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Adsorption, micellization and antimicrobial activity of formyl-containing cationic surfactant in diluted aqueous solutions

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ABSTRACT

Surfactants based on dynamic covalent bonds have attracted significant interest over the past few decades due to the coexistence of covalent and non-covalent bonds. However, studies on the fundamental properties of their precursors are rare. Herein, we synthesized a series of formyl-containing cationic surfactants (N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromides) bearing different hydrophobic chains, which can form dynamic imine bonds. The adsorption, micellization and antimicrobial activity were systematically investigated using surface tension, fluorescence, electrical conductivity, and ITC techniques. The results showed that the insertion of the 2-(4-formyl-phenoxy)ethyl group (equivalent to ~7 methylene groups) endows the surfactant with an asymmetrical double-chain structure, enhancing the hydrophobic interaction. As a result, the critical micelle concentration (cmc) and contribution per methylene group to the standard Gibbs free energy of micellization (ΔG_m^o) were significantly decreased, compared to conventional single surfactant. Upon increasing the hydrophobic chain length, the cmc, the negative logarithm of the surfactant concentration in the bulk phase required to produce a 20 $mN \cdot m^{-1}$ reduction in the surface tension of the solvent (pC_{20}) and maximum surface excess amount of the adsorbed surfactant (Γ_{max}) all decreased accompanied by an increase in the minimum molecular occupation area (A_{min}), while the ΔG_m^o and standard Gibbs free energy of adsorption (ΔG_{ads}^o) become more negative and thus more favorable for the formation of micelles and the adsorption film. Moreover, micellization changed from being entropy-driven to enthalpy-driven and is more sensitive toward NaCl than urea. In addition, the current formyl-containing cationic surfactants exhibit excellent antimicrobial activity against both Gram-positive and Gram-negative bacteria and fungi, especially the surfactant with a hydrophobic chain containing ~20 atoms. Such a study will be favorable for the design of new dynamic covalent surfactants and an understanding of the change in their aggregation.

1. Introduction

Surfactants are typical amphiphiles composed of a hydrophilic headgroup and hydrophobic tail. Due to their unique amphiphilic characteristics, surfactants prefer to adsorb onto the air/solution interface at low concentration, and self-assemble into various aggregates (including micelles, vesicle, liquid crystal, and so on) above the critical micellar concentration (cmc), giving them an important role in many industrial processes (cleaning, cosmetics, oil recovery, agriculture, dying and painting) and fundamental research [1–3].

Because of their special application performance and smart controllability, numerous responsive colloidal systems (wormlike micelles, liquid crystals, emulsions/microemulsions, foams, etc.) have continued to emerge over the past 30 years [4–8]. Whereas, the design and fabrication of smart colloidal systems cannot do without basic functional molecules, in which stimuli-responsive surfactants are an important representative [9,10]. Thus, stimuli-responsive surfactants that can change their surface activity upon responding to an external stimuli such as pH [11], temperature [12,13], light irradiation [14–16], CO_2/N_2 [17–20], redox [21–23] and magnetic field [24,25] have emerged over time.

Recently, dynamical combinational chemistry has been gradually applied toward the design of stimuli-responsive surfactants, i.e., dynamic covalent surfactants, which can switch their surface activity via the stimuli-induced formation and breakage of dynamic covalent bonds [26]. To date, dynamic covalent surfactants are mainly produced by mixing a formyl-containing moiety and amine-containing moiety to form an imine bond [27–29]. For instance, Takakura et al. [29] developed a micro-sized giant vesicle formed by a dynamic covalent surfactant, which was obtained via the in situ mixing of N-dodecyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide and dodecylamine. As a kind of formyl-containing precursor, N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide, has

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also been used to fabricate other dynamic covalent surfactants with different molecular structures or stimuli-responsiveness, such as Gemini structured, pH/redox and pH/light dual responsive surfactants. To better understand the aggregation in solution and at the interface, studies on the fundamental properties of formyl-containing precursors, including their adsorption and micellization properties, are highly desirable.

It is well known that the incorporation of an additive, as well as its molecular structure will affect the physicochemical properties, such as the degree of ionization, reaction rates and clouding/phase separation [32,33]. Thus, the effects of organic or inorganic additives on the fundamental properties is also crucial and cannot be ignored.

Herein, we have synthesized three formyl-containing surfactants bearing different hydrophobic tails, N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide (DOBAB, TOBAB and HOBAB corresponding to the C12-, C14- and C16-hydrophobic tail, Scheme 1), which can be used as the precursors of dynamic imine bond surfactants. Their molecular structures were characterized using ^{1}H NMR spectroscopy and ESI-MS, and the fundamental properties of their dilute solutions, including the adsorption at air/solution interface, micellization in solution, and antimicrobial activity, were investigated. This study may help to design novel dynamic covalent surfactants and understand aggregation before and after the formation of dynamic covalent bonds.

2. Experimental section

2.1. Materials

1,2-Dibromoethane (>99.0%), 4-hydroxybenzaldehyde (>99.0%), *N*, *N*-dimethylhexadecylamine (>98.0%), *N*,*N*-dimethyltetradecylamine (>90.0%), *N*,*N*-dimethyldodecylamine (>97.0%), Nile red (>99.0%), and all the other organic solvents used in this study were analytical-grade products from Admas-beta. These reagents were directly used without further purification. *S. aureus (ATCC6538)*, *E. coli (ATCC25922)* and *C. albicans (ATCC10231)* were obtained from BeNa culture collection (China). Water was triply distilled by a quartz water purification system ($R = 18$ MΩ cm).

2.2. Synthesis and characterizations of surfactant

The synthesized route of N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide was exhibited in Scheme 1.

2.2.1. Synthesis of 4-(2-bromoethoxy)benzaldehyde

In a 500 mL round-bottom flask, 1,2-dibromoethane (28.5 mL), acetonitrile (200 mL) and K_2CO_3 (8.2 g) were mixed and refluxed by heating. 4-Hydroxybenzaldehyde (4.1 g) was dissolved in acetonitrile (50 mL) and then the solution was dropwise added. The mixture was continuously stirred for 24 h under reflux and progress was controlled by TLC. After cooling to room temperature the mixture was extracted using water (150 mL) and diethyl ether (100 mL). The organic layers were washed with brine and solvents were removed under reduced pressure. The crude product was further purified by column chromatography (eluent: ethyl acetate/petroleum ether ± 1:5 *v*/v) to yield white crystals.

