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Lundberg, D., Stjerndahl, M., Holmberg, K. (2023). Ester-based surfactants: Are they stable enough?. Journal of Surfactants and Detergents, 26(3): 229-236. http://dx.doi.org/10.1002/jsde.12628

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Received: 6 July 2022 | Revised: 21 August 2022 | Accepted: 29 August 2022
DOI: 10.1002/jsde.12628

REVIEW

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Ester-based surfactants: Are they stable enough?

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Abstract

Surfactants with an ester bond connecting the polar headgroup and the hydrophobic tail are common. They are easy to synthesize, they can often be made from natural raw materials and their biodegradation profile is generally good, partly due to lipase or esterase catalyzed breakdown of the ester bond in sewage plants. A labile ester bond in the molecule may cause problems, however. Surfactants are often formulated at relatively high pH and it is important that they remain intact for a given period of time. In this article we discuss alkaline hydrolysis of different types of ester-based surfactants—cationic, anionic and nonionic—and also of surfactant mixtures. We show that the ester bond in a surfactant has a different hydrolysis pattern than ester bonds in non-surface active uncharged molecules. Cationic ester-based surfactants are hydrolyzed rapidly while anionic and also nonionic ester-containing surfactants are relatively resistant to hydrolysis.

KEYWORDS
ester, hydrolysis, micellar catalysis, micellar protection, surfactant

INTRODUCTION

Surfactants with an ester bond connecting the polar headgroup and the hydrophobic tail are common. Examples include anionic surfactants such as dialkyl sulfosuccinate, alkylsulfoacetates, isethionates, and sulfonated fatty acid methyl esters, nonionic surfactants such as sugar, oligoglycerol, and oligo(ethylene glycol) esters of fatty acids, and cationic surfactants such as the so-called "ester quats." Many of the amphiphiles produced by fermentation by yeast or bacteria also contain ester bonds (De et al., 2015; Holmberg, 2019). Surfactants containing an ester bond in the molecule are examples of so-called "cleavable surfactants," a term coined by Jaeger (Jaeger, 1995). Cleavable surfactants can be regarded as a subgroup of "stimuli-responsive surfactants" (Brown et al., 2013). Other examples of cleavable surfactants include amide-, carbonate-, and ortho ester-containing amphiphiles (Stjerndahl et al., 2019). Having an easily cleavable linkage in the surfactant molecule is often a way to improve the rate of biodegradation (Bhadani et al., 2020; Holmberg, 2019; Tehrani-Bagha & Holmberg, 2007). It can also be a way to control a process, for instance breaking an emulsion at a given stage by using an emulsifier that contains a labile bond (Belenki et al., 2013).

The ester bond is particularly common as "suicidal linkage." Esters are easy to synthesize, and the starting materials are usually non-toxic and readily available. Ester bonds are degraded in sewage plants by the action of lipases and esterases, which facilitates the ultimate biodegradation of the surfactant. Ester-based amphiphiles are therefore often regarded as environmentally benign.

The ease with which ester bonds degrade may constitute a problem, however. A surfactant must be stable under the conditions and during the time of its intended use. The purpose of this paper is to demonstrate that ester-based surfactants have a hydrolysis pattern that is very different from that of regular non-surface active esters. This knowledge is practically important when formulating surfactants.

CATIONIC ESTER-BASED SURFACTANTS

Introduction of the so-called "ester quats" in the end of the last century is probably the best example of an

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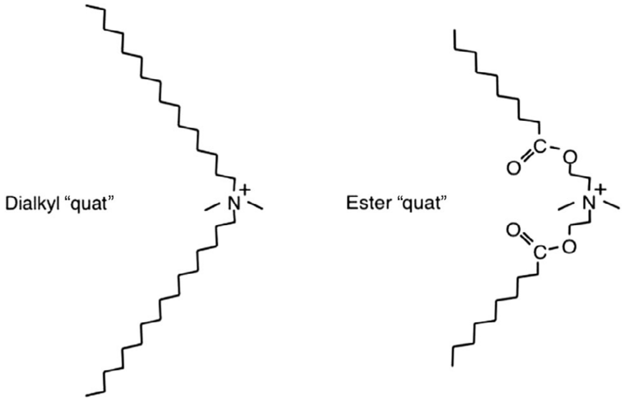

