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Synthesis and Surface Activity of Heterogemini Imidazolium Surfactants

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A series of heterogemini imidazolium surfactants with two-methylene spacer groups ([C_m-2-$C_n$im]Br_2, m, n=8, 10, 12, 14, 16; $m \neq n$) have been synthesized and characterized by ^{1}H NMR and ESI-MS spectroscopy. The effects of various reaction parameters, including stoichiometry, reaction temperature and time, were investigated. In addition, the surface activity study about heterogemini imidazolium surfactants was carried out and the influences of dissymmetric degree on the surface properties were also discussed.

Key words: Heterogemini imidazolium surfactants, Synthesis, Optimal conditions, Surface activity, Dissymmetric degree

I. INTRODUCTION

Gemini surfactants are composed of two amphiphilic moieties covalently connected by a rigid or flexible spacer at the level of the head groups. As a new generation of surfactants, gemini surfactants [1−3] demonstrate remarkable features in reducing surface tension and forming micelles. In addition, they have special physicochemical properties, such as high density, low Krafft point, and unique rheological properties [4]. Consequently, gemini surfactants have promising applications in skin care, chemical separations, organic synthesis, emulsifier, medicine, electrochemistry, nanomaterial synthesis, and biocatalysis [5], *etc.* Compared with the conventional gemini surfactants, gemini imidazolium surfactants [6] have several advantages and potential applications in many areas. For example, owing to the charge density dispersion of imidazolium head groups, this kind of gemini imidazolium surfactants show the inherent ionic nature of ionic liquids [7]. As cationic micelle systems, they display a significantly stronger tendency toward self-aggregation due to the distinct polarizability of imidazolium head groups and thus they can be used as supramolecular templates for the synthesis of functional materials [8]. As the reverse-micelle systems, the reverse micelles with big imidazolium head groups show higher capacity for solutes than those of quaternary ammonium cationic gemini surfactants. Besides, they can form compact membranes owing to the strong attraction between imidazolium head groups and aromatic rings through π-π interaction [9], which extends their potential applications in biology [18].

Heterogemini surfactants are a relatively new class of gemini surfactants which have the dissymmetric molecular structures with two different hydrophobic chains or two different hydrophilic head groups, linked by a rigid or flexible spacer group. On the account of more molecular structure factors that can be regulated and governed, some novel results have been obtained, such as, enhanced driving force of enthalpy factor, constructed counterions-free systems by the heterogeminis containing cationic-anionic head groups and bound vesicles formed by heterogeminis making use of their different length alkyl chains, *etc.* [10−14]. These gemini surfactants offer additional ways to control the shape of surfactant assemblies by varying the difference in the length of the hydrocarbon chains or the nature of the head groups. Oda and co-workers [15, 16] studied dissymmetric cationic quaternary ammonium gemini surfactants with the general structure [$C_mH_{2m+1}(CH_3)_2N$-$(CH_2)_s$-$N(CH_3)_2C_nH_{2n+1}]Br_2$, designated as $C_mC_sC_nBr_2$ series ($m \neq n$). Their results indicated that the hydrophobic chain length and dissymmetry of the surfactants have a strong influence on the micellization process. Sikirić *et al.* reported that $C_{12}C_2C_{14}Br_2$ exhibited peculiar properties in aqueous solution [17], *i.e.*, high polydispersity and the coexistence of three populations of differently sized aggregates. Therefore, it is significant to study the synthesis and properties of heterogemini surfactants.

To explore the field of heterogemini imidazolium surfactants based on symmetric gemini imidazolium surfactants, the synthesis, characterization, and properties of symmetric gemini imidazolium surfactants have been investigated extensively [18−21]. However, because of the difficulty for synthesis, the preparation of heterogemini imidazolium surfactants has not been focused on. Hence we made an attempt to synthesize and study the surface properties of heterogemini imidazolium surfactants with different long hydrocarbon groups.