2.2.2. Synthesis of N-alkyl-N,N-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide

In a 250 mL flask, 4-(2-bromoethoxy)benzaldehyde (9.16 g, 0.04 mol) and *N*,*N*-dimethylhexadecylamine (12.94 g, 0.048 mol) were mixed in 100 mL EtOH and refluxed for 24 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and then the crude product was recrystallized from acetone to yield *N*, *N*-dimethyl-N-hexadecyl-N-p-oxybenzylethylammonium bromide (HOBAB) as a white solid (8.1 g). DOBAB and TOBAB were obtained through the same route.

The molecular structure was characterized by ^{1}H NMR (Bruker Advance III 400 MHz spectrometer, Bruker, Switzerland) and ESI-MS (Waters MALDI SYNAPT MS, USA).

^{1}H NMR of DOBAB [400 MHz, ($CDCl_3$), Fig. S1]: δ/ppm = 0.87–0.90 (t, 3H, J = 6 Hz), 1.26–1.38 (m, 20H), 1.85 (s, 2H), 3.53(s, 6H), 3.62–3.66 (t, 2H, J= 8 Hz), 4.32–4.34 (d, 2H), 4.67–4.68 (d, 2H), 7.08–7.10 (d, 2H), 7.86–7.88 (d, 2H), 9.91 (s, 1H). MS of DOBAB (Fig. S2): Calcd: 362.0 (M – Br^-). Found: m/z = 362.3.

^{1}H NMR of TOBAB [400 MHz, ($CDCl_3$), Fig. S3]: δ/ppm = 0.87–0.91 (t, 3H, J= 8 Hz), 1.26–1.39 (m, 22H), 1.81–1.87 (m, 2H), 3.55 (s, 6H), 3.65–3.69 (m, 2H), 4.34–4.37 (t, 2H, J = 6 Hz), 4.67–4.69 (t, 2H, J = 6 Hz), 7.08–7.10 (d, 2H), 7.86–7.88 (d, 2H), 9.91 (s, 1H). MS of DOBAB (Fig. S4): Calcd: 391.2 (M – Br^-). Found: m/z = 391.2.

^{1}H NMR of HOBAB [400 MHz, ($CDCl_3$), Fig. S5]: δ/ppm = 0.87–0.90 (t, 3H, J = 6 Hz), 1.27–1.39 (m, 20H), 1.84 (s, 2H), 3.56(s, 6H), 3.65–3.69 (m, 2H), 4.36–4.38 (t, 2H, J = 8 Hz), 4.67–4.69 (m, 2H, J = 6 Hz), 7.08–7.10 (d, 2H), 7.87–7.89 (d, 2H), 9.92 (s, 1H). MS of HOBAB (Fig. S6): Calcd: 418.37 (M – Br^-). Found: m/z = 418.3.

2.3. Surface tension

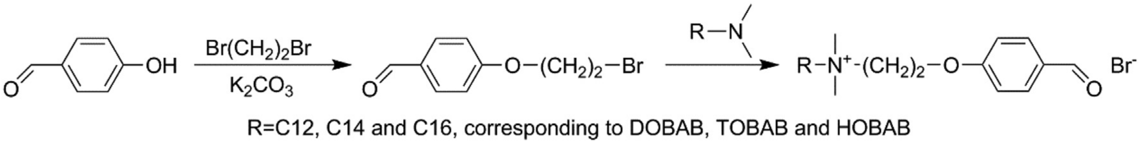
The surface tension (γ) was measured with a Krüss K100 tensiometer by the automatic du Noüy ring model at 25 ± 0.1 °C. A cover was used to minimize the evaporation of water. To obtain equilibrium γ, measurements were made every 3 min until the change was below 0.03 $mN \cdot m^{-1}$. Prior to measurement, the tensiometer was calibrated with triple-distilled water at 25 ± 0.1 °C (reference value 71.97 $mN \cdot m^{-1}$).

2.4. Conductivity

A FE30 conductometer (Mettler Toledo, USA) was used to measure the electrical conductivities of the surfactant solutions. The temperature was controlled by a thermostatic water-circulator bath (accuracy ±0.05 °C). Every sample was measured for three times, and the conductivity was the average value. Before measurement, the instrument was calibrated by inserting the electrode into a solution of KCl (0.01 mol L^{-1}) and adjusting the constant to 1.57.

2.5. Fluorescence experiment

Fluorescence of Nile red in surfactant solution was measured using a Varian Cary Eclipse spectrometer (Varian Inc. USA) equipped with a thermostatic water-circulator bath. The excitation wavelength was set at 550 nm, and the excitation and emission slit widths were both set at 5 nm. 10 μL solution of 2 $mmol \cdot L^{-1}$ Nile red in THF was added to



Scheme 1. Synthesized route of N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromide.

5 mL aqueous solution of surfactant, and then the sample was ultra-sonicated for 30 min [19,34]. Prior to measurement, all the samples were kept at 25 ± 0.1 °C no less than 12 h.

2.6. Isothermal titration calorimetry (ITC)

An isothermal titration calorimeter (MicroCal VP-ITC, Malvern, U.K.) was used to measure the enthalpies of micellization at 25 ± 0.1 °C. Twenty-eight 10 μ L aliquots of surfactant stock solution were injected sequentially into a 1400 μ L titration cell initially loaded with Milli-Q water. Each injection lasted 30 s, with an interval of 120 s between successive injections. The solution in the titration cell was stirred at a speed of 242 rpm throughout experiments. Before experiment, the instrument was calibrated by injecting Milli-Q water [35]. The enthalpy change of the micelle formation was obtained from the calorimetric curves.

2.7. Antimicrobial activity

The antimicrobial performance of the formyl-containing surfactants was evaluated using the Minimum Inhibitory Concentration (MIC) assay. The MIC is defined as the minimal concentration for antimicrobial agent that inhibited the visible growth after 24 h of incubation. *S. aureus (ATCC6538), E. coli (ATCC25922) and C. albicans (ATCC10231)* were chosen as the representatives of typical Gram-positive and Gram-negative bacteria and fungi, respectively. The MIC was determined using 96-well microtiter plates by a 2-fold serial dilution method.

