Catanionic Mixtures Forming Gemini-like Amphiphiles

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Abstract: The properties of aqueous mixtures of cationic species with alkyl dicarboxylic acid compounds have been studied. The cationic compounds used in this study were tertiary amine-type *N*-methyl-*N*-(2,3-dioxypentyl)hexadecylamine (C16amine) and quaternary ammonium-type *N,N*-dimethyl-*N*-(2,3-dioxypentyl)hexadecylammonium chloride (C16Q). The alkyl dicarboxylic acid compounds used were HOOC(CH₂)₁₀COOH (C12H) and its sodium salt (C12Na). Three aqueous mixtures were examined in this study: (System I) C16amine + C12H, (System II) C16Q + C12Na, and (System III) C16Q + C12H. The solution pH was set at 12 for System III. The combination of ¹H-NMR and mass spectroscopy data has suggested that a stoichiometric complex is formed in the aqueous solutions at a mole fraction of C12H (or C12Na) = 0.33. Here, the C12H (or C12Na) molecule added to the system bridges two cationic molecules, like a spacer of gemini surfactants. In fact, the static surface tensiometry has demonstrated that the stoichiometric complex behaves as gemini-like amphiphiles in aqueous solutions. Our current study offers a possible way for easily preparing gemini surfactant systems.

Key words: gemini surfactant, catanionic surfactant, alkylamine, alkyl dicarboxylic acid, surfactant mixture

1 INTRODUCTION

Gemini surfactants are dimers of monomeric surfactants linked with a spacer at the level of hydrophilic headgroups. The properties of aqueous solutions of gemini surfactants from the physicochemical aspect have been reviewed in earlier literature¹⁻³. One of the key properties of gemini surfactants is their remarkably low critical micelle concentration (cmc) in aqueous media, which enables us to reduce total consumption of surfactants in water-borne chemical products. Gemini surfactants are, therefore, called "environmentally friendly green materials". Unfortunately, however, the synthesis and subsequent purification process of gemini surfactants is generally more complicated than that of conventional monomeric surfactants. This causes difficulties in developing novel gemini surfactants as well as in finding applications for them in the formulation of high-performance chemical products in the fields of cosmetics, personal care, and in medical applications. Although we have recently developed a wide variety of oleic acid-based gemini surfactants through relatively simple chemical reactions to achieve cost-effective syntheses⁴⁻⁷, it is still necessary to find an effective way to formulate gemini surfactants.

On the basis of this background, we propose an alternative method for the easy preparation of new gemini surfac-

tant systems by using aqueous mixtures of a cationic compound (either an alkylamine or a quaternary ammonium-type cationic surfactant) with an alkyl dicarboxylic acid. The physicochemical properties of the aqueous mixtures of alkylamine with alkyl monocarboxylic acid have been studied from the standpoint of their phase behaviors⁸⁻¹⁰. The key conclusion in these studies is that a proton transfer from the acid to the amine results in the aqueous surfactant properties, i.e., we can see various surfactant-like phases such as hexagonal, cubic, and lamellar phases in their ternary phase diagrams with water. These phase behaviors are largely dependent not only on the chain length of the acid and the amine but also on the balance of the chain lengths⁸⁻¹⁰. A number of studies have focused on the aqueous properties of cationic-anionic mixed surfactants¹¹. Such mixtures are sometimes called "catanionic surfactants".

The use of alkyl dicarboxylic acid instead of alkyl monocarboxylic acid may provide an opportunity to develop gemini-like surfactants in aqueous media as a result of mixing with a cationic species. A similar concept has been reported previously¹²⁻¹⁴. For example, it has been suggested that an alkylamine compound with sugar moieties forms a stoichiometric complex with alkyl dicarboxylic acid when mixed at a molar ratio of 2:1 in aqueous solutions¹².

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Accepted June 15, 2011 (received for review May 24, 2011)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

The aqueous solution mixtures of an alkyl monocarboxylic acid and a bola-type alkyldiamine have also been studied, where the amine compound bridges two acid molecules, like a spacer of gemini surfactants¹³⁾. These studies are quite interesting but a physicochemical understanding of such aqueous mixtures is still not enough, particularly in the region of low concentrations. We believe that the dilute aqueous solution properties are important for characterizing the stoichiometric complex systems as gemini surfactants.

