Alkylaldehyde-bisulfite adducts as cleavable surfactants

Yoshihiro Itoh,* Junpei Horiuchi, Ken Takahashi

Department of Functional Polymer Science, Faculty of Textile Science and Technology,

Shinshu University

3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

yositoh@giptc.shinshu-u.ac.jp

* Corresponding author. Tel.: +81 268 21 5489; fax: +81 268 21 5489.

E-mail address: yositoh@giptc.shinshu-u.ac.jp (Y. Itoh)

Abstract

Alkylaldehyde-bisulfite adducts with octyl, decyl, and dodecyl groups (C_nS: n=8,10,12) were synthesized and the surface-active properties of the water-soluble compounds were compared. Exchange of the counter anions of $C_{10}S$ and $C_{12}S$ from sodium to tetramethylammonium solubilized them in water. The latter ammonium salt ($C_{12}S$-QA) had surface activities as good as a classical surfactant, sodium dodecylsulfate, and dissociated promptly in weakly basic solution at room temperature to be a non-surfactant. It was also found that $C_{12}S$-QA solubilized a hydrophobic substrate (solid), *N,N*-dimethyl-3-nitroaniline, in water and then separated it as a precipitate after alkali treatment.

Keywords: Cleavable Surfactant; Anionic Surfactant; Hydrolysis; Aldehyde-bisulfite Adduct

1. Introduction

Recently much attention has been paid to chemically cleavable surfactants because of not only environmental concerns but also potential applications in industrial fields [1-4]. Most of the surfactants reported so far usually contain a hydrolysable bond between the hydrophilic head group and the hydrophobic tail. For practical reasons, such cleavable surfactants have a number of basic requirements: i.e., simple synthesis, surface activities comparable to those of classical surfactants, high stability before and during their use, high and controlled cleavability under mild condition after their use, etc. In addition, environmental safety and new functionality of the cleaved products will be favored. Until now a few types of surfactants which would satisfy the above requirements have been reported: betaine ester (cationic) [5-7], ortho ester (nonionic, cationic, etc.) [8,9], and acyclic acetal (anionic) [10]. These surfactants decompose promptly at room temperature in weakly acidic or basic solution.

In the present paper, we report the surface-active and dissociative properties of water-soluble alkylaldehyde-bisulfite adducts (C_nS) as a novel type of cleavable surfactants. Aldehyde-bisulfite derivatives are frequently used for protection of aldehydes in the field of synthetic chemistry due to their stabilities in solid state and their ease of preparation and deprotection. However, their use as surfactants has been limited [11] and no study on the cleavability has been reported. It should be further noted that their dissociated products, alkylaldehyde and bisulfite (or its decomposition products), are frequently used as ingredients of perfumes and deoxidants, respectively, and thus will be nontoxic.

2. Experimental

2.1. Materials

Sodium dodecylsulfate (SDS) was purchased from Tokyo Kasei (reagent for ion-pair chromatography) and used as received.

Sodium and ammonium alkylaldehyde-bisulfites (C_nS-S and C_nS-A) were prepared by reacting the corresponding alkylaldehyde with sodium bisulfite and ammonium bisulfite, respectively, in aqueous ethanol at room temperature. The precipitates were washed with cold water and acetone repeatedly and then dried. A water-soluble product, C_8S-S, was

further purified by precipitation from water to acetone: yield, 67 %; ^{1}H NMR (D$_2$O) δ 0.82 (t, 3H), 1.24-1.93 (m, 12H), 4.33 (dd, 1H).

Tetramethylammonium decylaldehyde-bisulfite (C$_{10}$S-QA) and tetramethylammonium dodecylaldehyde-bisulfite (C$_{12}$S-QA) were prepared by an ion exchange method: An Amberlite IR-122NA resin in the H$^+$ form was charged with tetramethylammonium ion (QA) by using a tetramethylammonium chloride solution and then washed with water. The suspended solutions of C$_{10}$S-S and C$_{12}$S-S in water were stirred with the resin in the QA form (more than 3-fold ion equivalent). The solutions were further passed through a column of the resin (more than 2.5-fold ion equivalent) and the eluted solutions were lyophilized.

