Cleavable Surfactants

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ABSTRACT: Cleavable surfactants are of interest for several reasons. Above all, the development of surfactants with weak bonds deliberately built into the structure is driven by the need for improved biodegradability of amphiphiles. The breakdown may be catalyzed by enzymes, and biodegradation would be the normal mechanism in sewage plants. Alternatively, the surfactant may degrade by chemical means, e.g., induced by acid, alkali, ultraviolet (UV) light, heat, or ozone. Acid- and alkali-labile surfactants have attracted particular attention, and there is often a compromise between required stability at one stage and ease of breakdown at a subsequent stage. The paper reviews the main routes used to prepare cleavable surfactants and points out advantages and disadvantages of the different approaches. Emphasis is placed on the development during recent years. Cyclic and acyclic acetals, ketals, and ortho esters are the most important types of bonds for the preparation of acid-labile surfactants, whereas alkali-labile amphiphiles usually are based on ester bonds. The ester bond approach has been particularly important for cationic surfactants, and so-called ester quats have rapidly taken a large share of the traditional market for quats. Betaine esters constitute a special class of ester with very pronounced pH dependence. UV-labile surfactants based, for instance, on an azo bond, offer promise for the future.

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By tradition, surfactants are stable species. Among the surfactant workhorses are anionics such as alkylbenzenesulfonates and alkyl sulfates, nonionics such as alcohol ethoxylates and alkylphenol ethoxylates, and cationics such as alkyl quats and dialkyl quats; only alkyl sulfates are not chemically stable under normal conditions. Through the years the susceptibility of alkyl sulfates to acid-catalyzed hydrolysis has been seen as a considerable problem, particularly well-known for the most prominent

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member of the class, sodium dodecyl sulfate. The general attitude has been that weak bonds in a surfactant may cause handling and storage problems and should therefore be avoided.

In recent years the attitude toward easily cleavable surfactants has changed. Environmental concerns have become one of the main driving forces for the development of new surfactants, and the biodegradation rate has become a major issue. One of the main approaches taken to produce readily biodegradable surfactants is to build into the structure a bond with limited stability. For practical reasons, the weak bond is usually the bridging unit between the polar head group and the hydrophobic tail of the surfactant, which means that degradation immediately leads to destruction of the surface activity of the molecule, an event usually referred to as the primary degradation of the surfactant. Biodegradation then proceeds along various routes, depending on the type of primary degradation product. The ultimate decomposition of the surfactant, often expressed as the quantity of carbon dioxide evolved during a 4-wk exposure to appropriate microorganisms, expressed as a percentage of the amount of carbon dioxide that could theoretically be produced, is the most important measure of biodegradation. Seemingly, for most surfactants containing easily cleavable bonds, the values for ultimate decomposition are also higher than for the corresponding surfactants lacking the weak bond. Thus, the strong trend toward more environmentally benign products favors the cleavable surfactant approach on two accounts.

A second incentive for the development of cleavable surfactants is to avoid complications such as foaming or formation of unwanted, stable emulsions after use of a surfactant formulation. Cleavable surfactants potentially can eliminate some of these problems. If the weak bond is present between the polar and the nonpolar part of the molecule, cleavage will lead to one water-soluble and one water-insoluble product. Both moieties can usually be removed by standard work-up procedures. This approach

has been of particular interest for surfactants used in preparative organic chemistry and in various biochemical applications.

A third use of surfactants with limited stability arises from new functionality of their cleavage product. For instance, a surfactant used in personal-care formulations may decompose on application to form products beneficial to skin. Surfactants that impart a new function after cleavage are sometimes referred to as functional surfactants.

Finally, surfactants that break down into nonsurfactant products in a controlled way may find use in specialized applications, e.g., in the biomedical field. Thus, cleavable surfactants that form vesicles or microemulsions can be of interest for drug delivery, provided the metabolites are nontoxic.

Most cleavable surfactants contain a hydrolyzable bond. Chemical hydrolysis is either acid- or alkali-catalyzed, and many papers discuss the surfactant breakdown in terms of either of these mechanisms. In the environment, bonds susceptible to hydrolysis are often degraded by enzymatic catalysis, but few papers dealing with cleavable surfactants have investigated such processes *in vitro*. Other approaches that have been taken include incorporation of a bond that can be destroyed by ultraviolet (UV) irradiation or use of an ozone-cleavable bond. This review is subdivided according to the type of weak linkage present in the surfactant.

ACID-LABILE SURFACTANTS

Cyclic acetals. Cyclic 1,3-dioxolane (five-membered ring) and 1,3-dioxane (six-membered ring) compounds, illustrated in Scheme 1, have been studied in depth by the groups of Burczyk, Takeda, and others as examples of acid-labile surfactants. They are typically synthesized from a long-chain aldehyde by reaction with a diol or a higher polyol. Reaction with a vicinal diol gives the dioxolane (1–3), and 1,3-diols yield dioxanes (4,5).