FIGURE 1 A dialkyl quat and an ester quat. The main difference is that the two long alkyl chains are connected to the cationic headgroup by ester bonds in the ester quat but not in the dialkyl quat

intended use of a labile surfactant in formulations. Ester quats typically consist of two long-chain fatty acids attached to a quaternary nitrogen via ester bonds, the other two substituents on the nitrogen atom being methyl or other small substituents. The ester quats replaced the "stable dialkyl quats," which contain two long and two very short alkyl chain substituents on the quaternary nitrogen as the active ingredient in fabric softeners. Typical structures are shown in Figure 1. The two types of quaternary ammonium amphiphiles have similar physical–chemical properties but the ester quats contain linkages that are susceptible to enzymatic and chemical hydrolysis in the sewage plants. Therefore, the ester quats, but not the dialkyl quats, met the criteria for aquatic toxicity and biodegradability, which already at that time were needed to pass the environmental requirements in Europe and the United States. More recently, surfactants of the ester quat type have been found to be efficient bactericides and fungicides (Migahed et al., 2016).

All ester bonds are susceptible to alkali but the ester quats are more labile than uncharged ester surfactants. The rate of alkali-catalyzed ester hydrolysis is influenced by the adjacent electron-withdrawing quaternary ammonium group. The inductive effect will lead to a decreased electron density at the ester bond; hence, alkaline hydrolysis, which starts by a nucleophilic attack by hydroxide ions at the ester carbonyl carbon, will be favored. Such esters are unusually labile on the alkaline side but stable under acidic conditions (Para et al., 2016). The effect of the quaternary ammonium group on the alkaline and acid rates of hydrolysis is due to a stabilization/destabilization of the ground state.

In ester quats there are three atoms, two carbons and one oxygen, between the quaternary nitrogen and the carbonyl carbon of the ester bond. In betaine ester surfactants there is only one carbon separating the two atoms, see Figure 2. This means that the electron-withdrawing effect exerted by the quaternary nitrogen becomes extremely strong. Therefore, the hydrolytic stability of such ester surfactants becomes unusually pH dependent. They undergo alkaline hydrolysis already at neutral pH. Acid hydrolysis, on the other hand, is highly unfavorable because it would involve a dicationic intermediate and does not occur unless the pH is extremely low. This is illustrated in Figure 2. 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 (Kronberg et al., 2014).

An ester bond situated close to a positive charge is generally more susceptible to alkaline hydrolysis than an ester without an adjacent positive charge and the closer the charge to the ester linkage the more labile it is, as has been discussed above. However, for surface active esters there is an additional enhancement of the hydrolysis rate by an effect that is often referred to as "micellar catalysis," although the term "catalysis" is not adequate in a strict sense (Bunton, 1991). The surface active esters, such as quats and betaine esters, form micelles above the critical micelle concentration (CMC). The highly positively charged micelles attract anions, including hydroxide ions. This means that the hydroxide ion concentration, that is, the pH, becomes higher in the vicinity of the micelles than in bulk. Alkaline hydrolysis will therefore occur at a higher rate with cationic ester surfactants self-assembled into micelles than with individual unimers. This type of reasoning is based on the so-called pseudophase ion exchange model, in which the micelles and the bulk aqueous solution are regarded as two distinct reaction regions, or pseudophases (Romsted, 1977). Provided that the exchange of material between the bulk and the micellar pseudophase is fast enough so that the reaction does not disturb the equilibrium distribution of the reactants, which has been shown to be true for most reactions, the observed reaction rate will be the weighted sum of the rates in the micellar and the aqueous pseudophases. The net result will be that the rate of alkaline hydrolysis will be much enhanced for surface active esters compared to non-surface active esters and the rate increase will be more pronounced the lower the CMC because a lower CMC means that a larger fraction of the ester surfactant will be in the form of micelles. This has been thoroughly studied for long-chain betaine esters (Lundberg & Holmberg, 2004; Thompson & Allenmark, 1992).

Base-catalyzed hydrolysis is a second-order process. However, at a fixed pH, that is, when the concentration of hydroxide ions is constant, the hydrolysis proceeds according to the first-order rate equation

$$\ln[A] = -k_1 t + \ln[A]_0.$$

where k_1 is the pseudo first-order rate constant (s^{-1}), $[A]$ is the ester concentration at time t, and $[A]_0$ is the initial ester concentration.