In this work, a series of heterogemini imidazolium surfactants with two-methylene spacer groups are de-

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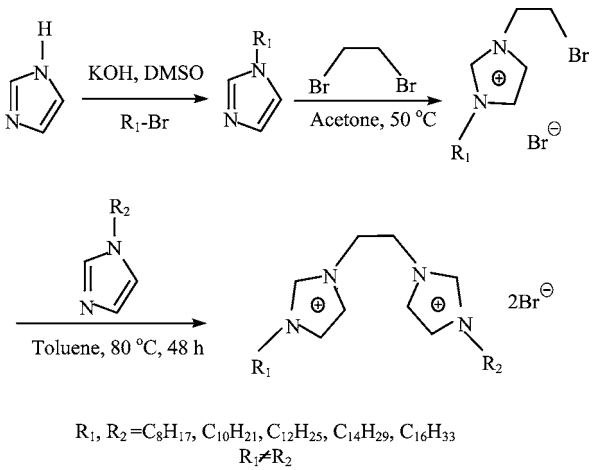

R_1, R_2=C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$
$R_1 \neq R_2$

Scheme 1 Synthetic procedure of $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$.

signed and synthesized ($[C_m\text{-}2\text{-}C_n\text{im}]Br_2$, m, n=8, 10, 12, 14, 16; $m \neq n$) (Scheme 1). Their structures are clearly confirmed by ^{1}HNMR and ESI-MS spectroscopy. Besides, optimized reaction conditions and surface properties of $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$ are researched. The effects of the hydrophobic chain length and dissymmetry on the surface adsorption and the formation of micelles are explored in detail.

II. EXPERIMENTS

A. Materials and methods

All chemicals were of analytical grade and used without any further purifications. ^{1}H NMR were recorded on a Bruker 500 MHz spectrometer. Mass spectra were performed by a Finnigan TSQ Quantum ultra AM mass spectrometer. The surface tension and critical micelle concentration (cmc) of the products were determined by a BZY-2 fully automatic surface tensiometer using the Wilhelmy Type method at 25.0 °C.

B. Synthesis of heterogemini imidazolium surfactants ($[C_m\text{-}2\text{-}C_n\text{im}]Br_2$)

1. *N*-alkylimidazole

A mixture of imidazole (14.7 mmol), potassium hydroxide (14.7 mmol) and dimethyl sulfoxide (5 mL) was placed in a 50 mL three-necked flask. After vigorous shaking for 2 h at room temperature, 1-bromoalkane (14.0 mmol) was dropped slowly into the above reaction mixture and the mixture was stirred for additional 4 h and monitored by thin layer chromatography (TLC) analysis. Upon completion, the distilled water (15 mL) was poured into the flask followed by extraction with chloroform (5×15 mL) in a separatory funnel. The combined organic layers were collected then dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was subjected to flash chromatography with ethyl acetate as eluant to give *N*-alkylimidazole. The yields of *N*-octyl imidazole, *N*-decyl imidazole, *N*-dodecyl imidazole, *N*-tetradecyl imidazole, and *N*-cetyl imidazole are 82.3%, 81.2%, 80.5%, 80.4% and 79.8%, respectively.

N-octyl imidazole: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.44 (s, 1H, CH), 7.03 (s, 1H, CH), 6.88 (s, 1H, CH), 3.90 (t, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.24-1.27 (m, 10H, CH_2), 0.85 (t, 3H, CH_3); MS (ESI): m/z 181.10 ($[M+H]^+$). *N*-decyl imidazole: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.41 (s, 1H, CH), 6.99 (s, 1H, CH), 6.86 (s, 1H, CH), 3.88 (t, 2H, CH_2), 1.74 (m, 2H, CH_2), 1.21-1.25 (m, 14H, CH_2), 0.85 (t, 3H, CH_3); MS (ESI): m/z 209.07 ($[M+H]^+$). *N*-dodecyl imidazole: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.44 (s, 1H, CH), 7.03 (s, 1H, CH), 6.88 (s, 1H, CH), 3.90 (t, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.23-1.27 (m, 18H, CH_2), 0.88 (t, 3H, CH_3); MS (ESI): m/z 237.08 ($[M+H]^+$). *N*-tetradecyl imidazole: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.43 (s, 1H, CH), 7.01 (s, 1H, CH), 6.88 (s, 1H, CH), 3.89 (t, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.22-1.26 (m, 22H, CH_2), 0.85 (t, 3H, CH_3); MS (ESI): m/z 265.19 ($[M+H]^+$). *N*-cetyl imidazole: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.45 (s, 1H, CH), 7.05 (s, 1H, CH), 6.90 (s, 1H, CH), 3.91 (t, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.25-1.32 (m, 26H, CH_2), 0.87 (t, 3H, CH_3); MS (ESI): m/z 293.29 ($[M+H]^+$).

