J Surfact Deterg (2011) 14:497–504
DOI 10.1007/s11743-011-1254-7

ORIGINAL ARTICLE

# A Novel Zwitterionic Imidazolium-Based Ionic Liquid Surfactant: 1-Carboxymethyl-3-Dodecylimidazolium Inner Salt

**Xue-feng Liu · Li-li Dong · Yun Fang**

Received: 23 September 2010 / Accepted: 29 January 2011 / Published online: 9 March 2011

**Abstract** A novel zwitterionic imidazolium-based ionic liquid (IL) surfactant, 1-carboxymethyl-3-dodecylimidazolium inner salt, was synthesized. The molecule structure was confirmed by means of electrospray ionization mass spectrometry, $^{1}$H nuclear magnetic resonance and elemental analysis. The isoelectric point (pI) is 3.8 ± 0.1 at 35 ± 0.1 °C. The other important physicochemical parameters such as the critical micelle concentration (CMC), the surface tension at CMC ($\gamma_{CMC}$), the adsorption efficiency ($pC_{20}$), the surface pressure at CMC ($\Pi_{CMC}$), the maximum surface excess ($\Gamma_m$), the minimum molecular cross-sectional area ($A_{min}$), the value of CMC/$C_{20}$ and the average number of aggregation ($N_m$) were determined by surface tension and steady-state fluorescence probe methods, respectively.

**Keywords** Zwitterionic surfactant · Imidazolium-based ionic liquid · Surface activity

## Introduction

The inherent amphiphilic imidazolium-based ([$C_n$mim]X) ionic liquids (ILs) has been one of the attractive aspects of the surface active ILs in recent years [1–22], here, $C_n$, m, im, and X stands for alkyl chain, methyl, imidazolium, and counter-ion, respectively. This particular aspect allows people to consider some long-chain ionic liquids (when dispersed in aqueous solutions), in fact, as new types of cationic surfactant, namely an IL surfactant [2, 6, 7, 23], surfactant-like ILs [14], and surface active ILs [18].

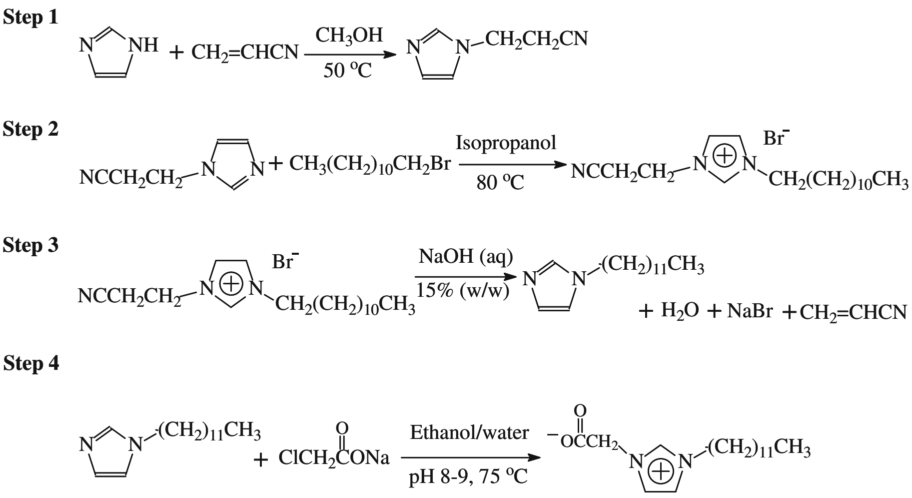
IL surfactants with single long-chain and Gemini IL surfactants have been reported [4, 24, 25]. Compared with single-chain IL surfactants, the IL-type Gemini ones have better surface activity and dispersion ability [26]. More recently, the hydroxyl-functionalized chiral IL surfactant [27] and novel IL surfactants, for instance, [$C_n$mim][$C_mH_{2m+1}SO_3$] [28] have been synthesized. From the electric charge characteristic of the ionic head groups, all the aforementioned IL surfactants are cationic. Interestingly, apart from a very recent paper [29], reports on the synthesis and the surface activity for zwitterionic imidazolium-based IL surfactants, by far, have seldom been reported yet.

Here, we synthesized a novel zwitterionic imidazolium-based IL surfactant, namely 1-carboxymethyl-3-dodecylimidazolium inner salt (CMDim, Scheme 1). The molecule structure was confirmed by means of electrospray ionization mass spectrometry (ESI–MS), $^{1}$H nuclear magnetic resonance ($^{1}$H NMR) and elemental analysis. In addition to the Krafft temperature ($T_K$) and the isoelectric point (pI), many important physicochemical parameters, such as the critical micelle concentration (CMC), the surface tension at the CMC ($\gamma_{CMC}$), the adsorption efficiency ($pC_{20}$), the surface pressure at the CMC ($\Pi_{CMC}$), the maximum surface excess ($\Gamma_m$), the minimum molecular cross-sectional area ($A_{min}$), the value of the CMC/$C_{20}$, the average number of aggregation ($N_m$) and the micellar microenvironment polarity were determined by using surface tension and fluorescence probe methods, respectively.