C$_{10}$S-QA : ^{1}H NMR (D$_2$O) δ 0.80 (t, 3H), 1.22-1.93 (m, 16H), 3.28 (s, 12H), 4.30 (dd, 1H).

C$_{12}$S-QA : ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 3H), 1.22-1.96 (m, 20H), 3.32 (s, 12H), 4.20 (dd, 1H).

Chemical structures and abbreviations of adducts are shown in Fig. 1.

2.2. Measurements

^{1}H NMR and Absorption spectra were recorded on a Bruker AVANCE400 spectrometer and a HITACHI U-3210 spectrophotometer, respectively.

Critical micelle concentrations (CMC) of surfactants were determined by measuring the conductivity of the aqueous solution as a function of surfactant concentration with a HORIBA DS-14 conductivity meter at 25 ^{o}C. The CMC values were determined from the inflection point of the conductivity vs. concentration plot.

Krafft points were determined by the naked eye for 1 wt% of aqueous surfactant solutions in a thermostat.

Foaming powers were determined by measuring the foam volume of the aqueous surfactant solution according to the literature with some modification [12]: A 7 ml of 0.1 wt% surfactant solution was placed in a 50 ml of graduated tube, shaken vigorously 100 times, and then allowed to stand for 3 min at 25 ^{o}C. The volume of the resulting foam was measured.

Solubilizing powers were determined by measuring the solubility of Oil Orange SS (Tokyo Kasei) in the surfactant solution according to the literature with some modification [13]: A mixture of 50 mg Oil Orange SS (solid) and 0.25 wt% surfactant solution (50 ml)

was placed in a 50 ml of graduated tube, shaken vigorously 100 times, and then allowed to stand for 3 h at 25 $^{\circ}$C. The residual solid was removed by filtration with a membrane filter (ADVANTEC, cellulose acetate, pore size 0.45 μm), and the concentration of Oil Orange SS in the filtrate was determined spectrophotometrically.

Dispersing powers were determined as follows: A mixture of 70 mg carbon black (Sigma-Aldrich) and 0.25 wt% surfactant solution (50 ml) was placed in a 50 ml of graduated tube, shaken vigorously 100 times, and then allowed to stand for 3 h at 25 $^{\circ}$C. The supernatant fraction of the solution was diluted to one fiftieth and then the absorption efficiency (%) at 500 nm in a 1-cm cuvette was measured.

In the similar manner, surface-active properties of C_{12}S-QA after the treatment in 10 mM of aqueous NaOH for 20 min at 25 $^{\circ}$C were examined. For reference, the properties of SDS were also examined under the same conditions.

The conversion yields, or dissociation degrees, of C_{12}S-QA were determined by HPLC. Test tubes containing a 4 ml of buffer solution (50 mM, pH 6-11) were allowed to stand for 30 min at 25 $^{\circ}$C: NaH_2PO_4-NaOH (pH 6-7), sodium borate-NaOH (pH 8-10), Na_2HPO_4 (pH 11) were used as buffers. The decomposition was started by adding a 1 ml of C_{12}S-QA (40 mM) in H_2O to each test tube and the solution was stirred for 10 min. The reaction was terminated by adding a drop of concentrated aqueous HCl. The conversion yields of C_{12}S-QA were determined with a Jasco liquid chromatography system equipped with a refractive-index detector (830-RI) and a reverse-phase C18 column (SHISEIDO CAPCELL PAK C18 MG). A mixture of methanol-0.2 M aqueous sodium perchlorate (80/20) was employed as an eluent. 2-Methylnaphthalene was used as an internal standard.

The dissociation of C_{12}S-QA was also followed by measuring the turbidity (transmittance (%) at 500 nm in a 1-cm cuvette) for the 10 mM of C_{12}S-QA in 50 mM buffer solution at regular time intervals at 25 $^{\circ}$C. The stabilities of C_{12}S-QA in aqueous HCl solutions (pH 3.4 and pH 1.3) were checked by the same method.