If the diol contains an extra hydroxyl group, such as in glycerol, a hydroxy acetal is formed and the remaining hydroxyl group can subsequently be derivatized to give anionic or cationic surfactants, as is illustrated in Scheme 2. It is claimed that glycerol gives ring closure to dioxolane,
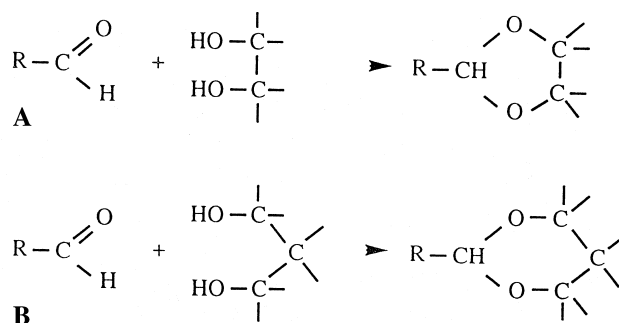
SCHEME 1

yielding a free, primary hydroxyl group, but it is likely that some dioxane with a free, secondary hydroxyl group is formed as well. The free hydroxyl group can be treated with SO_3 and then neutralized to give the sulfate (6), it can be reacted with propane sultone to give the sulfonate (7), or it can be substituted by bromine or chlorine and then reacted with dimethylamine to give a tertiary amine as polar group. The amine can then be quaternized in the usual manner, e.g., with methyl bromide (8). An analogous reaction with pentaerythritol as diol yields a 1,3-dioxane with two unreacted hydroxymethyl groups which can be reacted further, e.g., to give a dianionic surfactant (7). The remaining hydroxyl group may also be ethoxylated to give nonionic chemodegradable surfactants (9). The rate of decomposition in sewage plants of this class of nonionic surfactants is much higher than that of conventional ethoxylates (10).

Hydrolysis splits acetals into aldehydes, which are intermediates in the biochemical β-oxidation of hydrocarbon chains. Acid-catalyzed hydrolysis of unsubstituted acetals is generally facile and occurs at a reasonable rate at pH 4–5 at room temperature. Electron-withdrawing substituents such as hydroxyl, ether oxygen, and halogens reduce the hydrolysis rate, however (11). Anionic acetal surfactants are more labile than cationic (1), a fact that can be ascribed to the locally high oxonium ion activity around such micelles. The same effect can be seen also for surfactants forming vesicular aggregates, again undoubtedly due to differences in the oxonium ion activity in the pseudophase
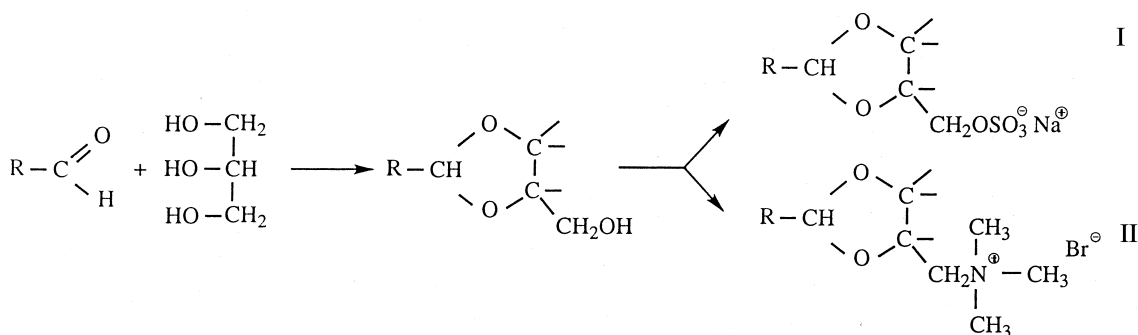
SCHEME 2

surrounding the vesicle. Acetal surfactants are stable at neutral and high pH.

The advantage of using a cleavable acetal surfactant instead of a conventional amphiphile has been elegantly demonstrated in a work by Bieniecki and Wilk (12). A cationic 1,3-dioxolane derivative served as the surfactant in a microemulsion formulation that was employed as reaction medium for an organic synthesis. When the reaction was complete, the surfactant was decomposed by addition of acid and the reaction product easily recovered from the resulting two-phase system. By this procedure the problems of foaming and emulsion formation, frequently encountered with conventional surfactants, could be avoided.

The 1,3-dioxolane ring has been found to correspond to approximately two oxyethylene units with regard to effect on critical micelle concentration (CMC) and adsorption characteristics (3). Thus, surfactant type I in Scheme 2 should resemble ether sulfates of the general formula $R–(OCH_2CH_2)_2OSO_3Na$. This is interesting since some commercial alkyl ether sulfates contain two to three oxyethylene units.

Acyclic acetals. Alkyl glucosides, often somewhat erroneously referred to as alkyl polyglucosides or APG, are cyclic compounds; but since the ring does not involve the two geminal hydroxyl groups of the aldehyde hydrate, it is here included in the category of acyclic acetals. Alkyl glucosides are by far the most important type of acetal surfactant. Since this surfactant class has been the topic of several recent reviews (13–15), it will be outlined only briefly below.