---

X. Liu (✉) · L. Dong · Y. Fang
School of Chemical and Material Engineering,
Jiangnan University, 214122 Wuxi,
People's Republic of China
e-mail: xfliu@jiangnan.edu.cn

**Scheme 1** The synthesis routes of CMDim



## Experimental Section

### Materials

Imidazole, 1-bromododecane, sodium chloroacetate, acrylonitrile, $D_2O$ and other reagents were purchased from Sinopharm Chemical Reagent Company (Shanghai, China), and were used without further purification. Deionized water was obtained from a Millipore Milli-Q water purification system (Millipore, USA).

### The Synthesis of CMDim

The synthesis routes of CMDim are shown in Scheme 1. For a general procedure, imidazole (0.2 mol, 13.6 g) and acrylonitrile (0.27 mol, 14.3 g) were dissolved in 20 mL methanol. The mixture was stirred at 50 °C for 8 h under nitrogen. The solvent methanol and the unreacted acrylonitrile were subsequently removed under vacuum. After that, 1-bromododecane (0.14 mol, 34.9 g) was added with isopropanol (40 mL) and the mixture was refluxed at 80 °C for 18 h under nitrogen. The isopropanol was removed under vacuum when the reaction was completed. The residue was dissolved in a 15 wt% NaOH aqueous solution (100 mL) and extracted by chloroform (50 mL). The chloroform layer was washed several times with deionized water. The residual solvent was removed under vacuum to give *n*-dodecylimidazole 29.7 g (90% yields). The *n*-dodecylimidazole (0.09 mol, 21.2 g) and sodium chloroacetate (0.09 mol, 10.5 g) were dissolved in ethanol–water (volume ratio 1:1), and was stirred at 75 °C for 8 h under nitrogen. The pH was maintained in the range of 8–9. The solvent was removed under reduced pressure when the reaction was completed. The product was dissolved in anhydrous ethanol and the inorganic salt was eliminated by filtration. And the unreacted *n*-dodecylimidazole was washed away by acetone. The objective compound was purified by recrystallization in deionized water at 3–4 °C and then dried under a vacuum for 3 days (yield 73.2%). The corresponding CMDim is white acicular crystal powder at room temperature.

The melting point of CMDim is 69.0 ± 0.3 °C. By the definition [30], the organic salts are called ILs when the melting point is lower than 100 °C, so we can also call CMDim an IL.

### The Measurements of ESI–MS, $^1$H NMR and Elemental Analysis

The ESI–MS measurement was carried out using a Maldi Synapt Q-TOF MS (waters) under a positive ion mode (see Fig. 1).

The $^1$H-NMR spectrum was obtained with an Avance III 400 MHz digital NMR spectrometer (Bruker) using $D_2O$ as solvent. And the NMR peak of $D_2O$ ($\delta = 4.710$ ppm) was used as the reference in determining the chemical shifts of protons in CMDim (see Fig. 2).

The elemental analysis measurements were conducted on a Vario EL III elementar analyzer (Elementar). All the experiments were performed at room temperature (about 25 °C).

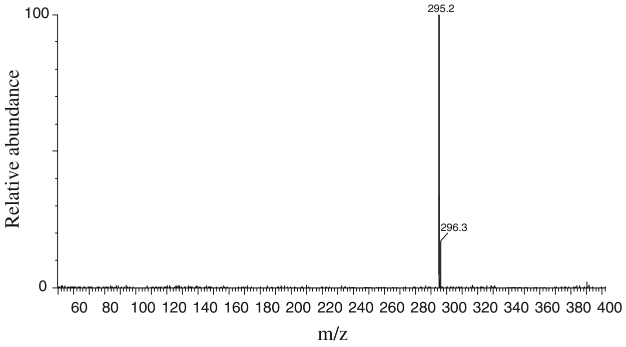


**Fig. 1** The ESI–MS spectrum of CMDim with positive ion mode

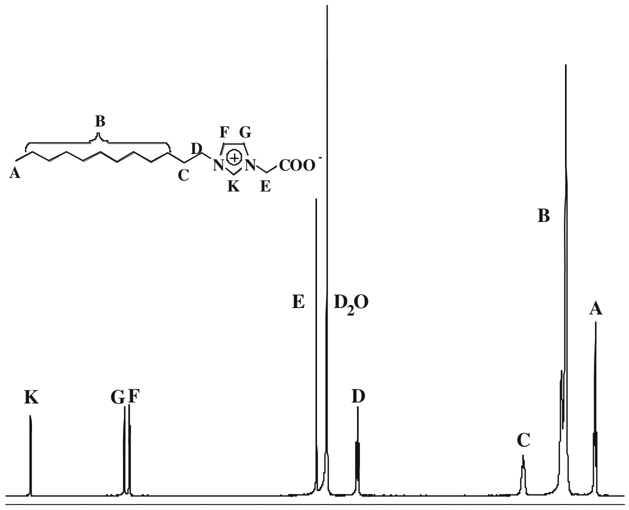


**Fig. 2** The $^1$H-NMR spectrum of CMDim

## The Measurements of Isoelectric Point, Surface Tension, and Fluorescence Emission Spectra

The isoelectric point (pI) of CMDim was determined by means of a Zeta potentiometer (Malvern) at 25 ± 0.1 °C, the electric field intensity was 15 V $cm^{-1}$. The concentration of the sample solutions was constant at $3.4 \times 10^{-3}$ mol $L^{-1}$ which is about 2.7 times of the CMC of the surfactant CMDim. The pHs of the sample solutions were adjusted by adding definite amount of HCl and NaOH, respectively. And the pI was determined by the plot of the Zeta potential versus pH (see Fig. 3).