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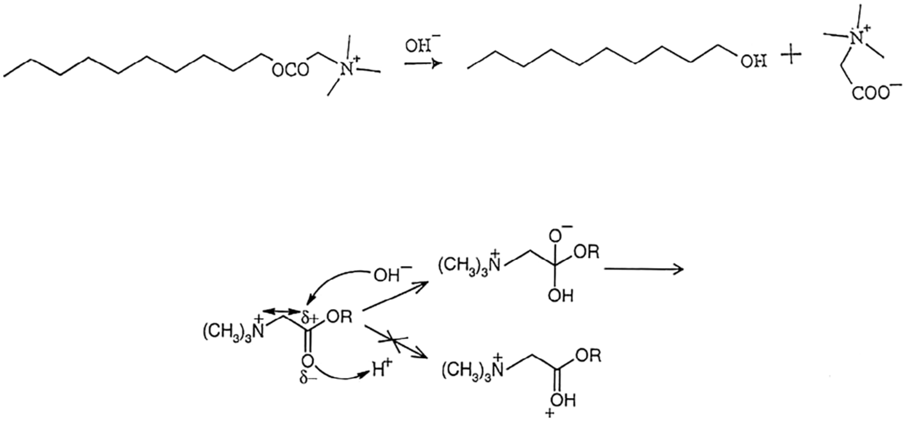

FIGURE 2 Top: Alkaline hydrolysis of a betaine ester surfactant; Bottom: The electron-withdrawing effect exerted by the positive charge on the nitrogen atom facilitates alkaline hydrolysis but disfavors acid hydrolysis

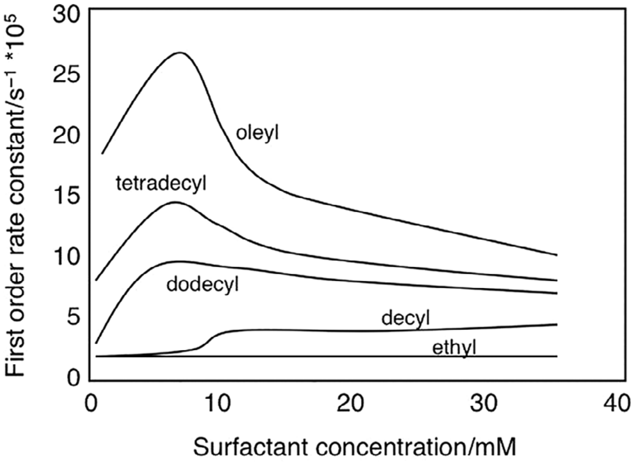

FIGURE 3 Hydrolysis of betaine ester surfactants with varying length of the hydrophobic tail. A non-surface active betaine ester, ethyl betainate, is also shown as a reference (from Lundberg & Holmberg, 2004)

Figure 3 shows pseudo-first order rate constants for alkaline hydrolysis of betaine esters with from 10 to 18 carbons in the hydrophobic tail (*R* in Figure 2). As can be seen, the rate constant is higher the longer the tail, which is due to a larger fraction of the surfactant being in self-assembled form when the hydrophobic tail is long (lower CMC value). This is a typical example of micellar catalysis, that is, an effect of a locally higher hydroxide ion concentration in the micellar pseudophase. The surfactant with the longest tail, oleyl betainate, has approximately 30 times higher rate constant at the optimum concentration than the non-surface active ethyl betainate.

The initial increase in hydrolysis rate with increasing surfactant concentration is due to a larger fraction of the surfactant being present in micelles. The rate constant reaches a maximum and then starts to decline. The decrease in reaction rate at higher concentrations for the surface active betaine esters is due to a competition between the surfactant counterion, which is chloride in this case, and the hydroxide ions around the micelle surface. The hydroxide ion concentration in the solution is constant while the chloride ion concentration increases as more and more surfactant is added. Chloride ions are more polarizable than hydroxide ions which means that they show stronger affinity to the charged micelle surface (Leontidis, 2002). This, in turn, implies that there will be a decrease in the locally elevated hydroxide ion concentration in the micellar pseudophase as the concentration of chloride ions increase (as a consequence of the increasing surfactant concentration). This effect can be fully accounted for by the pseudophase ion exchange model. If an even more polarizable anion, such as bromide, is used as surfactant counterion, the micellar catalysis would be considerably smaller. Addition of extra salt will also impact the micellar catalysis. The hydroxide ions will not be able to compete for the micelle surface if the total concentration of other anions is too high.