The samples were added to a 96-well microtiter plate and were diluted with sterile water to a series of concentrations. Each well contains 100 μL sample solution and 100 μL prepared bacterial suspension (10^6 CFU/mL). In addition, 100 μL sterile water plus 100 μL liquid medium was used as a negative control and 100 μL sterile water plus 100 μL bacterial suspension was used as a positive control. After that, the 96-well plates were placed in an incubator at 37 °C or 28 °C for 24 h and measured the OD (optical density) values at 600 nm. The rise in turbidity as well as OD values reflected the increase in both mass and bacteria number. The minimum concentration corresponding to the well that does not produce turbidity as well as the turning point of OD values is the MIC of the sample against the bacteria. All items used in the experiments were sterilized by high temperature and high pressure, and all the steps were proceeded in a sterile environment.

3. Results and discussion

3.1. Surface tension

Due to their unique molecular structures, surfactants are generally adsorbed onto the air/liquid interface in an oriented fashion, and thereby decrease the interfacial tension (air solution). As shown in Fig. 1, the equilibrium surface tension (γ) of the formyl-containing cationic surfactants first underwent a rapid decrease with increasing the logarithm of the surfactant concentration and then tended toward a constant beyond a critical value, corresponding to the cmc. There is no minimum in either of the surface tension curves, ruling out the presence of any surface-active impurities. Although the chemical compositions of hydrophobic tails are almost identical, the minimum γ above the cmc (γ_{cmc}) showed a slight decrease with shortening the hydrophobic tail. This may be related to the maximum surface excess amount of the adsorbed surfactant (Γ_{max}). A larger Γ_{max} generally leads to a more compact air/liquid interfacial film possessing stronger effectiveness in reducing the surface tension [1].

Many properties of the surfactant solution undergo a dramatic change above the cmc. Thus, the cmc plays an important role in the practical applications. Similar to most homologous straight-chain ionic surfactants, the cmc of the formyl-containing surfactants decreased by about one order of magnitude upon increasing the hydrophobic tail by two $-CH_2-$ groups. Upon plotting the logarithm of the cmc as a function of the number of carbon atoms (n) in the hydrophobic chain, a relation can be found in the form of $\log cmc = A - Bn$, where A and B are both positive constants relating to the molecular structure of the surfactant. A represents the effect of hydrophilic head on micellization, while B signifies the mean contribution to micellization per methene group. Generally, the larger the A value is, the weaker the micellization ability of the surfactant. For the current formyl-containing surfactants, A = 1.64, which is lower than those of alkyltrimethylammonium bromides (2.0) and alkylpyridinium bromides (1.7) [1], reflecting its stronger micellization ability. In fact, the lower cmc of the current formyl-containing surfactant compared to their corresponding alkyltrimethylammonium bromides and alkylpyridinium bromides [1], also confirm its strong micellization ability. This means that the insertion of the 2-(4-formyl-phenoxy)ethyl group enhances the hydrophobic interactions between the molecules, i.e., favoring micellization. Thus, if 2-(4-formyl-phenoxy)ethyl group is extended by forming an imine bond, the dialkyl-chain surfactant will be formed and the micellization ability will be further enhanced and become controllable. These will be discussed in another work.

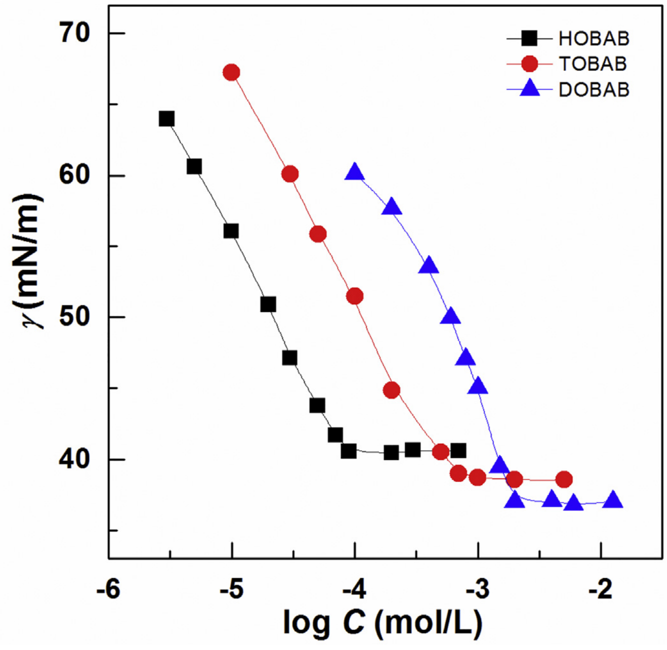


Fig. 1. Plots of surface tension as a function of the logarithm of surfactant concentration at 25 °C.

Upon comparison, it can be found that the cmc of DOBAB was between those of N-dodecyl-N-octyl-*N*,*N*-dimethylammonium bromide (1.50 $\text{mmol}\cdot\text{L}^{-1}$) and N-dodecyl-N-hexyl-*N*,*N*-dimethylammonium bromide (3.29 $\text{mmol}\cdot\text{L}^{-1}$) [36], implying that the 2-(4-formyl-phenoxy)ethyl group is approximately equivalent to 7 methylene groups. Therefore, the contribution of the 2-(4-formyl-phenoxy)ethyl group to the hydrophobicity was relatively large. In other words, the current formyl-containing surfactant can be regarded as an asymmetrical double-chain surfactant.

For the adsorption of surfactant at the air/water interface, the Γ_{max} and minimum molecular occupation area (A_{min}) can be calculated by applying Gibbs adsorption eqs. (1) and (2) [1], respectively,

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{\partial\gamma}{\partial \log C}\right) \tag{1}$$

$$A_{min} = \frac{1}{N\Gamma_{max}} \tag{2}$$

where R is the universal gas constant (8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), C is the surfactant concentration ($\text{mol}\cdot\text{L}^{-1}$), and N is the Avogadro constant. The value of n, which stands for the effective

Table 1
Surface activity parameters for synthesized formyl-containing cationic surfactants at 25 °C.

