Study on the Surface Properties and Aggregation Behavior of Quaternary Ammonium Surfactants with Amide Bonds

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ABSTRACT: A number of techniques, including conductivity, surface tension, dynamic light scattering, transmission electron microscopy, and ^1H nuclear magnetic resonance (^1H NMR), Fourier transform infrared (FT-IR), and ^1H – ^1H 2D nuclear Overhauser effect spectroscopy (^1H – ^1H 2D NOESY), have been used to investigate the effect of amide bonds on the interfacial and assembly properties of a cationic surfactant, *N*-anilinoformylmethyl-*N*-cetyl-*N,N*-dimethyl ammonium chloride (AMC- C_{16}), in aqueous solutions. The adsorption of AMC- C_{16} has been found to be much better than that of the conventional cationic surfactant, benzyl cetyldimethylammonium chloride (BAC-16) at the air/water interface and in solution. The surface tension measurements show the presence of two critical aggregation concentrations (CAC_1 and CAC_2) for AMC- C_{16} . The presence of a strong intermolecular hydrogen bond of AMC- C_{16} was confirmed by ^1H NMR and FT-TR. The molecular interactions of AMC- C_{16} were detected by ^1H – ^1H 2D NOESY. The results show that the rigid group (phenyl) of AMC- C_{16} was partially overlapped with its alkyl chain in aqueous solution, and the possible aggregation behavior for AMC- C_{16} was proposed. The effects of an inorganic salt (NaCl) and an organic salt ($\text{C}_6\text{H}_5\text{COONa}$) to the aggregates of AMC- C_{16} have been discussed.

INTRODUCTION

In the past few decades, researchers have conducted numerous studies on surfactant properties and applications because of the self-assembly of surfactant molecules in aqueous solution to form various microstructures.^{1–6} Surfactants can form a variety of different aggregates in aqueous solution such as vesicles, micelles, nanocrystals, and so forth.^{7,8} These different aggregates have great application value in mimicking biological membranes and drug delivery.^{9,10} Encapsulation of a drug into vesicles may favor controlled drug release and lower side effects.^{11,12} In part, the development of advanced materials can be attributed to molecular self-assembly because the self-assembly can form nanomaterials, and the application of nanomaterials in design and manufacture has attracted considerable attention in recent years.^{13,14} To form different aggregates types, the relationship between structure and aggregation of surfactants have been studied.

It has been reported that the introduction of an ester group or amide group into the molecular structure of a surfactant can cause a significant change in its surface activity and aggregation behavior.^{15–18} Compared with the surfactants without amide bonds, the presence of the amide bond in the molecular structure makes it easy to form intermolecular bonding to promote intermolecular aggregation.^{19–22} Because hydrogen bonds interaction is the driving force for self-assembly of

single-chain surfactants to form a double-layer vesicle.^{23,24} A series of anionic surfactants based on amino acids have been synthesized by Roy and Dey; the surface activity and self-assembly behaviors have been studied in aqueous solution.^{25–27} The results show that these anionic surfactants stepwise aggregate with two CAC values (CAC_1 and CAC_2). It has been proved that the special aggregation behavior can be attributed to the intermolecular amide hydrogen bond interaction. In the past few years, some single-chain nicotinic acid-based anionic surfactants were synthesized.^{7,28} Two CAC values (CAC_1 and CAC_2) have been obtained by the surface tension of different surfactant concentrations. It was confirmed by Fourier transform infrared (FT-IR) and ^1H NMR spectra. The formation of intermolecular hydrogen bonding between the amide bonds plays an important role in the aggregation process. This phenomenon of stepwise aggregation was also observed in the surfactant/polymer system.²⁹ It also has been discovered that the ability of the surfactant aggregation could

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Scheme 1. Synthesis Steps of AMC-C₁₆ and BAC-16

be improved by enhancing the hydrophobic interactions.³⁰ From the previous review, it has been reported that there are two CAC values or various aggregate types during aggregation in some anionic surfactants or surfactant/polymer systems. However, this phenomenon rarely occurs in single-chain cationic surfactant systems without any additives.