In this study, we have characterized the aqueous mixtures of cationic species with alkyl dicarboxylic acid. The aim of this study is to demonstrate whether the mixtures behave as gemini-like amphiphiles in their dilute aqueous solutions. The cationic compounds employed in this study were *N*-methyl-*N*-(2,3-dioxypropyl)hexadecylamine (C16amine) and *N,N*-dimethyl-*N*-(2,3-dioxypropyl)-hexadecylammonium chloride (C16Q). The chemical structures are shown in Fig. 1. We expect that the glycerin unit covalently bound to the amine or quaternary ammonium head-group results in increased water solubility (compared with glycerin-unmodified compounds, such as *N,N*-dimethylhexadecylamine or hexadecyltrimethylammonium chloride) and hence allows highly hydrophilic stoichiometric complex systems to form, which do not precipitate even at an equivalent molar mixing with alkyl dicarboxylic acid. This expectation is supported by the experimental results in which the glycerin-modified cationic surfactant (C16Q) narrows the precipitation region in its three-phase diagram with an anionic surfactant and water and the catanionic surfactants form vesicular assemblies which are well-dispersed in aqueous media¹⁵⁾. The alkyl dicarboxylic acid compounds reported herein were bola-type, as shown in Fig. 1, and the number of methylene units was fixed at ten as a typical example. Hereafter we call the alkyl dicarboxylic acid compounds "C12H" and "C12Na".

2 EXPERIMENTAL PROCEDURES

2.1 Materials

C12H was purchased from Wako. C12Na was obtained through the ion exchange of the C12H sample. For the

synthesis of C16amine, we used the following chemicals: 3-methylamino-1,2-propanediol (Wako), 1-bromohexadecane (Tokyo Chemical Industry, TCI), sodium hydroxide (Wako), and methanol (Wako). These chemicals were of analytical grade and used without further purification. The cationic surfactant (C16Q) was synthesized according to the procedure mentioned in our previous paper¹⁵⁾. The water used in this study was deionized with a Barnstead NANO Pure Diamond UV system and filtered with a Millipore membrane filter (0.22 µm pore size).

2.2 Synthesis and molecular characterization of C16amine

C16amine was synthesized according to the reaction scheme shown in Fig. 1. 3-methylamino-1,2-propanediol (10.5 g, 0.1 mol) was mixed with 1-bromohexadecane (10.1 g, 0.033 mol) in methanol, and then the mixture was reacted for 24 h at 80°C under magnetic stirring. After evaporation of the reaction solvent, sodium hydroxide (4 g, 0.1 mol) was added to the residue in the presence of water. The aqueous mixture was refluxed for 12 h at ca. 90°C, and then cooled to room temperature. Hot-filtration was performed five times to rinse the crude product, then the product was dried under a reduced pressure. The yield was 89%. The final product was characterized with analytical techniques which included ¹H-NMR (JEOL-ECP 500 MHz) and ESI-MS (FT-ICR MS Varian 910-MS) spectroscopies, and elemental analysis (PerkinElmer 2400 Series II CHNS/O Analyzer). The characterization data are shown below.

¹H-NMR (CDCl₃): δ 0.87-0.89 (t, 3H, CH₃), 1.26 (s, 28H, 14CH₂), 1.43-1.48 (q, 2H, CH₂CH₂N), 2.27-2.59 (m, 7H, CH₃NCH₂CH(OH)CH₂OH), 3.48-3.51 (q, 1H, NCH₂CH(OH)CH₂OH), and 3.73-3.79 ppm (m, 2H, CH(OH)CH₂OH).

ESI-MS: [M + H]⁺ 330.35 (Calc. 330.41).

Elemental analysis: Found (Calc.) C: 73.16 (72.89), H: 13.28 (13.15), and N: 4.20 (4.25).

2.3 Physicochemical analysis

Static surface tension measurements were performed by using a Krüss K100C Wilhelmy auto surface tensiometer with a platinum plate. Continuous measurements were carried out until a change in the surface tension was

Fig. 1 Chemical structures of C16amine, C16Q, C12H, and C12Na. The synthetic route of C16amine is also shown here.

reduced to less than 0.01 mN m^{-1} per 90 s.

Unless otherwise stated, all measurements reported herein were performed at 25°C (or at a room temperature of ca. 25°C).

