Kinetics and Mechanism for the Sonochemical Degradation of a Nonionic Surfactant

Ritu Singla, Franz Grieser, and Muthupandian Ashokkumar*

Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Victoria 3010, Australia

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The sonolytic degradation of the nonionic surfactant, octaethylene glycol monododecyl ether ($C_{12}E_8$), has been studied at various initial concentrations below and above its critical micelle concentration (CMC). It has been observed that the degradation rate increases with an increase in the initial concentration of the surfactant until the CMC is reached. Above the CMC an almost constant degradation rate is observed, suggesting that the surfactant in its monomer form is involved in the degradation process. The degradation process of $C_{12}E_8$ involves two distinct primary processes occurring at the bubble/solution interface: (a) hydroxylation/oxidation of the surfactant and (b) pyrolytic fragmentation of the surfactant. The oxidative cleavage of ethylene oxide units provides evidence for OH radical attack. Hydroxylation of the ethoxy chain gives rise to various short-chain carboxyalkyl−polyethylene glycol intermediates. The polyethylene glycol chain formed, due to the scission of the $C_{12}E_8$ molecule, undergoes rapid hydroxylation/oxidation to yield simple compounds that have the potential to undergo further degradation. The detection of multiple intermediates indicates that several processes affect the complete degradation pathways of the surfactant molecule. TOC analysis, however, indicates that the sonolytic mineralization of the surfactant is difficult to achieve at reasonable rates due to the relatively low surface activity of the degradation products formed during sonolysis.

Introduction

Over the past few decades, nonionic surfactants have increased their market share to reach about 40% of the total worldwide surfactant production.[1] Nonionic surfactants do not produce ions in aqueous solutions and are less sensitive to electrolytes than are ionic surfactants. As a consequence, they are compatible with other types of surfactants and are excellent components for use in complex mixtures, as is commonly found in a large number of domestic and industrial products. Nonionic surfactants are also good detergents, wetting agents, and emulsifiers, and some have good foaming properties. Some types exhibit very low toxicity levels and are therefore used in pharmaceuticals, cosmetics, and food products.[1]

In general, the surfactant market is dominated to a large extent by nonionics, especially by polyethoxylated products, that is, those whose hydrophilic group is a polyethylene glycol chain produced by the polycondensation of ethylene oxide onto a hydroxyl or amine group. Of the several types of polyethoxylated products, the alkylphenol ethoxylates (APE) are the most widely used.[2] The use of APE has been restricted since the discovery in 1984 that they are only partially degraded and their breakdown products are more toxic and more persistent in the environment than APE themselves.[3] For example, nonyl phenol is approximately 10 times more toxic than its ethoxylate precursor.[4] Therefore, eco-friendly alternatives, linear alcohol ethoxylates (LAE), were developed.

Currently, linear alcohol polyglycol ethers ($R(OCH_2CH_2)_nOH$) represent the economically most important group of nonionic surfactants. The widespread use of LAE unfortunately also increases their importance as environmental pollutants. The question of their biodegradability and ultimately their environmental fate constitutes the decisive criterion in their environmental compatibility assessment. However, experimental results from many biodegradation studies[5] suggest that these surfactants ultimately degrade in the environment.

Kravetz et al.[6] observed >80% primary degradation in 28 days for LAE and 40% for branched alcohol ethoxylates (AE). Balson and Felix[7] suggested that the breakdown of these compounds yields a hydrophobe and a polyethoxylate unit, effectively achieving primary degradation. On the other hand, studies[8] dealing with the degradation of the polyethylene glycol structure and short-chain homologues have shown that polyethylene glycols with low molecular mass (less than 400 units) are biodegradable, but those with high molecular mass cannot be completely degraded.[9] It has also been suggested in some reviews[1,9] that the polyethylene glycol chain of LAE is the slower degradable moiety of the surfactant molecule. In all of these studies, an understanding of the degradation routes leading to the mineralization and assimilation of the surfactant molecule in the environment through intermediates is still lacking.

