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ORIGINAL ARTICLE

Synthesis and Self-Aggregation of a Hydroxyl-Functionalized Imidazolium-Based Ionic Liquid Surfactant in Aqueous Solution

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Abstract This paper deals with the synthesis and self-aggregation of a hydroxyl-functionalized imidazolium-based ionic liquid (IL) surfactant, namely 1-hydroxyethyl-3-dodecylimidazolium chloride ([C_2OHC_{12}im]Cl). The molecular structure was confirmed by means of electrospray ionization mass spectrometry (ESI–MS), ^{1}H nuclear magnetic resonance (^{1}H NMR) and elemental analysis. Many important physicochemical parameters, such as the critical micelle concentration (CMC), the surface tension at CMC (γ_{CMC}), the adsorption efficiency (pC_{20}), the surface pressure at CMC (Π_{CMC}), the maximum surface excess (Γ_m), the minimum molecular cross-sectional area ($A_{\min}$), the value of CMC/C_{20}, the average number of aggregation (N_m) and the micellar microenvironment polarity were determined by surface tension-concentration curves, fluorescence spectra, and electrical conductivity. The phenomena of the second CMC, the concentration dependence of N_m, and the critical average aggregation number ($N_{m,c}$) of imidazolium-based IL surfactants are reported for the first time in this paper.

Keywords Hydroxyl-functionalized · Imidazolium-based · Ionic liquid surfactant · The second CMC · The critical aggregation number

Introduction

According to the generally accepted definition, ionic liquids (ILs) are liquid organic salts at, or below 100 °C [1]. ILs have drawn increasing interest for their promising roles as alternative media in a variety of catalytic [2], separation [3, 4], and electrochemical processes [5] as a result of their unique chemical and physical properties [6].

In recent years, one of the attractive aspects of ILs, for instance imidazolium-based ILs ([$C_n$mim]X), is their inherent amphiphilic character as surfactants in some conditions [7–28]. Here, C_n, m, im, and X stand for alkyl chain, methyl, imidazolium, and counter-ion, respectively. This particular aspect allows us to consider some long-chain ionic liquids (when dispersed in aqueous solutions), in fact, as a new type of cationic surfactants, namely IL surfactants [6, 8, 12, 13], surfactant-like ILs [20], and surface active ILs [24]. Therefore, IL surfactants would form self-organized aggregates in aqueous solutions (or the solutions containing water), e.g., the adsorbed layer at water–air interfaces, micelles and wormlike ones [29], microemulsions [30–33], and lyotropic liquid crystals [34, 35], etc.

Surveying the recent literature, two classes of IL surfactants can be identified, namely single-chain IL surfactants and IL-type Gemini surfactants [10, 36, 37]. In the light of the hydrophilic head group, four families of single-chain IL surfactants, i.e. pyridinium-, piperidinium-, pyrrolidinium-, and imidazolium-based surfactants have been synthesized and investigated widely. The effects of the length of the hydrocarbon chain, counter ions, temperature, and co-existing neutral inorganic salts on the surface activities of IL surfactant have been explored in detail. Compared with single-chain imidazolium-based IL surfactants, the Gemini surfactants

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have better surface activities and dispersion ability [38]. More recently, a series of complex IL surfactants $[C_n\text{mim}][C_mH_{2m+1}SO_3]$ [39] and a chiral IL surfactant [40] have been synthesized.

Hydroxyl-functionalized imidazolium-based ILs exhibit an excellent ability to dissolve $HgCl_2$ and $LaCl_3$ [41]. Moreover, hydroxyl group(s) in the side chain of ILs may play a unique role in the control of metal nanoparticles size and distribution [42, 43]. Thus, we expect that hydroxyl-functionalized imidazolium-based IL surfactants and their aggregates may have potential applications in the fields of the controllable synthesis for metal nanoparticles. The surface activity and aggregation behavior of such surfactants are essential. However, except for a very recent report [40], the surface activity and aggregation behavior of hydroxyl-functionalized IL surfactants have rarely been reported.

