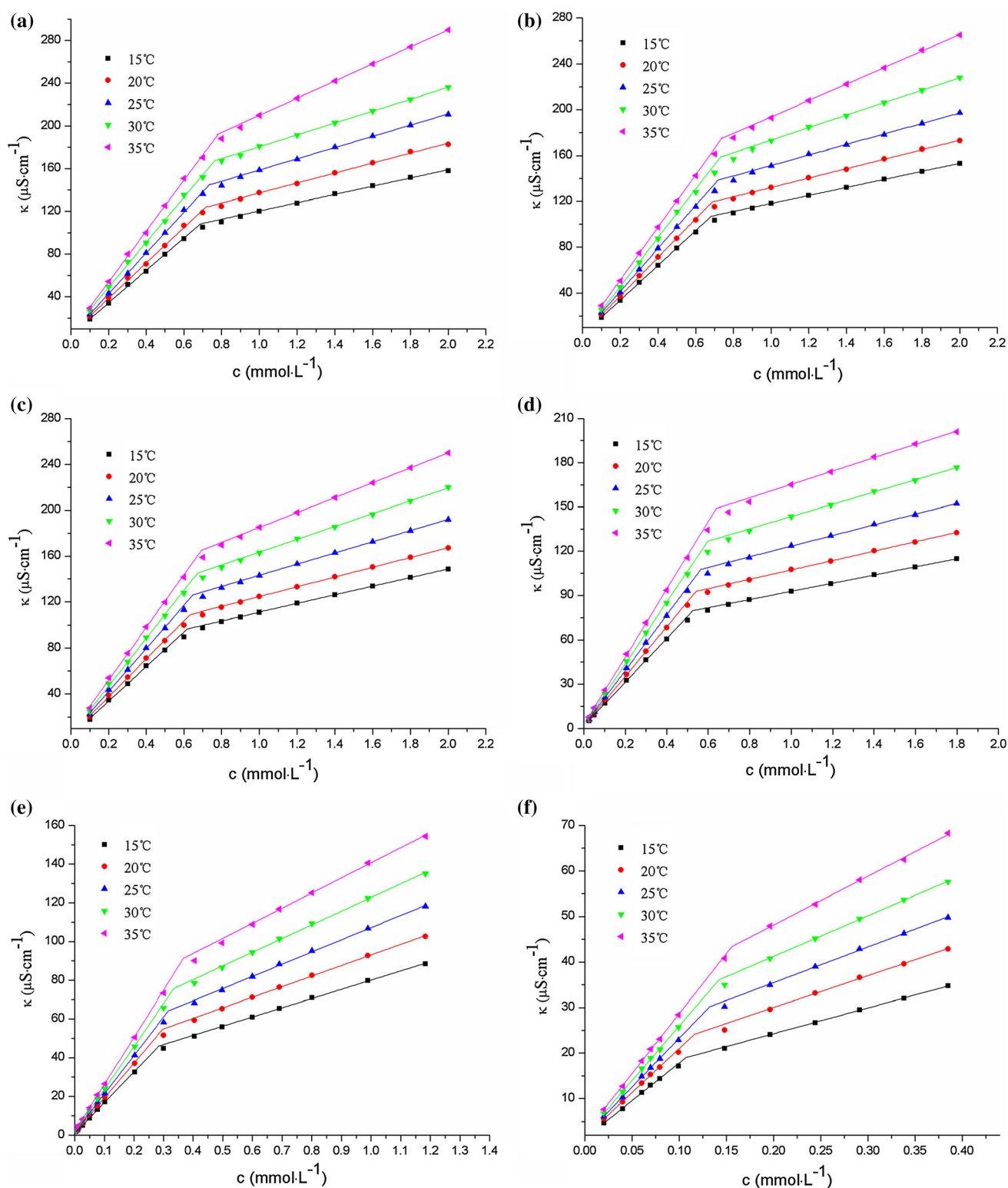
that the longer hydrophobic chains were more prone to bending.

