Synthesis and Characterization of Cleavable Surfactants Derived from Poly(ethylene glycol) Monomethyl Ether

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ABSTRACT: A series of noncyclic acetal-linked cleavable surfactants were simply prepared by condensation of aldehydes with poly(ethylene glycol) monomethyl ethers. All of the products were characterized by ^{1}H nuclear magnetic resonance. Their hydrophile–lipophile balance, surface tension, cloud point, critical micelle concentration, and foam height were determined. Hydrolysis kinetic studies, followed by gas chromatography, showed that they had higher hydrolytic reactivity in acidic solution than cyclic acetal-linked cleavable surfactants.

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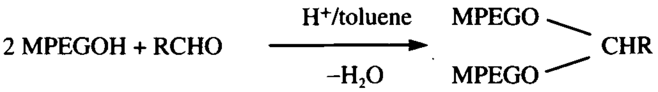
KEY WORDS: Acetals, cleavable surfactants, hydrolysis, poly(ethylene glycol) monomethyl ether, surface-active properties.

Surfactants have many applications. In some cases, the presence of an intact surfactant after its use can result in complications in subsequent manipulations. To solve this problem, many efforts have been made to find cleavable surfactants. Cleavable surfactants are surfactants that can decompose into nonsurface-active species or into new surface-active compounds with different properties upon exposure to acid (1–12), alkali (13), salt (14), heat (15), or light (16) after fulfilling their original functions. Cleavage of surfactants into nonsurfactants is also important to the environment, because the ultimate degradation of surfactants is usually determined by their primary degradation (degradation of surfactants into nonsurfactants). Among the various types of known cleavable surfactants, compounds in which the decomposition property can be controlled through adjustment of the solution pH seem to be the most common. They are known as acid-sensitive or alkali-sensitive surfactants.

Several acid-sensitive surfactants have been reported. Most of them contain a dioxolane (1–11) or a 1,3-dioxane ring (17–19). The study of noncyclic acetal linkages in acid-sensitive surfactants is limited (12,20) . The noncyclic acetals have the merit of relatively high hydrolytic reactivity, which is very important to practical applications. Most of the reported acid-sensitive surfactants are ionic surfactants. Nonionic surfactants, which have shown more than average growth in recent years, have many advantages over ionic surfactants (21). Here a group of nonionic surfactants, derived from poly(ethylene glycol) (PEG) monomethyl ether (MPEGOH) and all having a noncyclic acetal linkage, have been synthesized (Scheme 1, where MW = molecular weight). The hydrolysis kinetics of these surfactants in acidic solution and the fundamental surface-active properties, such as critical micelle concentration (CMC), surface tension, cloud point, and foam height, have been determined.



$$2\ \text{MPEGOH} + \text{RCHO} \xrightarrow[-\text{H}_2\text{O}]{\text{H}^+/\text{toluene}} (\text{MPEGO})_2\text{CHR}$$

Ia: $MW_{MPEGOH} = 550$, $R = -(CH_2)_{10}CH_3$
Ib: $MW_{MPEGOH} = 550$, $R = -(CH_2)_7CH_3$
Ic: $MW_{MPEGOH} = 550$, $R = -CH_2CH(CH_3)CH_2C(CH_3)_3$
IIa: $MW_{MPEGOH} = 350$, $R = -(CH_2)_{10}CH_3$
IIb: $MW_{MPEGOH} = 350$, $R = -(CH_2)_7CH_3$
IIc: $MW_{MPEGOH} = 350$, $R = -CH_2CH(CH_3)CH_2C(CH_3)_3$

SCHEME 1

EXPERIMENTAL PROCEDURES

Materials. All aldehydes and MPEGOH were purchased from Aldrich (Milwaukee, WI) and used without further purification.

Analytical instruments. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on an IBM-Bruker (Danbury, CT) AM-200 NMR spectrometer. Gas chromatography (GC) was performed with an HP 5690A gas chromatograph equipped with an HP-101 capillary column (Hewlett-Packard, Avondale, PA).

Synthesis of acetal I and II. MPEGOH (MW is 350 or 550), 0.05 mole of nonyl aldehyde (or 3,5,5-trimethyl hexanal or dodecanal), 150 mL toluene, and 0.1 g *p*-toluene sulfonic acid were azeotropically distilled until no more water separated. Toluene was removed under reduced pressure and the residue was washed with hexane. The crude product was

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dissolved in 300 mL 5% potassium carbonate plus 10% sodium chloride solution, and the aqueous solution was extracted by 100 mL ethyl acetate three times. The combined organic layer was washed with 100 mL saturated sodium chloride solution. After drying with anhydrous sodium sulfate, ethyl acetate was removed under reduced pressure. Yields were 70–80%.