Here, we prepared a hydroxyl-functionalized imidazolium-based IL surfactant, namely1-hydroxyethyl-3-dodecylimidazolium chloride ($[C_2OHC_{12}\text{im}]Cl$, Scheme 1). The molecular structure was confirmed by means of electrospray ionization mass spectrometry (ESI–MS), ^1H nuclear magnetic resonance (^1H NMR) and elemental analysis. Many important physicochemical parameters, such as the critical micelle concentration (CMC), the surface tension at CMC (γ_{CMC}), the adsorption efficiency (pC_{20}), the surface pressure at the CMC (Π_{CMC}), the maximum surface excess (Γ_m), the minimum molecular cross-sectional area (A_{min}), and the value of CMC/C_{20}, the average number of aggregation (N_m) and the micellar microenvironment polarity were determined by surface tension-concentration curves, fluorescence spectra, and electrical conductivity. The phenomena of the second CMC, the concentration dependence of N_m, and the critical average aggregation number ($N_{m,c}$) of imidazolium-based IL surfactants are reported for the first time in this paper.

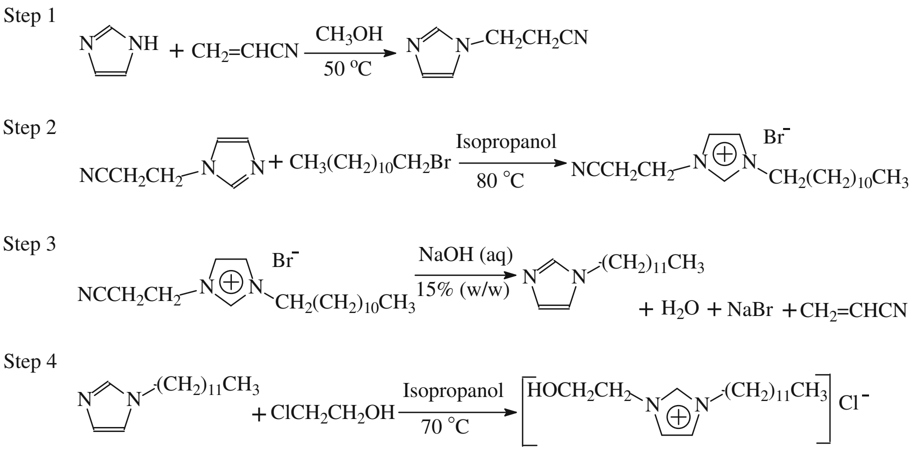
Experimental Section

Material

Imidazole, 1-bromododecane, 2-chloroethanol, 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 $[C_2OHC_{12}\text{im}]Cl$

The synthesis route of $[C_2OHC_{12}\text{im}]Cl$ is shown in Scheme 1. For a typical 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 ± 1 °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 ± 1 °C for 18 h under nitrogen. After the reaction was completed, isopropanol was removed under vacuum. The residue was dissolved in a mixture solution of 15% NaOH (w/w, 100 mL)-chloroform (50 mL), and then was stirred at room temperature until an interface between organic and aqueous phases was observed. The aqueous phase was removed, and the resulting 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). Using 30 mL isopropanol as solvent, *n*-dodecylimidazole (0.13 mol, 29.7 g) and 2-chloroethanol (0.7 mol, 56.4 g) were stirred at 70 °C for 24 h under nitrogen. The solvent and the unreacted 2-chloroethanol were removed under reduced pressure. The product was purified several times by recrystallization in acetone at −15 °C and then dried under vacuum for 2 days.



Scheme 1 The synthesis routes of $[C_2OHC_{12}\text{im}]Cl$

The corresponding [C_2OHC_{12}im]Cl is a pale yellow solid at −15 °C (ESM Fig. 1). The melting point of [C_2OHC_{12}im]Cl is 29.5 ± 0.5 °C. By definition, the organic salts are called ILs when the melting point is lower than 100 °C [1], so we can also call [C_2OHC_{12}im]Cl as IL.

The Measurements of ESI–MS, ^{1}H NMR and Elemental Analysis

The ESI–MS spectra were obtained using a Maldi Synapt Q-TOF MS (Waters) under positive ion mode. The ^{1}H-NMR spectra were 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 [C_2OHC_{12}im]Cl. The elemental analysis measurements were conducted on a Vario EL III elementar analyzer (Elementar). In the elemental analysis measurements, the chloride ion of [C_2OHC_{12}im]Cl was exchanged into nitrate ion by means of ion-exchange technique.