2. 1-(2-Bromoethyl)-3-alkylimidazolium bromide

The *N*-alkyl imidazole (in which alkyl=octyl, decyl, dodecyl) was reacted with a large excess (more than 3-fold) of 1,2-dibromoethane in dry acetone at 50 °C under nitrogen atmosphere. The reaction was monitored by TLC analysis. At the end of the reaction, the solvent was removed by evaporation *invacuo* and the unreacted 1,2-dibromoethane was washed out thoroughly with hexane. The resulting viscous pale yellow oil was purified by silica column chromatography (acetone:MeOH=10:1) to afford 1-(2-bromoethyl)-3-alkylimidazolium bromide. The yields of 1-(2-bromoethyl)-3-octylimidazolium bromide, 1-(2-bromoethyl)-3-decylimidazolium bromide, 1-(2-bromoethyl)-3-dodecylimidazolium bromide are 72.5%, 74.1%, and 76.8%, respectively.

1-(2-Bromoethyl)-3-octylimidazolium bromide: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 10.23 (s, 1H, CH), 7.81 (s, 1H, CH), 7.37 (s, 1H, CH), 4.94 (t, 2H, CH_2), 4.29 (t, 2H, CH_2), 3.93 (t, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.23-1.31 (m, 10H, CH_2), 0.84 (t, 3H, CH_3); MS (ESI): m/z 289.10 ($[M\text{-}Br]^+$). 1-(2-Bromoethyl)-3-decylimidazolium bromide: ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 10.33 (s, 1H, CH), 7.78 (s, 1H, CH), 7.35 (s, 1H, CH), 4.96 (t, 2H, CH_2),

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4.29 (t, 2H, CH_2), 3.93 (t, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.23-1.31 (m, 14H, CH_2), 0.86 (t, 3H, CH_3); MS (ESI): m/z 317.07 ($[M\text{-}Br]^+$). 1-(2-Bromoethyl)-3-dodecylimidazolium bromide: ^{1}H NMR (500 MHz, $CDCl_3$ δ/ppm 10.27 (s, 1H, CH), 7.76 (s, 1H, CH), 7.34 (s, 1H, CH), 4.96 (t, 2H, CH_2), 4.30 (t, 2H, CH_2), 3.93 (t, 2H, CH_2), 1.92 (m, 2H, CH_2), 1.23−1.32 (m, 18H, CH_2), 0.87 (t, 3H, CH_3); MS (ESI): m/z 345.26 ($[M\text{-}Br]^+$).

3. $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$

A mixture of the intermediates 1-(2-bromoethyl)-3-alkylimidazolium bromide (alkyl=octyl, decyl, dodecyl) and two equiv of *N*-alkyl imidazole (in which the alkyl chains were different from the intermediates) in toluene was stirred at 80 °C for 48 h under nitrogen atmosphere. After the reaction completed, the solution was cooled down to the room temperature. A white precipitate was isolated, recrystallized in acetone for three times and dried under vacuum to yield $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$ as a white powder. The yields of $[C_8\text{-}2\text{-}C_{12}\text{im}]Br_2$, $[C_8\text{-}2\text{-}C_{14}\text{im}]Br_2$, $[C_8\text{-}2\text{-}C_{16}\text{im}]Br_2$, $[C_{10}\text{-}2\text{-}C_{12}\text{im}]Br_2$, $[C_{10}\text{-}2\text{-}C_{14}\text{im}]Br_2$, $[C_{10}\text{-}2\text{-}C_{16}\text{im}]Br_2$, $[C_{12}\text{-}2\text{-}C_{14}\text{im}]Br_2$ and $[C_{12}\text{-}2\text{-}C_{16}\text{im}]Br_2$ are 85.5%, 87.3%, 88.2%, 89.0%, 88.6%, 89.4%, 88.7% and 88.3%, respectively.