Surface tension/CMC. Surface tension was measured by a du Nouy ring at a concentration of 0.1% in deionized water. The equipment used was a Lauda tensionmeter TC 1C/3. To obtain CMC, surface tension at different concentration was measured, and the breakpoint on the plot of surface tension vs. concentration was taken as CMC.

Foam height. Foam height was measured by rotating a water solution in a 500-mL measuring cylinder at room temperature. The product (0.5 g) was carefully dissolved in 200 mL deionized water. The measuring cylinder was put on an axis and rotated manually 40 times in one minute. The height of the foam was measured after 1 and 5 min.

Cloud point. The cloud points were determined by the naked eye with 1% solutions of the surfactants (22). The procedure used was to weigh 0.1 g surfactant into a test tube and add 10 g deionized water. Stir until dissolved. Warm in hot-water bath until cloudy, stirring occasionally with a thermometer. Remove from heat. Place in a stand and continue stirring occasionally until the solution is clear again. Record its temperature.

Hydrophile–lipophile balance (HLB) values. HLB values were calculated by Griffin's method (23): HLB = (wt% of oxyethylene) × 0.2. We calculated the terminal methyl group of the PEG as part of the lipophile.

Hydrolysis kinetics. Hydrolysis kinetics in pH = 3 buffer and 5% sulfuric acid solution at room temperature were evaluated by determining by GC the relative quantity of aldehydes released during the hydrolysis. About 0.06 mmol of the surfactant was dissolved in 3 mL pH = 3 buffer or 5% sulfuric acid solution. Hexane (3 mL) and about 0.06 mmol of *p*-xylene were added into this solution (as internal standard). The solution was shaken continuously in a 25°C water bath. Some of the solution was sampled from the hexane layer after a certain period. Our method was slightly different from the method reported before (24). Instead of using calibration curves to calculate the absolute amount of aldehydes released from hydrolysis at different times, we determined the relative amount of aldehydes released at different times to the amount of aldehydes released at 100% hydrolysis (I_t/I_{100}). In a plot of $-\log(1-I_t/I_{100})$ vs. time, the slope of the linear line was equal to a pseudo first-order kinetic constant. At pH = 3, some of the surfactants could not hydrolyze completely. The amount of aldehydes released at 100% hydrolysis was obtained by lowering the solution pH to 0.5 and raising the temperature to 40–50°C overnight.

RESULTS AND DISCUSSION

A series of noncyclic acetal-linked cleavable surfactants were simply prepared by condensation of MPEGOH with aldehydes. Purification of the products was easily achieved by washing the products with hexane to remove possible remaining aldehydes and by extracting the aqueous solution of the products with ethyl acetate to separate the products from unreacted MPEGOH. Unlike some PEG-based surfactants with lower HLB values, these surfactants, except compound **IIa**, are immiscible with hexane. **IIa**, which has the lowest HLB value, is miscible with hexane if a small amount of hexane is added. To avoid formation of persistent emulsions, washing with hexane was applied to the products instead of to the aqueous solution of the products. When **IIa** was washed with hexane, a relatively large amount of hexane was applied; otherwise, the solution would not separate into two layers. All of these compounds were characterized by ^{1}H NMR. The ^{1}H NMR analytical data results of compounds **I(a–c)** and **II(a–c)** are: **Ia**: 4.57 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 94H, PEG backbone); 3.38(*s*, 6H, -OC$\underline{H}_3$); 1.61 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group); 1.26 [*s*, 18H, -(C$\underline{H}_2$)$_9$ in the hydrophobe]; 0.88 (*t*, 3H, -C$\underline{H}_3$ in the hydrophobe); **Ib**: 4.57 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 94H, PEG backbone); 3.38 (*s*, 6H, -OC$\underline{H}_3$); 1.61 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group); 1.26 [*s*, 12H, -(C$\underline{H}_2$)$_6$ in the hydrophobe]; 0.88 (*t*, 3H, -C$\underline{H}_3$ in the hydrophobe); **Ic**: 4.63 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 94H, PEG backbone); 3.38 (*s*, 6H, -OCH$_3$); 1.65 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group);