3 RESULTS AND DISCUSSION

Three aqueous mixtures were examined in this study: (System I) C16amine + C12H, (System II) C16Q + C12Na, and (System III) C16Q + C12H. The solution pH was set at 12 for System III by using an aqueous solution of 100 mmol dm^{-3} NaOH. No additional electrolytes were added to the three systems. Under these experimental conditions, neither precipitation nor phase separation was seen for Systems II and III, at least up to the total concentration of the two components of 100 mmol dm^{-3} ($0 \leq X_c \leq 1$, where X_c is the mole fraction of C12H or C12Na).

Figure 2 shows the visual appearance of the C16amine and C12H mixtures in aqueous solutions (System I). The total concentration of the two components was fixed at 10 mmol dm^{-3} and the mole fraction of the components was varied. The solubility of C16amine in water is less than 10 mmol dm^{-3} at 25°C and hence a cloudy solution with some suspended aggregates was obtained for the single C16amine system ($X_c = 0$). An increased mole fraction of C12H resulted in the disappearance of the suspended aggregates but the sample solution prepared at $X_c = 0.1$ was still cloudy. Interestingly, the sample solutions became transparent in the range of $0.2 \leq X_c \leq 0.33$, without any precipitants. In particular, the sample solution prepared at $X_c = 0.33$ exhibited the most significant foaming capability among the sample solutions obtained in System I. This indicates that $X_c = 0.33$ is a key mole fraction for studying the aqueous C16amine and C12H mixtures. It is obvious that this mole fraction corresponds to the optimum charge neutralization point if the stoichiometric complex formation occurs between the two components. The poor solubility of C12H in water resulted in precipitation in the range of $0.5 \leq X_c \leq 1$.

In order to confirm the complex formation between the cationic species and the alkyl dicarboxylic acid compounds, nano-ESI-MS and $^1\text{H-NMR}$ spectroscopy measurements were performed at a fixed $X_c = 0.33$. Similar ESI-MS analyses have been reported by Blanzat *et al.*, where the stoichiometric complex formation was suggested to have occurred for the mixture of alkylamine and alkyl dicarboxylic acid compounds¹². Nano-ESI-MS spectra are shown in Fig. 3 for the C16amine + C12H mixture (System I) and the C16Q + C12Na mixture (System II). The m/z values calculated for [the stoichiometric complex + H]⁺ are 889.89 and 917.92. In this figure, it is possible to see the corresponding peaks at 889.90 m/z for System I and at 917.76 m/z for System II, which are quite consistent with the calculated

Fig. 2 Visual appearance of aqueous mixtures of C16amine and C12H (System I). The total concentration of the two components is fixed at 10 mmol dm^{-3} and the mole fraction of C12H is varied from 0 to 1. C16amine and C12H were added to the pure water in the sample vials, and then the samples were mixed under ultrasonic irradiation for 2 h and finally equilibrated in a water-shaker bath for 12 h. These pictures were taken after gentle hand-shaking.

m/z values. This is good evidence that gemini-like stoichiometric complex molecules are present in the bulk solution, as expected. We note that it was not possible to perform nano-ESI-MS spectroscopy measurements for System III because of its high electrolyte concentration and its highly alkaline nature.

Further evidence regarding the formation of the gemini-like complex was suggested on the basis of $^1\text{H-NMR}$ data. These $^1\text{H-NMR}$ measurements were performed in D_2O in the presence of sodium (3-trimethylsilyl)-1-propanesulfonate as an NMR standard reagent. In the case of System III, NaOD was used for the pH adjustment. The poor solubility of C16amine ($X_c = 0$) and C12H ($X_c = 1$) in water caused difficulties in measuring their $^1\text{H-NMR}$ spectra (System I), so only Systems II and III were examined here. In these systems, we could measure their $^1\text{H-NMR}$ spectra at $X_c = 0$ and 1 and hence see any shifts of characteristic signals when C16Q was mixed with C12Na or C12H ($X_c = 0.33$). The chemical shifts of the characteristic signals are summarized in Table 1 for Systems II and III. For both systems the mixing resulted in changes in the chemical shift: one can see the decreased chemical shift (i.e., upfield shift) of the characteristic signals assigned as A and B protons (originated from C12Na or C12H) and the slightly increased chemical shift (i.e., downfield shift) of the characteristic signals assigned as d, e, and f protons (originated from C16Q). This suggests a change in the electrostatic field around the C16Q and C12H (or C12Na) molecules to occur as a result of their mixing, which supports our hypothesis that the stoichiometric complex is present in the aqueous solutions.