The typical effect of the disymmetry on the cmc can be found from the disymmetric  $[C_mC_4C_n\text{im}]\text{Br}_2$  series (Fig. 2b), those surfactants with the same total carbon number of 24 in two hydrocarbon chains. Higher structural disymmetry resulted in a lower cmc by employing  $m/n$  as the degree of disymmetry and a similar conclusion was also observed in other disymmetric Gemini surfactants [29, 34, 36]. Clearly, the introduction of disymmetry to the hydrophobic chains can strengthen the aggregation behavior, and adding two methylene groups to one longer chain was more efficient in lowering the cmc than adding each of them to two chains separately. The hydrophobic interactions had two contributions to the aggregation behavior, intermolecular and intramolecular. The latter will be weaker because the spacer groups kept the two hydrophobic chains apart. For the symmetric Gemini surfactants, the hydrophobic interactions will be minimized due to the equal number of hydrophobic units for both intramolecular and intermolecular interactions. However, for the disymmetric Gemini surfactants, as  $m/n$  increased, the ratio of hydrophobic units interacting intermolecularly to those intramolecularly will increase [41]. Therefore, the overall hydrophobic interactions were gradually improved with the increasing  $m/n$ , which made a positive contribution to the formation of micelles. On the other hand, both the  $\gamma_{\text{cmc}}$  and  $A_{\text{min}}$  values increased with the increase of  $m/n$ , implying that the Gemini surfactants with a higher disymmetry were packed more loosely at the air/water interface. This might be attributed to the fact that the longer hydrocarbon chain for  $[C_{18}C_4C_6\text{im}]\text{Br}_2$  with the highest disymmetry was more prone to bend at the interface, which

made the surface area per molecule larger, and therefore resulted in the larger  $\gamma_{\text{cmc}}$  value. The  $\gamma_{\text{cmc}}$  and  $A_{\text{min}}$  values showed the opposite relation with the disymmetry in comparison with  $C_mC_3C_n\text{PB}$  ( $m+n=24$ ,  $m=12, 14, 16$ ). Furthermore, the increase in  $\text{cmc}/C_{20}$  indicated that the adsorption at the air/water interface was more favored over the micellization process for those surfactants with the higher disymmetry. The same conclusion could also be speculated from the variation in  $pC_{20}$  values.

### Degree of Counterion Binding to Micelles

The degree of counterion binding to micelles ( $\beta$ ), a fundamental feature of the ionic surfactant micelles, is certain to have an important role in the micellization process and various aggregation behaviors in aqueous solutions. An understanding of  $\beta$  can provide insight into the specific properties of ionic surfactants and a further investigation of new ionic Gemini surfactants. The electrical conductivity measurements are often used to determine the cmc and  $\beta$  values. For each of  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  or  $[C_mC_4C_n\text{im}]\text{Br}_2$  series, Fig. 3 gives the plots of the conductivity ( $\kappa$ ) versus surfactant concentration ( $c$ ) at five different temperatures. It was evident that all plots had breakpoints, and that the concentration corresponded to the cmc. This was a result of the reduction of effective charges in the solution, due to the binding of some counterions to the micelles above the cmc. Moreover, the degree of counterion dissociation ( $\alpha$ ) can be taken as the ratio of the slopes of two fitted lines above and below the cmc. Thus, the  $\beta$  values could be obtained by using  $\beta = 1 - \alpha$ . The cmc and  $\beta$  values of  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  and  $[C_mC_4C_n\text{im}]\text{Br}_2$  series at five different temperatures are listed in Table 2. It can be seen that the cmc



**Fig. 3** Plots of electrical conductivity vs. surfactant concentration at five different temperatures. The error of electrical conductivity value is  $\pm 0.2 \mu\text{S}/\text{cm}$ .  $[\text{C}_{12}\text{C}_4\text{C}_{12}\text{im}]\text{Br}_2$  (a),  $[\text{C}_{14}\text{C}_4\text{C}_{10}\text{im}]\text{Br}_2$  (b),  $[\text{C}_{16}\text{C}_4\text{C}_8\text{im}]\text{Br}_2$  (c),  $[\text{C}_{18}\text{C}_4\text{C}_6\text{im}]\text{Br}_2$  (d),  $[\text{C}_{14}\text{C}_4\text{C}_{12}\text{im}]\text{Br}_2$  (e),  $[\text{C}_{14}\text{C}_4\text{C}_{14}\text{im}]\text{Br}_2$  (f)

values for all the studied surfactants increased upon raising the temperature, and that the cmc values estimated from the electrical conductivity at 25 °C were in accordance with

those obtained from the surface tension. A reasonable explanation was that the ordered water molecules around the hydrophobic chains may be broken at a higher