Alkyl glucosides are made either by direct condensation of glucose and a long-chain alcohol or by transacetalization of a short-chain alkyl glucoside, such as butyl glucoside, with a long-chain alcohol, in both cases in the presence of an acid catalyst (Scheme 3). The procedure leads to some degree of sugar ring condensation, the extent of which can be governed by various means, e.g., the ratio of long-chain alcohol to sugar.

The alkyl glucoside surfactants break down into glucose and long-chain alcohol under acidic conditions. On the alkaline side, even at very high pH, they are stable to hydrolysis. Their cleavage profile, along with their relatively straightforward synthesis, makes these surfactants interesting candidates for various types of cleaning formulations.

Polyoxyethylene-based cleavable surfactants have been synthesized by reacting end-capped poly(ethylene glycol) (PEG) with a long-chain aldehyde, as is shown in Scheme 4 (16,17). During acid hydrolysis, these compounds will re-
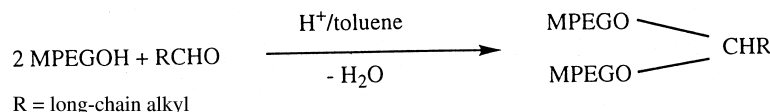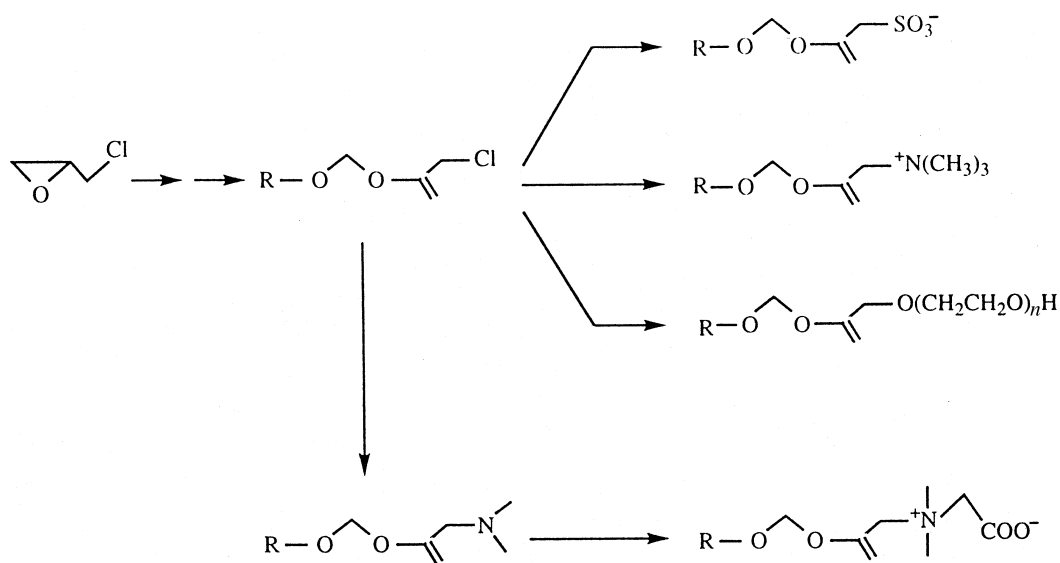

R = long-chain alkyl
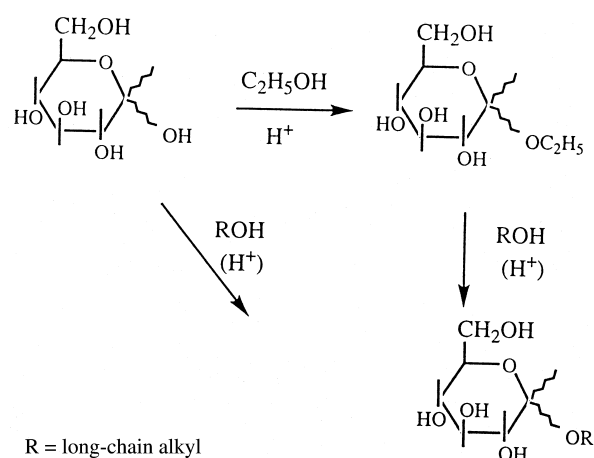
SCHEME 3

vert to the original fatty aldehyde and end-capped PEG. Studies of the relationship between structure and hydrolytic reactivity have shown that the hydrolysis rate increases as the hydrophobe chain length decreases when the hydrophilic part is kept constant. This has been attributed to decreased hydrophobic shielding of the acetal linkage from oxonium ions. No effect on the hydrolysis rate was seen when the hydrophilic part was varied while the hydrophobic part was kept constant or when the structure of the hydrophobe was varied from linear to branched. Furthermore, the hydrolytic reactivity for nonaggregated is higher than for micellized surfactants (18,19).

Ono *et al.* (20,21) have synthesized series of open acetal surfactants—anionics, nonionics, cationics, and amphoterics—and made a systematic study of the influence of the polar head group on hydrolytic reactivity (Scheme 5). The hydrophobic tail as well as the connecting group was kept constant, and the time for complete decomposition was recorded. The results, shown in Table 1, constitute a nice illustration of the effect of the micelle surface on the hydrolysis rate. With negatively charged micelles, the reaction is very fast, with positively charged micelles the process is sluggish, and with the noncharged micelles the rate is intermediate.