As we all know, the different salt types have different influence on the surfactant aggregation process.³¹ Most inorganic and organic salts reduce the electrostatic interaction between the surfactant head groups by adsorbing on the surface of the aggregates and affect the aggregation of surfactant molecules. Besides reducing electrostatic interaction, the phenyl group of organic salts induce strong hydrophobic interaction by penetrating into aggregates, thereby reducing electrostatic repulsion of the surfactant headgroups more effectively, and it is more favorable for the aggregation of surfactant molecules compared with inorganic salts.^{31,32}

In the present study, AMC-C₁₆ was synthesized according to refs 22 and 33. The adsorption and aggregation behavior of AMC-C₁₆ has been investigated by conductivity, surface tension, dynamic light scattering (DLS), and transmission electron microscopy (TEM). It has been found that the amide bond can improve the ability of intermolecular aggregation. The novel aspect of this work is AMC-C₁₆ stepwise aggregates with two CAC values (CAC₁ and CAC₂) with the concentration increase. The intermolecular hydrogen bond and the interaction of the rigid group (phenyl) and the alkyl chain of AMC-C₁₆ have been confirmed by NMR technology. Furthermore, the effect of inorganic and organic salts on the aggregates of AMC-C₁₆ has been studied. This work helps to further understand the effect of amide bonds on the aggregation behavior of single-chain cationic surfactants. The molecular structures of the AMC-C₁₆ and benzyl cetyldimethylammonium chloride (BAC-16) are given in Scheme 1.

RESULTS AND DISCUSSION

Surface Tension Studies. The critical aggregation concentration (CAC) of AMC-C₁₆ and BAC-16 were determined by the surface tension method. The plots of surface tension (γ) versus concentration (C) of AMC-C₁₆ and BAC-16 are shown in Figure 1.

It is clear from Figure 1 that there are two break points (CAC₁ and CAC₂) for AMC-C₁₆ but one break (CAC₁) for BAC-16. For AMC-C₁₆, the CAC was given by the first break; the second break may be due to the onset of secondary aggregation. To confirm whether the second breakpoint was caused by impurities, the purity of AMC-C₁₆ was verified by ¹H NMR spectrum and liquid chromatography–mass spectrometry (LC–MS) spectrum (Figures S1 and S2), and there was no minimum value near the breakpoint. This indicates that AMC-C₁₆ may form two different morphologies of aggregates within the concentration range studied. It has been reported that two break points are caused by post-micellar aggrega-

Figure 1. Plot of surface tension (γ) vs concentration (C) of AMC-C₁₆ and BAC-16.

tion.^{7,24–27,34} The post-micellar aggregation in AMC-C₁₆ may be due to the presence of amide bonds in the AMC-C₁₆ molecular structure. It is easy to form intermolecular bonding to promote intermolecular aggregation.^{21,22}

The CAC values obtained are listed in Table 1. It is clear that AMC-C₁₆ has lower CAC₁ value than BAC-16. The introduction of the amide group in the surfactant molecular structure leads to a further reduction in the CAC value.^{16,17,35} It shows that the micellization is more favorable for AMC-C₁₆. As listed in Table 1, the γ_{CAC} value of AMC-C₁₆ is lower than that of BAC-16. This indicates that AMC-C₁₆ has good surface activity.

Furthermore, the surface excess concentration (Γ_{max}) and the area occupied (A_{min}) by a single surfactant molecule at the air/water interface at the interface are crucial to the interpretation of the surface activities of surfactants.³⁶ The values of Γ_{max} and A_{min} were calculated by the Gibbs adsorption equations.³⁷ The Gibbs adsorption eqs 1 and 2 are given as follows

$$\Gamma_{\text{max}} = -[1/(2.303nRT)][d\gamma/(d\log C)] \quad (1)$$

$$A_{\text{min}} = 1/(N_A \Gamma_{\text{max}}) \quad (2)$$

where $d\gamma/d\log C$ is the maximum slope before CAC, $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $T = 298.15 \text{ K}$, N_A is Avogadro's number, and $n = 2$ for the monovalent ionic surfactant.³⁸

