Preparation and Properties of Novel Double-Chain Nonionic Surfactants with Acid Decomposition Function

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Abstract: Novel double-chain nonionic surfactants with an acid decomposition function were prepared by acid-catalyzed condensation of chloroacetone with fatty alcohols (octyl, decyl, and dodecyl), followed by a Williamson reaction with polyethylene glycol without any expensive reagents and special equipment. These surfactants showed easy micelle formation compared to those of polyoxyethylene (n=9) dodecyl ether (C₁₂EO₉), and good foaming properties. The emulsion stability of these surfactants was almost the same as that of C₁₂EO₉. They decomposed completely after 30 min at pH 1. After 28 days they were more than 60% biodegradable and were almost the same as sodium dodecanoate.

Key words: chemocleavable surfactants, acetal type, nonionic surfactants, double-chain surfactants, biodegradation

1 INTRODUCTION

Surfactants are used in many applications, such as detergents, paints, toiletries and pharmaceuticals. The development of surfactants with excellent surface-active properties, additional functions, or good biodegradability has become desired. Therefore, chemocleavable surfactants, which decompose to give nonsurface-active species or other surfactants with different properties after fulfilling their original functions, have become the focus of great interest in the field of surfactant chemistry. In particular, many reports exist concerning the acid-decomposition types of amphiphilic compounds.¹⁻⁹

We have been investigating the preparation and properties of a series of acid- and alkali-cleavable ionic surfactants.¹⁰⁻²⁴ We have mentioned that the chemocleavable moiety (the noncyclic acetal group, 1,3-dioxolane ring or ester) has a positive effect on the various surface-active properties (especially the micelle formation and solubility in water)¹⁴⁻¹⁷,²⁰⁻²⁴ and clarified that they are decomposed easily under acid or alkali conditions. The biodegradability of some of these surfactants was very good.

On the other hand, few reports have been made on nonionic chemocleavable surfactants with two lipophilic groups. Generally, nonionic surfactants have better surface-active properties than ionic surfactants, and can be used with any other surfactants. In addition, it is known that double-chain surfactants have much smaller cmc and lower surface tension at cmc than the corresponding surfactants having one lipophilic part in the molecule.

Here, we report that novel double-chain nonionic chemocleavable surfactants with the noncyclic acetal group were prepared by acid-catalyzed condensation of chloroacetone with fatty alcohols, followed by a Williamson reaction with polyethylene glycol without any expensive reagents and special equipment (Scheme 1). We clarified their surface-active properties and the decomposition profiles in water upon exposure to acid, and compared them with those of single-chain conventional surfactants. We then evaluated their biodegradability because biodegradable surfactants are desired from an ecological standpoint.

Scheme 1 Preparation of Double-Chain Chemocleavable Surfactants.
2 EXPERIMENTAL

2.1 Materials and instruments

Fatty alcohols and chloroacetone were obtained commercially (Tokyo Chemical Industry Co., Inc.). The target chemocleavable double-chain surfactants were synthesized by acid-catalyzed condensation of chloroacetone with fatty alcohols and a subsequent Williamson reaction with polyethylene glycol.

Infrared spectra were recorded on a Shimadzu FT-IR DR-8100. 1H-NMR spectra were measured in CDCl₃ with a JEOL JNM-EX270 (270 MHz) spectrometer using TMS as the internal standard. Elemental analysis data were obtained on an EA1110 elemental analyzer (CE instruments).

2.2 Synthesis

2.2.1 Double-chain acetal compound (1a), as a typical procedure

In a round-bottomed flask fitted with a stirrer and a Dean-Stark receiver, octyl alcohol (3.91 g, 30 mmol), chloroacetone (0.93 g, 10 mmol) and p-toluenesulfonic acid (p-TsOH) (0.10 g, 0.5 mmol) were dissolved in hexane (40 mL). The solution was refluxed for 4 h. The hexane solution was washed twice with 5% NaHCO₃ aqueous solution (30 mL) and saturated NaCl aqueous solution (30 mL). The organic layer was dried with MgSO₄, and the solvent was evaporated. The oily product (1a) was obtained by Kugelrohr distillation of the residue (150°C/0.1 Torr); yield: 4.72 g (70%).

All other compounds 1 were also isolated by distillation with Kugelrohr equipment. The conditions of distillation were as follows: 1b, 180°C/0.1 Torr; 1c, 200°C/0.1 Torr.

2.2.2 Double-chain surfactant (2a), as a typical procedure

A mixture of 1a (3.34 g, 10 mmol), poly(ethylene glycol) (MW400) (12.0 g, 30 mmol), powdered sodium hydroxide (1.60 g, 40 mmol), tetrabutylammonium bisulfate and dioxane (20 mL) was stirred at 60°C for 5 h. After filtration and subsequent evaporation of the filtrate, 2a was isolated as a liquid by silica-gel column chromatography with a hexane:acetone (6:4, v/v) eluent; yield: 2.48 g (32%).

The chemical yields and analytical data of the products (1 and 2) are summarized in Table 1.