Acetal surfactants have been found to resemble traditional surfactants in terms of physicochemical properties. However, reportedly, the CMC values for acetal-containing surfactants are somewhat lower than for the corresponding conventional surfactants. Furthermore, the efficiency of the surfactants, expressed as the concentration required to produce a 20 mN/m reduction in surface tension, was higher for the cleavable surfactants (20). Evidently, the acetal linkage connecting the hydrophobic tail and the

$$2\ MPEGOH + RCHO \xrightarrow[-\ H_2O]{H^+/toluene} \begin{array}{c} MPEGO \\ MPEGO \end{array}\!\!\diagdown\!\!\diagup CHR$$

R = long-chain alkyl
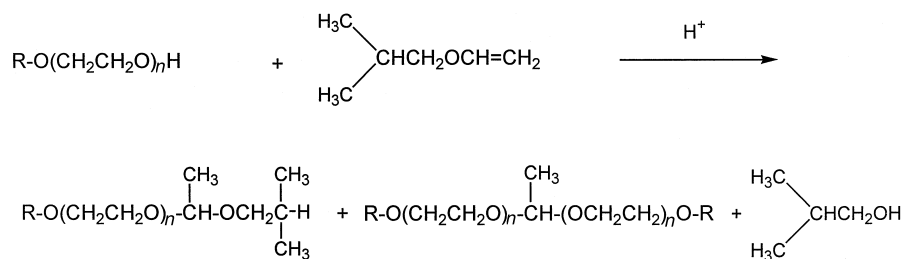
SCHEME 4

SCHEME 5

SCHEME 6

polar head group contributes to surfactant hydrophobicity, resulting in higher adsorption efficiency at the air–water interface and an increased tendency to aggregate into micelles.

Acetal linkages have also been used in end-capped surfactants. By reacting a fatty alcohol alkoxylate with an alkyl vinyl ether, such as isobutyl vinyl ether, low-foaming surfactants with excellent biodegradation have been obtained (22). Through a transacetalization process, a mixture of an isobutyl-blocked fatty alcohol alkoxylate and a di(fatty alcohol alkoxylate) acetal is formed, as shown in

TABLE 1
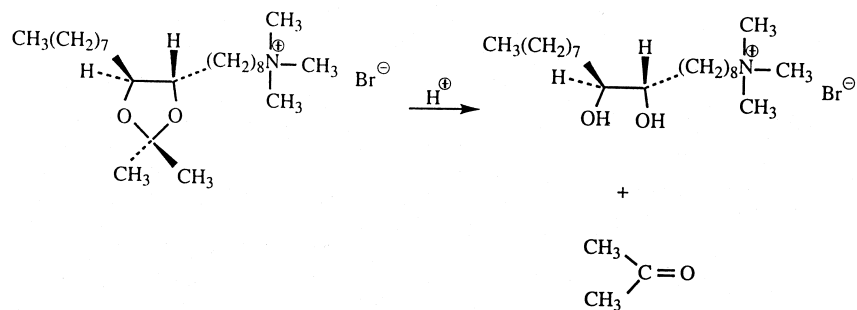**Times for Decomposition of Acetal Surfactants with Various Head-Group Charges[a]**

Surfactant type	2% DCl	pD 1	pD 3
Anionic	Immediately	Immediately	30 min
Cationic	48 h	1 wk	>2 wk
Nonionic	Immediately	15 min	90 h
Amphoteric	3 h	24 h	>1 wk

[a]Experiments were made at 25°C under varying conditions. D_2O was used as solvent to permit monitoring the hydrolysis reactions by nuclear magnetic resonance (Ref. 20).

Scheme 6. Transacetalization has made it possible to prepare PEG-poly(propylene glycol) (PPG) block copolymers with improved biodegradation characteristics (23). Hydrolysis of these compounds yields 1 mol of acetaldehyde and 2 mol of alcohol [which might be fatty alcohol alkoxylate, poly(alkylene glycol) or isobutanol].

Ketals. Surfactants containing ketal bonds can be prepared from long-chain ketones and a diol in analogy with the reaction schemes given in Schemes 1 and 2 for the preparation of acetal surfactants (24). Recently, nonionic cleavable surfactants based on a long-chain carbonyl compound, glycerol, and a polyoxyethylene chain have been commercialized. Both long-chain ketones and aldehydes can be used. Upon condensation with glycerol, they form cyclic ketals and acetals, respectively, as discussed above for cyclic acetals. Ketones give primarily 4-hydroxymethyl-1,3-dioxolanes, whereas aldehydes give a mixture of 4-hydroxymethyl-1,3-dioxolanes and 5-hydroxy-1,3-dioxanes. The remaining hydroxyl function is alkoxylated in the presence of a conventional base catalyst (9,10).

These acid-labile surfactants have found use in the electroreduction of hexachlorobenzene, which is performed in a microemulsion. After dehalogenation, the pH is reduced

SCHEME 7

to below 3, leaving a solution without surface-active properties and allowing straightforward recovery of the electrolysis products from the solution (25).