Figure 4 shows the static surface tension data obtained for the three systems as a function of the total concentration of the cationic and anionic species at a fixed $X_c = 0.33$. Also shown here are the surface tension data of aqueous C16Q solutions measured in pure water and at pH 12. For

Fig. 3 Nano-ESI-MS spectra of aqueous mixtures of (a) C16amine + C12H (System I) and (b) C16Q + C12Na (System II).

all the mixtures in regions of low concentrations, the surface tension decreases sharply with increasing concentration and attains a break point. Then the surface tension becomes constant even when the total concentration is increased further at the constant X_c . This is a general trend we can see in aqueous surfactants systems and the concentration corresponding to the break point is assumed to be the cmc of each mixture. Physicochemical parameters estimated on the basis of the static surface tension data are listed in **Table 2**: cmc, surface tension measured at each cmc (γ_{cmc}), surface excess concentration estimated at the cmc (Γ_{cmc}), occupied area per stoichiometric complex molecule adsorbed at the air/aqueous solution interface (A_{cmc}), and pC_{20} ($= -\log C_{20}$, where the C_{20} value is defined to be the concentration where a decrease in the surface tension of 20 mN m^{-1} from pure water is recorded, and therefore, this value is indicative of an efficiency in lowering the

surface tension)¹⁶⁾. Here the Γ_{cmc} and A_{cmc} values are calculated according to the following equations¹⁶⁾:

$$\Gamma_{cmc} = -\frac{1}{2.303iRT} \left(\frac{d\gamma}{d \log C} \right)_T \quad (1)$$

$$A_{cmc} = \frac{1}{N_A \Gamma_{cmc}} \quad (2)$$

where i is the number of adsorption species, T is the absolute temperature, N_A is the Avogadro constant, and R is the gas constant. It is not easy to find accurate i values for cationic mixtures (especially for Systems I and II), so the Γ_{cmc} and A_{cmc} values for these systems are not shown in **Table 2**. We also note here that adjusting the pH to 12 requires the addition of a small volume of NaOH aqueous solution into the system, and this necessarily causes an increased background electrolyte concentration. At this pH the background electrolyte concentration is estimated to be much higher than the resultant cmc(s), and therefore,

Table 1 ^1H -NMR chemical shifts measured for systems II and III.

	C16Q (ppm)	C12Na (ppm)	System II (ppm)	$\Delta\delta_{\text{II}}$ (ppm)	C16Q ^{*)} (ppm)	C12H ^{*)} (ppm)	System III ^{*)} (ppm)	$\Delta\delta_{\text{III}}$ ^{*)} (ppm)
a	0.81–0.84		0.81–0.84	≈ 0	0.81–0.83		0.81–0.83	≈ 0
b	1.25, 1.31		1.24, 1.31	≈ 0	1.24, 1.31		1.26, 1.31	≈ 0
c	1.72		1.72	≈ 0	1.72		1.72	≈ 0
d	3.32–3.57		3.34–3.58	+0.01	3.14–3.54		3.16–3.55	+0.02
e	3.14, 3.15		3.15, 3.16	+0.01	3.10, 3.11		3.11, 3.13	+0.02
f	4.19–4.22		4.21–4.24	+0.02	4.03–4.08		4.06–4.10	+0.03
A		2.13–2.17	2.07–2.09	–0.07		2.14–2.17	2.09–2.11	–0.06
B		1.51–1.54	1.49–1.51	–0.03		1.51–1.53	1.48–1.51	–0.03
C		1.27	1.27	≈ 0		1.27	1.26	–0.01

$\text{CH}_3^-(\text{CH}_2)_{13}-\text{CH}_2-\text{CH}_2-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2-\text{CHOH}-\text{CH}_2\text{OH}) \text{ Cl}^-$
 a b c d e d f d

$\text{HOOC}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_2-\text{COOH}$ (or 2Na^+)
 A B C B A

^{*)} Measured at pH 12.