The extraordinary pH dependence of the hydrolysis of surface active betaine esters have made them candidates for use as "soft antimicrobial agents," that is, microbicides with a temporary action. In the case of amphiphilic betaine esters, they would be biologically active under slightly acidic conditions but decompose into harmless products, the natural amino acid betaine and a fatty alcohol, as the pH is raised to neutral or above. The antimicrobial effect has been tested on a number of bacteria including *Salmonella typhimurium* (Ahlström & Edebo, 1998; Lindstedt et al., 1990). Disinfection in the poultry industry (or other food industries) is a typical application. In food production the lines are continuously cleaned and disinfected. Using a disinfectant whose antimicrobial effect disappears after rinsing with dilute alkali is attractive from a hygiene perspective. Another typical application for a soft antimicrobial agent is wound disinfection. More recently, soft microbicides with an amide bond as the weak linkage have been explored (Hoque et al., 2012).

An even higher rate of alkaline hydrolysis of ester bonds in cationic surfactants was found for gemini surfactants. Several types of gemini surfactants containing ester bonds in either the spacer unit or in the side

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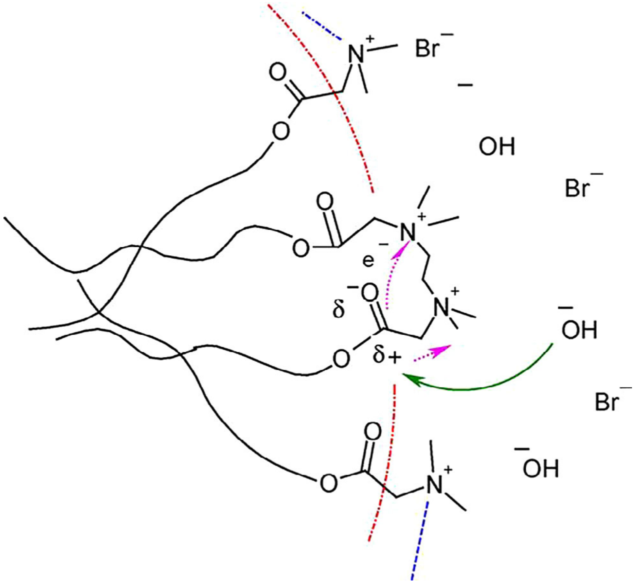

FIGURE 4 Alkaline hydrolysis of a gemini betaine ester surfactant may be accelerated through a neighboring group participation mechanism (redrawn from Tehrani-Bagha et al., 2007)

chains have been synthesized and characterized by the group of Abe and several others (Bhadani et al., 2014, 2015, 2020). The susceptibility to alkaline hydrolysis of gemini surfactants with the long side chains connected to the quaternized nitrogens by ester bonds which were either in "ester quat mode" or "betaine ester mode" (see Figures 1 and 2, respectively) has been thoroughly evaluated (Tehrani-Bagha et al., 2007) and the hemolytic activity for gemini surfactants of betaine ester type has also been determined (Luczynski et al., 2013). For both the ester quat and the betaine type of ester bond the rate of hydrolysis was considerably faster for the gemini than for the monomeric surfactant. This may be related to the fact that the counterion binding was found to be considerably lower for the gemini surfactant micelles than for the micelles of the corresponding monomeric surfactant (Tehrani-Bagha et al., 2007). This means that micelles of the gemini surfactant will more efficiently attract other anions, for example, hydroxide ions. Thus, the local pH around the micelle surface will be higher around micelles of the gemini surfactants than around micelles of the corresponding monomeric surfactants.

Another possible reason for the fast degradation of the gemini surfactants is shown in Figure 4 (Tehrani-Bagha et al., 2007). The hydrolysis starts as a nucleophilic attack by the hydroxide ion at one of the carbonyl carbons of the gemini surfactant. As discussed above, the reaction is faster than for normal esters because the adjacent quaternary ammonium group pulls electrons away, rendering the site of attack very electrophilic. For a gemini surfactant, the second quaternary nitrogen may lend anchimeric assistance, a kind of neighboring group participation, to the hydrolysis. As is illustrated in the figure, the result will be that the carbonyl carbon will be depleted of electrons by two mechanisms, rendering it extremely electrophilic.

As has been discussed above, cationic ester-based surfactants are generally susceptible to base catalyzed hydrolysis. However, the rate of cleavage of the ester bond can be manipulated by a number of factors such as (i) the proximity of the cationic charge, (ii) micellar catalysis, and (iii) neighboring group participation. As with all hydrolysis reactions, steric hindrance is also likely to be an important factor. The effect of steric hindrance on the hydrolysis rate seems not to have been systematically investigated for cationic ester-based surfactants but it has been studied for nonionic surfactants carrying an ester bond between the oligo(ethylene glycol) chain and the hydrophobic tail, see *Nonionic ester-based surfactants*.