Ketal-based surfactants have also been prepared in good yields from esters of keto acids by either of two routes, as shown in Scheme 7 (26–28). The biodegradation profiles of the dioxolane surfactants of Scheme 7 are shown in Figure 1 (27). As expected, the degradation rate is highly dependent on the alkyl chain length. The process is markedly faster with labile surfactants (and particularly for structure I which contains an extra ether oxygen) than with the conventional carboxylate surfactant of the same alkyl chain length used as reference. Ketal surfactants are generally more labile than the corresponding acetal surfactants. As an example, a ketal surfactant kept at pH 3.5 was cleaved to the same extent as an acetal surfactant of similar structure kept at pH 3.0 (29). The relative lability of the ketal linkage is due to the greater stability of the carbocation formed during ketal hydrolysis compared to the carbocation formed during acetal hydrolysis (30). [It is noteworthy that biodegradation of an acetal surfactant was found to be faster than for a ketal surfactant of very similar structure

(27). Evidently, there is no strict correlation between ease of biodegradation and rate of chemical hydrolysis.]

Jaeger (31–34) introduced the term "second-generation cleavable surfactant" for labile surfactants that on cleavage give another surfactant together with a small water-soluble species. The daughter surfactant generally has a higher CMC than the parent surfactant. Scheme 8 shows a typical example of a second-generation cleavable surfactant. The concept has been applied to a variety of structures, including phospholipid analogs (34), and several applications of this specific type of cleavable surfactants have been proposed in the papers by Jaeger *et al.* (31–34).

Double-chain, double-head-group second-generation surfactants have also been synthesized. The geometry of the molecules may be varied by the position of the link between the hydrocarbon tails. Surfactants with both symmetrical and unsymmetrical cross-linking with respect to the head groups have been prepared (1,35,36). These surfactants can be seen as examples of gemini surfactants. In one approach, labile gemini surfactants were synthesized that, on acid treatment, broke down into single-chain, single-head-group surfactants (36). They are of interest in

FIG. 1. Rate of biodegradation vs. time for four ketal surfactants and for sodium decanoate as reference. I and II relate to the compounds of Scheme 6; a: R = $C_{12}H_{25}$, n = 2; b: R = $C_{16}H_{33}$, n = 2 [Reprinted from *J. Am. Oil Chem. Soc. 72*:853 (1995) with permission of the AOCS Press].

SCHEME 8

model investigations, e.g., to study the morphology of aggregates. Their preparation is cumbersome, however, which means that their practical usefulness is limited.

Ortho esters. Ortho esters are a new class of surfactants that have been described recently (37). Surfactant ortho esters are conveniently prepared by transesterification of a low-molecular-weight ortho ester (such as triethyl orthoformate) with fatty alcohol and PEG. An example of structure and a typical method of preparation are given in Scheme 9. Due to the trifunctionality of the ortho ester, a distribution of species is obtained. Furthermore, if the reactant alcohol is difunctional, cross-linking will occur and a large network may be formed. Such compounds have been shown to be effective foam depressants, and an example based on PPG and PEG is shown in Scheme 10 (38). By varying the number and types of substituents (fatty alcohol, alkyleneoxy group, end-blocking), the properties of the ortho ester-based surfactant or block copolymer can be tailor-made for a specific field of application.

Hydrolysis of ortho esters occurs by a mechanism analogous to that of acetals and ketals and gives rise to 1 mol of formate and 2 mol of alcohol (39,40). Both formates and alcohols can be regarded as nontoxic substances. Recent research by Bergh *et al.* (41) has shown that surface-active formates (similar to surface-active alcohols and esters but in contrast to surface-active aldehydes) have little or no dermatological effect, evaluated in terms of sensitizing capacity and irritancy. Ortho ester-based surfactants undergo acid-catalyzed cleavage much more readily than acetal-based surfactants under the same conditions (25; Hellberg, P.-E., and K. Bergström, unpublished data). For instance, a water-soluble ortho ester based on octanol and monomethyl-PEG is hydrolyzed to 50% in 2 h at pH 5. The structure of the surfactant has been found to influence the hydrolysis rate and, in general, a more hydrophilic surfactant has a higher decomposition rate.

Ortho ester linkages can also be used to improve biodegradation properties in long-chain ethoxylates or block copolymers. A conventional PEG-PPG copolymer with a molecular weight of 2200 biodegrades to only 3% in 28 d. However, an equivalent molecule built up from PEG 350 and PPG 400, connected by ortho ester links, will reach 62% biodegradation within 28 d and thus be classified as "readily biodegradable" (38).