The Measurements of Surface Tension, Electrical Conductivity and Fluorescence Spectra

The surface tension measurements of [C_2OHC_{12}im]Cl aqueous solutions were conducted on a surface tensiometer with a drop volume method (the accuracy of temperature controlling and volume measuring were ±0.1 °C and ± 0.001 mL, respectively). The specific conductivity, κ (μS cm^{-1}), of the surfactant solutions was measured as a function of concentration with a low-frequency conductivity analyzer (Model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd, accuracy of ±1%).

The fluorescence spectral measurements were carried out on a RF5301PC spectrofluorophotometer (Shimadzu, Japan). The fluorescence emission spectra of surfactant micelle-solubilized pyrene were employed for the determinations of CMC, microenvironment polarity [44] and N_m. The concentration of pyrene was fixed at 1.0×10^{-7} mol L^{-1}. The excitation wavelength is 335 nm. The N_m was determined from benzophenone-mediated steady-state fluorescence quenching of micelle-solubilized pyrene. All the measurements of surface tension, electrical conductivity and fluorescence spectra were conducted at both 25 ± 0.1 and 35 ± 0.1 °C.

Results and Discussion

Structural Characterization of [C_2OHC_{12}im]Cl

The ESI–MS technique was employed to measure the molecular weight of the objective product [C_2OHC_{12}im]Cl in this work. Under the positive ion mode, only the cationic [C_2OHC_{12}im]$^+$ should be detected (Fig. 1). The mass-to-charge ratio (*m/z*) of [C_2OHC_{12}im]$^+$ is 281.2, which matches well with the theoretical calculation result (281.4) of the molecule ion weight for [C_2OHC_{12}im]$^+$. The results of elemental analysis for [C_2OHC_{12}im]NO_3 (C 59.41%, H 9.69%, O 18.64%, and N 12.26%) match well with the theoretical calculation compositions (C 59.45%, H 9.68%, O 18.63%, and N 12.24%). In order to get the molecule structural information in detail, the ^{1}H-NMR spectrum of [C_2OHC_{12}im]Cl was obtained (Fig. 2). The interpretation results of the ^{1}H-NMR spectrum are also shown in Fig. 2. The NMR signal of the OH– is overlapped with that of the solvent D_2O. All of the results of ESI–MS, elemental analysis and ^{1}H NMR indicate that the [C_2OHC_{12}im]Cl as prepared presents a sufficient purity.

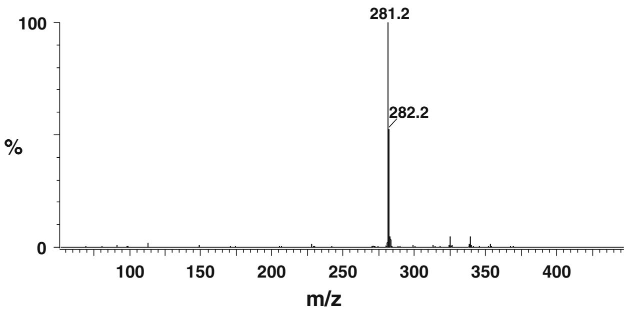


Fig. 1 The ESI–MS spectrum of [C_2OHC_{12}im]Cl at positive ion mode

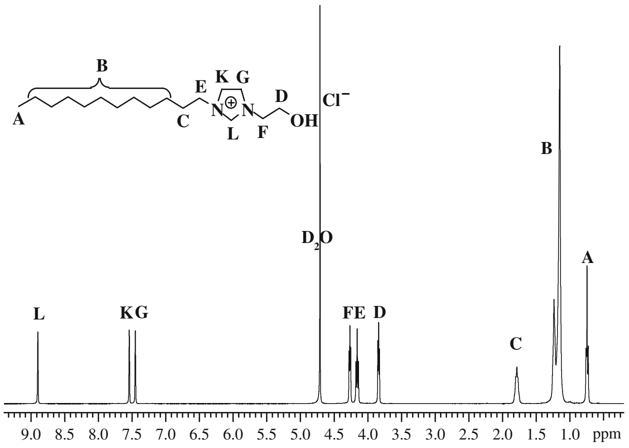


Fig. 2 The ^{1}H-NMR spectrum of [C_2OHC_{12}im]Cl

The Surface Properties of [C_2OHC_{12}im]Cl Aqueous Solution

The concentration dependence of the surface tension for [C_2OHC_{12}im]Cl in aqueous solutions at 25 and 35 °C are shown in Fig. 3. The surface tension (γ, mN m^{-1}) gradually