More recently, cationic gemini surfactants with ester bonds in the side chains and amide bonds in the spacer unit have been synthesized and characterized (Wu et al., 2020). The ester bonds are susceptible to alkali while the amide bonds undergo acid hydrolysis more readily. Such surfactants will have an unusual hydrolysis profile.

ANIONIC ESTER-BASED SURFACTANTS

Anionic surfactants with an ester linkage in the molecule usually have a sulfonate group as the polar headgroup. Dialkylsulfosuccinates, sulfonated fatty acid methyl esters, and isethionates are well-known examples.

These surfactants usually come with sodium as counterion. All ester sulfonate surfactants exhibit an unusually high stability towards alkaline hydrolysis of the ester bond. The main reason for the alkaline stability is that hydroxide ions do not readily attack the negatively charged micelles. The situation is opposite to that for ester surfactants carrying a positive charge in the polar headgroup. As discussed above, such micelles attract counterions and the pH around the micelles is higher than the bulk pH. For negatively charged surfactant micelles the hydroxide ion concentration, that is, the pH, around the micelles is lower than in the bulk phase. We can here talk about "micellar protection" of the surfactant esters.

Since the ester bonds present in the strongly negatively charged surfactant micelles are protected from attack by hydroxide ions, only ester surfactants present as unimers in bulk are subject to hydrolysis. This means that alkali-catalyzed hydrolysis of anionic ester surfactants at a fixed pH is in practice a pseudo-zero order reaction provided that the major part of the surfactant is present in the micelles. In zero order reactions the rate is independent of both reacting species, the surfactant unimers in solution and the hydroxide

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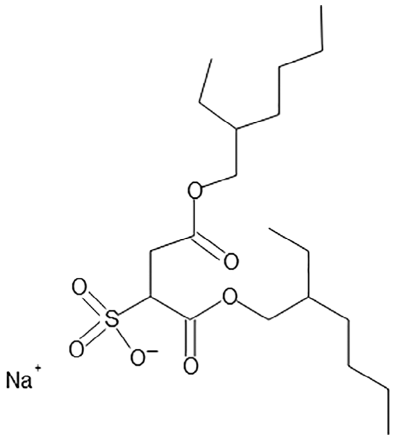

FIGURE 5 The anionic ester-containing surfactant sodium bis (2-ethylhexyl)sulfosuccinate

ions. Below the CMC the concentration of surfactant unimers stays constant and the hydrolysis proceeds at a constant rate. The micelles supply new unimers to keep the concentration in the bulk at a constant value, the CMC. Only when the hydrolysis has progressed so far that the CMC has been reached will the unimer concentration in the bulk phase start to decrease and the reaction then becomes first order.

The net result from the above discussion is that anionic ester-based surfactants are much more stable than one might expect from a water-soluble ester because the surfactants present in micelles are protected from attack by hydroxide ions. This, in turn, means that the surfactant stability increases with a decrease in CMC value because a lower CMC means fewer unimers in solution.

The rate of alkaline hydrolysis of unimers of ester-based anionic surfactants will be influenced by the inductive effect exerted by the adjacent negative charge, which makes the carbonyl carbon of the ester bond less electrophilic, as well as to steric hindrance around the ester bond. Take the well-known surfactant bis(2-ethylhexyl)sulfosuccinate as an example. This surfactant, see Figure 5, is often referred to as Aerosol OT or AOT and is frequently used in formulations at relatively high pH, although it undergoes alkaline hydrolysis at a reasonable speed at a pH of around 11 at room temperature.

The surfactant is a diester of sulfosuccinic acid. The sulfonate group will push electrons towards the carbonyl carbon of the two ester bonds making them less electrophilic than for normal esters and more so for the ester bond that is in direct proximity to the sulfonate group. That carbonyl carbon will also be more sterically hindered. One may therefore expect that the surfactant when subjected to alkali will first be degraded to the monoester which would contain two negatively charged groups, a sulfonate and a carboxylate. That would still be a surfactant but a very hydrophilic one. The alcohol generated, 2-ethylhexanol, is also a surface active species but a very hydrophobic one. Thus, one may expect that the two hydrolysis products will both enter the micelles of the diester. The monoester will push the CMC to a higher value and the alcohol will drive it in the opposite way.