The effectiveness of surface tension decrease (π_{CAC}) and the adsorption efficiency (pC_{20}) is calculated as the following eqs 3 and 4

$$\pi_{\text{CAC}} = \gamma_0 - \gamma_{\text{CAC}} \quad (3)$$

$$pC_{20} = -\lg C_{20} \quad (4)$$

where γ_0 is the surface tension of pure water and γ_{CAC} is the surface tension of the solution at CAC. C_{20} is the surfactant concentration needed to reduce the surface tension of pure water by 20.0 mN/m. The values of π_{CAC} , pC_{20} , Γ_{max} and A_{min} are listed in Table 1.

Table 1. Surface Properties of AMC-C₁₆ and BAC-16 in Aqueous Solution at 25 °C Obtained by Different Techniques

surfactant	CAC ₁ (mM)	CAC ₂ (mM)	γ_{CAC} (mN·m ⁻¹)	π_{CAC} (mN·m ⁻¹)	Γ_{max} ($\mu\text{mol}\cdot\text{m}^{-2}$)	A_{min} (nm ²)	pC ₂₀	β	$\Delta G_{\text{agg}}^{\circ}$ (kJ·mol ⁻¹)	$\Delta G_{\text{ads}}^{\circ}$ (kJ·mol ⁻¹)
AMC-C ₁₆	0.10	1.44	37.5 (CAC ₁) 32.4 (CAC ₂)	34.52	2.04	0.82	4.62	0.54	-30.49	-47.38
BAC-16	0.43 0.40 ^a		40.5 39.6 ^a	31.55	1.49 1.46 ^a	1.11 1.14 ^a	3.87 4.13 ^a	0.44	-27.51	-44.38

^aThe data of corresponding surfactant BAC-16 reported in ref 23.

It can be seen that the pC₂₀ value of AMC-C₁₆ is larger than the pC₂₀ value of BAC-16, which indicates that AMC-C₁₆ is superior to BAC-16 in the adsorption efficiency. The values of Γ_{max} and A_{min} reflect the adsorption and arrangement of the molecules at the air/water interface, respectively. It is worth noting that the value of A_{min} for AMC-C₁₆ is lower than that for BAC-16; thus, large aggregates may form in the case of AMC-C₁₆. This can be attributed to the intermolecular amide hydrogen bond interactions, which cause the surfactant molecules to pack tightly. The standard free energy of aggregation per mole of surfactant ($\Delta G_{\text{agg}}^{\circ}$) and the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) were calculated by the eqs 5 and 6.^{16,39}

$$\Delta G_{\text{agg}}^{\circ} = (1 + \beta)RT \ln \text{CAC} \quad (5)$$

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{agg}}^{\circ} - \pi_{\text{CAC}}/\Gamma_{\text{max}} \quad (6)$$

where R is the gas constant, T is the temperature (K), $\beta = 1 - \alpha$. The degree of counterion dissociation (α) was given by the ratio of the slopes of the κ versus C curve above and below CAC (Figure S3). The counterion binding parameter (β) gives the average number of counterions per surfactant ion in the micelle and can be estimated from the ratio of the slopes.¹⁶ The values of β , $\Delta G_{\text{agg}}^{\circ}$, and $\Delta G_{\text{ads}}^{\circ}$ are listed in Table 1. The larger the negative values of $\Delta G_{\text{ads}}^{\circ}$, the more favorable is the aggregate formation in aqueous solution compared with $\Delta G_{\text{agg}}^{\circ}$.

DLS Studies. To obtain the size distribution of aggregates, DLS was carried out on the aqueous solution of AMC-C₁₆ and BAC-16. The sizes and distributions of the aggregates are shown in Figure 2.

It is clear from Figure 2 that there are two size-distributions in the concentration of 6 mM (4 times the CAC₂) of AMC-C₁₆, and the average hydrodynamic diameter (D_h) of the aggregates is about 5 and 119 nm, respectively. However, there was only one size-distribution, about 60 nm, in the concentration of 1.74 mM (4 times the CMC) of BAC-16.