$[C_8\text{-}2\text{-}C_{12}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.13 (s, 2H, CH), 7.82 (s, 2H, CH), 7.68 (s, 2H, CH), 4.70 (s, 4H, CH_2), 4.13 (t, 4H, CH_2), 1.74 (m, 4H, CH_2), 1.20-1.24 (m, 28H, CH_2), 0.85 (t, 6H, CH_3); MS (ESI): m/z 222.16 ($[M\text{-}2Br]^{2+}$). $[C_{10}\text{-}2\text{-}C_{12}\text{im}]Br_2$/$[C_8\text{-}2\text{-}C_{14}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.16 (s, 2H, CH), 7.81 (s, 2H, CH), 7.68 (s, 2H, CH), 4.70 (s, 4H, CH_2), 4.12 (t, 4H, CH_2), 1.73 (m, 4H, CH_2), 1.18-1.23 (m, 32H, CH_2), 0.85 (t, 6H, CH_3); MS (ESI): m/z 236.22 ($[M\text{-}2Br]^{2+}$). $[C_{10}\text{-}2\text{-}C_{14}\text{im}]Br_2$/$[C_8\text{-}2\text{-}C_{16}\text{im}]Br_2$: δ/ppm 9.17 (s, 2H, CH), 7.82 (s, 2H, CH), 7.69 (s, 2H, CH), 4.72 (s, 4H, CH_2), 4.13 (t, 4H, CH_2), 1.74 (m, 4H, CH_2), 1.18-1.24 (m, 36H, CH_2), 0.85 (t, 6H, CH_3); MS (ESI): m/z 250.39 ($[M\text{-}2Br]^{2+}$). $[C_{10}\text{-}2\text{-}C_{16}\text{im}]Br_2$/$[C_{12}\text{-}2\text{-}C_{14}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.17 (s, 2H, CH), 7.80 (s, 2H, CH), 7.68 (s, 2H, CH), 4.69 (s, 4H, CH_2), 4.13 (t, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.19-1.23 (m, 40H, CH_2), 0.84 (t, 6H, CH_3); MS (ESI): m/z 264.21 ($[M\text{-}2Br]^{2+}$). $[C_{12}\text{-}2\text{-}C_{16}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.07 (s, 2H, CH), 7.80 (s, 2H, CH), 7.64 (s, 2H, CH), 4.67 (s, 4H, CH_2), 4.11 (t, 4H, CH_2), 1.72 (m, 4H, CH_2), 1.18-1.23 (m, 44H, CH_2), 0.84 (t, 6H, CH_3); MS (ESI): m/z 278.33 ($[M\text{-}2Br]^{2+}$).

C. Synthesis of 1,2-bis(3-alkylimidazolium-1-yl) ethane bromide ($[C_m\text{-}2\text{-}C_m\text{im}]Br_2$)

A solution of the *N*-decyl imidazole, *N*-dodecyl imidazole or *N*-tetradecyl imidazole (5 mmol) and 1,2-dibromoethane (2 mmol) in isopropanol (10 mL) was refluxed for three days 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 two days. The resulting white powder $[C_m\text{-}2\text{-}C_m\text{im}]Br_2$ was obtained. The yields of $[C_{10}\text{-}2\text{-}C_{10}\text{im}]Br_2$, $[C_{12}\text{-}2\text{-}C_{12}\text{im}]Br_2$ and $[C_{14}\text{-}2\text{-}C_{14}\text{im}]Br_2$ are 92.4%, 94.7% and 93.3%, respectively.

$[C_{10}\text{-}2\text{-}C_{10}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.13 (s, 2H, CH), 7.81 (s, 2H, CH), 7.68 (s, 2H, CH), 4.70 (s, 4H, CH_2), 4.11 (t, 4H, CH_2), 1.73 (m, 4H, CH_2), 1.19-1.24 (m, 28H, CH_2), 0.85 (t, 6H, CH_3); MS (ESI): m/z 222.24 ($[M\text{-}2Br]^{2+}$). $[C_{12}\text{-}2\text{-}C_{12}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.16 (s, 2H, CH), 7.81 (s, 2H, CH), 7.68 (s, 2H, CH), 4.70 (s, 4H, CH_2), 4.12 (t, 4H, CH_2), 1.73 (m, 4H, CH_2), 1.18-1.23 (m, 36H, CH_2), 0.84 (t, 6H, CH_3); MS (ESI): m/z 250.23 ($[M\text{-}2Br]^{2+}$). $[C_{14}\text{-}2\text{-}C_{14}\text{im}]Br_2$: ^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 9.12 (s, 2H, CH), 7.80 (s, 2H, CH), 7.66 (s, 2H, CH), 4.69 (s, 4H, CH_2), 4.11 (t, 4H, CH_2), 1.72 (m, 4H, CH_2), 1.20-1.25 (m, 44H, CH_2), 0.83 (t, 6H, CH_3); MS (ESI): m/z 278.15 ($[M\text{-}2Br]^{2+}$).