Mukherjee et al. have made a detailed study on alkaline hydrolysis of Aerosol OT (Mukherjee et al., 1994). Their work confirmed that the initial hydrolysis occurred at the ester bond with one carbon in-between the sulfonate group and the carbonyl carbon of the ester bond. They measured the enthalpy of the first hydrolysis step at different surfactant concentrations and found that the ΔH values were more negative above the CMC than below the CMC. They also found that at concentrations above the CMC, the values remained more or less constant. This is all in line with a zero-order hydrolysis reaction above the CMC.

The relatively high stability of hydrophobic anionic ester surfactants is of practical importance. It means that such surfactants can be used also in alkaline formulations provided that the surfactant concentration is far above the CMC, which is normally the case. On dilution, which may occur during a rinsing step, and which will ultimately take place in a sewage plant, the concentration will fall below the CMC, the hydrolysis rate will be relatively fast, and the biodegradation will be facilitated.

NONIONIC ESTER-BASED SURFACTANTS

At first sight noncharged ester-containing surfactants appear to be more straight-forward when it comes to hydrolysis of the ester linkage. The absence of charges at the micelle surface should mean that there will be neither an accumulation nor a depletion of hydroxyl ions in the micellar pseudophase. This is not completely true, however. These surfactants are typically fatty acid esters of either an oligo(ethylene glycol) chain or a sugar. When the ester bond is cleaved, a fatty acid salt is generated together with the uncharged polar headgroup. The fatty acid salt is an anionic amphiphile and will enter the micelles of the nonionic surfactant. Mixed micelles will form, and these will carry a negative charge. Thus, the initial degradation will lead to an increased hydrolytic stability of the remaining nonionic surfactant, provided that the concentration of the surfactant is well above the CMC. This is illustrated in Figure 6, which shows the half-life of tetra(ethylene glycol) monoester of octanoic acid at various initial concentrations of the surfactant (Stjerndahl & Holmberg, 2003). The CMC value for the surfactant is 50 mM. As can be seen from the figure, at that concentration the half-life of the surfactant starts to increase in a linear fashion. This is a clear indication of the ester-containing nonionic surfactant being protected from attack by hydroxide ions when present in micelles.

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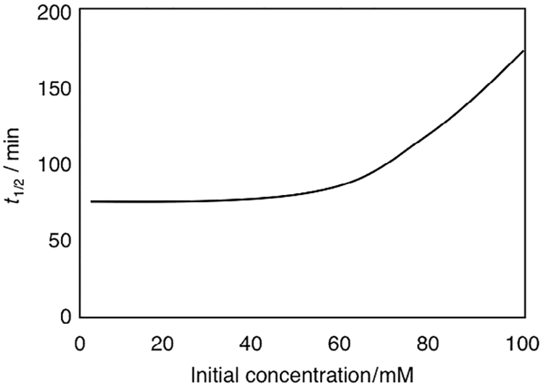

FIGURE 6 Half-life, $t_{1/2}$, versus initial concentration of the surfactant tetra(ethylene glycol) monoester of octanoic acid. The CMC of the surfactant is 50 mM (Redrawn from Stjerndahl & Holmberg, 2003)

As mentioned above, steric hindrance is also likely to play a role for the stability of ester-containing surfactants. This has been investigated in some detail for the series of four tetra(ethylene glycol) monoesters of carboxylic acids with different substitution pattern close to the carbonyl carbon of the ester bond, shown in Figure 7 (Stjerndahl & Holmberg, 2003).

Figure 7 shows that the substitution on carbon atom 2 in the alkanoic acid chain plays a big role for the rate of hydrolysis. A methyl substituent does not influence the rate much compared to the situation with no substituent while an ethyl substituent gives a much more sluggish hydrolysis. This is a bit surprising.

The four surfactants were also subjected to enzyme-catalyzed hydrolysis using either *Mucor miehei* lipase or *Candida antarctica B* lipase as catalyst (Stjerndahl et al., 2003). The rate of hydrolysis was even more influenced by the substitution pattern and there was a considerable rate difference between the unsubstituted ester (Surfactant 1 in Figure 7) and the methyl-substituted ester (Surfactant 2 in Figure 7). The rate of biodegradation of the four surfactants was also determined using the Closed Bottle test, the classical test method for "ready biodegradability," and the results are shown in Figure 8. As can be seen, the biodegradation rate was the same for Surfactants 1, 2, and 3 but much slower for Surfactant 4. Surfactants 1–3 passed the degradation threshold of 60% degradation in 28 days, which is an important criterion in the assessment of biodegradability. Surfactant 4 was too slow to pass the threshold.