**Table 2** Thermodynamic parameters of micellization for the disymmetric Gemini imidazolium surfactants at different temperatures

Surfactant	<i>m/n</i>	Temperature (°C)	cmc (mmol/L)	$\beta$	$\Delta G_m^\theta$ (kJ/mol)	$\Delta H_m^\theta$ (kJ/mol)	$T\Delta S_m^\theta$ (kJ/mol)
[C <sub>12</sub> C <sub>4</sub> C <sub>12</sub> im]Br <sub>2</sub>	1	15	0.706	0.745	−47.12	−5.059	42.06
		20	0.723	0.742	−47.75	−5.227	42.52
		25	0.738	0.730	−48.14	−5.370	42.77
		30	0.758	0.726	−48.72	−5.539	43.18
		35	0.765	0.709	−49.00	−5.667	43.33
[C <sub>14</sub> C <sub>4</sub> C <sub>10</sub> im]Br <sub>2</sub>	1.4	15	0.682	0.768	−47.88	−5.858	42.03
		20	0.687	0.757	−48.38	−6.026	42.35
		25	0.717	0.756	−48.99	−6.229	42.76
		30	0.731	0.737	−49.19	−6.370	42.82
		35	0.740	0.715	−49.31	−6.499	42.81
[C <sub>16</sub> C <sub>4</sub> C <sub>8</sub> im]Br <sub>2</sub>	2	15	0.619	0.751	−47.83	−6.769	41.06
		20	0.631	0.743	−48.36	−6.974	41.38
		25	0.649	0.739	−48.95	−7.197	41.75
		30	0.672	0.731	−49.39	−7.406	41.98
		35	0.693	0.716	−49.63	−7.586	42.04
[C <sub>18</sub> C <sub>4</sub> C <sub>6</sub> im]Br <sub>2</sub>	3	15	0.525	0.813	−50.24	−12.52	37.72
		20	0.542	0.810	−50.88	−12.93	37.95
		25	0.565	0.807	−51.48	−13.36	38.13
		30	0.599	0.802	−51.93	−13.77	38.16
		35	0.639	0.800	−52.43	−14.21	38.22
[C <sub>14</sub> C <sub>4</sub> C <sub>12</sub> im]Br <sub>2</sub>	1.17	15	0.284	0.700	−49.61	−15.02	34.59
		20	0.297	0.696	−50.17	−15.51	34.66
		25	0.316	0.682	−50.34	−15.91	34.43
		30	0.335	0.680	−50.88	−16.43	34.45
		35	0.367	0.679	−51.30	−16.97	34.33
[C <sub>14</sub> C <sub>4</sub> C <sub>14</sub> im]Br <sub>2</sub>	1	15	0.107	0.658	−52.26	−22.20	30.06
		20	0.116	0.638	−52.20	−22.70	29.50
		25	0.132	0.635	−52.47	−23.44	29.03
		30	0.142	0.628	−52.83	−24.13	28.70
		35	0.156	0.593	−52.16	−24.40	27.76

temperature, which would be unfavorable for the formation of micelles [42]. All the values of  $\beta$  showed a monotonous decrease with the increasing temperature, which indicated the decrease of charge density on the micelle surface. The same trends of cmc and  $\beta$  values with temperature have also been observed for the disymmetric Gemini pyrrolidinium surfactants C<sub>m</sub>C<sub>3</sub>C<sub>14</sub>PB and C<sub>m</sub>C<sub>3</sub>C<sub>n</sub>PB.

### Thermodynamics Parameters

The thermodynamic parameters for the micellization process of [C<sub>14</sub>C<sub>4</sub>C<sub>m</sub>im]Br<sub>2</sub> and [C<sub>m</sub>C<sub>4</sub>C<sub>n</sub>im]Br<sub>2</sub> series were investigated by employing the mass action model [43]. The standard Gibbs free energy change ( $\Delta G_m^\theta$ ), the standard enthalpy change ( $\Delta H_m^\theta$ ), and standard entropy change ( $\Delta S_m^\theta$ ) for the micellization process can be determined from Eqs. (5–7):

$$\Delta G_m^\theta = RT(1 + \beta) \ln X_{cmc} \quad (5)$$

$$\Delta H_m^\theta = \left[ \frac{\partial(\Delta G_m^\theta/T)}{\partial(1/T)} \right] \Delta H_m^\theta = -RT^2(1 + \beta) \frac{d \ln(X_{cmc})}{dT} \quad (6)$$

$$\Delta S_m^\theta = \frac{\Delta H_m^\theta - \Delta G_m^\theta}{T} \quad (7)$$

where  $R$  is the gas constant (8.314 J mol<sup>−1</sup> K<sup>−1</sup>),  $T$  is the absolute temperature in K,  $\beta$  is the degree of counterion binding to micelles which was obtained previously, and  $X_{cmc}$  is the cmc expressed in mol fractions.