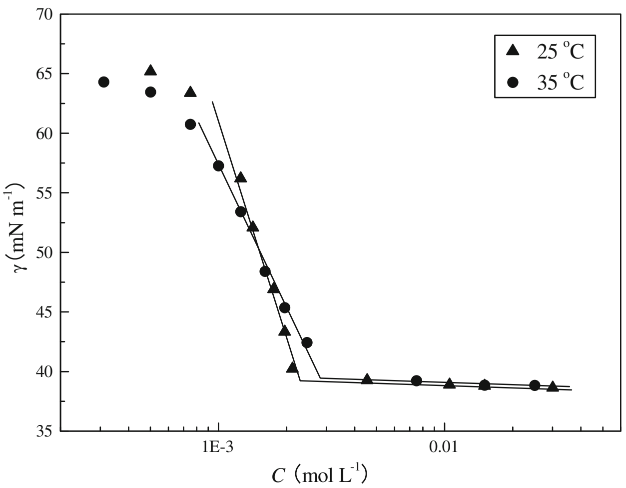


Fig. 3 The concentration dependence of the surface tension (γ) for $[C_2OHC_{12}im]Cl$ aqueous solution at 25 and 35 °C

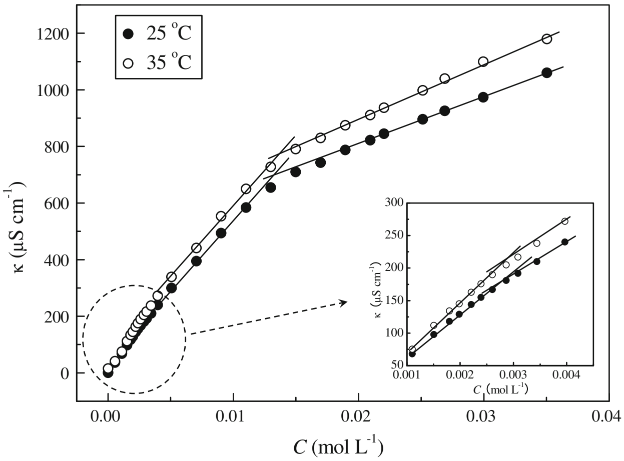


Fig. 4 The specific conductivity (κ) of $[C_2OHC_{12}im]Cl$ in aqueous solution at 25 and 35 °C

decreases to a plateau region with the $[C_2OHC_{12}im]Cl$ concentration (C, mol L^{-1}) increasing. A decrease in surface tension indicates that the surfactant molecules adsorbed at the air/solution interface. The break points appear in the γ-C curves suggests the formation of micelles in aqueous solutions. Here, it is worth mentioning that the purity of $[C_2OHC_{12}im]Cl$ was also confirmed from the observed sharp break points in the γ-C curves. The results of the CMC and γ_{CMC} for the surfactant were obtained from the γ-C curves. The values of CMC at 25 and 35 °C were also determined by means of electrical conductivity (Fig. 4) and fluorescence spectra (Fig. 5). From the surface tension data, several surface property parameters, such as the adsorption efficiency (pC_{20}), the surface pressure at the CMC (Π_{CMC}), the maximum surface excess (Γ_m), the minimum molecular cross-sectional area (A_{min}), and the value of CMC/C_{20} may be obtained.

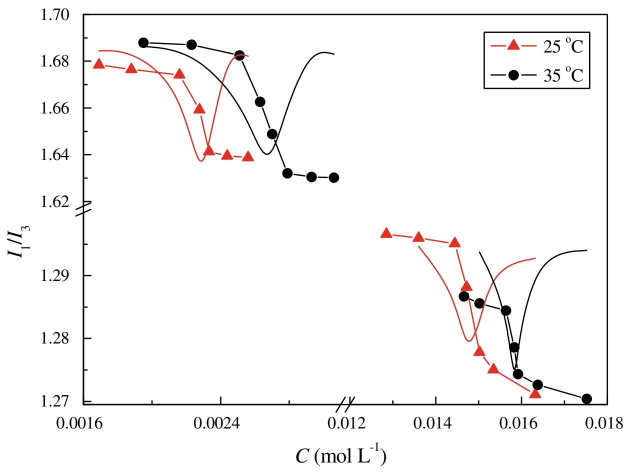


Fig. 5 The variation of I_1/I_3 with the concentration of $[C_2OHC_{12}im]Cl$ in aqueous solution at 25 and 35 °C

It is recognized that the pC_{20} value can measure the efficiency of surfactant adsorbing at the air/solution interface.

$$pC_{20} = -\log C_{20} \quad (1)$$

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 pC_{20}, the higher the adsorption efficiency of the surfactant is.