Surfactant	DOBAB	TOBAB	HOBAB
γ_{cmc} (mN·m^{-1})	37.04 ± 0.077	38.60 ± 0.097	40.48 ± 0.042
cmc (mmol·L^{-1})	2.11 ± 0.041[a]	0.590 ± 0.023[a]	0.0802 ± 0.00082[a]
	2.25 ± 0.10[b]	0.646 ± 0.076[b]	0.0873 ± 0.0022[b]
$10^{-6}\ \Gamma_{max}$ (mol·m^{-2})	1.89 ± 0.097	1.51 ± 0.085	1.45 ± 0.017
A_{min} (nm^2 per molecule)	0.88 ± 0.045	1.08 ± 0.038	1.15 ± 0.013
pC_{20}	3.32 ± 0.014	4.05 ± 0.023	4.76 ± 0.018
Π_{cmc} (mN·m^{-1})	34.93 ± 0.041	33.44 ± 0.082	31.49 ± 0.042

[a] Obtained from surface tension method.
[b] Obtained from fluorescence method using Nile red as probe.

number of species present at the interface, was taken to be 2 for a 1–1 type ionic surfactant [1]. The data listed in Table 1 showed that the Γ_{max} decreased from (1.89 ± 0.097) × 10^{-6} to (1.45 ± 0.017) × 10^{-6} mol·m^{-2} with a hydrophobic chain from C16 to C12, accompanied by an increase in the A_{min} from 0.88 ± 0.045 to 1.15 ± 0.013 nm^2 per molecule. This indicates that the interfacial film formed by DOBAB was the tightest, and that formed by HOBAB was the loosest. Therefore, the γ_{cmc} of DOBAB was the lowest, and the γ_{cmc} of HOBAB was the highest. Due to the insertion of the 2-(4-formyl-phenoxy)ethyl group, the current formyl-containing surfactants have larger A_{min} than conventional cationic surfactants, such as N-tetradecyl-*N*,*N*,*N*-trimethylammonium bromide (TTAB, 0.61 nm^2 per molecule at 30 °C) [1], N-cetyl-*N*-methylpyrrolidinium bromide (C16MPB, 0.45 nm^2 per molecule at 25 °C) [37], selenium-hybride C16MPB (0.43–0.59 nm^2 per molecule at 25 °C) [21,23]. Notwithstanding, their A_{min} values are very close to those of N-alkyl-N,N,N-tripropylammonium bromide [1], implying a positive contribution from the 2-(4-formyl-phenoxy)ethyl group to the hydrophilic headgroup.

The effectiveness in the γ reduction (Π_{cmc}) can be obtained using eq. (3):

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{3}$$

where γ_0 is the γ of pure water. As listed in Table 1, the Π_{cmc} of DOBAB, TOBAB, and HOBAB were relatively similar as a result of their similar γ_{cmc}. Nevertheless, small differences still exist. Due to the same solvent, the Π_{cmc} shows an opposite change with that of the γ_{cmc}. A larger Π_{cmc} denotes a stronger ability to decrease the γ. Therefore, DOBAB is more effective in reducing the γ than HOBAB. This is agreement with the conclusion deduced from the γ_{cmc} and Γ_{max}.

In addition, the adsorption efficiency of a surfactant is usually evaluated using the negative logarithm of the surfactant concentration in the bulk phase required to produce a 20 mN·m^{-1} reduction in the γ of the solvent (pC_{20}) [1]. The larger the pC_{20}, the higher the adsorption efficiency. As listed in Table 1, the pC_{20} of the formyl-containing surfactants linearly increased with the number of carbon atoms in the hydrophobic tail, which was consistent with the results obtained for conventional surfactants [1]. Obviously, the longer the hydrophobic chain, the larger the driving force for migration to the interface and the higher the adsorption efficiency.

3.2. Nile red fluorescence

Nile red is an oil-soluble fluorescent probe [19], which exhibits little fluorescence in water. However, when micelles are formed, Nile red can be solubilized in the hydrophobic interior and then fluoresce. Based on this property, Nile red is usually used as probe to determine the cmc. Fig. 2 showed the variation in the intensity of the Nile red fluorescence signal at 625 nm with the surfactant concentration. On the whole, below a critical concentration, the fluorescence intensity remains unchanged (~0), suggesting that no Nile red is solubilized. However, the fluorescence intensity starts to quickly increase above a critical concentration, which is usually interpreted to be the solubilization of Nile red in a hydrophobic microenvironment. That is to say, micelles are formed. Therefore, the critical concentration corresponds to the cmc. As listed in Table 1, the cmc obtained from the variation in the intensity of the Nile red fluorescence were 0.0873 ± 0.0022, 0.646 ± 0.076 and 2.25 ± 0.10 mmol·L^{-1} for HOBAB, TOBAB and DOBAB, respectively. These values are close to those obtained using the surface tension method.

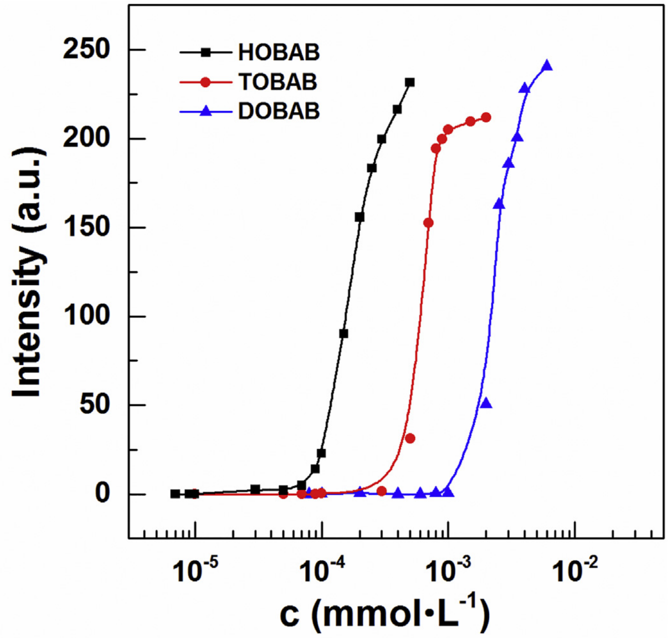


Fig. 2. Variations in the intensity of the Nile red fluorescence with surfactant concentration at 25 °C.