Ortho ester-based surfactants have been found to be roughly equivalent to conventional surfactants in terms of cleaning and emulsifying properties. Their CMC values are considerably lower than those of comparable alcohol ethoxylates (37; Hellberg, P.-E., and K. Bergström, unpublished data), probably due mainly to the presence of
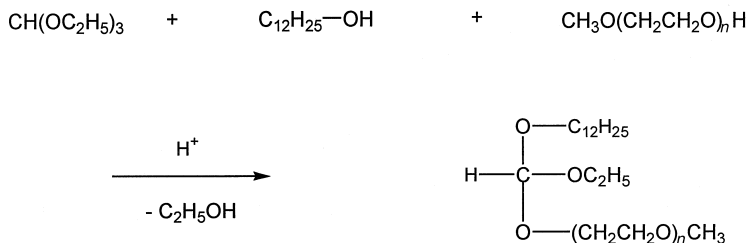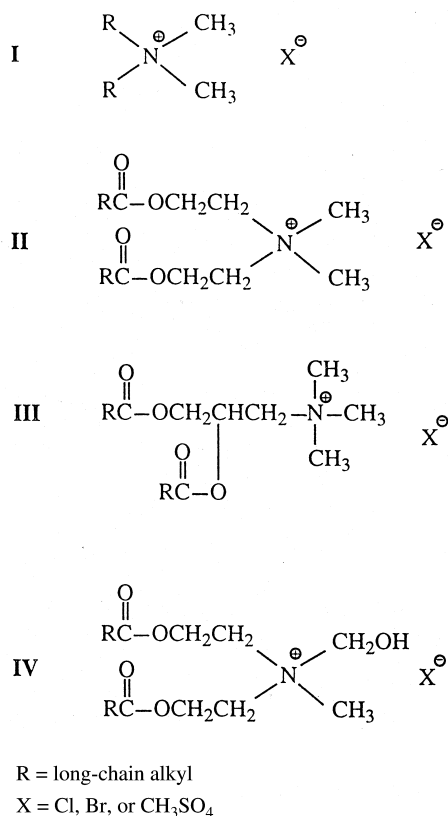

SCHEME 9
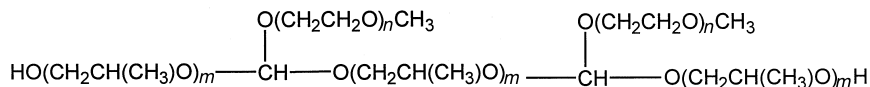
SCHEME 10

species with two alkyl chains, but the ortho ester linkage itself may also contribute to the hydrophobicity, as has been shown for acetal linkages (20).

ALKALI-LABILE SURFACTANTS

Normal ester quats. By "ester quat" we refer to surface-active quaternary ammonium compounds of the general formula $R_4N^+X^-$ in which the long-chain alkyl moieties, R, are linked to the charged head group by an ester bond, with X^- being a counter-ion. By "normal ester quats" we mean surfactants based on esters with one or more fatty acids and a quaternized amino alcohol. Scheme 11 shows examples of three different ester quats, all containing two long-chain and two short substituents on the nitrogen atom. The figure also shows the "parent," noncleavable quat. As can be seen, the ester-containing surfactants contain two carbon atoms between the ester bond and the nitrogen, which carries the positive charge. Cleavage of the ester bonds of surfactants **II–IV** yields a fatty acid soap in addition to a highly water-soluble quaternary ammonium di- or triol. These degradation products exhibit low fish toxicity and are degraded further by established metabolic pathways. The overall ecological characteristics of ester quats are much superior to those of traditional quats as represented by compound **I** of Scheme 11.

In Europe, dialkyl ester quats have largely replaced stable dialkyl quats as rinse-cycle softener, which is the single largest application for quaternary ammonium compounds. The switch from stable dialkyl quats to dialkyl ester quats represents the second-most dramatic change of product type in the history of surfactants, the switch from branched alkylbenzenesulfonate (ABS) to linear ABS being the most dramatic. Both changes were entirely environment-driven. Unlike stable quats, ester quats show excellent values for biodegradability and aquatic toxicity (42,43). Ester quats have also fully or partially replaced traditional quats in other applications of cationics, such as hair-care products and various industrial formulations (42).

The cationic charge close to the ester bond renders normal ester quats unusually stable to acid and labile to alkali. The strong pH dependence of the hydrolysis can be taken advantage of to induce rapid cleavage of the product. This phenomenon is even more pronounced for betaine esters. The mechanism of hydrolysis is discussed in some detail in the following section. The pH dependence of hydrolysis of ester quats has been investigated in detail (42). It was found that the hydrolysis rate goes through a minimum at pH 3–4 and accelerates strongly above pH 5–6. Evidently, formulations containing ester quats must be maintained at low pH.

Esters of choline have attracted special attention because the primary degradation products, choline and a fatty acid, are both natural metabolites in the body. Thus, choline esters should constitute a group of very nontoxic cationic surfactants. A series of choline esters has been synthesized and evaluated as disinfectants with controlled half-lives (44,45) (Scheme 12). Compounds with an alkyl group, R, of 9–13 carbons showed excellent antimicrobial effect. The *in vivo* hydrolysis was rapid, presumably due to catalysis by butyrylcholine esterase, which is present in human serum and mucosal membranes.