2.3 Physical properties

The cloud point (T_{cp}) of the surfactants was determined

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>1H-NMR(^b) (δ)</th>
<th>Anal. Found (Calc’d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>70(^c)</td>
<td>0.88 (t, 6H, J=6.6), 1.20-1.38 (m, 20H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.40-3.45 (m, 4H), 3.49 (s, 2H)</td>
<td>C, 68.13 (68.40), H, 11.72 (11.72)</td>
</tr>
<tr>
<td>1b</td>
<td>78(^c)</td>
<td>0.88 (t, 6H, J=6.6), 1.20-1.38 (m, 28H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.35-3.45 (m, 4H), 3.49 (s, 2H)</td>
<td>C, 70.64 (70.80), H, 12.11 (11.89)</td>
</tr>
<tr>
<td>1c</td>
<td>64(^c)</td>
<td>0.88 (t, 6H, J=6.6), 1.20-1.38 (m, 36H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.35-3.45 (m, 4H), 3.49 (s, 2H)</td>
<td>C, 72.52 (72.61), H, 12.40 (12.22)</td>
</tr>
<tr>
<td>2a</td>
<td>32(^d)</td>
<td>0.88 (t, 6H, J=6.8), 1.20-1.38 (m, 20H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.40-3.80 (m, 44H)</td>
<td>C, 62.33 (62.13), H, 10.74 (10.82)</td>
</tr>
<tr>
<td>2b</td>
<td>32(^d)</td>
<td>0.88 (t, 6H, J=6.8), 1.20-1.38 (m, 28H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.40-3.80 (m, 44H)</td>
<td>C, 64.03 (64.22), H, 11.01 (11.25)</td>
</tr>
<tr>
<td>2c</td>
<td>30(^d)</td>
<td>0.88 (t, 6H, J=6.8), 1.20-1.38 (m, 36H), 1.42 (s, 3H), 1.50-1.60 (m, 4H), 3.40-3.80 (m, 44H)</td>
<td>C, 65.50 (65.28), H, 11.24 (11.53)</td>
</tr>
</tbody>
</table>

\(^a\) IR spectra (neat): 1a, b, c: 2920, 1470 and 1120 cm\(^{-1}\); 2a, b, c: 3340, 2870, 1460 and 1100 cm\(^{-1}\).
\(^b\) In CDCl₃, TMS as the internal standard.
\(^c\) Based on chloroacetone.
\(^d\) Based on 1.
by the naked eye using a 1 wt% aqueous solution. The surface tension of a surfactant solution was measured with a Wilhelmy tensiometer (surface tensiometer CBVP-A3; Kyowa Kaimenkagaku Co., Ltd.; platinum plate) at 25°C. The foaming properties were evaluated by the semi-micro TK method with a 0.1 wt% aqueous solution at 25°C. The hydrodynamic diameter of surfactants was measured by dynamic light scattering (DLS) method (90° scattering angle) at 25°C. The DLS apparatus was model DLS-6000HL with a He-Ne ion laser manufactured by Otsuka Electronics Co., Ltd. The sample (0.02 M) was filtered through a 0.2 μm filter (Millipore). The decomposition properties of the surfactants (20 mM), by the addition of HCl, were measured using GLC analysis (Shimadzu, GC-14B; column: CBP1-W12-500; 2a: 120°C, 2b: 140°C, 2c: 160°C) of the fatty alcohol generated in hexane. The decomposition properties of the surfactants were evaluated by observing the separated water. The aqueous surfactant solution (0.25 wt%, 50 mL) and oil (soybean oil or liquid paraffin, 50 mL) were emulsified by a homogenizer (DIAX 900, Heidolph). After emulsification for 1 min (8000 rpm), the volume of the separated water was measured. The biodegradability was estimated by:

$$\text{Biodegradability} (\%) = \frac{\text{BOD}}{\text{TOD}} \times 100$$

where TOD means theoretical oxygen demand. The quantity of oxygen consumption was measured with a Coulrometer OM3100 (Ohkura Electronics Co.), which is a BOD meter for closed systems.

### 3 RESULTS AND DISCUSSION

The preparation of new types of nonionic double-chain chemocleavable surfactants (2a-c) with the noncyclic acetal group is shown in Scheme 1. The intermediates, acetal compounds (1), were synthesized by acid-catalyzed condensation of chloroacetone with fatty alcohols in the presence of p-TsOH in hexane. The compounds (1) were purified by Kugelrohr distillation. We usually use toluene as the solvent in acid-catalyzed condensation. The boiling point of chloroacetone (b.p. 119°C) was almost the same as that of toluene (b.p. 111°C). Although we used cyclohexane (b.p. 81°C) instead of toluene at first, the acetal compounds (1) were obtained in low yield. The target chemocleavable nonionic double-chain surfactants (2) were obtained by a general Williamson reaction of 1 with an excess of oligo (ethylene glycol). They were purified by silica gel column chromatography using acetone and hexane as the eluents.