The surface tension ($\gamma$) measurements of CMDim aqueous solutions were conducted on a drop volume tensiometer at 35 ± 0.1 °C. The outer radius of the glass capillary was 0.66 mm. During the procedure of $\gamma$ measurements, the sufficient aging time is necessary for the surfaces of the pendant drops formed at the tip of a capillary to reach the equilibrium state. Here, the aging time of the drop surface for the lowest sample solution was determined by the plot of $\gamma$ versus the drop detachment time $t$ (in s) (Fig. 4). Obviously, the $\gamma$ of the solution decreased with the drop detachment time increasing with a breakpoint at $t \approx 200$ s. The change of $\gamma$ was less than ±0.1 mN $m^{-1}$ in the region of $t > 300$ s. Under this condition, the $\gamma$ could be considered as an equilibrium surface tension. The lower concentration sample solution needs longer aging time for the drop surface to reach an equilibrium state. Thus, in order to make the drop surfaces reach the equilibrium state, all the drops of the surfactant solutions were aged for at least 10 min. Finally, the drop volume was calibrated by The surface activity parameters, such as the critical micelle concentration (CMC), the $\gamma$ at CMC ($\gamma_{CMC}$), the adsorption efficiency ($pC_{20}$), the surface pressure at the CMC ($\Pi_{CMC}$), the maximum surface excess ($\Gamma_m$), the minimum molecular cross-sectional area ($A_{min}$) and the value of CMC/$C_{20}$ were obtained from the $\gamma$-$C$ curves (Fig. 5).

The fluorescence emission spectral measurements were carried out on a RF5301PC spectrofluorophotometer (Shimadzu, Japan). Pyrene was used as the fluorescence probe. The concentration of pyrene was fixed at $1.0 \times 10^{-7}$ mol $L^{-1}$. The excitation wavelength was 335 nm.

The microenvironment polarity of the surfactant micelles and the value of CMC with pH = 7 were determined by means of the fluorescence emission spectral method [11, 31] (see Fig. 6). The value of $N_m$ was

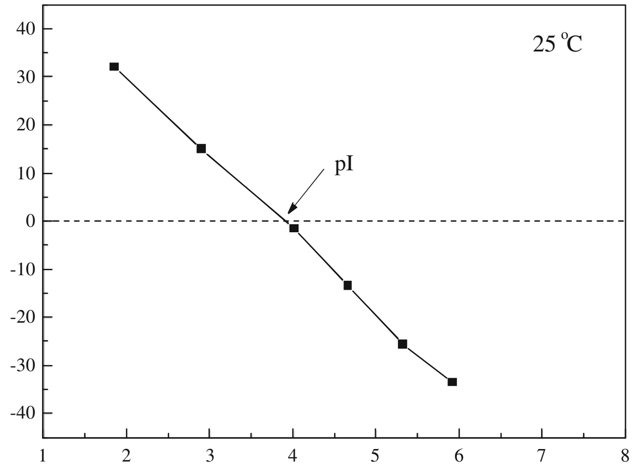


**Fig. 3** The relationship between Zeta potential and pH for CMDim in aqueous solutions, the surfactant concentration is $3.4 \times 10^{-3}$ mol $L^{-1}$, and the pH was adjusted by adding HCl and NaOH, respectively

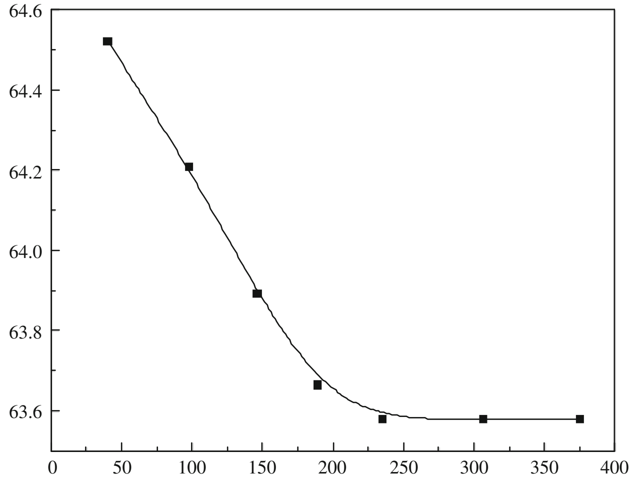


**Fig. 4** The aging curve of CMDim aqueous solution drop surface at 35 °C at a pH of 7, the concentration of the surfactant was $2.5 \times 10^{-3}$ mol $L^{-1}$