Solubilization and separation of a solid substrate, *N,N*-dimethyl-3-nitroaniline (DMNA; Tokyo Kasei), in aqueous SDS and C_{12}S-QA solutions were carried out as follow: A mixture of 20 mg DMNA and 5 ml of aqueous surfactant solutions ranging in concentration from 20 mM to 100 mM was sonicated in a bath (SHARP UT-105, 35 kHz) for 20 min at 25 $^{\circ}$C. The residual solid was separated by centrifugation (2000 rpm, 1 min) and the concentration of DMNA in the supernatant was determined spectrophotometrically. To a 3 ml of the supernatant, a 0.1 ml of aqueous NaOH (equivalent molar) was added and stirred for 30 min. The resulting precipitate was removed with the membrane filter (pore

size, 0.45 μm), and the concentration of DMNA in the filtrate was determined spectrophotometrically.

3. Results and discussion

3.1. Solubilities of C_nS

Solubilities of a series of adducts in water are summarized in Table 1. Sodium octylaldehyde-bisulfite (C_8S-S) was soluble in water at ambient temperature, while other sodium and ammonium salts were insoluble or partially soluble not only in water but also in most solvents. The Krafft temperature of $C_{12}S$-S in water was estimated to be about 65 ^oC. However, exchange of the counter cations of $C_{10}S$ and $C_{12}S$ from sodium to tetramethylammonium solubilized them moderately in water (>3 wt%) at room temperature. The Krafft temperature of $C_{12}S$-QA was estimated to be ca. 5 ^oC.

3.2. Surface-active properties of C_nS

In Table 2, several surface-active properties of water-soluble adducts, C_8S-S, $C_{10}S$-QA, and $C_{12}S$-QA, are compared with those of a classical surfactant, sodium dodecylsulfate (SDS). $C_{12}S$-QA had a somewhat larger CMC value and somewhat smaller foaming and dispersing powers than SDS, whereas the solubilizing power of the former was slightly larger than that of the latter. The inconsistency is probably because these parameters depend on many factors such as chemical structures of surfactants and counter ions, microstructures of micelles, and surfactant concentrations. It is, however, broadly true that the surface activities of $C_{12}S$-QA are almost comparable to those of SDS. The activities of C_nS naturally decreased with the decrease in the alkyl-chain length.

3.3. Dissociation of $C_{12}S$-QA in weakly basic solution

All water-soluble adducts dissociated in weakly basic solution at room temperature. Fig. 2 shows the time-course of the transmittance (%) at 500 nm for aqueous buffer solutions of $C_{12}S$-QA. Above pH 8 the solution became turbid within a few minutes, while little apparent change was observed below pH 6. These results indicate that the

dissociation of $C_{12}S$-QA and its conversion to a non-surfactant occur promptly in weakly basic solution. In fact, the conversion yield of $C_{12}S$-QA after the reaction for 10 min at 25 °C increased with pH in alkali region (pH >7), going up to almost 100 % at pH 11 (Fig. 3).

It has been shown that the important equilibriums for aldehydes (RCHO) and aldehyde-bisulfite adducts (RCH(OH)SO$_3^-$) in aqueous solution in the range of pH 1 to 10 involve dissociation of RCH(OH)SO$_3^-$ to RCHO and bisulfite anion (HSO$_3^-$) (eq. 1), hydration of RCHO (eq. 2), and two-step acid dissociations of sulfuric acid (H$_2$SO$_3$: eqs. 3 and 4) [15]:

$$\text{RCH(OH)SO}_3^- \underset{}{\overset{K_d}{\rightleftharpoons}} \text{RCHO} + \text{HSO}_3^- \tag{1}$$

$$\text{RCHO} + \text{H}_2\text{O} \underset{}{\overset{K_h}{\rightleftharpoons}} \text{RCH(OH)}_2 \tag{2}$$