Fig. 4 Static surface tension of aqueous mixtures of (a) C16amine + C12H (System I) and C16Q + C12Na (System II) and (b) C16Q + C12H at pH 12 (System III) as a function of the total concentration. The mole fraction of C12H (or C12Na) is fixed at 0.33. The surface tension data measured for C16Q are also shown in each figure.

we assume $i = 1$ when calculating the Γ_{cmc} and A_{cmc} values (whereas, the single C16Q system gives $i = 2$ because of its 1:1-type ionic surfactant nature)¹⁶⁾. Clearly, the gemini-like stoichiometric complex formation results in a lower cmc and a lower γ_{cmc} when compared with the monomeric surfactant (C16Q) examined under corresponding experimental conditions. In addition, the A_{cmc} values estimated for the stoichiometric complex (System III) are less than the $2 \times A_{\text{cmc}}$ values estimated for C16Q at pH 12, suggesting the closer packing of the complex molecules (per a hydrophobic “tail” chain) adsorbed at the air/aqueous solution interface^{§)}. These results confirm the excellent surface activity of the gemini-like stoichiometric complex^{§ §)}. Two reasons must be considered for this surface activity: one is the

^{§)} It was found that a decreased pH from 12 results in an increased surface tension: at a given total concentration of 1 mmol dm⁻³ (C16Q + C12H, at $X_c = 0.33$) in the presence of 100 mmol dm⁻³ NaCl as a background electrolyte, the surface tension is measured as 33–34 mN m⁻¹ at pH 10–12, and as 43–44 mN m⁻¹ at pH 6–8, respectively. It is possible to assume, therefore, that the stoichiometric complex formation in System III preferentially occurs under the alkaline condition, although the exact equilibrium constant between the stoichiometric complex and the free “monomers” is not known.

^{§ §)} We also performed surface tension measurements in System II as a function of X_c . The resultant surface tension data gave pC_{20} values of 4.6–4.7 in the range of $0.1 \leq X_c \leq 0.67$. These pC_{20} values are larger than those calculated for the single C16Q system (see Table 2). This indicates that the mixing of the two components (C16Q + C12Na) in the range of $0.1 \leq X_c \leq 0.67$, even not at $X_c = 0.33$, results in the complex formation that induces the surface tension lowering. No significant difference in the surface tension lowering capability (pC_{20}) was observed, at least in the range of $0.1 \leq X_c \leq 0.67$.

Table 2 Summary of static surface tension data.

	cmc (mmol dm ⁻³)	γ_{cmc} (mN m ⁻¹)	Γ_{cmc} (μ mol m ⁻²)	A_{cmc} (nm ²)	<i>i</i>	pC ₂₀
C16Q	0.61	40.6	0.92	1.8	2	4.3
System II (C16Q + C12Na)	0.15	36.4				4.7
System I (C16amine + C12H)	0.051	30.6				5.7
C16Q (pH 12)	0.18	36.5	3.2	0.53	1	4.6
System III (C16Q + C12H, pH 12)	0.0081	29.2	2.9	0.57	1	6.3

“gemini effect” (i.e., the surface activity is generally greater for gemini surfactants than for corresponding monomeric surfactants) and the other is the charge neutralization in our current case.

4 CONCLUSIONS

The properties of the aqueous mixtures of a cationic compound (either alkylamine-type C16amine or quaternary ammonium-type C16Q) with an alkyl dicarboxylic acid compound (either C12H or C12Na) have been studied. The alkyl dicarboxylic acid molecules added to the systems play the role of a spacer connecting two cationic molecules. This yields a gemini-like stoichiometric complex in aqueous solutions, which is supported by nano-ESI-MS and ¹H-NMR spectroscopies. The static surface tensiometry has demonstrated the greater surface activity of the gemini-like stoichiometric complex when compared with the monomeric surfactant (C16Q). In particular, it is interesting to note that the two intrinsically surface inactive components (C16amine and C12H) behave as gemini-like amphiphiles as a result of their mixing in aqueous solutions. The mixing of the cationic species with the alkyl dicarboxylic acid compounds is, therefore, a possible way of preparing new gemini surfactant systems. This is a fruitful finding in the field of surfactant chemistry, because the synthesis and purification of gemini surfactants having a covalently bound spacer is generally a hard work.

ACKNOWLEDGEMENTS

This work was financially supported by MEXT (The Ministry of Education, Culture, Sports, Science and Technology in Japan) Grant-in-Aid for Young Scientists (B) 21750199.

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