The Π_{CMC} is defined as

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (2)$$

where γ_0 is the surface tension of pure solvent. The value of Γ_m (in mol cm^{-2}) was estimated by applying the Gibbs adsorption isotherm to the surface tension data,

$$\Gamma_m = -\frac{1}{4.606RT}\left(\frac{\partial\gamma}{\partial \lg C}\right)_T \quad (3)$$

where R is the gas constant (8.314×10^7 ergs mol^{-1} K^{-1}), T is the experiment temperature (K), and the $\left(\frac{\partial\gamma}{\partial \lg C}\right)_T$ is the slope of the linear portion of the graph of surface tension against logarithmic concentration at a fixed temperature. The A_{min} (in square Angstroms) was calculated using Eq. 4, where N_A is Avogadro's number.

$$A_m = \frac{10^{16}}{N_A \times \Gamma_m} \quad (4)$$

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 physicochemical parameters are listed in Table 1.

The CMC of $[C_2OHC_{12}im]Cl$ increases with temperature increasing. At 25 °C, the value of CMC for

Table 1 The physicochemical parameters of [C_2OHC_{12}im]Cl and the other types of surfactants from references [11, 17, 44]

	[C_2OHC_{12}im]Cl		[C_{12}mim]Cl	[C_{14}mim]Cl	[C_{14}mim]Br
	35 °C	25 °C			
CMC (10^{-3} mol L^{-1})	2.82[a]	2.31[a]	13.17 [17][a]	2.98 [17][a]	2.80 [44][a]
	2.86[b]	2.69[b]	13.47 [17][b]	3.68 [17][b]	2.60 [11][b]
	2.67[c]	2.29[c]	14.0 [17][c]	3.65 [17][c]	2.90 [44][c]
γ_{CMC} (mN m^{-1})	38.8	38.6	42.0 [17]	45.0 [11]	39.2 [44]
Π_{CMC} (mN m^{-1})	31.6	33.4	–	–	33.8 [44]
Γ_m (10^{-10}mol cm^{-2})	1.51	1.82	–	–	1.96 [44]
pC_{20}	2.05	2.36	–	–	3.33 [44]
CMC/C_{20}	0.32	0.53	–	–	5.99[d]
A_m (Å^2)	110.2	91.2	72 [17]	–	84.7 [44]
I_1/I_3	1.63	1.64	–	–	1.25 [44]

[a] From surface tension methods

[b] From electrical conductivity methods

[c] From fluorescence methods

[d] Calculated from the data in [44]

[C_2OHC_{12}im]Cl is lower than that of [C_{12}mim]Cl [13, 17] and compares well with that of [C_{14}mim]Cl [11, 13, 17] and [C_{14}mim]Br [11, 45, 46]. This can be attributed to the longer side chain (hydroxyethyl group) in [C_2OHC_{12}im]Cl, i.e. the hydrophobicity of IL surfactants probably increases with the increase of the side chain length. On the other hand, the hydroxyl group will lower the CMC of [C_2OHC_{12}im]Cl [47]. In addition, the side chain length increase will enlarge the cationic head group of [C_2OHC_{12}im]Cl surfactant. Thus, it is reasonable that A_m of [C_2OHC_{12}im]Cl is slightly larger than that of [C_{14}mim]Br [45].

The Second CMC of [C_2OHC_{12}im]Cl

Generally, the spherical micelles are formed at the first CMC (CMC_1). And the appearance of the second CMC (CMC_2) indicates the structural transition, for instance, from spherical to rod-like ones [48]. Strong evidence for the existence of the CMC_2 within traditional surfactants has been proved [49–52]. For the traditional ionic surfactants, the value of CMC_2/CMC_1 ratio is in the range of 2–9 [49–52]. However, no reports on the CMC_2 for IL surfactants have been reported yet.