III. RESULTS AND DISCUSSION

A. Optimal reaction conditions

In the general synthesis of $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$, nucleophilic substitution of *N*-alkylimidazole and 1,2-dibromoethane was critical. Take the synthesis of 1-(2-bromoethyl)-3-dodecylimidazolium bromide for an example, the generation of symmetric gemini surfactants 1,2-bis(3-dodecylimidazolium-1-yl) ethane bromide($[C_{12}\text{-}2\text{-}C_{12}]Br_2$) is unavoidable. Thus, to effectively reduce symmetric gemini surfactants, quaternization reaction of *N*-dodecylimidazole and 1,2-dibromoethane was investigated under different reaction conditions (Table I). We find that the increase of 1,2-dibromoethane/*N*-dodecylimidazole molar ratio is beneficial to the formation of 1-(2-bromoethyl)-3-dodecylimidazolium bromide. Considering the effect of 1,2-dibromoethane, temperature and time on yields, we select the molar ratio of 4:1, reaction temperature of 50° and time of 10 h as the optimal conditions. Higher temperature and longer time will lead to produce more symmetric gemini surfactant, resulting in diminished yield. Besides, dry acetone as the reaction solvent should be excessive, which creates the dilution reaction environment thus makes against the formation of $[C_{12}\text{-}2\text{-}C_{12}]Br_2$.

B. Surface activity

It can also be found that $[C_m\text{-}2\text{-}C_n\text{im}]Br_2$ are immiscible with low polarity solvents, such as ethyl acetate, toluene, cyclohexane and petroleum ether, but miscible in methanol, chloroform and acetonitrile. The sur-

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TABLE I Optimization of reaction conditions on the synthesis of 1-(2-bromoethyl)-3-dodecylimidazolium bromide.

Ratio[a]	Temperature/°C	Time/h	Yield/%
1:1	50	10	40.6
2:1	50	10	53.5
3:1	50	10	66.4
3:1	50	12	64.0
3:1	60	10	61.6
4:1	50	10	76.8
4:1	50	12	73.3
4:1	60	10	70.6
5:1	50	10	77.9
5:1	50	12	77.2

[a] Molar ratio of 1,2-dibromoethane to *N*-dodecylimidazole.

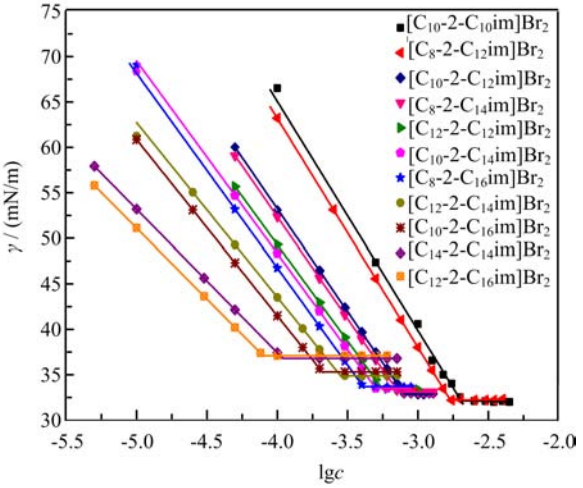

FIG. 1 Surface tension γ of heterogemini imidazolium surfactants [C_m-2-$C_n$im]Br_2 *vs.* concentration c at 25 °C.