From the DLS measurement results, the molecules of AMC-C₁₆ form different aggregate types in aqueous solution. It has been reported that the amide group in the surfactant molecular structure, because it is prone to form intermolecular hydrogen bonds, promotes molecular aggregation and forms different aggregate types.^{7,21,23} The size distribution at 5 nm corresponds to micelles.^{18,40} There was one obvious peak with an average apparent hydrodynamic radius of 100 nm, reflecting the typical size of a big aggregate,^{41,42} which is well consistent with the result of TEM observations.

Morphological Study by TEM Observations. To visually observe the morphology of the aggregates, TEM test was performed on the solution of AMC-C₁₆. The TEM pictures of AMC-C₁₆ solution are shown in Figure 3.

At 6 mM (4 times the CAC₂), different sizes of vesicles are observed. The sizes of large vesicles are in the range 20–100

Figure 2. Size distribution of the aggregates in aqueous solution [(a) AMC-C₁₆, (b) BAC-16].

nm, Figure 3a,b (marked by arrows). These results are consistent with the DLS measurements.

Viscosity of Surfactant Solution. The formation of different vesicles is normally manifested by the increase of bulk viscosity of the surfactant solution.^{28,43–46} Therefore, the relative viscosity of different concentrations of the aqueous solution of AMC-C₁₆ was measured. The variation of relative viscosity is shown in Figure 4.

As shown in Figure 4, the viscosity increased nonlinearly as the concentration of AMC-C₁₆ increased. Especially, the solution viscosity of AMC-C₁₆ relative to water increases very rapidly when the concentration is more than CAC₂. Therefore, the micelles may exist in solution of AMC-C₁₆ when the concentration exceeds CAC₂.⁴⁷ The results of the viscosity measurements are consistent with the DLS measurements.

Intermolecular Hydrogen Bonding. To explain intermolecular hydrogen bonding interactions, the NMR technique was applied. The ¹H NMR spectra of AMC-C₁₆ in DMSO-*d*₆ and DMSO-*d*₆ + H₂O are shown in Figure 5.

Figure 3. TEM micrographs of the aggregates for AMC-C₁₆ in aqueous solution [(a,b) 6 mM].

Figure 4. Plot of relative viscosity vs concentration of AMC-C₁₆ in aqueous solution.

It can be clearly observed from Figure 5 that as the amount of H₂O increases, the chemical shift of the amide proton (H₄) shifts to high field. The results show that there are strong intermolecular hydrogen bonds between AMC-C₁₆ and water molecules.

To further verify the existence of intermolecular hydrogen bonds, FT-IR spectra were used to record the change of amide stretching frequency of AMC-C₁₆, under conditions of dryness and the presence of water (Figures S4–S6). The NH-stretching frequency, amide I band, and amide II band of the CONH linkage appeared at higher frequency (3198, 1698, 1564 cm^{−1}) under conditions of dryness, but transferred to a lower frequency (3169, 169¹, 1546 cm^{−1}) in the presence of water. This result further confirmed that the hydrogen atom

Figure 5. ¹H NMR spectra of AMC-C₁₆ [(a) DMSO-*d*₆, (b) DMSO-*d*₆ + 10 μL H₂O, (c) DMSO-*d*₆ + 30 μL H₂O].

and oxygen atom of amide bond with water molecules could form the intermolecular hydrogen bond.

We speculated that the rigid group (phenyl) bends around the amide bond. It has been reported in the literature that such a bend will make the amide bond more favorable for the formation of intermolecular hydrogen bonds with water molecules during the formation of aggregates, therefore leading to greater hydration of the cationic headgroup region.²² In addition, with the concentration of the solution increasing, the rigid group (phenyl) hydrophobic interactions become strong enough to promote the bending around the flexible amide bond. Kamboj et al.²⁰ reported a cationic surfactant which contains an amide bond and morpholine ring near the headgroup. The morpholine ring coils back toward the interior of the micelle when cetyl is a hydrophobic chain. Moreover, Zhai et al.³⁰ reported a cationic surfactant containing a large rigid group and a flexible alkyl chain. The alkyl chain of the product was partially overlapped with its non-planar rigid structure in aqueous solution, and the possible aggregation process for the product was proposed.