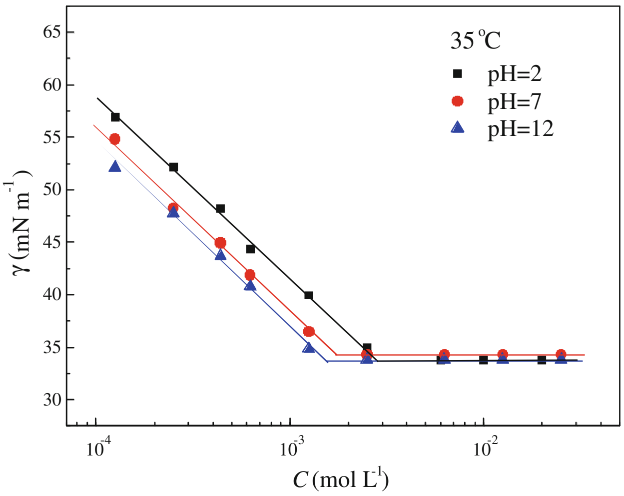


**Fig. 5** The concentration dependence of the surface tension for CMDim in aqueous solutions at 35 °C

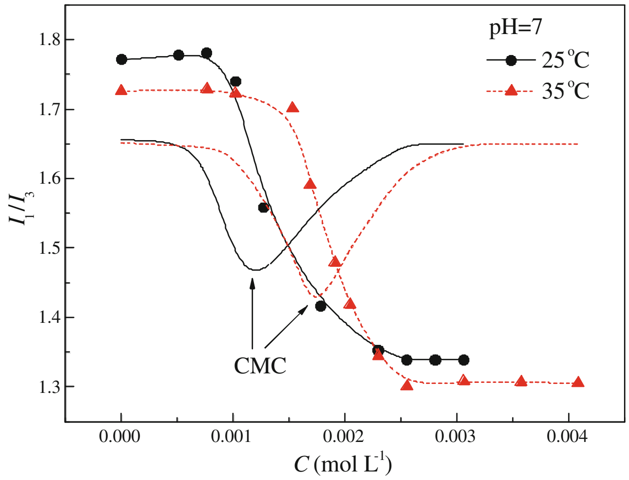


**Fig. 6** The $I_1/I_3$ versus the concentration of CMDim at 25 °C and 35 °C, pH = 7, the additional curves with minima are the first order derivatives of $I_1/I_3$-$C$, and the minima correspond to the CMC of CMDim at 25 °C and 35 °C, respectively

determined using a steady-state fluorescence quenching method [32, 33]. All the fluorescence spectral measurements were conducted at 25 ± 0.1 and 35 ± 0.1 °C, respectively.

## Results and Discussion

### Structural Characterization of CMDim

The ESI–MS technique was employed to measure the molecule weight of the objective product CMDim in this work. Under the positive ion mode, the cationic $[\mathrm{CMDim} + \mathrm{H}]^+$, i.e. one mole of CMDim inner salts were binding with one mole of protons, was detected (Fig. 1). The mass-to-charge ratio ($m/z$) of $[\mathrm{CMDim} + \mathrm{H}]^+$ is 295.2, which matches well with the theoretical calculation result (294.4 + 1) of the molecule ion weight for $[\mathrm{CMDim} + \mathrm{H}]^+$. The found results of elemental analysis for CMDim are C 69.26%, H 10.36%, O 9.56%, and N 10.82%, which matches well with the theoretical calculation compositions (C 69.40%, H 10.20%, O 9.52%, and N 10.88%).

In order to get the molecule structural information in detail, the $^1$H-NMR spectrum of CMDim was obtained. The interpreting results of the $^1$H-NMR spectrum using the signal of solvent $D_2O$ as a reference are also presented in Fig. 2. All of the results of ESI–MS, elemental analysis and $^1$H NMR indicate that the CMDim presents a sufficient purity.

### The Isoelectric Point of CMDim

The isoelectric point (pI), sometimes abbreviated to IEP, is the pH at which a particular molecule or surface carries no net electrical charge. Amphoteric molecules called zwitterions contain both positive and negative charges depending on the functional groups present in the molecule. The net charge on the molecule is affected by pH of their surrounding environment and can become more positively or negatively charged due to the loss or gain of protons ($H^+$). The pH dependence of the Zeta potential for CMDim in aqueous solutions is shown in Fig. 3. And the pI of the zwitterionic CMDim is 3.8 ± 0.1 at 25 ± 0.1 °C.

The pI value can affect the solubility of a molecule at a given pH. Such molecules have minimum solubility in water or salt solutions at the pH which corresponds to their pI and often precipitate out of the solution. Based on this particular aspect, the objective CMDim was purified by recrystallization in water with adjusting the pH of the aqueous solutions in the temperature range of 3–4 °C.

### The Surface Activity Parameters of CMDim

At a pH below their pI, zwitterions carry a net positive charge; above their pI they carry a net negative charge. The concentration dependence of the $\gamma$ for CMDim in aqueous solutions at various pHs are shown in Fig. 5. One can see that, the $\gamma$ (in mN $\mathrm{m}^{-1}$) gradually decreases to a plateau region with the increase of CMDim concentration ($C$, mol $\mathrm{L}^{-1}$). A decrease of surface tension indicates that the surfactant molecules adsorbed at the air-solution interface. The break point appears in the $\gamma$-$C$ curves suggests the formation of micelles in aqueous solutions. Here, it is worth mentioning that the purity of CMDim was also confirmed from the observed sharp break point in the

$\gamma$-$C$ curves. The values of the CMC and $\gamma_{CMC}$ for the surfactant at various pHs were obtained from the $\gamma$-$C$ curves.