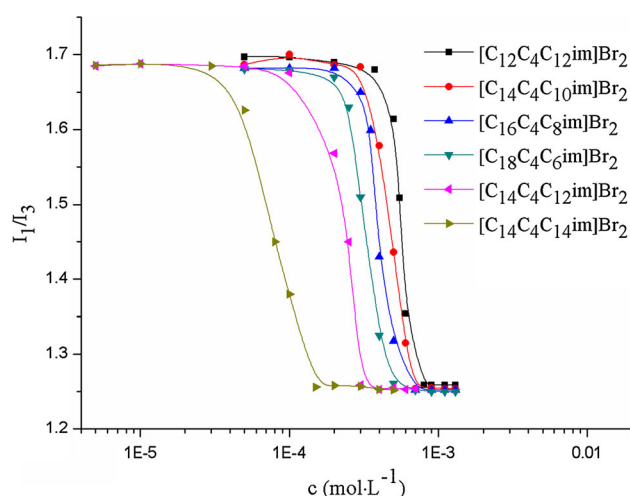
The corresponding thermodynamic parameters of micellization for all the investigated surfactants at five different temperatures are shown in Table 2. The values of  $\Delta G_m^\theta$  are all negative, meaning that the aggregation for each surfactant in aqueous solution is spontaneous. Notably, both the overall hydrophobic chain length and the disymmetry degree greatly



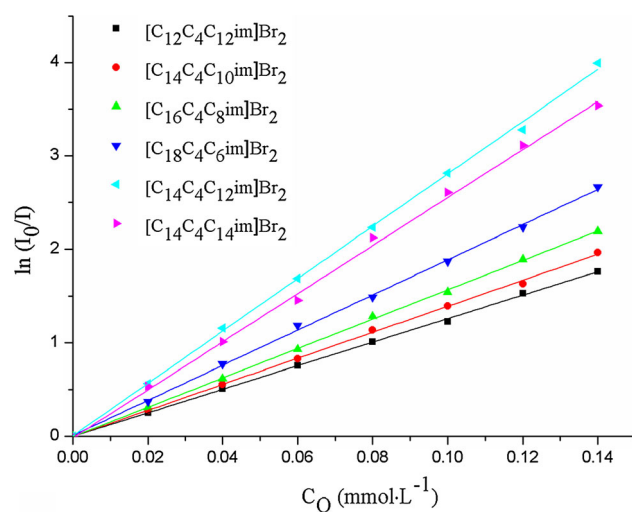
affected the thermodynamic parameters, or, in other words, the micellization process. The observed more negative  $\Delta G_m^0$  values for  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  series with longer overall hydrophobic chains indicated a stronger tendency to micellization due to greater hydrophobic interactions. Although the changes of  $\Delta G_m^0$  values for  $[C_mC_4C_n\text{im}]\text{Br}_2$  series with an increase of the dissymmetry were not so large, it demonstrated that the more negative  $\Delta G_m^0$  of  $[C_{18}C_4C_6\text{im}]\text{Br}_2$  with a higher dissymmetry was more beneficial to micellization than that of  $[C_{12}C_4C_{12}\text{im}]\text{Br}_2$ . Simultaneously, the values of the standard enthalpy ( $\Delta H_m^0$ ) for each surfactant were also negative, indicating that the formation process of micelles was exothermic, which can be attributed to possible surfactant–solvent interactions [17]. Additionally, all the  $\Delta H_m^0$  values changed little as the temperature increased, suggesting no significant changes in the environment around the hydrophobic chains of surfactant molecule. The data from Table 2 indicated the  $\Delta S_m^0$  values were positive in all cases and the values of  $T\Delta S_m^0$  were much larger than that of  $|\Delta H_m^0|$ . The negative values of  $\Delta G_m^0$  were mainly due to the larger positive  $\Delta S_m^0$ , implying that the micellization for  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  or  $[C_mC_4C_n\text{im}]\text{Br}_2$  series was entropy-driven. It can be concluded that the driving force of micellization process was the tendency of hydrophobic chains to transfer from the solvent to the interior of micelle. In general, there are mainly four contributions to  $\Delta H_m^0$  for the Gemini surfactants: the van der Waals interaction between the alkyl chains, the hydrophobic interaction, the head group repulsion and the configuration of spacer chains [44]. Among these interactions, the van der Waals interaction and the hydrophobic interaction will lead to the changes in the  $\Delta H_m^0$  values for the present investigated surfactants. As was previously discussed in our work, the hydrophobic interactions increased significantly with increasing  $N_c$  and  $m/n$ , which made the  $\Delta H_m^0$  values more negative. Consequently, the overall hydrocarbon chain length and the degree of dissymmetry had a significant effect on the contribution of  $\Delta H_m^0$  to  $\Delta G_m^0$ . For the  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  series, the contribution of  $\Delta H_m^0$  to  $\Delta G_m^0$  increased when the overall hydrocarbon chain length was increased, which was similar to those of the symmetric  $[C_mC_4C_m\text{im}]\text{Br}_2$  and the dissymmetric  $C_mC_3C_{14}\text{-PB}$ . The  $|\Delta H_m^0|$  values for  $[C_{14}C_4C_{14}\text{im}]\text{Br}_2$  were nearly equal to the values of  $T\Delta S_m^0$  with the increase in the temperature. On the other hand, for the  $[C_mC_4C_n\text{im}]\text{Br}_2$  series, a higher degree of dissymmetry can result in a higher contribution of  $\Delta H_m^0$  to  $\Delta G_m^0$ , being consistent with those of the dissymmetric  $C_mC_6C_n\text{Br}_2$  [34] and the dissymmetric  $C_mC_3C_n\text{PB}$ . From the data in Table 2, the changes of  $\Delta H_m^0$  values at 25 °C were from  $-5.370$  to  $-13.36$  kJ/mol as the dissymmetry increased. The introduction of dissymmetry to the hydrophobic chain shed new light on the possibility of adjusting micellization process further.