$$\text{H}_2\text{SO}_3 \underset{}{\overset{K_{a1}}{\rightleftharpoons}} \text{HSO}_3^- + \text{H}^+ \tag{3}$$

$$\text{HSO}_3^- \underset{}{\overset{K_{a2}}{\rightleftharpoons}} \text{SO}_3^{2-} + \text{H}^+ \tag{4}$$
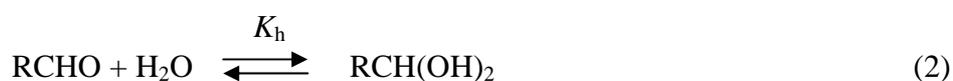
where K_d, K_h, and K_a (K_{a1} and K_{a2}) are dissociation constant, hydration constant and acid-dissociation constant, respectively. The K_d values for water-soluble alkylaldehyde-bisulfite adducts with a short alkyl chain in aqueous solution are estimated to be very small ($< 10^{-4}$) [15], implying the negligible dissociation of $C_{12}S$-QA. It is known that formaldehyde and acetaldehyde are relatively hydrated in aqueous solution (pK_h (-log K_h) = -3.3 and -0.1, respectively) and that alkylaldehydes with a longer alkyl chain have a decreased tendency of hydration (pK_h = 0.3 for butyraldehyde) [16]. Then the influence of hydration of dodecylaldehyde on the dissociation of $C_{12}S$-QA seems to be minor. The pK_{a1} and pK_{a2} values for H$_2$SO$_3$, are reported to be 1.85 and 7.2, respectively [17]. Therefore, the efficient dissociation of $C_{12}S$-QA in weakly basic solution (pH >7) will occur mainly via the acid dissociation of HSO$_3^-$ (eq. 4).

In Table 3, the surface-active properties of $C_{12}S$-QA after the alkali treatment, i.e., after the complete dissociation in 10 mM of aqueous NaOH, are compared with those of SDS. It is apparent that $C_{12}S$-QA loses its surface activities almost completely after the dissociation and SDS does not.

3.4. Stability of C_{12}S-QA in acidic solution

As for practical uses of the present type of adducts as surfactants, it is necessary to investigate their stability in acidic solution. The dissociation degrees of C_{12}S-QA in aqueous HCl solutions at pH 3.4 and 1.3 were followed by measuring the solution turbidity in the same manner as described above (Fig. 4). The pH 1.3 solution at room temperature became turbid slightly in a few hours probably because the dissociation is enhanced due to the protonation of HSO_3^- (eq. 3). The slight increase in the transmittance in the longer time region may be partially due to some aggregation of water-insoluble products. In contrast, the pH 3.4 solution exhibited only a negligibly small scattering after several hours, indicating the higher stability of C_{12}S-QA in weakly acidic solution. In fact, the solution could be stored for months without any precipitation in a refrigerator.

3.5. Solubilization and separation of solid substrate

To survey the utility of C_{12}S-QA as an extraction aid, the solubilization and separation of a hydrophobic substrate, *N,N*-Dimethyl-3-nitroaniline (DMNA), from its suspended solution was examined. Fig. 5 shows the concentration of DMNA solubilized in different concentrations of aqueous C_{12}S-QA and SDS solutions before and after addition of equimolar amounts of NaOH. As expected, the solubilities of DMNA in both solutions were almost the same, which increased linearly with the surfactant concentration. The addition of NaOH into the C_{12}S-QA solution caused precipitation of DMNA immediately. DMNA was recovered quantitatively as a solid from the C_{12}S-QA solutions of up to 40 mM, but the separation of DMNA from the more concentrated solutions was incomplete. Since the latter solutions remained surface activity (i.e., foaming), mutual aggregation of DMNA, dodecylaldehyde (dissociated product), and C_{12}S-QA may retard the C_{12}S-QA dissociation and the DMNA separation. In contrast, no apparent change was observed for the SDS solution: no precipitation of DMNA occurred. Thus, it can be safely said that C_{12}S-QA is used as an efficient extraction aid.