It is recognized that the p$C_{20}$ value can measure the efficiency of surfactant adsorbing at the air-solution interfaces.

$$pC_{20} = -\log C_{20} \tag{1}$$

where $C_{20}$ is defined as the surfactant concentration at which the surface tension of pure solvent is reduced by 20 mN m$^{-1}$. The larger the value of p$C_{20}$, the higher the adsorption efficiency of the surfactant is.

The $\Pi_{CMC}$ is defined as

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{2}$$

where $\gamma_0$ is the surface tension of pure solvent. The values of $\Gamma_m$ (in mol cm$^{-2}$) under the conditions of pH = 2, 7 and 12 were estimated by applying Eq. 3 [34] to the surface tension data in the surfactant concentration regions of $C < 10^{-3}$ mol L$^{-1}$. Thus, the activity of the surfactant can be replaced by the concentration in the procedure of the $\Gamma_m$ calculation.

$$\gamma_0 - \gamma = RT\Gamma_m \ln\left(\frac{C}{b} + 1\right) \tag{3}$$

where $R$ is the gas constant ($8.314 \times 10^7$ ergs mol$^{-1}$ K$^{-1}$), $T$ is the experiment temperature (K), and $b$ is the empirical constant. Equation 3 is a derivate form from the Gibbs adsorption equation. Thus, the prefactor in the Gibbs adsorption equation must be considered carefully. Here, the prefactor is 1 for the surfactant CMDim at pH = 7, because there is no counter ions binding with CMDim. Under the condition of pH = 2, the prefactor can be considered as 1. The reason is as following. The concentrations of both $H^+$ and $Cl^-$ (come from HCl, because we used HCl for pH adjustments) are $10^{-2}$ mol L$^{-1}$. Due to the chemical characteristic of carboxyl groups in CMDim, the $H^+$ will bind with the carboxyl groups. Then, the CMDim presents as a cationic surfactant (CMDim$^+$Cl$^-$). The remaining HCl should act as a coexisting electrolyte with the same counter ions as cationic surfactant CMDim$^+$Cl$^-$. The surface tension data used for Γm calculation are within the regions of $C < 10^{-3}$ mol L$^{-1}$. Thus, the concentration of the remaining HCl in solutions is, at least, one order of magnitude larger than the cationic surfactant. One can consider the condition is a state with the constant ion strength. Due to the analogous reasons discussed above, the prefactor is also 1 under the conditions of pH = 12.

The $A_{min}$ (in square angstroms) was calculated using Eq. 4, where $N_A$ is Avogadro's number.

$$A_{min} = \frac{10^{16}}{N_A \times \Gamma_m} \tag{4}$$

where $N_A$ is Avogadro constant. 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 interfaces than the tendency to form micelles. All aforementioned parameters may be obtained and are listed in Table 1.

The CMC of CMDim increases with pH decreasing due to the characteristic zwitterionic head group in CMDim molecule. This tendency is similar to that of traditional zwitterionic surfactants, for instance, carboxybetaines. The CMC of CMDim is higher in acid solutions than in alkaline solutions, because the CMDim is at least partly in the cationic form at low pH, and it is in the form of the anions in the case of high pH. As the pH lowering, the amount of the zwitterionic and then cationic form in solution increases, and the resulting CMCs of the anionic/zwitterionic, zwitterionic, zwitterionic/cationic, and then cationic surfactants increase. On the other hand, increasing the concentration of acid (here HCl was used) also increases the ionic strength of the solutions, which tends to lower the CMCs. However, compared with that of the pH, the effect of the ionic strength on the CMC of zwitterionic CMDim seems to be small (see Fig. 5; Table 1). It is attributed to that the pH can change the type of hydrophilic groups in CMDim (i.e. from the cationic to the neutral inner salt then to the anionic when the pH changes from the basic to the acidic); but the ionic strength does not change the hydrophilic group type of the surfactant.

**Table 1** The physicochemical parameters for CMDim from surface tension method in this work and the other types of surfactants with the same carbon chain from reference [34]

| Parameters | CMDim | | | $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$ |
|---|---|---|---|---|
| pH | 2.0 ± 0.1 | 7.0 ± 0.2 | 12.0 ± 0.1 | |
| CMC ($10^{-3}$ mol L$^{-1}$) | 2.78 | 1.71 | 1.52 | 1.8 (2.0)* |
| $\gamma_{CMC}$ (mN m$^{-1}$) | 33.8 | 34.3 | 33.8 | – |
| p$C_{20}$ | 3.52 | 3.69 | 3.77 | – |
| $\Pi_{CMC}$ (mN m$^{-1}$) | 36.6 | 36.1 | 36.6 | – |
| $\Gamma_m$ ($10^{-10}$ mol cm$^{-2}$) | 1.74 | 1.41 | 1.25 | 3.2* |
| $A_{min}$ (Å$^2$) | 95.4 | 117.5 | 133.1 | 59.0 (52.0)* |
| CMC/$C_{20}$ | 9.14 | 8.57 | 9.01 | 6.5** |

* At 25 °C; ** at 23 °C

The value of CMC, p$C_{20}$ and $\Gamma_m$ for CMDim under the condition of neutral pH are lower than that of $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$ [34, 35] without regard to the effect of experimental temperature. This can be attributed to the cross-sectional area ($A_{min}$) difference between these two surfactants. As shown in Table 1, the $A_m$ for CMDim is larger than that of $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$, which can be attributed to the larger bulk of carboxymethyl imidazolium group in the CMDim molecule. The value of CMC/$C_{20}$ for CMDim is larger than that of $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$, which indicates a greater steric effect on micellization than on adsorption at the air-solution interface for CMDim caused by the larger head groups.