## Micropolarity and Micellar Aggregation Number

It is well known that pyrene is used as a fluorescence probe to investigate the cmc and polarity of the micellar microenvironment. Normally, the fluorescence emission spectra of pyrene have five vibration bands after the excitation at 335 nm. The ratio of fluorescence intensity ( $I_1/I_3$ ) between the first vibronic band (373 nm) and the third vibronic band (384 nm) is strongly dependent on the position of the pyrene in micelles and thus can be seen as a measure for the polarity of the micellar microenvironment [45]. Once the surfactant molecules begin to form micelles, the extreme hydrophobic pyrene molecules will transfer from the water environment into the interior hydrophobic region, which was reflected as a sharp drop in the  $I_1/I_3$  value. The concentration corresponding to the sharp drop was taken as the cmc. Figure 4 gives the relationship between the  $I_1/I_3$  ratio and the concentration of all the investigated surfactants. For the  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  or  $[C_mC_4C_n\text{im}]\text{Br}_2$  series, the values of cmc determined from the fluorescence plots shown in Table 1 were consistent with those estimated by the methods of electrical conductivity and surface tension. The values of  $I_1/I_3$  were independent of the surfactant concentration above cmc and almost the same for the  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  or  $[C_mC_4C_n\text{im}]\text{Br}_2$  series, suggesting that the hydrophobic chains length and the dissymmetry have little effect on the micropolarity that was sensed by the pyrene. Moreover, the low  $I_1/I_3$  values indicated that the pyrene was solubilized in the palisade layer near the polar head groups [22]. On the one hand, as the  $N_c$  or  $m/n$  ratio increased, the hydrophobic interaction was gradually optimized. This was expected to result in a decrease of micropolarity, owing to the tighter packing of



**Fig. 4**  $I_1/I_3$  ratio of pyrene as a function of the concentration for the dissymmetric Gemini imidazolium surfactants in aqueous solution



**Fig. 5**  $\ln(I_0/I)$  of pyrene as a function of concentration of the quencher benzophenone in the surfactant aqueous solution

the surfactant alkyl chains. On the other hand, the tighter packing structure may make the pyrene slightly closer to the micellar surface and thus cause an increase of micropolarity, which compensated the first effect just discussed. As a result, the micropolarity of these investigated surfactants micelles that was sensed by the pyrene was observed to be almost the same.