Betaine esters. The rate of alkali-catalyzed ester hydrolysis is influenced by adjacent electron-withdrawing or electron-donating groups. A quaternary ammonium group is strongly electron-withdrawing. The inductive effect will lead to a decreased electron density at the ester bond; hence, alkaline hydrolysis, which starts by a nucleophilic attack by hydroxyl ions at the ester carbonyl carbon, will be favored. Compounds **II–IV** of Scheme 11 all have two carbon atoms between the ammonium nitrogen and the –O– oxygen of the ester bond. Such esters undergo alkaline hydrolysis at a faster rate than esters lacking the adjacent charge, but the difference is not very large. If, on the other hand, the charge is at the other side of the ester bond, the rate enhancement is much more pronounced. Such esters are extremely labile on the alkaline side but very stable

SCHEME 11

R = long-chain alkyl
X = Cl, Br, or CH_3SO_4
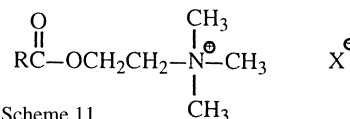
For R and X see Scheme 11.

SCHEME 12
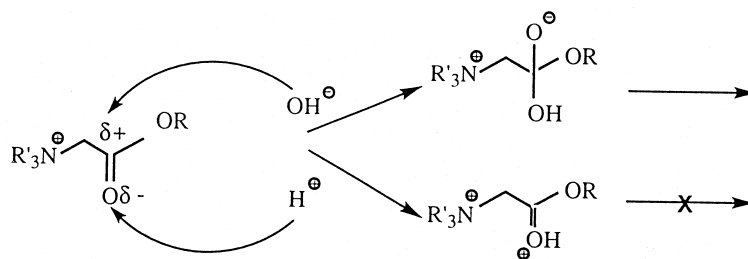
SCHEME 13

even under strongly acidic conditions (46). The large effect on the rate of alkaline and acid hydrolysis of the quaternary ammonium group is due to stabilization/destabilization of the ground state, as illustrated in Scheme 13. The charge repulsion, involving the carbonyl carbon atom and the positive charge at the nitrogen atom, is relieved by hydroxide ion attack, but augmented by protonation. The net result is that, compared with an ester lacking the cationic charge, the rate of alkaline hydrolysis is increased 200-fold, whereas the rate of acid hydrolysis is decreased 2000-fold (47). For surface-active betaine esters based on long-chain fatty alcohols, the rate of alkaline hydrolysis is further accelerated due to micellar catalysis (48). The presence of large, polarizable counter ions, such as bromide, can completely outweigh the micellar catalysis, however (49).

The extreme pH dependence of surface-active betaine esters makes them interesting as cleavable cationic surfactants. Shelf life is long under acid conditions, and the hydrolysis rate will then depend on the pH at which they are used. Single-chain surfactants of this type have been suggested as "temporary bactericides" for use in hygiene products, for disinfection in the food industry and in other instances where only short-lived bactericidal action is wanted (48). The patent literature also contains examples of betaine esters containing two long-chain alkyl groups (50–52). Two examples are given in Scheme 14.

Monoalkyl carbonates. Alcohol ethoxylates with a limited number of oxyethylene groups are viscous oils. Their incorporation into powder detergents constitutes a well-known problem. Carbonate salts of such surfactants have

been used as labile derivatives from which the surfactant can be readily regenerated. Such derivatives could be named "prosurfactants" by analogy with the term "prodrug" in medicine. Reaction of an alcohol ethoxylate with carbon dioxide gives a solid carbonate salt that decomposes under alkaline washing conditions to give the starting nonionic surfactant and carbonate, as illustrated in Scheme 15 (53). (Strictly speaking, the prosurfactant is also a surfactant although it is not meant to serve as such in the application step.) Conversion of an alcohol ethoxylate into a solid carbonate makes possible the incorporation of high levels of this surfactant into granular detergents of high bulk density.