face tension measurement is a classical method to study the surface properties of surfactants. The plots of surface tension versus log concentration (γ-lg$c$) for [C_m-2-$C_n$im]Br_2 by a surface tension apparatus using the Wilhelmy Type method at 25.0 °C are shown in Fig.1. A sharp break is shown in the surface tension plots, which are the indication of the critical micelle concentration (cmc) and the formation of micelles in the aqueous solutions. Here, it is worth mentioning that the purity of [C_m-2-$C_n$im]Br_2 was also confirmed from the observed sharp break points in the γ-lg$c$ plots, that is to say, the absence of a minimum around the breakpoints suggests there are no higher active substances in these heterogemini imidazolium surfactants. The values of the cmc are listed in Table II. The cmc shows a monotonous decrease with the increasing overall hydrophobic chain length (m+n) regardless of the dissymmetry, implying that the longer overall hydrophobic chain length, the higher the aggregation ability is. Therefore, [C_{14}-2-C_{14}im]Br_2 or [C_{12}-2-C_{16}im]Br_2 has the higher aggregation ability than the other Gemini surfactants. Besides, the cmc of surfactants with equal m+n, such as C_{10}-2-C_{10} and C_8-2-C_{12}, C_{10}-2-C_{12} and C_8-2-C_{14}, C_{12}-2-C_{12}, C_{10}-2-C_{14} and C_8-2-C_{16}, C_{12}-2-C_{14} and C_{10}-2-C_{16}, or C_{14}-2-C_{14} and C_{12}-2-C_{16}, decrease linearly as the n/m ratio increases, as presented in the Table II. This observation indicates that higher structural dissymmetry results in a lower cmc value by employing n/m as the degree of dissymmetry and a similar relationship can also be observed from the other dissymmetric Gemini surfactants [11, 22, 23]. Consequently, [C_{12}-2-C_{16}im]Br_2 possesses the highest aggregation ability in all the investigated heterogemini imidazolium surfactants. It is clear that the introduction of dissymmetry to the hydrophobic chains is more beneficial to the formation of micelles and adding two CH_2 groups to one longer chain is more efficient in lowering the cmc than adding each of them to two chains separately. The hydrophobic interactions have two contributions to the aggregation behavior, intermolecular and intramolecular. The latter will be the weaker interaction because the spacer group keeps the two hydrophobic chains apart. For the symmetric geminis, the number of hydrophobic units interacting will be the same for intramolecular and intermolecular interactions, and therefore the hydrophobic interaction will be minimized. However, for the dissymmetric geminis, as n/m ratio increases, the ratio of the number of hydrophobic units interacting intermolecularly to those interacting intramolecularly will increase [23]. Thus, the overall hydrophobic interaction is gradually improved with the increasing n/m ratio, which makes a positive contribution to the formation of micelles.

From the surface tension data, several surface property parameters, such as adsorption efficiency pc_{20}, the surface pressure at the cmc (π_{cmc}), the value of cmc/c_{20}, the maximum surface excess (Γ_{max}) and the minimum area occupied by a surfactant molecule at the air/solution interface (A_{min}) can be obtained. It is recognized that the pc_{20} value can measure the efficiency of surfactant adsorbing at the air/solution interface.

$$pc_{20} = -\lg c_{20} \tag{1}$$

where c_{20} is defined as the surfactant concentration at which the surface tension of pure solvent is reduced by 20 mN/m. The larger the value of pc_{20}, the higher the adsorption efficiency of the surfactant is.

The π_{cmc} is defined as:

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{2}$$

where γ_0 is the surface tension of pure solvent and γ_{cmc} is the surface tension of surfactant solution at the cmc. This parameter reflects the maximum reduction of surface tension caused by the dissolution of surfactant molecules and thus becomes an indication of the ability of the surfactant to lower the surface tension of the solvent.

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TABLE II Values of the cmc, surface tension at the cmc (γ_{cmc}), surface pressure at the cmc (π_{cmc}), adsorption efficiency pc_{20}, cmc/c_{20} with c_{20} being the surfactant concentration at which the surface tension of pure solvent is reduced by 20 mN/m, the maximum surface excess (Γ_{max}), and the minimum area occupied by a surfactant molecule at the air/solution interface (A_{min}) for heterogemini imidazolium surfactants.

Surfactant	n/m	cmc/(mmol/L)	γ_{cmc}/(mN/m)	π_{cmc}/(mN/m)	pc_{20}	cmc/c_{20}	Γ_{max}/(μmol/m^2)	A_{min}/nm^2
[C_{10}-2-C_{10}im]Br_2	1	2.10	32.0	40.0	3.48	6.34	1.47	1.13
[C_8-2-C_{12}im]Br_2	1.5	1.70	32.2	39.8	3.55	6.03	1.47	1.13
[C_{10}-2-C_{12}im]Br_2	1.2	0.80	32.9	39.1	3.94	6.97	1.32	1.26
[C_8-2-C_{14}im]Br_2	1.75	0.73	33.1	38.9	3.98	6.97	1.31	1.27
[C_{12}-2-C_{12}im]Br_2	1	0.56	33.4	38.6	4.13	7.55	1.24	1.34
[C_{10}-2-C_{14}im]Br_2	1.4	0.50	33.5	38.5	4.17	7.40	1.24	1.34
[C_8-2-C_{16}im]Br_2	2	0.41	33.7	38.3	4.24	7.13	1.25	1.33
[C_{12}-2-C_{14}im]Br_2	1.17	0.28	34.9	37.1	4.44	7.71	1.12	1.48
[C_{10}-2-C_{16}im]Br_2	1.6	0.21	35.3	36.7	4.54	7.28	1.13	1.47
[C_{14}-2-C_{14}im]Br_2	1	0.11	36.8	35.2	4.92	9.15	0.92	1.81
[C_{12}-2-C_{16}im]Br_2	1.33	0.08	37.1	34.9	5.06	9.19	0.91	1.83