## The Micelle Properties of CMDim

In this study, pyrene was used as a fluorescence probe to monitor the form of micelle for CMDim in aqueous solution and then to investigate the polarity of the microenvironment of micelles. The emission spectrum of pyrene presents five vibration bands. The first band ($I_1$, around 373 nm) may be enhanced in a polar microenvironment, while the third band ($I_3$, around 384 nm) is not sensitive to the surrounding environment. It is known that pyrene preferentially dissolves into hydrophobic regions. Thus, the ratio of $I_1/I_3$ may probe the formation of the micelles and the micropolarity of the surfactant aggregates [31, 32, 36].

The plots of $I_1/I_3$ versus the concentration of CMDim at 25 ± 0.1 and 35 ± 0.1 °C and the corresponding first order derivatives are shown in Fig. 6. The $I_1/I_3$ decreases with the surfactant concentration increasing. However, the dependence of $I_1/I_3$ on $C$ is sigmoid; the values of the CMC could be calculated by the inflection point of sigmoid $I_1/I_3$-$C$ curves [11]. The CMCs of CMDim calculated from the sigmoid $I_1/I_3$-$C$ curves are $1.74 \times 10^{-3}$ mol L$^{-1}$ (35 ± 0.1 °C) and $1.25 \times 10^{-3}$ mol L$^{-1}$ (25 ± 0.1 °C), respectively. Obviously, the value of the CMC at 35 ± 0.1 °C from the fluorescence probe method is very close to that from the surface tension method.

The variation for $I_1/I_3$ with the surfactant concentration indicates the formation of the micelles in aqueous solutions. The values of $I_1/I_3$ for pyrene are 0.60 and 1.90 under the conditions of cyclohexane [36] and pure water [37], respectively. One can see that the values of $I_1/I_3$ for the micelles are 1.34 and 1.31 at 25 ± 0.1 and 35 ± 0.1 °C, respectively, which suggests that the polarity of the CMDim micelle is lower than that of pure water while is larger than that of pure cyclohexane.

Here, we use the packing parameter, $V_H/l_CA_{min}$, for predicting the micelle shape of CMDim in aqueous solutions, the $V_H$ (the volume of the hydrophobic long carbon chain) is $27.4 + 26.9C_n$ Å$^3$ [34, 38], $l_C$ (the length of the long carbon chain) is $1.5 + 1.265C_n$ [38], the $C_n$ is the carbon number of the long-chain. The calculated values of $V_H/l_CA_{min}$ are in the range of 0.15–0.20 for CMDim under the various pHs conditions in this work. Based upon the geometry relationship between the micelle shape and the surfactant molecule structure [34], the calculated values of $V_H/l_CA_m$ allow us to consider that the shape of CMDim micelle is spherical.

The average aggregation number, $N_m$, of CMDim in aqueous solutions was determined by a steady-state fluorescence quenching method. This method is based on the procedure proposed by Turro and Yekta [32], and the main assumptions are that (1) the quenching rate constant is much larger than the probe decay rate constant and (2) the random distribution of the probe and quencher over the micelles results in a Poisson distribution. Here, pyrene and benzophenone were used as the probe and the quencher, respectively. Thus the $N_m$ was obtained by applying the Eq. 5 to the fluorescence data [29],

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_m \times C_Q}{C - \mathrm{CMC}} \tag{5}$$

where $I_0$ and $I$ are the fluorescence intensities of pyrene in the absence and presence of the quencher at a specific wavelength, $C_Q$ and $C$ are the concentration of the quencher and CMDim, respectively. The plots of $N_m$ versus the surfactant concentration at 25 ± 0.1 and 35 ± 0.1 °C with pH = 7 are shown in Fig. 7. The $N_m$ increases, in mass, with the concentration of CMDim increasing. The relevant mathematic equations can be written as (the coefficient constants are listed in the parentheses)

$$N_m = 2.44 \times 10^3 C + 25.25 \quad R^2 = 0.9589 \tag{6}$$

$$N_m = 1.54 \times 10^3 C + 33.09 \quad R^2 = 0.9555. \tag{7}$$

One can see an empirically linear relationship between the $N_m$ and the CMDim concentration. From the relationship between $N_m$ and the surfactant concentration, one of