3.3. Conductivity

The conductivity (κ) of the formyl-containing surfactant solutions was measured at 25, 35 and 45 °C, respectively. From the results exhibited in Fig. 3, it can be seen that κ showed a linear increase at both low and high concentrations, but the change in κ was not monotonous. At low concentrations, the change in κ was more appreciable than that at high concentrations because of the transition of the conducting species [1,21,38]. Namely, the κ-C curve can be divided into two linear segments by one breakpoint, corresponding to the cmc. The cmc of DOBAB, TOBAB and HOBAB at 25 °C obtained via conductivity measurements were 2.45 ± 0.070, 0.62 ± 0.021 and 0.089 ± 0.006 mmol·L^{-1}, respectively (Table 2), which are very close to those obtained by the surface tension measurements or fluorescence method (Table 1).

Generally, heating accelerates the migration of conducting ions in a solution, and thus leads to higher conductivity. Thus, with increasing the temperature, the slopes of the two linear segments both increased to some extent, and the breakpoints shifted to higher concentration, reflecting a larger cmc. As listed in Table 2, the cmc values increased from 2.45 ± 0.070, 0.62 ± 0.021 and 0.089 ± 0.006 mmol·L^{-1} to 3.11 ± 0.052, 0.72 ± 0.023 and0.16 ± 0.0042 mmol·L^{-1}, for DOBAB, TOBAB and HOBAB, respectively. This tendency is often observed in conventional ionic surfactants, such as C16MPB [37], selenium-hybride C16MPB [21]. Note that upon increasing the temperature from 25 to 45 °C, the cmc of DOBAB has an appreciable increase of 0.66 mmol·L^{-1}, but that of HOBAB only increased by 0.071 mmol·L^{-1}, approximately 1/10 of the amplification of DOBAB. In other words, the influence of temperature on the cmc is more prominent for short-chain surfactants than that of long-chain surfactants [37,39].

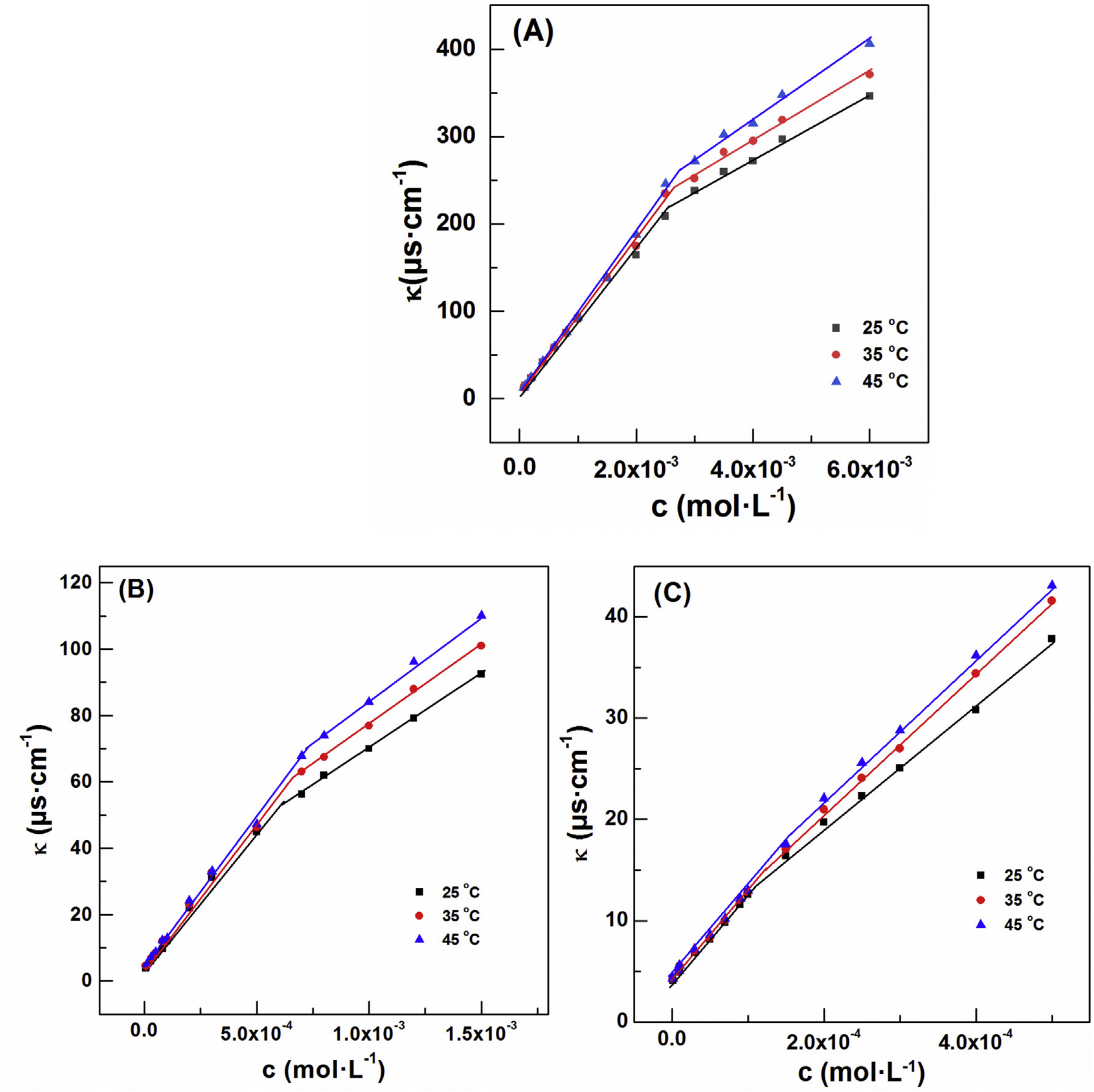


Fig. 3. Plotting the conductivity as a function of the concentration of (A) DOBAB, (B) TOBAB and (C) HOBAB at different temperatures.