The employment of “advanced oxidation techniques” has the advantage of providing information about the complete degradation of a pollutant and offers the opportunity to analyze all relevant degradation products. Several papers deal with the degradation of nonionics using advanced oxidation techniques; however, the majority of these studies have focused on the photochemical degradation of alkylphenol ethoxylates.[10−12] For example, Brand et al.[10] have reported the homogeneous photochemical degradation of APE in alkaline solutions of Fe(III) at $\lambda < 300$ nm, while Pelizzetti et al.[11] have reported the complete mineralization of APE using TiO_2 as a photocatalyst. A few studies have been carried out on the degradation of APE’s using ultrasonic irradiation.[13,14]

The chemical reactions ensuing from the ultrasonic irradiation of a solution are produced through the phenomenon of cavitation.[15] Cavitation refers to the rapid growth and implosive collapse of bubbles in a liquid resulting in an unusual reaction environment within and in the vicinity of bubbles. Compression of gas and vapor within the bubbles generates intense heat and

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* Corresponding author. E-mail: masho@unimelb.edu.au.

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can generate local hot spots. Recent measurements[16,17] carried out under experimental conditions similar to those used in the present study indicate that effective temperatures as high as 4500 K are reached within these collapsing bubbles. Because the core temperature reaches a value similar to that reported by Suslick et al.,[18] we speculate that the interfacial region would reach about 1900 K as suggested in their report.

According to "hot spot" theory, sonochemical reactions can occur in three different regions, that is, at the interior of the collapsing bubbles, at the interfacial region being the thin shell of fluid surrounding the collapsing cavitation bubble, and finally in the bulk of the solution.[19] The sonolysis of organic compounds in dilute aqueous solution proceeds by two-reaction pathways.[18] First, volatile compounds evaporate during the expansion cycle and degrade via pyrolytic and combustive reactions within the collapsing cavitation bubble.[20] Second, it occurs by the reaction of OH radicals with the solute adsorbed at the bubble interface, in the bulk, and to some extent within the bubbles.[21] The choice of the reaction pathway depends on the volatility, hydrophobicity, and surface activity of the compound.[22]

To our knowledge, data on the complete sonochemical degradation of a LAE have not been reported previously. Therefore, in this study, an attempt has been made to examine the sonochemical reaction kinetics of a representative LAE, octaethylene glycol monododecyl ether ($C_{12}E_8$) (eight ethylene oxide units as the hydrophilic group and C_{12} alkyl chain as the lipophilic group of the surfactant), along with its sonochemical degradation pathway.

Experimental Setup

Materials. The nonionic surfactant octaethylene glycol monododecyl ether ((Biochemica, $C_{12}E_8$) was used as received. Water was obtained from a three-stage Milli-Q water purification system with conductivity of $<10^{-6}$ S cm^{-1} and surface tension of 72 mN m^{-1} at 25 °C.

Sonolysis and Reaction Conditions. Sonolysis experiments were performed at an ultrasound frequency of 355 kHz in continuous wave mode. The ultrasound unit used was an ELAC LVG-60 RF generator coupled with an ELAC Allied signal transducer with a plate diameter of 54.5 mm. The power output on the RF generator for all of the experiments was 30 W. The effective calorimetric power[23] delivered to the solutions was 18 W. The volume of the solutions sonicated was 200 mL. Experiments were carried out under atmospheric conditions and at room temperature. To maintain the reaction conditions at room temperature (20 ± 5 °C), water was circulated through a double walled jacketed cell.

Analytical Determinations. Solute concentration was monitored over time using electrospray mass spectrometry (ESMS). The mass spectrometer used was a Micromass QUATTRO 11 coupled to a Hewlett-Packard series 1100 degasser. The instrument was calibrated using its automatic tuning procedure with respect to the parent compound as the standard. The mass range scanned was m/z 50−700, and several spectra were obtained across each chromatographic peak. All of the mass spectra were the averages of 3−4 spectra obtained across the top of each chromatographic peak with background noise substraction. The analysis was carried out in positive electrospray ionization mode at cone voltages of 30, 50, and 80 V. The mobile phase consisted of 50% acetonitrile and 50% water. The flow rate of the solvent was 0.03 mL min^{-1}, and the capillary voltage was set at 3.5 kV. To the test sample was added 1% formic acid to enhance the relative peak height of $C_{12}E_8$ and its degradation intermediates.