Study of Aggregation Behavior. In order to understand the formation process of the AMC-C₁₆ aggregates, ¹H–¹H 2D NOESY was used to detect the molecular interactions of AMC-C₁₆ in aqueous solution. The ¹H–¹H 2D NOESY spectra of AMC-C₁₆ are shown in Figure 6.

As can be seen from Figure 6, the proton of phenyl (H₁, H₂, and H₃) shows strong correlations with the protons on the flexible alkyl (H_{7–10}) (marked with rounded rectangles).

Figure 6. ¹H–¹H 2D NOESY spectra of AMC-C₁₆ in D₂O.

Usually, if the distance between protons is less than 5 Å, the cross-peak signals will appear in the ^1H – ^1H 2D NOESY spectrum.^{31,48,49} The amide proton (H_4) has shown correlations with the protons on the flexible alkyl (H_{7-10}) (marked with rectangles). Also, the protons on methylene (H_5) have shown weak correlations with the proton of phenyl (H_2 and H_3). This indicates that the hydrophobic chains are close to the rigid group (phenyl) in AMC-C₁₆ aggregates.

Salt Effect on AMC-C₁₆ Aggregation. It is well known that the presence of salts has a very significant effect on the aggregation of ionic surfactants. The surface tension curves of AMC-C₁₆ at different concentrations of NaCl and C₆H₅COONa are presented in Figure 7. The CAC values obtained from Figure 7 were plotted against the different concentrations of salts, as shown in Figure S7.

Figure 7. Plot of surface tension (γ) vs concentration (C) of AMC-C₁₆ at different salt concentrations: (a) NaCl, (b) C₆H₅COONa.

As shown in Figures 7 and S7, as the concentration of inorganic salt (NaCl) and organic salt (C₆H₅COONa) increases, the values of CAC and γ_{CAC} decrease. The addition of salts in the aqueous solution of AMC-C₁₆ can effectively promote the aggregation and adsorption at the interface of AMC-C₁₆. This is because the addition of salts can effectively reduce the electrostatic repulsion between the surfactant headgroups.

It was worth noting that the first platform of the curve becomes shorter and eventually disappears as the salt concentration increases (Figure 7). Because the concentration of AMC-C₁₆ increases, the hydrophobic and the amide bonds effect of the rigid group (phenyl) should promote aggregation and molecular conformational changes.^{18,31,50} Hence, the secondary aggregation is much more sensitive to ionic strength.

Additionally, at the same concentration of salts, compared with the addition of the inorganic salt (NaCl), the organic salt

(C₆H₅COONa) can be more effective in pushing the second turning point toward the first turning point. This means that the aggregates of AMC-C₁₆ change significantly with the addition of salts.

Furthermore, the changes of AMC-C₁₆ aggregates in the presence of different salts were studied by the DLS technique. The concentrations of AMC-C₁₆ are 0.3 mM (between CAC₁ and CAC₂) and 6 mM (>CAC₂), the concentration of the salts is different. It is 2.5–15 mM for NaCl and 2–17 mM for C₆H₅COONa. The size distributions of the aggregates of AMC-C₁₆ at different salt concentrations are shown in Figures 8 and 9.

Figure 8. Size distribution of the aggregates for 0.3 mM AMC-C₁₆ at different salt concentrations: (a) NaCl, (b) C₆H₅COONa.

As the concentration of inorganic salts (NaCl) increases, there are two types of aggregates, spherical micelles (8 nm) and small-size vesicles (about 75–112 nm) in solution (Figure 8a). However, as the concentration of the organic salt (C₆H₅COONa) increases, only one type of aggregate exists in the solution, which may be large vesicles (about 130 nm) (Figure 8b).