3.4. Micellization thermodynamics by conductivity

As mentioned above, the κ-C curve is composed of two linear segments. The ratio the slopes of two linear segments above and below the cmc in Fig. 3 is generally defined as the degree of ionization (β). Consequently, 1-β is defined as the degree of binding of the counterions to the micelles for a 1–1 ionic surfactant.

As shown in Table 2, the 1-β values gradually decreased with increasing the temperature, which is mainly attributed to the faster migration of ions at high temperature. Namely, the higher the temperature, the lower the degree of binding of the counterions to the micelles. Similar phenomena are also observed for other ionic surfactants [21,37–40]. Furthermore, the 1-β of DOBAB was the largest, 0.5897–0.4775 (25–45 °C), but the 1-β of HOBAB was the smallest,

Table 2
The thermodynamic parameters and *cmc* of the formyl-containing cationic surfactants at different temperatures.

Surfactant	T (K)	cmc (mmol·L^{-1})	1-β	ΔG_m^o (kJ·mol^{-1})	ΔH_m^o (kJ·mol^{-1})	$-T\Delta S_m^o$ (kJ·mol^{-1})	ΔS_m^o (J·mol^{-1}·K^{-1})	ΔG_{ads}^o (kJ·mol^{-1})
DOBAB	298	2.45 ± 0.070	0.5897 ± 0.037	−39.51 ± 0.32	−14.22 ± 0.24	−25.29 ± 0.41	84.83 ± 0.64	−58.10 ± 0.38
	308	2.74 ± 0.059	0.5524 ± 0.028	−39.42 ± 0.41	−14.83 ± 0.17	−24.60 ± 0.35	79.82 ± 0.58	
	318	3.11 ± 0.052	0.4775 ± 0.041	−38.24 ± 0.28	−15.05 ± 0.14	−23.20 ± 0.28	72.91 ± 0.39	
TOBAB	298	0.62 ± 0.021	0.4765 ± 0.043	−42.28 ± 0.41	−18.55 ± 0.23	−23.73 ± 0.44	79.58 ± 0.48	−63.35 ± 0.49
	308	0.66 ± 0.015	0.4468 ± 0.024	−42.15 ± 0.58	−19.42 ± 0.10	−22.73 ± 0.37	73.77 ± 0.57	
	318	0.72 ± 0.023	0.4277 ± 0.051	−42.34 ± 0.29	−20.43 ± 0.25	−21.92 ± 0.56	68.89 ± 0.32	
HOBAB	298	0.089 ± 0.006	0.3505 ± 0.075	−44.62 ± 0.61	−27.25 ± 0.46	−17.38 ± 0.40	58.28 ± 0.44	−66.28 ± 0.60
	308	0.12 ± 0.0048	0.2205 ± 0.058	−44.75 ± 0.37	−29.30 ± 0.54	−15.45 ± 0.62	46.88 ± 0.51	
	318	0.16 ± 0.0042	0.1908 ± 0.049	−44.27 ± 0.54	−30.36 ± 0.39	−13.91 ± 0.57	40.57 ± 0.38	

Standard uncertainty (u) is u (T) = 0.35 K (level of confidence = 0.68). Relative standard uncertainties (ur) are ur (cmc) = ± 6.7%, ur (ΔG_m^o) = ± 1.4%, ur (ΔH_m^o) = ± 1.8%, ur (ΔS_m^o) = ± 1.1%, ur (ΔG_{ads}^o) = ± 1.0%.

0.3505–0.1908 (25–45 °C). This implies that the longer the hydrophobic chain, the lower the degree of binding of the counterions to the micelles. Similarly, Das et al. found that in the alkyltrimethylammonium bromides series, the degree of binding of the counterions to the micelles decreased with the chain length [41]. Zana ascribed a decrease in the 1-β to be a consequence of a decrease in the surface charge density, i.e., an increase of surface area per ionic head group [42]. Compared with DOBAB, the larger A_{min} for HOBAB also indirectly confirmed the smaller 1-β.

According to the mass action model, the standard free energy of micellization per mole of monomer unit (ΔG_m^o) of ionic surfactants is related to the molar fraction of the surfactant at the cmc (X_{cmc}) by the following relationship [1]:

$$\Delta G_m^o = (2-\beta)RT\ln X_{cmc} \tag{4}$$

All the ΔG_m^o values were calculated and summarized in Table 2. The ΔG_m^o values remained almost unchanged with changing molar fraction of the surfactant at the temperature for every surfactant. However, the ΔG_m^o values become more negative with increasing the chain length. From the viewpoint of energy, a more negative ΔG_m^o is more favorable for micellization. Namely, HOBAB bearing the most negative ΔG_m^o is the easiest to form micelles, as verified by the smallest cmc.

Based on the thermodynamic relationship and calculated ΔG_m^o, the standard enthalpy (ΔH_m^o) and standard entropy (ΔS_m^o) of micellization can be obtained according to eqs. (5) and (6) [1]:

$$\Delta H_m^o = \left[\frac{\partial(\Delta G_m^o/T)}{\partial(1/T)}\right] = RT^2\left(\frac{\mathrm{d}\ln X_{cmc}}{dT}\right) \tag{5}$$

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \tag{6}$$

As listed in Table 2, the ΔH_m^o and ΔS_m^o values gradually decreased accompanied by a steady increase in the $-T\Delta S_m^o$ values upon increasing the temperature from 25 to 45 °C. This is mainly because heating decreases the amount of ordered water molecules, which includes the water structured surrounding the hydrophobic alkane chains and the water bound to the trimethylammonium headgroups [1,43].

The ΔH_m^o values were always higher than the $-T\Delta S_m^o$ values for DOBAB and TOBAB, but a reversal occurred for HOBAB. This means that the micellization processes of DOBAB and TOBAB are primarily governed by the entropy gain associated with it, but HOBAB is mainly dominated by the enthalpy. Briefly, upon increasing the chain length, the ΔH_m^o values decrease, while the $-T\Delta S_m^o$ values increase, and then they cross over.

From Table 2 it can be seen that at a given temperature, the ΔG_m^o decreased by approximately ~1.37 kJ/mol per -CH_2- group, which is no more than half of those obtained for conventional single-chain or symmetric Gemini surfactants (~3 kJ/mol per -CH_2- group) [1,44]. Likewise, the ΔH_m^o decreased by ~3.37 kJ/mol and the ΔS_m^o increased by ~2.20 J/mol with the addition of each -CH_2- group.