The micellar aggregation number,  $N_{agg}$ , was measured by fluorescence quenching experiments [46] and calculated by Eq. (8):

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{agg}C_Q}{C_S - cmc} \quad (8)$$

where  $I_0$  and  $I$  are the fluorescence intensities of pyrene in the absence and presence of the quencher at a specific wavelength of 373 nm, and  $C_Q$  and  $C_S$  are the molar concentration of quencher and surfactant, respectively.

Figure 5 shows the variation of  $\ln(I_0/I)$  as a function of  $C_Q$  for  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  and  $[C_mC_4C_n\text{im}]\text{Br}_2$  series. The concentrations were all  $2.0 \text{ mmol L}^{-1}$  for the  $[C_mC_4C_n\text{im}]\text{Br}_2$  series, and  $1 \text{ mmol L}^{-1}$  for the  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  ( $m = 12, 14$ ) series. Each plot was fitted into a straight line and the slope was obtained. The  $N_{agg}$  values of  $[C_{14}C_4C_{10}\text{im}]\text{Br}_2$ ,  $[C_{14}C_4C_{12}\text{im}]\text{Br}_2$  and  $[C_{14}C_4C_{14}\text{im}]\text{Br}_2$  were found to be 18, 20 and 22, respectively, implying that  $N_{agg}$  increased with increasing  $N_c$  for the disymmetric  $[C_{14}C_4C_m\text{im}]\text{Br}_2$  series. For the disymmetric  $[C_mC_4C_n\text{im}]\text{Br}_2$  series,  $N_{agg}$  were 16, 18, 21 and 27 for  $m = 12, 14, 16$  and 18, respectively, as listed in Table 1. Obviously, the  $N_{agg}$  values were dependent on  $m/n$ , increasing from 16 to 27 as  $m/n$  increased from 1 to 3. The possible explanation was that the surfactant with the higher  $N_c$  or  $m/n$  can form a more compact micellar structure, because of the enhancement in the hydrophobic interaction. Such a trend of

increasing  $N_{agg}$  values with increasing  $m/n$  has been found in the disymmetric  $C_mC_6C_n\text{Br}_2$ . However, the opposite relationship of decreasing  $N_{agg}$  values with increasing  $N_c$  or  $m/n$  was observed in the disymmetric  $C_mC_3C_{14}\text{PB}$  or  $C_mC_3C_n\text{PB}$ , and this might result from the formation of premicelles. The more premicelles that could be formed, the lower the  $N_{agg}$ .

**Acknowledgments** We are grateful for the financial support from the Six Talent Peaks Program of Jiangsu Province, China (Project No. JNHB-001).