4. Conclusion

A water-soluble dodecylaldehyde-bisulfite adduct, $C_{12}S$-QA, is stable in weakly acidic solution, but the addition of alkali dissociates it promptly to be non-surface-active components. Therefore, it works as a novel type of alkali-cleavable surfactant. In addition, $C_{12}S$-QA solubilizes a hydrophobic substrate and separates it as a solid almost quantitatively after alkali treatment, though under limited conditions. These results imply many potential applications of this type of surfactants in separation technology.

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Table 1

Solubilities of C_nS in water at room temperature[a]

Surfactant	Alkyl Chain (C_n)		
	C_8	C_{10}	C_{12}
C_nS-S	◯	✕	✕
C_nS-A	✕	△	✕
C_nS-QA	—[b]	◯	◯

[a] ◯, soluble; △, partially soluble; ✕, insoluble.

[b] Not prepared.

Table 2

Surface-active properties of water-soluble C_nS in water

Surfactant	CMC[a] (mM)	Foaming[b] (ml)	Dispersing[c] (%)	Solubilizing[d] (mg/l)
C_8S-S	—	0	22	0
$C_{10}S$-QA	18	6	38	1.1
$C_{12}S$-QA	11	15	54	4.3
SDS	8 (8)[e]	39	78	3.2

[a] By conductivity method.

[b] Foam volume of shaked solution; [surfactant]=0.1 wt%.

[c] % absorption of carbon black-dispersed solution; [surfactant]=0.25 wt%.

[d] Solubility of Oil Orange SS in aqueous solution; [surfactant]=0.25 wt%.

[e] Ref. 14.

Table 3

Surface-active properties of $C_{12}S$-QA before and after alkali treatment[a]

Surfactant	Alkali treatment[b]	Foaming[c]	Dispersing (%)	Solubilizing (mg/l)
$C_{12}S$-QA	before	◯	54	4.3
	after	✕	3	0.7
SDS	before	◯	78	3.2
	after	◯	65	2.8

[a] See Table 2.

[b] Treatment of $C_{12}S$-QA (0.25 wt%) in 10 mM NaOH for 20 min at 25 °C.

[c] Foaming, ◯; non-foaming, ✕.

Figure Captions

Fig. 1 Chemical structures of C_nS.

Fig. 2 Change in transmittance (%) for aqueous buffer solutions (pH 6-9) of $C_{12}S$-QA at 500 nm at 25°C: ◯, pH 9.0; △, pH 8.0; ▽, pH 7.0; □, pH 6.0; [$C_{12}S$-QA]=10 mM; [buffer]=50 mM.

Fig. 3 pH dependence of conversion for $C_{12}S$-QA in 40 mM buffer solution at 25°C: [$C_{12}S$-QA]=8 mM; reaction time, 10 min.

Fig. 4 Change in transmittance (%) at 500 nm for acidic $C_{12}S$-QA solutions at 25°C: ◯, pH 3.4; △, pH 1.3; [$C_{12}S$-QA]=10 mM.

Fig. 5 Solubilization and separation of DMNA in different concentrations of aqueous $C_{12}S$-QA and SDS solutions at 25 °C: open symbols, before addition of NaOH; closed symbols, after addition of equimolar NaOH; circle, $C_{12}S$-QA; triangle, SDS; y-axis indicates the concentration of DMNA solubilized in the solution.

Fig. 1

$$CH_3-(CH_2)_{n-2}-\overset{\overset{\textstyle OH}{|}}{CH}-SO_3^{\ominus} \ M^{\oplus}$$

$$(\ n = 8,10,12 \ )$$

$M^{\oplus}:$ $Na^{\oplus}$ **C_nS-S**

       $NH_4^{\oplus}$ **C_nS-A**

       $N(CH_3)_4^{\oplus}$ **C_nS-QA**

Fig. 2

Fig. 3

Fig. 4

Fig. 5