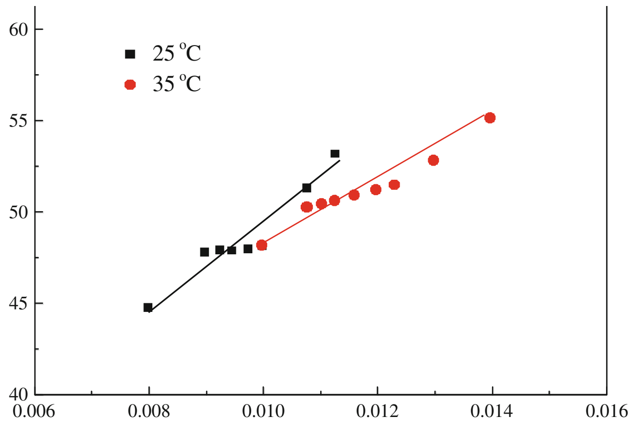


**Fig. 7** The concentration dependence of $N_m$ for CMDim with pH = 7 at 25 °C and 35 °C

the most important parameters, the critical average aggregation number ($N_{m,c}$), can be obtained by reverse extending the Eqs. 6 and 7 to CMCs, respectively. Here, the parameter $N_{m,c}$ describes the surfactant monomers number of the first micelle corresponding to the definite CMC in solution at certain temperature. This parameter is hardly obtained by other routine methods. Corresponding to the value of CMCs at 25 ± 0.1 and 35 ± 0.1 °C, the $N_{m,\ c}$ is 28.3, and 35.8, respectively. The former is smaller than that of $C_{12}H_{25}N^{+}(CH_3)_2CH_2COO^{-}$ (about 80–85) [34], which indicates that the CMDim micelle presents a much looser structure. It is also attributed to the higher steric effects among the larger bulk head groups in CMDim molecules.

**Acknowledgments** This work was sponsored by the Qing Lan Project (2010) of Jiangsu Province, the Fundamental Research Funds for the Central Universities (JUSRP21110), the Jiangsu Key Laboratory of Fine Petrochemicals (KF0903), and the Zhejiang Zanyu Technology Co.,Ltd Research Funds.