The degradation intermediates were identified by comparing the chromatograms to those of known compounds using mass spectrometry and HPLC. The HPLC used was a Shimadzu LC-10 AT VP system with a Shimadzu SPD-10 AVP UV−visible absorbance detector. The detector wavelength was set at 210 nm. To quantitatively analyze the formation of acids, an Alltech 5 μm Prevail organic acid column was used. The mobile phase used was a solution containing 0.025 M KH_2PO_4 and 0.015 M H_3PO_4. The flow rate of the solvent was 1.0 mL min^{-1}.

TOC was determined with a total organic carbon analyzer, which utilizes oxidative combustion followed by infrared detection. The TOC analyser used was a TOC-V_{CSH} (Shimadzu) programmed by TOC-Control V Software. The instrument was calibrated before each use with standardized TOC solutions in the range of 1−1000 mg L^{-1}.

Gaseous products were quantitatively analyzed using a Shimadzu GC-17A gas chromatograph. Calibration curves of methane, ethane, ethylene, and acetylene gases were constructed by injecting known amounts into the column. Product yields were determined by converting the calibration curve peak areas into gas concentrations. The solubility of these gases in aqueous solution was also taken into account in the calculations.

The concentration of H_2O_2 was determined to gauge the amount of OH radicals generated. Samples of varying concentrations of $C_{12}E_8$ were sonicated for 10 min, and the H_2O_2 concentration was measured using a standard technique.[24] Iodide ions were oxidized by sonochemically produced hydrogen peroxide to form molecular iodine, which then reacts with free iodide to form I_3^-. The concentration of I_3^- was determined spectrophotometrically by following its absorbance at 353 nm and using the molar extinction coefficient of I_3^- (26 400 M^{-1} cm^{-1}).[24]

In the Results and Discussion, the quantity G_{SC} has been used to interpret the observed degradation rate of surfactant molecules, the formation of H_2O_2, and the formation of hydrocarbon products per calorimetric power delivered into the aqueous solution per second. That is,

$$G_{SC} = X/Y \tag{1}$$

where X is the number of moles of solute degraded, and Y is the calorimetric power delivered (J/s) (Y × sonication time (s) = the energy "dose").

Results and Discussion

Sonolytic Degradation. The sonochemical degradation of the nonionic surfactant $C_{12}E_8$ was studied over a wide range of concentrations spanning the critical micelle concentration (CMC). The amount of $C_{12}E_8$ degraded with dose/sonication time for different initial $C_{12}E_8$ concentrations is shown in Figure 1. It can be observed that the amount of $C_{12}E_8$ degraded increases with dose for all concentrations. In Figure 2, G^i_{SC} is calculated and plotted as a function of initial $C_{12}E_8$ concentration. G^i_{SC} represents the initial concentration of $C_{12}E_8$ degraded (30 min of sonication; this concentration was chosen to avoid product interference at longer sonication time) per unit of calorimetric power delivered.

The data shown in Figure 2 reveal two distinct concentration regimes. First, the G^i_{SC} increases linearly with increasing concentrations of $C_{12}E_8$ up to ~90 μM. However, above this $C_{12}E_8$ concentration, the G^i_{SC} changes by a far smaller extent or, within experimental error, remains the same. It is of relevance

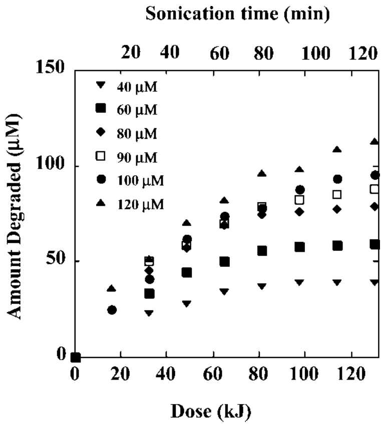


Figure 1. Amount of $C_{12}E_8$ degraded at different initial concentrations at an ultrasound frequency of 355 kHz as a function of dose and sonication time.