## References

1. Song LD, Rosen MJ (1996) Surface properties, micellization, and premicellar aggregation of Gemini surfactants with rigid and flexible spacers. *Langmuir* 12:1149–1153
2. Zana R (2002) Dimeric and oligomeric surfactants, behavior at interfaces and in aqueous solution: a review. *Adv Colloid Interface Sci* 97:205–253
3. Chevalier Y (2002) New surfactants: new chemical functions and molecular architectures. *Curr Opin Colloid Interface Sci* 7:3–11
4. Zhong X, Guo JW, Feng LJ (2014) Cationic Gemini surfactants based on adamantane: synthesis, surface activity and aggregation properties. *Colloids and Surfaces A* 441:572–580
5. Zheng O, Zhao JX (2006) Solubilization of pyrene in the aqueous micellar solutions of Gemini surfactant  $C_{12}\text{-s-C}_{12}\text{-2Br}$ . *J Colloid Interface Sci* 300:749–754
6. Lu T, Lan Y, Liu C, Huang J, Wang Y (2012) Surface properties, aggregation behavior and micellization thermodynamics of a class of Gemini surfactants with ethyl ammonium head groups. *J Colloid Interface Sci* 377:222–230
7. Ding YS, Zha M, Zhang J, Wang SS (2007) Synthesis of a kind of geminal imidazolium ionic liquid with long aliphatic chains. *Chin Chem Lett* 18:48–50
8. Tookazu Y, Miri B, Keisuke M (2009) Surface properties and aggregate morphology of partially fluorinated carboxylate-type anionic gemini surfactants. *J Colloid Interface Sci* 339:230–235
9. Zhou LM, Chen H, Jiang XH, Lu F, Zhou YF (2009) Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants. *J Colloid Interface Sci* 332:16–21
10. Song CP, Wu DQ, Zhang F, Liu P, Lu QH, Feng XL (2012) Gemini surfactant assisted synthesis of two-dimensional metalnanoparticles/graphene composites. *Chem Commun* 48:2119–2121
11. Zhou Y, Cheng Y, Han CY, Lai JL, Sui L, Luo GX (2014) Synthesis and surface properties of anionic Gemini surfactants having N-acylamide and carboxylate groups. *J Surfact Deterg* 17:727–732
12. Jain T, Tehrani-Bagha AR, Shekhar H, Crawford R, Johnson E, Norgaard K (2014) Anisotropic growth of gold nanoparticles using cationic gemini surfactants: effects of structure variations in head and tail groups. *J Mater Chem C* 2:994–1003
13. Sharma VD, Lees J, Hoffman NE, Brailoiu E, Madesh M, Wunder SL, Ilies MA (2014) Modulation of pyridinium cationic lipid–DNA complex properties by pyridinium Gemini surfactants and its impact on lipoplex transfection properties. *Mol Pharmaceutics* 11:545–559
14. Alami E, Beinert G, Marie P, Zana R (1993) Alkanediyl- $\alpha,\omega$ -bis(dimethylalkylammonium bromide) Surfactants. 3. Behaviour at the Air–Water Interface. *Langmuir* 9:1465–1467
15. Silva SMC, Sousa JJS, Marques EF, Pais AACC, Michniak-Kohn BB (2013) Structure activity relationships in alkylammonium