UV-LABILE SURFACTANTS

The concept of triggering cleavage by UV light is attractive because it allows an extremely fast breakdown of the surfactant to occur. An alkyl aryl ketone sulfonate, which bears some structural resemblence to ABS surfactants, has been synthesized (54). This compound is photocleaved into a water-soluble aryl sulfonate and a mixture of two methyl-branched olefins, as shown in Scheme 16. The surfactant is of interest for solubilization of proteins since the work-up procedure is greatly facilitated by the instantaneous elimination of surfactant from the solution. The wavelength required for this type of photolysis, a so-called Norrish Type II cleavage, is 300 nm and above. This low-energy radiation should be harmless to proteins. Another approach has been to insert the light-sensitive diazosulfonate group between the polar head group and the tail of an anionic surfactant (55–57). As can be seen from Scheme
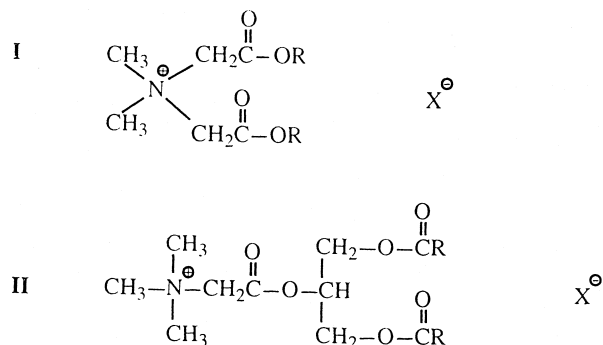
SCHEME 14
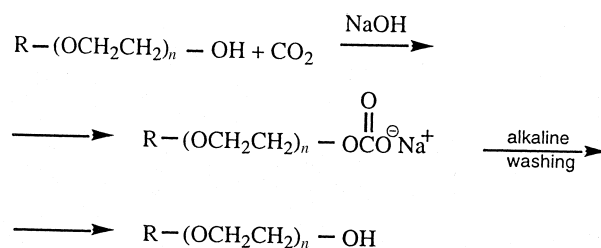
SCHEME 15
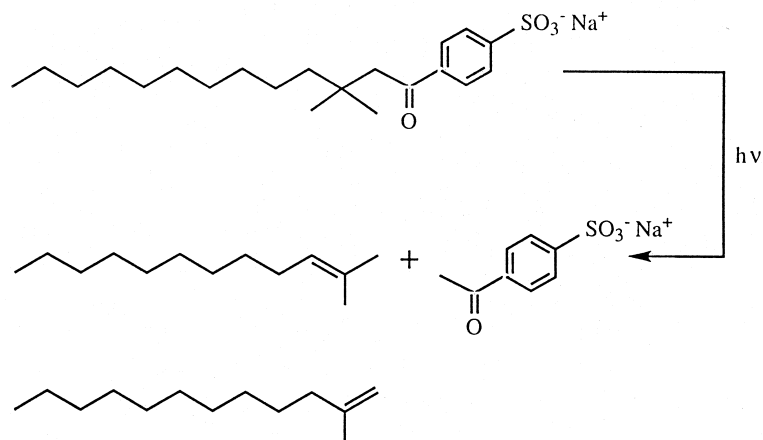
SCHEME 16

17, these surfactants are also similar in structure to the commonly used ABS. A comparison of CMC values for the diazosulfonate and the normal sulfonate surfactants with the same R substituent shows lower values for the former, indicating a contribution of hydrophobicity from the azo linkage. Photochemical cleavage yielded sulfate ion and the remaining diazonium compound which was further photolyzed in a second step.

An interesting use of photolabile surfactants is as emulsifiers in emulsion polymerization (58,59). The use of a photolabile emulsifier opens the possibility to control the latex coagulation process simply by exposing the dispersion to UV irradiation. The ionic head group of the surfactant would be split off by photolysis, leading to aggregation of the latex particles. Such latexes could be of interest for coating applications.

A recent paper reported the synthesis of a double-chain surfactant that contains Co(III) as complexing agent for two single-chain surfactants based on ethylenediamine in the polar head group. UV irradiation, or merely sunlight, causes reduction of Co(III) to Co(II). The latter gives a very

labile complex, and the double-chain surfactant immediately degrades into two single-chain moieties (60).

MISCELLANEOUS

Apart from the product classes discussed above, which we believe include the most important types of cleavable surfactants, several more or less exotic examples of surfactants with limited half-life have been reported. For instance, isethionate esters with very high degree of alkali lability have been developed. These products, made by esterification of an alkyl polyoxyethylene carboxylic acid with the sodium salt of isethionic acid, have been claimed to be partially cleaved when applied to the skin (61). Surfactants containing the Si–O bond have also been developed as cleavable surfactants susceptible to both alkaline and acid hydrolysis (31,62). Cleavable quaternary hydrazinium surfactants have been explored as amphiphiles containing a bond which splits very easily. The surfactants are cleaved by nitrous acid under extremely mild conditions (63). Ozone-cleavable surfactants have been developed as ex-
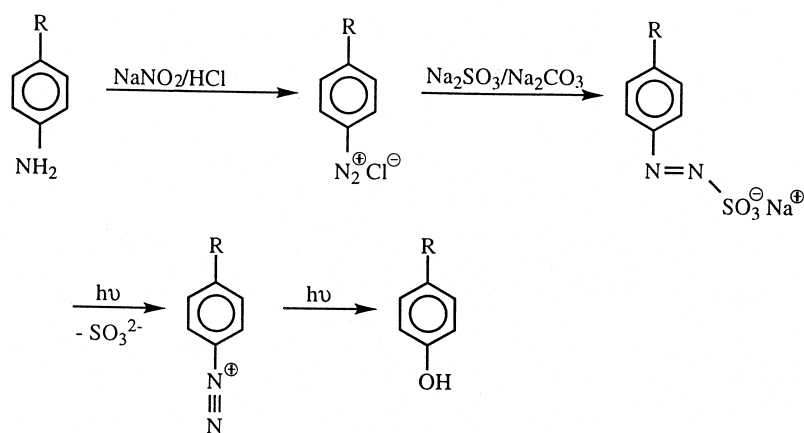
SCHEME 17

amples of environmentally benign amphiphiles. These surfactants, which contain unsaturated bonds, break down easily during ozonization of water, which is a water purification process of growing importance (64).

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