An observation that follows from the results from the alkaline hydrolysis, the lipase catalyzed hydrolysis and the biodegradation of the four ester-based nonionic surfactants is that neither chemical hydrolysis, nor enzymatic hydrolysis can be used as a tool to predict the outcome of the biodegradation test. The biodegradation test is made by exposing the surfactant to a sample of activated sludge from a sewage plant. The biodegradation pathways are obviously very complex and cannot be extrapolated to simple chemical or enzymatic breakdown. Nevertheless, the results indicate that an ester bond in a typical nonionic surfactant can be readily degraded in a sewage plant provided the substitution in the close vicinity of the ester bond is not too severe.

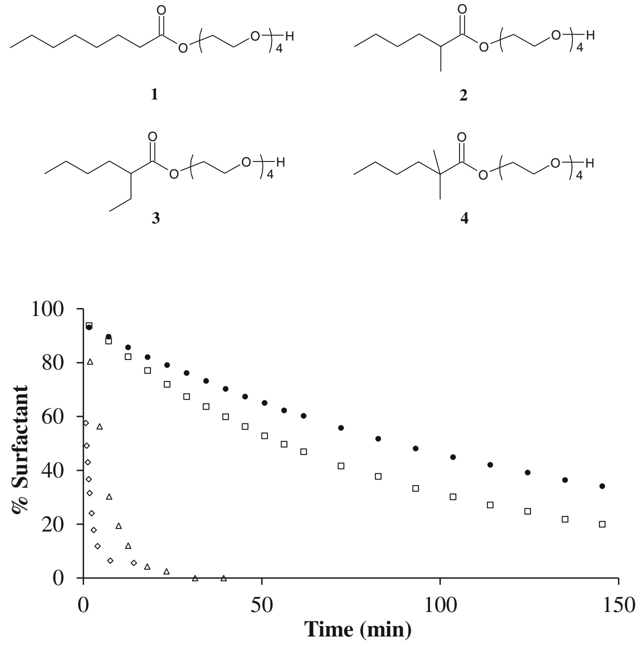

FIGURE 7 Top: Structure of four monoesters of tetra(ethylene glycol) with different substitution pattern close to the ester bond. Bottom: Degradation of the four surfactants at pD 13 monitored by ^{1}H NMR. (◇) Surfactant **1**, (△) Surfactant **2**, (□) Surfactant **3**, and (●) Surfactant **4** (redrawn from Stjerndahl & Holmberg, 2003)

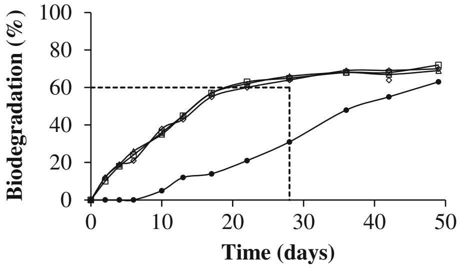

FIGURE 8 Biodegradation versus time of the four surfactants shown in Figure 7 (redrawn from Stjerndahl et al., 2003)

SURFACTANT MIXTURES

Many surfactant-based formulations contain more than one type of amphiphile. For instance, household cleaning formulations are often based on a combination of an anionic and a nonionic surfactant and combinations of a nonionic and a cationic surfactant are frequently

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used for hard surface cleaning. When ester-based surfactants are used it is of interest to investigate the stability of the individual species.

Such a study was made for a mixture one ester-containing cationic surfactant, decyl betainate, and one ester-containing nonionic surfactant, tetra(ethylene glycol) mono-n-octanoate (Lundberg et al., 2005). Alkaline hydrolysis of the individual components of the mixture has been discussed above in the sections *Cationic ester-based surfactants* and *Nonionic ester-based surfactants*, respectively. The structures are shown in Figures 2, top and 7 top, (structure 1). The CMC values for the two surfactants were in the same range, 7 mM for the nonionic and 10 mM for the cationic surfactant, indicating that the mixed micelles that will form in solution will contain appreciable amounts of both species. The micelles will carry a positive charge, which means that the hydroxide ion concentration in the micellar pseudophase will be higher than in the bulk. Thus, micellar catalysis may accelerate the hydrolysis not only of the cationic ester-containing surfactant but also of the nonionic ester-based amphiphile.