According to Rosen et al. [1], the free energy to transfer amphiphilic molecules in solution to the air–water interface at molar fraction of the surfactant at the cmc was defined as the standard Gibbs free energy of adsorption (ΔG_{ads}^o), which can be calculated using eq. (7):

$$\Delta G_{ads}^o = \Delta G_m^o - \frac{\pi_{cmc}}{\Gamma_{\max}} \tag{7}$$

From eq. (7), the ΔG_{ads}^o values obtained for the formyl-containing surfactants were -58.10 ± 0.38, -63.35 ± 0.49 and -66.28 ± 0.60 kJ/mol for DOBAB, TOBAB and HOBAB, respectively. Compared with those of traditional alkyltrimethylammonium bromides [41], the absolute value of ΔG_{ads}^o is larger, indicating a rather higher adsorption efficiency. By examining the surfactant structures, it is clear that the insertion of the 2-(4-formyl-phenoxy)ethyl group produces a positive contribution to the adsorption of surfactants at the air/water interface.

The minimum work needed to make a surface area per mole or free energy change accompanied by transition from the bulk phase to the surface phase of the solution is defined as the minimum free energy (G_{min}) by Sugihara [45], which can be evaluated using eq. (8):

$$G_{min} = \gamma_{cmc} A_{min} N \tag{8}$$

From eq. (8), the G_{min} values of the formyl-containing surfactants were obtained as 17.72, 24.30 and 27.78 kJ/mol for DOBAB, TOBAB and HOBAB, respectively. This indicates that the longer the chain length, the more difficult the formation of a thermodynamically stable surface is. These results are also in agreement with the change in the γ_{cmc}.

3.5. Micellization thermodynamic by ITC

In addition to the conductivity method, the cmc and observed enthalpy (ΔH) can also be determined utilizing ITC technology. As exhibited Fig. 4, all the ΔH values were endothermic, similar to that observed in conventional alkyltrimethylammonium bromides [43] or cationic Gemini surfactants [46]. The ΔH-C curve can be roughly divided into three regions: two approximate plateaus and one rapid mutation zone. At low concentrations, the ΔH only underwent a slight decrease with concentration, or even remained unchanged, forming the first plateau. Above a critical concentration, the ΔH started to dramatically decrease in a small concentration range. The decrease in the ΔH levelled off over another critical value, forming the second plateau.

According to the classification proposed by Engberts et al. [47], the enthalpograms for TOBAB and DOBAB are type A, but the enthalpogram for HOBAB belongs to type B. In other words, the former can be regarded as a "textbook" example, in which the surfactants behave ideally and no solute-solute interactions occur [47]. Whereas, in the latter case, the effect of the solute-solute interactions on the enthalpy change is no longer negligible. This suggests that dilute solutions of TOBAB and DOBAB can be assumed to be ideal, but that of HOBAB not.

The cmc is obtained from the first derivative of the ΔH-C curve and the micellization enthalpy (ΔH_{mic}) is obtained from the difference between the observed enthalpies of the two linear segments of the curve [43,48]. Table 3 shows the cmc values determined from the ITC experiments, which correspond fairly well with the values determined from

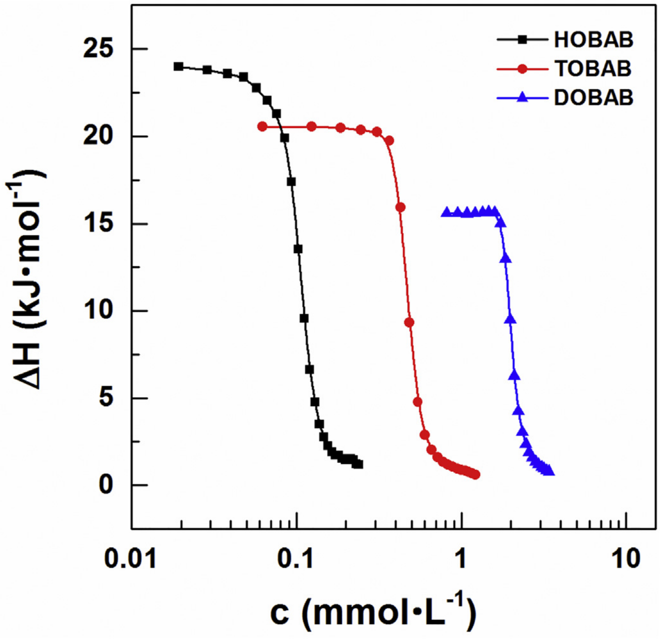


Fig. 4. Variations in the observed enthalpy (ΔH_m^o) with surfactant concentration at 25 °C.

Table 3
Critical micelles concentration and micellization enthalpy of formyl-containing cationic surfactants obtained from the enthalpograms by ITC at 25 °C.

	cmc($\mathrm{mmol \cdot L^{-1}}$)	ΔH_{mic} ($\mathrm{kJ \cdot mol^{-1}}$)
HOBAB	0.0784 ± 0.0011	−20.3748 ± 0.29
TOBAB	0.581 ± 0.048	−18.7196 ± 0.11
DOBAB	2.07 ± 0.15	−13.9089 ± 0.12

the surface tension and fluorescence methods (Table 1). All the ΔH_{mic} are exothermic for the surfactants studied, and the ΔH_{mic} becomes a larger negative value with increasing the chain length. These results are similar to those obtained from the conductivity measurements. However, all the ΔH_{mic} are less negative than those obtained from the conductivity measurements. This may be related to the change in the aggregation number of the micelles with temperature [1].