## References

1. Galgano PD, El Secoud OA (2010) Micellar properties of surface active ionic liquids: a comparison of 1-hexadecyl-3-methylimidazolium chloride with structurally related cationic surfactants. J Colloid Interface Sci 345:1–11
2. Merrigan TL, Bates ED, Dorman SC Jr, Davis JH (2000) New fluorous ionic liquids function as surfactants in conventional room-temperature ionic liquids. Chem Commun 20:2051–2052
3. Miskolczy Z, Sebők-Nagy K, Biczók L, Göktürk S (2004) Aggregation and micelle formation of ionic liquids in aqueous solution. Chem Phys Lett 400:296–300
4. Baltazar QQ, Chandawalla J, Sawyer K, Anderson JL (2007) Interfacial and micellar properties of imidazolium-based monocationic and dicationic ionic liquids. Colloids Surf A 302:150–156
5. Jungnickel C, Łuczak J, Ranke J, Fernández JF (2008) Micelle formation of imidazolium ionic liquids in aqueous slution. Colloids Surf A 316:278–284
6. Łuczak J, Hupka J, Thöming J, Jungnickel C (2008) Self-organization of imidazolium ionic liquids in aqueous solution. Colloids Surf A 329:125–133
7. Blesic M, Marques MH, Plechkova NV, Seddon KR, Rebelo LPN, Lopes A (2007) Self-aggregation of ionic liquids: micelle formation in aqueous solution. Green Chem 9:481–490
8. Smirnova NA, Vanin AA, Safonova EA, Pukinsky IB, Anufrikov YA, Makarov AL (2009) Self-assembly in aqueous solutions of imidazolium ionic liquids and their mixtures with an anionic surfactant. J Colloid Interface Sci 336:793–802
9. Goodchild I, Collier L, Millar SL, Prokeš I, Lord JCD, Butts CP, Bowers J, Webster JRP, Heenan RK (2007) Structural studies of the phase, aggregation and surface behavior of 1-alkyl-3-methylimidazolium halide + water mixtures. J Colloid Interface Sci 307:455–468
10. Inoue T, Ebina H, Dong B, Zheng L (2007) Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. J Colloid Interface Sci 314:236–241
11. El Seoud OA, Pires PAR, Abdel-Moghny T, Bastos E (2007) Synthesis and micellar properties of surface-active ionic liquids: 1-alkyl-3-methylimidazolium chlorides. J Colloid Interface Sci 313:296–304
12. Ao M, Xu G, Zhu Y, Bai Y (2008) Synthesis and properties of ionic liquid-type Gemini imidazolium surfactants. J Colloid Interface Sci 326:490–495
13. Thomaier S, Kunz W (2007) Aggregates in mixtures of ionic liquids. J Mol Liq 130:104–107
14. Zhao Y, Chen X, Wang X (2009) Liquid crystalline phases self-organized from a surfactant-like ionic liquid $C_{16}$mimCl in ethylammonium nitrate. J Phys Chem B 113:2024–2030
15. Blesic M, Lopes A, Melo E, Petrovski Z, Plechkova NV, Lopes JNC, Seddon KR, Rebelo LPN (2008) On the self-aggregation and fluorescence quenching aptitude of surfactant ionic liquids. J Phys Chem B 112:8645–8650
16. Zhao Y, Gao S, Wang J, Tang J (2008) Aggregation of ionic liquids [Cnmim]Br ($n = 4, 6, 8, 10, 12$) in D2O: a NMR study. J Phys Chem B 112:2031–2039
17. Gaillon L, Sirieix-Plenet J, Letellier P (2004) Volumetric study of binary solvent mixtures constituted by amphiphilic ionic liquids at room temperature (1-alkyl-3-methylimidazolium bromide) and water. J Solution Chem 33:1333–1347
18. Dong B, Li N, Zheng L, Yu L, Inoue T (2007) Surface adsorption and micelle formation of surface active ionic liquids in aqueous solution. Langmuir 23:4178–4182
19. Wang J, Wang H, Zhang S, Zhang H, Zhao Y (2007) Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids [C4mim][BF4] and [Cnmim]Br ($n = 4, 6, 8, 10, 12$) in aqueous solutions. J Phys Chem B 111:6181–6188
20. Pino V, Yao C, Anderson J (2009) Micellization and interfacial behavior of imidazolium-based ionic liquids in organic solvent-water mixtures. J Colloid Interface Sci 333:548–556
21. Łuczak J, Jungnickel C, Joskowska M, Thöming J, Hupka J (2009) Thermodynamics of micellization of imidazolium ionic liquids in aqueous solutions. J Colloid Interface Sci 336:111–116
22. Wang H, Wang J, Zhang S, Xuan X (2008) Structural effects of anions and cations on the aggregation behavior of ionic liquids in aqueous solution. J Phys Chem B 112:16682–16689
23. Rebelo LPN, Lopes JNC, Esperança JMSS, Guedes HJR, Łachwa J, Najdanovic-Visak V, Visak ZP (2007) Accounting for the unique, doubly dual nature of ionic liquids from a molecular thermodynamic and modeling standpoint. Acc Chem Res 40:1114–1121
24. Ao M, Xu G, Pang J, Zhao T (2009) Comparison of aggregation behaviors between ionic liquid-type imidazolium Gemini surfactant [C12–4-C12im]Br2 and its monomer [C12 mim]Br on silicon wafer. Langmuir 25:9721–9727
25. Ding YS, Zha M, Zhang J, Wang SS (2007) Synthesis, characterization and properties of geminal imidazolium ionic liquids. Colloid Surf A 298:201–205
26. Liu Y, Yu L, Zhang S, Yuan J, Shi L, Zheng L (2010) Dispersion of multiwalled carbon nanotubes by ionic liquid-type Gemini imidazolium surfactants in aqueous solution. Colloid Surf A 359:66–70
27. Li XW, Gao YA, Liu J, Zheng LQ, Chen B, Wu LZ, Tung CH (2010) Aggregation behavior of a chiral long-chain ionic liquid in aqueous solution. J Colloid Interface Sci 343:94–101
28. Blesic M, Swadźba-Kwaśny M, Holbrey JD, Lopes JNC, Seddon KR, Rebelo LPN (2009) New catanionic surfactants based on 1-alkyl-3-methylimidazolium alkylsulfonates, $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$: mesomorphism and aggregation. Phys Chem Chem Phys 11:4260–4268
29. Tondo DW, Leopoldino EC, Souza BS, Micke GA, Costa ACO, Fiedler HD, Bunton CA, Nome F (2010) Synthesis of a new zwitterionic surfactant containing an imidazolium ring. Evaluating the chameleon-like behavior of zwitterionic micelles. Langmuir 26:15754–15760
30. Dupont J, Souza RF, Suarez PAZ (2002) Ionic liquid (Molten salt) phase organometallic catalysis. Chem Rev 102:3667–3692

31. Aguiar J, Carpena P, Molina-Bolívar JA, Ruiz CC (2003) On the determination of the critical micelle concentration by the pyrene 1:3 ratio method. J Colloid Interface Sci 258:116–122
32. Turro NJ, Yekta A (1978) Luminescent probes for detergent solutions. A simple procedure for determination of the mean aggregation number of micelles. J Am Chem Soc 100:5951–5952
33. Dong B, Zhao X, Zheng L, 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
34. Rosen MJ (2004) Surfactants and interfacial phenomena, 3rd edn. Wiley, New Jersey, pp 82–130
35. Amin-Alami A, Kamenka N, Partyuka S (1987) Interfacial properties of zwitterionic surfactants: N-dodecylbetaine. Thermochim Acta 122:171–179
36. Kalyansundaram K, Thomas JK (1977) Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. J Am Chem Soc 99:2039–2044
37. Turro NJ, Kuo PL (1986) Pyrene excimer formation in micelles of nonionic detergents and of water-soluble polymers. Langmuir 4(2):422–438
38. Tanford C (1972) Micelle shape and size. J Phys Chem 76(21):3020–3024

## Author Biographies

**Xue-feng Liu** received his M.Sc. Degree from Wuxi University of Light Industry, and his Ph.D. degree from Jiangnan University in China. He is an associate professor at the School of Chemical and Material Engineering at Jiangnan University in China. His research field is colloid and interface chemistry.

**Li-li Dong** is a graduate student, majoring in Applied Chemistry in the School of Chemical and Material Engineering at Jiangnan University in China.

**Yun Fang** is a professor in the School of Chemical and Material Engineering at Jiangnan University in China. His research field is colloid and interface chemistry.