- C<sub>12</sub>-Gemini surfactants used as dermal permeation enhancers. *AAPS J* 15:1119–1127
16. Zhou L, Jiang X, Li Y, Chen Z, Hu X (2007) Synthesis and properties of a novel class of Gemini pyridinium surfactants. *Langmuir* 23:11404–11408
  17. Ao MQ, Xu GY, Zhu YY, Bai Y (2008) Synthesis and properties of ionic liquid-type Gemini imidazolium surfactants. *J Colloid Interface Sci* 326:490–495
  18. Liu GY, Gu DM, Liu HY, Ding W, Li Z (2011) Enthalpy-entropy compensation of ionic liquid-type Gemini imidazolium surfactants in aqueous solutions: a free energy perturbation study. *J Colloid Interface Sci* 358:521–526
  19. Jiang Z, Li X, Yang G, Cheng L, Cai B, Yang Y, Dong J (2012) pH-responsive surface activity and solubilization with novel pyrrolidone-based Gemini surfactants. *Langmuir* 28:7174–7181
  20. Cai B, Dong JF, Cheng L, Jiang Z, Yang Y, Li XF (2013) Adsorption and micellization of gemini surfactants with pyrrolidinium head groups: effect of the spacer length. *Soft Matter* 9:7637–7643
  21. Cai B, Li XF, Yang Y, Dong JF (2012) Surface properties of Gemini surfactants with pyrrolidinium head groups. *J Colloid Interface Sci* 370:111–116
  22. Ao MQ, Huang PP, Xu GY, Yang XD, Wang YJ (2009) Aggregation and thermodynamic properties of ionic liquid-type gemini imidazolium surfactants with different spacer length. *Colloid Polym Sci* 287:395–402
  23. Ao MQ, Xu GY, Pang JY, Zhao TT (2009) Comparison of aggregation behaviors between ionic liquid-type imidazolium Gemini surfactant [C12-4-C12im]Br 2 and its monomer [C12mim]Br on silicon wafer. *Langmuir* 25:9721–9727
  24. Ren CC, Wang F, Zhang ZQ, Nie HH, Li N, Cui M (2015) Synthesis, surface activity and aggregation behavior of Gemini imidazolium surfactants 1,3-bis(3-alkylimidazolium-1-yl) propane bromide. *Colloids Surf A* 467:1–8
  25. Antonietti M, Kuang DB, Smarsly B, Zhou Y (2004) Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures. *Chem Int Ed* 43:4988–4992
  26. Paul BK, Motra R (2005) Water solubilization capacity of mixed reverse micelles: effect of surfactant component, the nature of the oil, and electrolyte concentration. *J Colloid Interface Sci* 288:261–279
  27. Leodidis EB, Hatton TA (1990) Amino acids in AOT reversed micelles. 1. Determination of interfacial partition coefficients using the phase-transfer method. *J Phys Chem* 94:6400–6411
  28. Fry AJ (2003) Strong ion-pairing effects in a room temperature ionic liquid. *J Electroanal Chem* 546:35–39
  29. Bai GY, Wang JB, Wang YJ, Yan HK (2002) Thermodynamics of hydrophobic interaction of disymmetric Gemini surfactants in aqueous solutions. *J Phys Chem B* 106:6614–6616
  30. Alami E, Holmberg K, Eastoe J (2002) Adsorption properties of novel Gemini surfactants with nonidentical head groups. *J Colloid Interface Sci* 247:447–455
  31. Peresykin AV, Menger FM (1999) Zwitterionic geminis, coacervate formation from a single organic compound. *Org Lett* 1:1347–1350
  32. Menger FM, Peresykin AV (2001) A combinatorially-derived structural phase diagram for 42 zwitterionic geminis. *J Am Chem Soc* 123:5614–5615
  33. Menger FM, Peresykin AV (2003) Strings of vesicles: flow behavior in an unusual type of aqueous gel. *J Am Chem Soc* 125:5340–5345
  34. Wang XY, Wang JB, Wang YL (2003) Micellization of a series of disymmetric Gemini surfactants in aqueous solution. *J Phys Chem B* 107:11428–11432
  35. Sikirić M, Primožič I, Filipović-Vinceković N (2002) Adsorption and association in aqueous solutions of disymmetric Gemini surfactant. *J Colloid Interface Sci* 250:221–229
  36. Zou M, Dong JF, Yang GF, Li XF (2015) A comprehensive study on micellization of disymmetric pyrrolidinium headgroup-based gemini surfactants. *Phys Chem Chem Phys* 17:10265–10273
  37. Kamboj R, Singh S, Chauhan V (2014) Synthesis, characterization and surface properties of *N*-(2-hydroxyalkyl)-*N'*-(2-hydroxyethyl) imidazolium surfactants. *Colloids and Surfaces A* 441:233–241
  38. Wettig SD, Verrall RE (2001) Thermodynamic studies of aqueous m-s-m Gemini surfactant systems. *J Colloid Interface Sci* 235:310–316
  39. Dong B, Li N, Zheng LQ, Inoue T (2007) Surface adsorption and micelle formation of surface active ionic liquids in aqueous solution. *Langmuir* 23:4178–4182
  40. Dong B, Zhao XY, Zheng LQ, Zhang J, Li N, Inoue T (2008) Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment. *Colloids Surf A* 317:666–672
  41. Wang XD, Li QT, Chen X, Li ZH (2012) Effects of structure disymmetry on aggregation behaviors of quaternary ammonium Gemini surfactants in a protic ionic liquid EAN. *Langmuir* 28:16547–16554
  42. Ruiz CC, Díaz-López L, Aguiar J (2007) Self-assembly of tetradecyltrimethylammonium bromide in glycerol aqueous mixtures: a thermodynamic and structural study. *J Colloid Interface Sci* 305:293–300
  43. Tan JL, Zhao PJ, Ma DP, Feng SY, Zhang CQ (2013) Effect of hydrophobic chains on the aggregation behavior of cationic silicone surfactants in aqueous solution. *Colloid Polym Sci* 291:1487–1494
  44. Fan YR, Li YJ, Cao MW, Wang JB, Wang YL, Thomas RK (2007) Micellization of disymmetric cationic Gemini surfactants and their interaction with dimyristoylphosphatidylcholine vesicles. *Langmuir* 23:11458–11464
  45. Keyes-Baig C, Duhamel J, Wetting S (2011) Characterization of the behavior of a pyrene substituted Gemini surfactant in water by fluorescence. *Langmuir* 27:3361–3371
  46. Wang XQ, Liu J, Yu L, Jiao JJ, Wang R, Sun LM (2013) Surface adsorption and micelle formation of imidazolium-based zwitterionic surface active ionic liquids in aqueous solution. *J Colloid Interface Sci* 391:103–110

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