Furthermore, from Figure S8, with the addition of salt, the solution state of AMC-C₁₆ is obviously different. The solution of AMC-C₁₆ is always a clear solution as the concentration of NaCl increases. However, the solution of AMC-C₁₆ turns into a colloidal solution when the concentration of C₆H₅COONa is more than 5 mM. This indicates that increase in the concentration of C₆H₅COONa is beneficial to stabilize the vesicles. This unexpected observation could be attributed to the different interactions between NaCl and C₆H₅COONa with AMC-C₁₆.

NaCl affects the aggregation of surfactant only by reducing the electrostatic repulsion between the surfactant headgroup by adsorption on the surface of the aggregates. However, the

Figure 9. Size distribution of the aggregates for 6 mM AMC-C₁₆ at different salt concentrations: (a) NaCl, (b) C₆H₅COONa.

aromatic counterions affect the micellization of surfactants both electrostatically as well as hydrophobically because of the C₆H₅COO[−] anion's greater tendency of penetrating the head group region of the surfactant aggregates and reducing the electrostatic repulsion among the surfactant headgroups.^{31,47} Therefore, the C₆H₅COO[−] anion shows more pronounced stabilization of the vesicles and is more beneficial to aggregation of the surfactant molecules. Therefore, the organic salt stabilizes the vesicles.

From Figure 9, when the concentration of AMC-C₁₆ is 6 mM (>CAC₂), as the concentration of inorganic salts (NaCl) increases, the vesicle peak gradually becomes smaller (Figure 9a). Also, when the concentration of organic salts (C₆H₅COONa) is above 2 mM, only one type of aggregate exists in the solution, which may be large vesicles (about 20–500 nm) (Figure 9b). These results imply that the addition of proper salts can effectively adjust the structure of the surfactant aggregates. It is helpful in understanding the effect of both inorganic and organic salts on the aggregation behavior of surfactants. This phenomenon was also previously reported.^{51,52}

CONCLUSIONS

The effects of the amide bond on the adsorption and aggregation behavior of AMC-C₁₆ have been investigated in aqueous solution by various techniques. The presence of the amide bond, prone to hydrogen bonds, has been found to favor the AMC-C₁₆ molecular adsorption or aggregation in the interface or aqueous solution. This can be attributed to the presence of the hydrogen bond, which can counterbalance effectively the electrostatic repulsion of the AMC-C₁₆ molecular headgroup. The introduction of the amide bond leads to AMC-C₁₆ with higher surface activity and enhanced

tendency to form aggregates above the CAC having hydrodynamic diameters in the range 0.88–119 nm compared to BAC-16 and to earlier reported cationic surfactants.^{15,16,22,53,54}

Surface tension measurements at different concentrations indicate stepwise aggregate of AMC-C₁₆ and thus produce two critical aggregation concentration (CAC₁ and CAC₂). With the concentration increasing, the vesicles were formed by AMC-C₁₆ at suitable concentrations without any additives, which have been confirmed by TEM. In addition, the rigid group (phenyl) bends into the hydrophobic region when vesicles are formed as revealed by ¹H–¹H 2D NOESY experiments. The AMC-C₁₆ may have potential application value in the pharmaceutical industry as a drug-delivery vehicle.

EXPERIMENTAL SECTION

Instruments and Material. All reagents were of analytical grade, were commercially available, and used as received without further purification. Melting points (mp) were determined using an MPA100 Optimelt Automated Melting Point System, Stanford Research Systems Company, U.S.A. FT-IR was recorded using Frontier type infrared spectrometer, PerkinElmer Corp., U.S.A. ¹H NMR was recorded by using Avance 600 superconducting NMR, Bruker Company, Switzerland. Mass spectra were recorded on a Waters Xevo UPLC/G2-QT instrument, Agilent Company, U.S.A. Conductivity was measured on Alvarez DDS-307 conductivity analyzer, Shanghai Precision and Scientific Instrument Company. Surface tensions were determined on a K100 tension meter, Krüss Company, Germany. DLS measurements were performed on a Malvern Autosizer, Malvern, U.K. TEM image was obtained with an H-7650, Hitachi Instruments Company. Relative viscosities were measured in thermostatted Ubbelohde viscometers, Shanghai Huake Labware Co. All samples were prepared using Milli-Q water (18.25 MΩ·cm). All measurements were carried out at room temperature (25.0 ± 0.1 °C).