Plots of surface tension vs. concentration for compounds 2a-c are shown in Fig. 1. The cloud point ($T_{cp}$), the critical micelle concentration (cmc), the ability to lower surface tension ($\gamma_{cmc}$), and foaming properties of these surfactants

![Fig. 1 Surface Tension-Concentration Plots of Aqueous Surfactant Solutions of Compounds 2 at 25°C: □, 2a; ○, 2b; △, 2c.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{cp}$</th>
<th>cmc</th>
<th>$\gamma_{cmc}$</th>
<th>Foam volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>C_{12}H_{25}O(CH_{2}CH_{2}O)H</td>
<td>80.0</td>
<td>0.066</td>
<td>30.0</td>
</tr>
<tr>
<td>2b</td>
<td>C_{10}H_{21}</td>
<td>69.5</td>
<td>0.20</td>
<td>29.0</td>
</tr>
<tr>
<td>2c</td>
<td>C_{8}H_{17}</td>
<td>77.0</td>
<td>1.3</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table 2 Surface-Active Properties of Double-Chain Surfactant (2) and the Reference Compound

- a) At 25°C.
- b) At 1 wt%.
- c) At 0.1 wt%.

are summarized in Table 2, along with reference data for polyoxyethylene (n = 9)dodecyl ether (C12EO9) measured under the same conditions.

All surfactants 2 prepared in this work were readily soluble in water, which is significant for practical use. The $T_{\text{m}}$ values of 2 decrease about 8°C with an increase of two methylene groups in the hydrophobic group. Although the $T_{\text{m}}$ values of compound 2c bearing dodecyl groups was 61.0°C, that of C12EO9 was 80.0°C because it has two hydrophobic groups.

The cmc values of a series of chemocleavable surfactants 2 decrease about one order of magnitude with an increase of two methylene groups in the hydrophobic group. The cmc of C12EO9 was about six times larger than that of 2c, which had the same alkyl chain length. The $\gamma_{\text{cmc}}$ values of 2b and 2c were below 30 mN/m, and were smaller than that of C12EO9. A clear correlation between $\gamma_{\text{cmc}}$ and the length of R is not observed. It had been expected that double-chain surfactants 2 would show much better micelle formation and the ability to lower surface tension than conventional surfactants in this work because double-chain surfactants are generally more tightly packed at the surface than single-chain surfactants. But actually, the cmc values of chemocleavable surfactants were smaller than that of C12EO9, but the $\gamma_{\text{cmc}}$ values of 2 were somewhat smaller than that of C12EO9. The presence of aggregates with a hydrodynamic diameter of about 20 nm (2c) was observed by DLS analysis. It can be assumed that the aggregates of 2c were not be vesicles or spherical micelles, but cylindrical micelles. Therefore, these surfactants 2 would be somewhat more tightly packed than single-chain surfactants. It is predicted that the bulkiness of the nine oxyethylene units in the hydrophilic group would make a negative contribution to the intermolecular hydrophobic interaction. In the range of this work, the series of chemocleavable surfactants 2 has better micelle formation and a little better ability to lower surface tension than conventional surfactants.

The foaming ability and foam stability of surfactants 2 were excellent. The foaming ability of surfactants 2 and C12EO9 was almost the same, but the foam stability of 2 was much better than that of C12EO9. Surfactants 2 had good foaming properties.

The emulsion stability of 2c is shown in Fig. 2. The emulsion stability of soy bean oil was better than that of liquid paraffin in both surfactants 2c and C12EO9. The emulsion stability of 2c was almost the same as that of C12EO9.

The decomposition properties of surfactants 2, by the addition of HCl, were measured using GLC. The decomposition profiles of 2a are summarized in Table 3, along with reference data for the previously reported soap type of cleavable surfactant 3a measured under the same conditions. Surfactants 2a decomposed immediately at 1 M HCl, and in 30 min at pH 1. The degradation of 2a proceeded almost completely after 90 min at pH 3. It was reported that surfactants 3a required 40 min to decompose at pH 1 and were stable for a week at pH 3. We discussed the decomposition rate order of the chemocleavable surfactants with different types of hydrophilic groups and ascribed the differences in reactivities of anionic and nonionic surfactants to a combination of electrostatic and micellar effects in our previous report\textsuperscript{23}. The local concentrations of protons near the surface of anionic and nonionic micelles may be higher than or similar to the concentration of protons in the bulk phase. But in the case of surfactants 3a, protons are consumed to neutralize the carboxylate anions on the surface of micelles before they attack the acetate groups under the investigated conditions. Similar decomposition rates were also observed in the case of 2b and 2c. It has also been confirmed that these compounds 2 are stable at ambient temperature for at least 1 yr.

Finally, the biodegradability of compounds 2 was measured by the BOD method in the presence of activated sludge. Biodegradability data for the compounds after 4 wk are shown in Fig. 3, along with the data for C12EO9, sodium dodecanoate and sodium n-dodecylbenzenesulfonate (LAS) measured under the same conditions.

The test chemicals giving results of greater than 60%
Double-chain chemocleavable surfactants were easily prepared by relatively simple methods from easily accessible commercial reagents. These surfactants had good water-solubility, smaller cmc and lower surface tension at cmc compared to conventional surfactants. The foaming properties of 2 was good. The emulsion stability of 2 was almost the same as that of C_{12}EO9. They also have an acid-decomposition property and good biodegradability.

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