TABLE 1
Cloud Point, HLB Value, Critical Micelle Concentration, Surface Tension, and Foam Height (both at 1 and 5 min) of Compounds I and II (at room temperature)[a]

Compounds	Cloud point (°C)	HLB	CMC (mM)	Surface tension (mN/m)	Foam height (mm) 1 min	Foam height (mm) 5 min
Ia	92	16.3	0.08	34.0	87	52
Ib	81.5	16.9	0.1	28.1	80	48
Ic	74.5	16.9	0.3	25.1	40	21
IIa	77	14.4	0.08	33.5	69	28
IIb	72	15.4	0.3	27.6	58	23
IIc	64	15.4	0.3	24.5	29	12

[a] Cloud points reported here are apparent cloud points; HLB, hydrophile–lipophile balance; CMC, critical micelle concentration.

1.45 (*m*, 1H, -C$\underline{H}$ in the hydrophobe); 0.85–1.30 (*m*, 14H, other protons in the hydrophobe); **IIa**: 4.57 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 58H, PEG backbone); 3.38 (*s*, 6H, -OC$\underline{H}_3$); 1.61 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group); 1.26 [*s*, 18H, -(C$\underline{H}_2$)$_9$ in the hydrophobe]; 0.88 (*t*, 3H, -C$\underline{H}_3$ in the hydrophobe); **IIb**: 4.57 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 58H, PEG backbone); 3.38 (*s*, 6H, -OC$\underline{H}_3$); 1.61 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group); 1.26 [*s*, 12H, -(C$\underline{H}_2$)$_6$ in the hydrophobe]; 0.88 (*t*, 3H, -C$\underline{H}_3$ in the hydrophobe); **IIc**: 4.63 (*t*, 1H, acetal -C$\underline{H}$); 3.66 (*m*, 58H, PEG backbone); 3.38 (*s*, 6H, -OCH$_3$); 1.65 (*m*, 2H, -C$\underline{H}_2$ next to the acetal group); 1.45 (*m*, 1H, -C$\underline{H}$ in the hydrophobe); 0.85–1.30 (*m*, 14H, other protons in the hydrophobe).

The surface-active properties of compounds **I** and **II** are given in Table 1. Lowering of the surface tension of pure water by addition of the compounds reported here shows that they are surface-active agents. Surface tensions of our cleavable surfactants are from 25 to 35 mN/m, slightly lower than typical noncleavable ethoxylates, which range from 30 to 40 mN/m (25). The foaming height test reported here proved that acetals produced less foaming and the foams have a shorter lifetime than surface-active ethoxylated alcohols (20). This could be advantageous for many industry applications. Compounds reported here differ from the classical ethoxylated surfactants by the presence of a terminal methyl group in the hydrophilic head. It has been reported that, for nonionic surfactants C_mEO_n, the presence of a terminal hydroxyl group is not necessary to obtain good surface properties (26).

The cloud points of these compounds are lower than typical noncleavable ethoxylates with similar HLB values and are dependent on their structures. The presence of terminal methyl groups in the hydrophilic head may play a role in lowering the cloud points (27). For noncleavable ethoxylates, cloud points increase as the length of the hydrophobes decreases and as branching of the hydrophobes decreases if the hydrophiles are kept the same. Cloud points also increase as the MW of the hydrophiles increases if the hydrophobes are kept the same (28). However, the cloud points of compounds reported here decrease as the length of the hydrophobes decreases, which is contradictory to what was reported for noncleavable ethoxylates. The possible reason for this disagreement is that these acetals may have hydrolyzed partially during measuring of the cloud points. We have found that cloud points of these acetal-linked compounds decreased dramatically as the extent of hydrolysis increased. As **Ib** and **IIb** can hydrolyze much faster than **Ia** and **IIa**, the extent of cloud points' lowering of **Ib** and **IIb** may be higher than the extent of cloud points' lowering of **Ia** and **IIa** during the heating process. In this situation, it is possible that the measured cloud points of **Ib** and **IIb** become lower than those of **Ia** and **IIa**, even if the true cloud points are higher than those of **Ia** and **IIa**. Thus, the cloud points reported here are apparent cloud points, not true cloud points. The appreciable smell of these solutions after measuring cloud points indicated partial hydrolysis.