The micellar interaction parameter, β, for the mixture was determined from the CMC values for varying mixtures of the two surfactants and found to be -2.4, indicating a moderate net attraction, which is according to expectations.

The hydrolysis rate of the ester-containing betaine surfactant was found to follow the pseudophase ion exchange model discussed above. The rate was higher above than below the CMC, which is indicative of micellar catalysis, and it decreased with decreasing ratio of cationic to nonionic surfactant, most likely due to dilution of the positive charges on the micelle surface.

Thus, alkaline hydrolysis of the cationic ester-containing surfactant proceeded according to expectations with the rate decreasing due to less pronounced micellar catalysis with the mixed micelles. The nonionic ester-based amphiphile, which was also present in the mixed micelles, was not affected by the increase in hydroxide ion concentration in the micellar pseudophase, however. It remained stable during the course of the experiment. Evidently, at the bulk pH and buffer strength used in the experiment, 8.5 and 100 mM, respectively, micellar catalysis will induce hydrolysis of the ester bond in the cationic but not in the nonionic surfactant. This is obviously due to the high electrophilicity of the carbonyl carbon in the betainate surfactant but not in the nonionic ester surfactant.

To the best of our knowledge, related experiments have not been conducted and reported for mixtures of an anionic and a nonionic ester-containing surfactant. However, one may anticipate that the "micellar protection" effect, discussed in the section *Anionic ester-based surfactants* will be applicable not only for the anionic but also for the nonionic surfactant; thus, the more vulnerable nonionic surfactant ester will be protected from alkaline hydrolysis by the anionic amphiphile when present in mixed micelles. The same protection is of course likely to be provided also by anionic surfactants that lack an ester group. This is important from a practical point of view. An alkali-sensitive nonionic surfactant becomes more stable to hydrolysis when it is combined with an anionic surfactant.

CONCLUSIONS

In this article we demonstrate that amphiphilic esters show hydrolysis patterns different from that of regular uncharged and non-surface active esters. Cationic surfactants undergo alkaline hydrolysis readily and the rate is higher the lower the CMC of the surfactant. This is due to micellar catalysis. Cationic gemini surfactants with ester bonds connecting the spacer and the tails exhibit an even higher rate of ester bond cleavage.

Anionic surfactants are protected from alkaline hydrolysis when present in micelles. This is the opposite to micellar catalysis and is referred to as micellar protection. The lower the CMC of the surfactant, that is, the higher the proportion of self-associated surfactant, the more pronounced is the micellar protection. Also nonionic ester surfactants, which are usually fatty acid esters, exhibit micellar protection. When such a surfactant starts to hydrolyze, the generated fatty acid salt will enter the nonionic surfactant micelles. The mixed micelles that form will then carry a negative charge, which hinders approach of hydroxide ions. At constant pH the breakdown of the surfactant becomes a zero-order reaction. Only surfactant unimers participate in the hydrolysis reaction and the concentration of unimers is constant below the CMC.

We have demonstrated that in a mixture of a cationic and a nonionic surfactant the cationic surfactant breaks down rapidly due to micellar catalysis. The hydrolysis of the nonionic amphiphile is not accelerated, however. We have not shown, but we speculate that for a mixture of an anionic and a nonionic ester-containing surfactant the hydrolysis of both amphiphiles will be slow due to the micellar protection effect.

From a practical point of view, it is important to remember that both micellar catalysis and micellar protection assumes surfactant concentrations exceeding the CMC values. On dilution, such as in the effluent that reaches the sewage plant, the surfactant concentration becomes very low, which means that the specific effects on the hydrolysis rate disappear.

AUTHOR CONTRIBUTIONS

Dan Lundberg: Conceptualization, investigation. **Maria Stjerndahl**: Conceptualization, investigation. **Krister Holmberg**: Conceptualization, writing.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest. Dan Lundberg is currently employed by AstraZeneca R&D, 431 83 Gothenburg, Sweden. Maria Stjerndahl is employed by Sahlgrenska University Hospital, 41,345 Gothenburg, Sweden.

ETHICS STATEMENT

We hereby declare that this article is our own work and has not been published elsewhere. All sources used in the paper are properly cited. No human or animal subjects were used in this research.

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How to cite this article: Lundberg D, Stjerndahl M, Holmberg K. Ester-based surfactants: Are they stable enough? J Surfact Deterg. 2023;26(3):229–36. https://doi.org/10.1002/jsde.12628

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