Synthesis and Characterization. Scheme 1 shows the synthesis steps of AMC-C₁₆ and BAC-16.

Synthesis and Characterization of Chloroacetanilide. Chloroacetanilide was synthesized. The solution of chloroacetyl chloride (45 mmol) in acetone (15 mL) was slowly dropped into the solution of aniline (30 mmol) and K₂CO₃ (24 mmol) in acetone (45 mL) under cooling with an ice-water bath; then, the mixture was stirred under nitrogen for 2.5 h. Acetone was evaporated off under reduced pressure (525–675 mmHg) at 40–45 °C. The oily liquid crude product was obtained, and distilled water (50 mL) was added. The precipitate formed was filtered and washed with distilled water (20 mL × 5). Then, recrystallization from anhydrous ethanol gave pure chloroacetanilide as a white solid (77% yield).

¹H NMR (600 MHz, CDCl₃): δ 8.23 (s, 1H, NH), 7.56 (d, 2H, *J* = 8.4 Hz, PhH), 7.36 (t, 2H, *J* = 7.8 Hz, PhH), 7.18 (t, 1H, *J* = 7.2 Hz, PhH), and 4.20 (s, 2H, O=C–CH₂).

Synthesis and Characterization of *N*-Anilinoformylmethyl-*N*-cetyl-*N,N*-dimethyl Ammoniumchloride (AMC-C16). The AMC-C₁₆ was synthesized. A mixture of chloroacetanilide (9.1 mmol), *N,N*-dimethyl-*N*-hexadecylamine (10.9 mmol), and acetonitrile (40 mL) was heated to 80 °C for 5 h. Acetonitrile was evaporated off under reduced pressure at room temperature to obtain the crude product. The crude product was purified by recrystallization from ethyl acetate for at least 4 to 6 times till the purity of the compound was

confirmed by thin liquid chromatography (TLC). A white solid powder of **AMC-C₁₆** was obtained with a yield of 94%.

FT-IR (KBr pellet) ν (cm⁻¹): 3198 (N–H stretching, amino), 3037 (C–H stretching, benzene ring), 2920 (C–H stretching, methyl), 2851 (C–H stretching, methylene), 1698 (O=C stretching, carbonyl), 1605, 1500, 1446 (skeleton stretching vibration, benzene ring), and 722 (alkyl chain bending, methylene). ¹H NMR (600 MHz, CDCl₃): 11.73 (s, 1H, NH), 7.80 (d, 2H, *J* = 8.4 Hz, PhH), 7.31 (t, 2H, *J* = 7.5 Hz, PhH), 7.13 (t, 1H, *J* = 7.2 Hz, PhH), 4.88 (s, 2H, CH₂–N⁺), 3.62 (t, 2H, *J* = 8.4 Hz, N⁺–CH₂CH₂–), 3.42 (s, 6H, N⁺–CH₃), 1.81 (q, 2H, N⁺–CH₂CH₂–), 1.25–1.35 (m, 26H, –CH₂(CH₂)₁₃–CH₃), and 0.88 (t, 3H, *J* = 6.6 Hz, CH₃). ESI-MS (positive ions) *m/z*: calcd, 403.3683 for [M – Cl]⁺; found, 403.3676. mp: 131.5–134.6 °C.

Synthesis and Characterization of Benzylcetyl Dimethylammonium Chloride (BAC-16). A mixture of benzyl chloride (30 mmol), *N,N*-dimethyl-*N*-hexadecylamine (36 mmol), and acetonitrile (50 mL) was heated to 80 °C for 5.5 h. Acetonitrile was evaporated off under reduced pressure at room temperature to obtain the crude product. The crude product was purified by recrystallization from ethyl acetate and acetone for at least 4 to 6 times till the purity of the compound was confirmed by TLC. A white solid powder of **BAC-16** was obtained with a yield of 86%.