The value of cmc/c_{20} ratio is correlated with structural factors in the micellization and adsorption processes. The surfactant with larger cmc/c_{20} ratio has the greater tendency to adsorb at the interface than the tendency to form micelles. As can be shown in Table II, both pc_{20} and cmc/c_{20} ratio increase with the increase of the total carbon number of hydrophobic chains, which suggests that the adsorption at the interface is much easier than the micellization process for [C_{14}-2-C_{14}im]Br_2 or [C_{12}-2-C_{16}im]Br_2. This is probably because that the greater repulsion action of longer hydrophobic chains makes them easily stretch into the external environment. [C_{10}-2-C_{10}im]Br_2 has the lower γ_{cmc} and higher π_{cmc} value than other Gemini surfactants, indicating the higher effectiveness of surface tension reduction. However, the values of γ_{cmc}, pc_{20}, cmc/c_{20} and π_{cmc} change a little upon raising the n/m ratio for the surfactants with the same overall hydrophobic chains, which means the degree of dissymmetry has no significant effect on the surface activity of heterogemini imidazolium surfactants.

The packing densities of surfactants at the air/aqueous solution interface are important for the interpretation of the surface activity. Γ_{max} is a measure of how much of the air/solution interface changed by the surfactant adsorption and depends on the molecular structure of a surfactant molecule and its orientation at the interface. A_{min} reflects the packing densities. The higher the effectiveness of adsorption, the smaller the interfacial area occupied by a surfactant molecule. Γ_{max} was calculated by applying the Gibbs adsorption isotherm Eq.(3). A_{min} can be estimated from the relation Eq.(4).

$$\Gamma_{max} = \frac{-1}{2.303nRT}\frac{d\gamma}{d\lg c} \quad (3)$$

$$A_{min} = \frac{10^{24}}{N_A\Gamma_{max}} \quad (4)$$

where n represents the number of species at the interface; Γ_{max} is in μmol/m^2, R is the gas constant (8.314 J/(mol·K), T is the temperature in Kelvin, and ($d\gamma$/d$\lg c$) is the slope in the surface tension isotherm when the concentration is near the cmc. In aqueous solutions of [C_m-2-$C_n$im]Br_2 surfactants, n is taken as 3 due to the fact that the solute molecule dissolves into three ions-one divalent and two monovalent [24]. N_A is Avogadros number and A_{min} is in nm^2/molecule. Both the Γ_{max} and A_{min} values are listed in Table II. The A_{min} values increase as the overall hydrophobic chain length is increased, which suggests that [C_{10}-2-C_{10}im]Br_2 has higher molecular compactness at the air/aqueous solution interface than those surfactants with longer overall hydrophobic chains. A reasonable explanation is that the longer hydrophobic chains are more prone to bend and thus make the surface area per molecule larger [25]. On the other hand, surfactants with the same total carbon number of hydrophobic chains have similar A_{min} values. The surface adsorption properties, Γ_{max} and A_{min}, do not depend on the symmetry degree but only on the overall hydrophobicity of the surfactants.

IV. CONCLUSION

In summary, we have successfully developed a facile and efficient method to prepare [C_m-2-$C_n$im]Br_2 (m, n=10, 12, 14, 16; $m\neq n$). The surface properties of heterogemini imidazolium surfactants are investigated. Compared with their symmetric imidazolium gemini surfactants, the degree of dissymmetry (n/m) of heterogemini imidazolium surfactants shows a marked effect on the cmc values. For those surfactants with the same overall hydrophobic chains, as the n/m ratio increases, the cmc decreases linearly, suggesting greater ability to form micelles. However, the effects of n/m on the pc_{20},

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cmc/c_{20}, $\pi_{\rm cmc}$ and $A_{\rm min}$ are very small. This synthetic method also provides an opportunity to prepare more derivatives by changing the spacer chains and further study other properties of heterogemini imidazolium surfactants, such as aggregation behavior, thermodynamic parameters of micellization ($\Delta G_m^{\ominus}$, $\Delta S_m^{\ominus}$, $\Delta H_m^{\ominus}$), *etc.*

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