All six compounds were stable in 5% NaOH solution for 24 h and hydrolyzable in acidic aqueous solution. The hydrolysis kinetics of these compounds in pH = 3 buffer at room temperature were studied by GC. The times required for 100% hydrolysis in 5% sulfuric acid solution also were determined. All hydrolytic reactions followed pseudo first-order kinetics in pH = 3 buffer at their early stages. The results are listed in Table 2. The kinetic studies were made at concentrations of 20 mM, well above their CMC, because cleavable surfactants are usually used at concentrations greater than their CMC. Thus, the hydrolytic kinetic constants obtained are the kinetic constants of the micelles.

In addition to the GC method used here, hydrolysis of acetals in acidic solution also could be studied by ^{1}H NMR or ultraviolet (UV) methods. Many hydrolysis studies have been done in DCl/D$_2$O solution by measuring ^{1}H NMR spectra at various times (12,29). Others employed a UV technique to follow carbonyl group formation during hydrolysis in acidic aqueous/dioxane solution (30). Neither of these methods could give the true hydrolytic kinetic constants of the micelles, because the first one has solvent isotope effects and the second one has organic solvent effects. The organic solvent can interfere with the formation of micelles and thus affect the hydrolytic kinetics. The UV method is a convenient method for studying hydrolytic kinetics of unaggregated molecules.

Compared with our previous study on corresponding cyclic acetal-linked cleavable surfactants, these noncyclic acetal-linked surfactants hydrolyze three orders of magnitude faster. Hydrolytic reactivity is important to practical applications. In most cases, cleavable surfactants are expected to be easily cleavable under mild conditions. To the best of our knowledge, the only report about hydrolytic reactivity of noncyclic acetal-linked PEG-based surfactant was made by Ono *et al.* (29). They reported the hydrolytic reactivity of compound **Vd** ($C_{12}H_{25}OCH_2OC(=CH_2)CH_2O(CH_2CH_2O)_6OH$). It took 90 h to complete the hydrolysis in pD = 3 D$_2$O solution. For pseudo first-order hydrolysis, $t_{1/2} = t_{final}/10$, because at 10 half lives, the remaining unhydrolyzed product is only $(1/2)^{10} \times 100\% = 0.098\%$. Then a completion time of 90 h corresponds to a half life of 540 min. Considering the solvent isotope effects, usually in the range of $k(D_3O^+)/k(H_3O^+)$

TABLE 2
Results of Acid-Catalyzed Hydrolysis of Surfactants I(a–c) and II(a–c) at 25°C

Compounds	Pseudo first-order rate constant $k \times 10^3$ (1/min)^a	Half-life $t_{1/2}$(min)^a	Time for complete decomposition (h)^b
Ia	0.2	3470	>5
Ib	1.7	410	2.0
Ic	1.4	500	1.5
IIa	0.1	6930	3.5
IIb	1.4	500	2.5
IIc	1.7	410	2.0

^{a}pH = 3 buffer.
^{b}In 5% sulfuric acid.

= 2–3 (31), the hydrolytic reactivity of Ono's compound is lower than our **Ib**, **Ic**, **IIb**, and **IIc** in pH = 3 buffer. But Ono *et al.* (29) reported that **Vd** hydrolyzed completely immediately in 2% DCl/D_2O solution, much faster than our compounds in 5% sulfuric acid.

The hydrolytic reactivity reported here may not be high enough for some applications. To improve the hydrolytic reactivity, we will make some new noncyclic acetal-linked surfactants by employing α,β-unsaturated aldehydes as starting material. It has been reported that the presence of the conjugated double bond will greatly enhance the hydrolytic reactivity by stabilizing the intermediate formed during hydrolysis (32).

In regard to hydrolytic reactivity–structure relations, the hydrolytic reactivity increases as the hydrophobe chainlength decreases if the hydrophiles are kept the same (**Ia** < **Ib**, **IIa** < **IIb**). This may be attributed to the decreasing hydrophobic shielding of the acetal linkage from aqueous protons. Comparing the hydrolytic rate constants of **Ib** and **Ic**, **IIb** and **IIc** in pH = 3 buffer, we found that the structure of the hydrophobe itself (linear hydrophobe or branched hydrophobe) could not determine the hydrolytic reactivity. Similarly, the size of the hydrophile itself could not determine the hydrolytic reactivity either. It is more reasonable that the hydrolytic reactivity is determined by the overall structure of the surfactant, because the structure of the micelles is determined by both the hydrophile and the hydrophobe of a surfactant, and the hydrolytic reactivity in the form of micelles should depend on the structure of the micelles.

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