3.6. Effects of additives on micellization

NaCl and urea are chosen as inorganic and organic representatives, respectively, to study the effects of additives on the micellization of HOBAB (Fig. S7, 8). It is well known that the presence of an inorganic electrolyte causes the double-electric layer of an ionic surfactant to be compressed, decreasing the thickness of the ionic atmosphere surrounding the ionic head groups, and thus leads to a depression of the cmc [1]. Similarly, the addition of NaCl leads to a considerable reduction in the cmc for HOBAB. As listed in Table 4, only a minor amount of NaCl, as low as 10 $\mathrm{mmol \cdot L^{-1}}$, leads to a decline of an order of magnitude in the cmc, suggesting that HOBAB is very sensitive to NaCl. Meanwhile, the ΔG_m^o value becomes more negative with the addition of NaCl. The cmc and ΔG_m^o continued to decrease upon further increasing NaCl, but the changes were very small. These results suggest that the introduction of an inorganic electrolyte can significantly enhance the self-assemble ability of formyl-containing cationic surfactants. Moreover, in the previous experiment we found that HOBAB was separated at high NaCl concentration (>50 $\mathrm{mmol \cdot L^{-1}}$). Namely, the salt-out effect starts to dominate.

On the other hand, the data listed in Table 4 show that the effect of urea on the micellization of HOBAB is relatively small. In the presence of urea, the cmc of HOBAB was slightly above that in pure water (Table 1) and the ΔG_m^o remained basically unchanged. With increasing urea from 100 to 300 $\mathrm{mmol \cdot L^{-1}}$, the cmc of HOBAB only exhibited a very small change from 0.0944 ± 0.0011 to 0.0997 ± 0.0013 $\mathrm{mmol \cdot L^{-1}}$, which is lower than that induced by heating (Table 1) and NaCl (Table 4). The increases in the cmc and ΔG_m^o both indicate that urea is unfavorable for self-assembly, but the influence is very limited.

3.7. Antimicrobial performance

The antibacterial and antifungal activity of the formyl-containing surfactants were assessed using the minimum inhibitory concentration (MIC) assay. As listed in Table 5, all the samples exhibited prominent antibacterial activity against *S. aureus* and *E. coli*, and antifungal activity against *C. albicans*. The antimicrobial performance of TOBAB against bacteria or fungi was the best, exhibiting the lowest MIC. Especially for *S. aureus* and *E. coli*, the antibacterial activity of TOBAB was comparable to that of an asymmetric Gemini cationic surfactant (14–2-8), but higher than that of traditional single-head-single-tail myristyltrimethylammonium bromide [49]. Minbiole et al. [50] argued for that compound bearing a hydrophobic chain between 20 and 24 carbon atoms usually displayed optimal antimicrobial activity. For the current surfactants, the total number of carbon atom in the hydrophobic chain of TOBAB was the closest to 20. Hence, it may be a good alternative candidate as an antimicrobial agent.

Table 5
Minimum inhibitory concentration (MIC) for prepared formyl-containing cationic surfactants.

Sample	MIC ($\mathrm{\mu mol \cdot L^{-1}}$)		
	S. aureus	*E. coli*	*C. albicans*
HOBAB	7.84 ± 0.056	62.70 ± 0.042	7.84 ± 0.017
TOBAB	1.96 ± 0.027	3.92 ± 0.013	7.84 ± 0.018
DOBAB	7.84 ± 0.031	7.84 ± 0.022	15.68 ± 0.023

4. Conclusions

In summary, a series of formyl-containing cationic surfactants (N-alkyl-*N*,*N*-dimethyl-N-(2-(4-formyl-phenoxy)ethyl) ammonium bromides) bearing different hydrophobic chains were synthesized and investigated for the first time. Upon increasing the alkyl chain from C12 to C16, the effectiveness in reducing the γ showed a small decrease as reflected by the larger γ_{cmc} and smaller Π_{cmc}, as a result of a decrease in the density of the adsorption film. Similar to conventional ionic surfactants [1], the cmc and pC_{20} decrease with the chain length, indicating a strong hydrophobic interaction and adsorption efficiency the at air/solution interface. The longer the hydrophobic chain, the more negative the ΔG_m^o and ΔG_{ads}^o, and the more favorable it is to form micelles in the bulk and to adsorb at the air/solution interface. However, the long chain is unfavorable for forming a s surface, as verified by the large G_{min}. The contributions of enthalpy and entropy to ΔG_m^o undergo an inversion with increasing the hydrophobic tail length and the contribution per methylene group to the ΔG_m^o is evidently lower than traditional single-chain or Gemini surfactants [1,44] due to the asymmetric double-chain structure [51]. The micellization is more sensitive to inorganic electrolytes than organic additives. In addition, TOBAB exhibits the best antimicrobial activity against both Gram-positive and Gram-negative bacteria and fungi, because its total carbon atoms number in the hydrophobic chaintable is very close to 20. Understanding the fundamental properties of the formyl-containing reactive surfactants in dilute solutions is favorable for the design of new responsive surfactants and aggregates, and their potential applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4
Critical micelles concentration and micellization enthalpy of HOBAB in the presence of NaCl or urea at 25 °C.

	Concentration ($\mathrm{mmol \cdot L^{-1}}$)	cmc ($\mathrm{mmol \cdot L^{-1}}$)	ΔG_m^o ($\mathrm{kJ \cdot mol^{-1}}$)	ΔH_m^o ($\mathrm{kJ \cdot mol^{-1}}$)	$-T\Delta S_m^o$ ($\mathrm{kJ \cdot mol^{-1}}$)
NaCl[a]	10	0.00455 ± 0.000069	−80.88 ± 0.44	/	/
	30	0.00442 ± 0.000095	−80.99 ± 0.53	/	/
	50	0.00426 ± 0.000040	−81.21 ± 0.61	/	/
Urea[b]	100	0.0944 ± 0.0011	−45.73 ± 0.52	−18.84 ± 0.29	27.04 ± 0.17
	200	0.0987 ± 0.0028	−45.73 ± 0.48	−17.65 ± 0.30	28.08 ± 0.23
	300	0.0997 ± 0.0013	−45.57 ± 0.25	−19.20 ± 0.22	26.35 ± 0.19

[a] Obtained by surface tension method, and the ΔG_m^o was calculated by $\Delta G_m^o = 2RTlnX_{cmc}$.
[b] Obtained by ITC method.

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Appendix A. Supplementary data

Some additional results including ^{1}H NMR and ESI-MS spectra, changes in surface tension with HOBAB concentration in the presence of NaCl, and variations in ΔH_m^o with HOBAB concentration in the presence of urea. Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.115168.

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