Figures 4 and 5 are the results of CMC measurements by means of electrical conductivity and fluorescence spectra, respectively. In addition to the traditional breakpoints (corresponding to the CMC_1), the second breakpoints (corresponding to the CMC_2) were observed in the relative higher concentration regions. The CMC_2 (mmol L^{-1}) of [C_2OHC_{12}im]Cl were obtained (25 °C: 13.29 and 14.78, from electrical conductivity and fluorescence spectra, respectively; 35 °C: 13.79 and 15.83, from electrical conductivity and fluorescence spectra, respectively.). The temperature dependence of the CMC_2 is in accordance with that of dodecyl dimethyl benzyl ammonium bromide in aqueous solutions [52]. The values of CMC_2/CMC_1 are 4.94 (electrical conductivity) and 6.45 (fluorescence spectra) at 25 °C, 4.82 (electrical conductivity) and 5.93 (fluorescence spectra) at 35 °C, respectively. The phenomena of the second CMC should deepen the understanding of the unique properties for IL surfactants.

In order to investigate the polarity of the microenvironment for the micelles, pyrene was used as a fluorescence probe. It is known that pyrene preferentially dissolves into hydrophobic regions. 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. Thus, the ratio of I_1/I_3 may not only probe the micropolarity of the surfactant aggregates, but is also used to obtain the CMC of the surfactant in aqueous solution [53].

As shown in Fig. 5, the I_1/I_3 decreases with the surfactant concentration increasing. When the surfactant concentration reaches the CMC_1, the I_1/I_3 is about 1.64, which is higher than that of [C_{12}mim]Br [45], [C_{14}mim]Br [45], and [C_{14}hpim]Br [40]. It is also probably attributed the existence of the side-chain (the hydroxylethyl group) in the head group of [C_2OHC_{12}im]Cl. This side-chain probably produces a larger steric hindrance effect between the head groups of [C_2OHC_{12}im]Cl, which leads to a relative looser packing mode within the formed micelles. That the relative small aggregation number (*discussed in the next section*) of the micelles in the range of CMC_1 to 8.53 mmol L^{-1} will probably be the evidence, at least in part, to the aforementioned conjecture. As the concentration of the surfactant higher than the CMC$_2$, the value of I_1/I_3 further decreases to about 1.26, which is comparable with the results in the literature [40, 45]. In this case, the smaller result of I_1/I_3 is in accordance with the relative large aggregation number (discussed in the next section).

The Concentration Dependence of N_m for [C$_2$OHC$_{12}$im]Cl

The aggregation number (N_m) of [C$_2$OHC$_{12}$im]Cl in aqueous solutions at 35 °C were determined by a steady-state fluorescence quenching technique. Pyrene and benzophenone were used as the probe and the quencher, respectively. The N_m was obtained by applying the Eq. 5 to the fluorescence data.

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_\mathrm{m} \times C_\mathrm{Q}}{C - \mathrm{CMC}} \tag{5}$$

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 concentrations of the quencher and [C$_2$OHC$_{12}$im]Cl, respectively. And the CMC is the CMC$_1$ when the surfactant concentration is in the range of CMC$_1$ to CMC$_2$. When the surfactant concentration is larger than CMC$_2$, the CMC in Eq. 5 should be the CMC$_2$. The plot of N_m versus the surfactant concentration at 35 °C is shown in Fig. 6. The N_m increases, in the mass, with the concentration of [C$_2$OHC$_{12}$im]Cl increasing. The N_m grows as an empirical power law [54] of the total surfactant concentration in the ranges of 5.82–8.53 and 26.7–70.9 mmol L^{-1}, respectively. The relevant mathematic equations can be written as (the coefficient constants are listed in the parentheses)