FT-IR (KBr pellet) ν (cm⁻¹): 3008 (C–H stretching, benzene ring), 2922 (C–H stretching, methyl), 2853 (C–H stretching, methylene), 1616, 1472, 1456 (skeleton stretching vibration, benzene ring), and 723 (alkyl chain bending, methylene). ¹H NMR (600 MHz, CDCl₃): δ 7.65 (d, 2H, *J* = 7.2 Hz, PhH), 7.45–7.49 (m, 3H, PhH), 5.02 (s, 2H, CH₂–N⁺), 3.49 (t, 2H, *J* = 8.4 Hz, N⁺–CH₂CH₂–), 3.31 (s, 6H, N⁺–CH₃), 1.81 (br s, 2H, N⁺–CH₂CH₂–), 1.26–1.35 (m, 26H, –CH₂(CH₂)₁₃–CH₃), and 0.88 (t, 3H, *J* = 6.9 Hz, CH₃). ESI-MS (positive ions) *m/z*: calcd, 360.3625 for [M – Cl]⁺; found, 360.3615. mp: 58–60 °C.

Conductivity. The conductivities of the solutions of **AMC-C₁₆** and **BAC-16** were determined by using a digital conductivity meter at 25 °C. The solutions were thermostated at 25.0 ± 0.1 °C using a thermostatic bath during the measurements. The conductivity values of the solutions of different concentrations were tested by a dilution method.⁴ The measurements were repeated 3 times.

Surface Tension. Surface tension was determined using a Krüss K100 automatic tensiometer by the Du Nouy ring method at 25.0 ± 0.1 °C. The temperature of the solution was strictly controlled during the measurement. The surface tension values of the solution of different concentrations were tested by a dilution method. The instrument was calibrated using Milli-Q water before every experiment began and the standard deviation was kept within ±0.1 mN/m. The measurements were repeated 3 times.

Dynamic Light Scattering. DLS measurements were performed using a Malvern Autosizer light scattering apparatus at a scattering angle of 90°. The sample solution was filtrated through a membrane filter with a pore size of 0.45 μm just before the measurements. The samples were thermally equilibrated for 10 min at 25 °C before measurement. The measurements were repeated 3 times.

Transmission Electron Microscopy. Transmission electron microscopy was performed with an H-7650 operating at 100 kV. The solution of the surfactant needs to equilibrate for 12 h before performing the transmission electron microscopic

measurements. Freshly prepared phosphotungstic acid solution (2%) was used as a staining agent. One drop of the solution was placed on a carbon formvar-coated copper grid (200 mesh), and the excess solution was removed with a filter paper to obtain a thin liquid film on the copper grid. Subsequently, a staining agent was dropped on the liquid film for 2 min, and the excess liquid was removed with a filter paper. The prepared samples were dried in air and tested.

Relative Viscosity. The Ubbelohde viscometer was used to measure the relative viscosities of the surfactant solution. The viscosity of Milli-Q water was used as the control. The solutions were heated at 25.0 °C using a thermostatic bath during the measurements. The measurements were repeated 3 times and averaged.

NMR Measurement. ¹H NMR spectra were recorded on a 600 MHz Bruker Avance NMR spectrometer at room temperature of 25.0 ± 0.1 °C. DMSO-*d*₆ (99.9%) and CDCl₃ (99.9%) were used to prepare the stock solution of the cationic surfactants. About 1 mL of the solution was transferred to a 5 mm NMR tube for each measurement. TMS is an internal standard on a Bruker AV 600 MHz. The signal assignment of the proton of surfactant molecules was measured by ¹H–¹H 2D NOESY using D₂O as the solvent.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c00294>.

¹H NMR spectrum, LC–MS spectrum, conductivity, FT-IR spectra, CAC values, and physical appearance (PDF)

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Notes

The authors declare no competing financial interest.

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