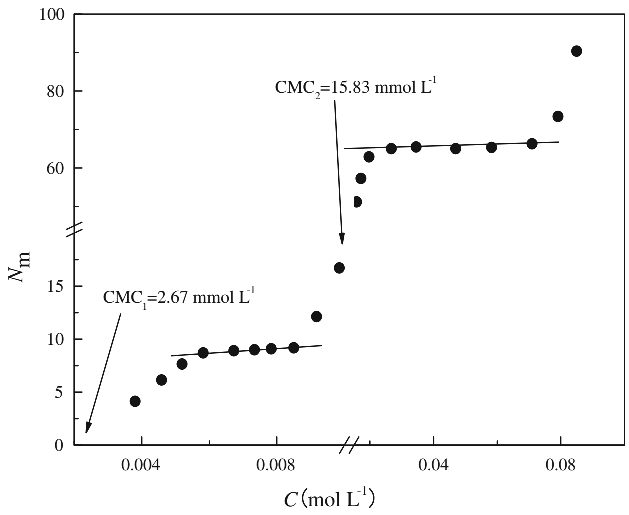


Fig. 6 The concentration dependence of N_m for [C$_2$OHC$_{12}$im]Cl in aqueous solution at 35 °C

$$N_\mathrm{m} = 16.9C^{0.13} \quad (R^2 = 0.9985) \tag{6}$$

$$N_\mathrm{m} = 71.6C^{0.03} \quad (R^2 = 0.9982) \tag{7}$$

One can see that an obvious increment for N_m in the range of 8.53–19.70 mmol L^{-1}. This is probably due to a structural transition of the micelles as the concentration increases [48, 54]. Similarly, the sharp increment of N_m in the range of 70.94–84.98 mmol L^{-1} suggests a newer structural change for the micelles. In addition, the experimental results of N_m in the range of 3.81–5.19 mmol L^{-1} do not obey the empirical power law. This may be the experimental deviation resulting from the relative small micelle concentration [55] in the range of 3.81–5.19 mmol L^{-1}. However, the aforementioned structural transition should be investigated by means of cryo transmission electron microscopy [56], and this part of work is under way.

Here, we can use the packing parameter, $V_\mathrm{H}/l_\mathrm{C}A_m$, for predicting the micelle shape of [C$_2$OHC$_{12}$im]Cl in aqueous solutions [57], the V_H (the volume of the hydrophobic long carbon chain) is 27.4 + 26.9 C$_n$ Å^3 [58], l_C (the length of the long carbon chain) is 1.5 + 1.265 C$_\mathrm{n}$ [58], where C$_\mathrm{n}$ is the number of carbons in the long-chain. The calculated value of $V_\mathrm{H}/l_\mathrm{C}A_m$ is 0.19 at 35 °C. Based upon the geometry relationship between the micelle shape and the surfactant molecule structure [57], the calculated value of $\mathrm{V_H}/l_\mathrm{C}A_m$ allows us to consider that the shape of [C$_2$OHC$_{12}$im]Cl micelles is spherical in aqueous media in the range of CMC$_1$ to 8.53 mmol L^{-1}.

In order to estimate the reasonableness of the experimental results for N_m, we used a simple theoretical model [57, 58] for calculating the possible maximum N_m in a spherical micelle of [C$_2$OHC$_{12}$im]Cl. In this simple model, we tacitly assumed the surfactant micelle is spherical with a hydrophobic core radius of l_C. Thus, the volume of the hydrophobic core for the [C$_2$OHC$_{12}$im]Cl micelles is $N_m \times V_\mathrm{H}$ which equals to $\frac{4}{3}\pi(l_\mathrm{C})^3$ [57]. The calculated result for the possible maximum N_m is 55.5 at 35 °C, which matches well with the results in the case of sodium dodecyl sulfate [55, 58]. Our experimental results of N_m in the range of CMC$_1$ to 8.53 mmol L^{-1} is smaller than that of the calculated value (55.5). This may be attributed to the larger "rebelling" effects between the head groups of the surfactants in micelles. Thus, the micelles present a very loose packing mode, which can be demonstrated, on the other hand, by the relative larger I_1/I_3 in the range of CMC$_1$ to 8.53 mmol L^{-1}.

From the relationship between N_m and the surfactant concentration, one of the most important parameters, the critical average aggregation number ($N_{m,\mathrm{c}}$), can be obtained by reversely extending the linear Eqs. 6 and 7 to CMC. Here, the parameter $N_{m,\mathrm{c}}$ describes the surfactant monomer number of the first micelle corresponding to the definite CMC in solution. This parameter is obtained by the routine methods only with great difficulty. Corresponding to the CMC_1 and CMC_2, the first $N_{m,c}$ is 8, and the second one is 63, respectively. The former is quite small, which indicates that the first spherical micelle presents a very loose structure. And the later is relative larger indicating that the micelle has a closer packing structure.

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