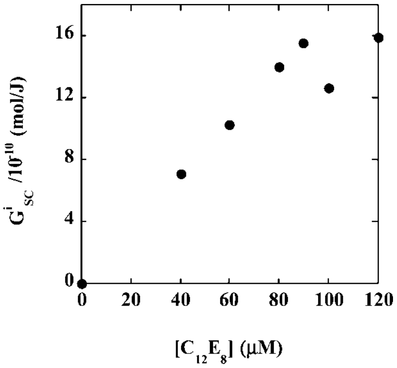


Figure 2. G^{i}_{SC} (where, i represents the initial concentration of $C_{12}E_8$ degraded (30 min sonication time)) as a function of initial $C_{12}E_8$ concentration at an ultrasound frequency of 355 kHz.

to note that about 90 μM approximately corresponds to the CMC value of $C_{12}E_8$.[25]

An almost constant G^{i}_{SC} value above the CMC suggests that only surfactant in the monomer form is involved in the degradation process.[14] This implies that the sonolytic degradation of $C_{12}E_8$ is primarily an interfacial event. Hydrophobic organic compounds tend to partition at the collapsing cavitation bubble/solution interface and degrade mainly by direct thermal decomposition leading to the formation of byproducts.[26] Conversely, nonvolatile hydrophilic compounds degrade to produce oxidation byproducts by reacting with hydroxyl radicals that diffuse out of the cavitation bubbles.[27]

The nonionic surfactant $C_{12}E_8$ is composed of both hydrophobic and hydrophilic moieties. The ethoxy chain is hydrophilic and lies in the aqueous phase, whereas the hydrophobic hydrocarbon chain is oriented into the bubble. Therefore, two possible degradation pathways exist for the $C_{12}E_8$ monomer: (a) OH radical attack on the monomer at the bubble surface and/or (b) thermolytic decomposition of the monomer at the bubble/solution interface either directly or following radical attack.

Sostaric and Riesz[26] in their sonochemical study of $C_{10}E_8$ by an EPR spin trapping technique reported that the ethoxy and alkyl chains of $C_{10}E_8$ undergo pyrolytic decomposition, and they deduced that this was most likely after initial attack by OH radicals at the bubble/solution interface. The efficiency with which a surfactant molecule reacts with hydroxyl radicals generated in a sonochemical process is related to its interfacial concentration,[26] which is proportional to the extent of adsorption at the bubble/solution interface. Henglein and Kormann[28] reported that the greater the hydrophobicity of a solute in an aqueous medium, the more efficient is the solute as an OH radical scavenger. Vinodgopal et al.[14] and Ashokkumar et al.[29] showed similar results in their studies on the sonochemical degradation of surfactants in air-saturated aqueous solutions.

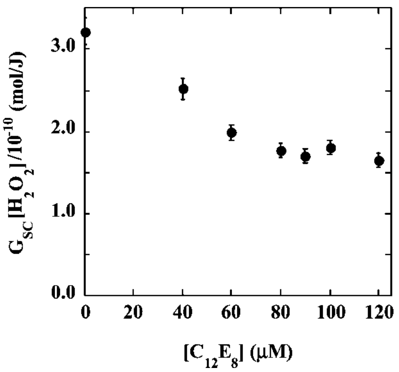


Figure 3. The H_2O_2 yield as a function of initial $C_{12}E_8$ concentration. Initial G_{SC} represents the H_2O_2 yield in pure water. The aqueous solutions in the presence and absence of $C_{12}E_8$ were sonicated for 10 min at an ultrasound frequency of 355 kHz.

However, in the absence of a scavenger, some of the primary OH radicals undergo recombination to form H_2O_2 in the bulk of the solution.[30] Henglein and Kormann[28] stated that an aqueous solution of solutes with higher hydrophobicity exhibits lower H_2O_2 yields during sonolysis. Similar results were observed in the case of $C_{12}E_8$ as shown in Figure 3. The $G_{SC}(H_2O_2)$ decreased with an increase in the $C_{12}E_8$ concentration. The decrease in the $G_{SC}(H_2O_2)$ can be explained on the basis that surfactant molecules tend to exist at relatively high concentrations in the hot shell of the hotspot.[19] They can scavenge a proportion of the primary radical species in this region, thus competing with the primary radical recombination processes. Thus, even in solutions containing a very low concentration of solute, only a small fraction of OH radicals escape from the bubble/solution interface and reach the bulk phase of the liquid.

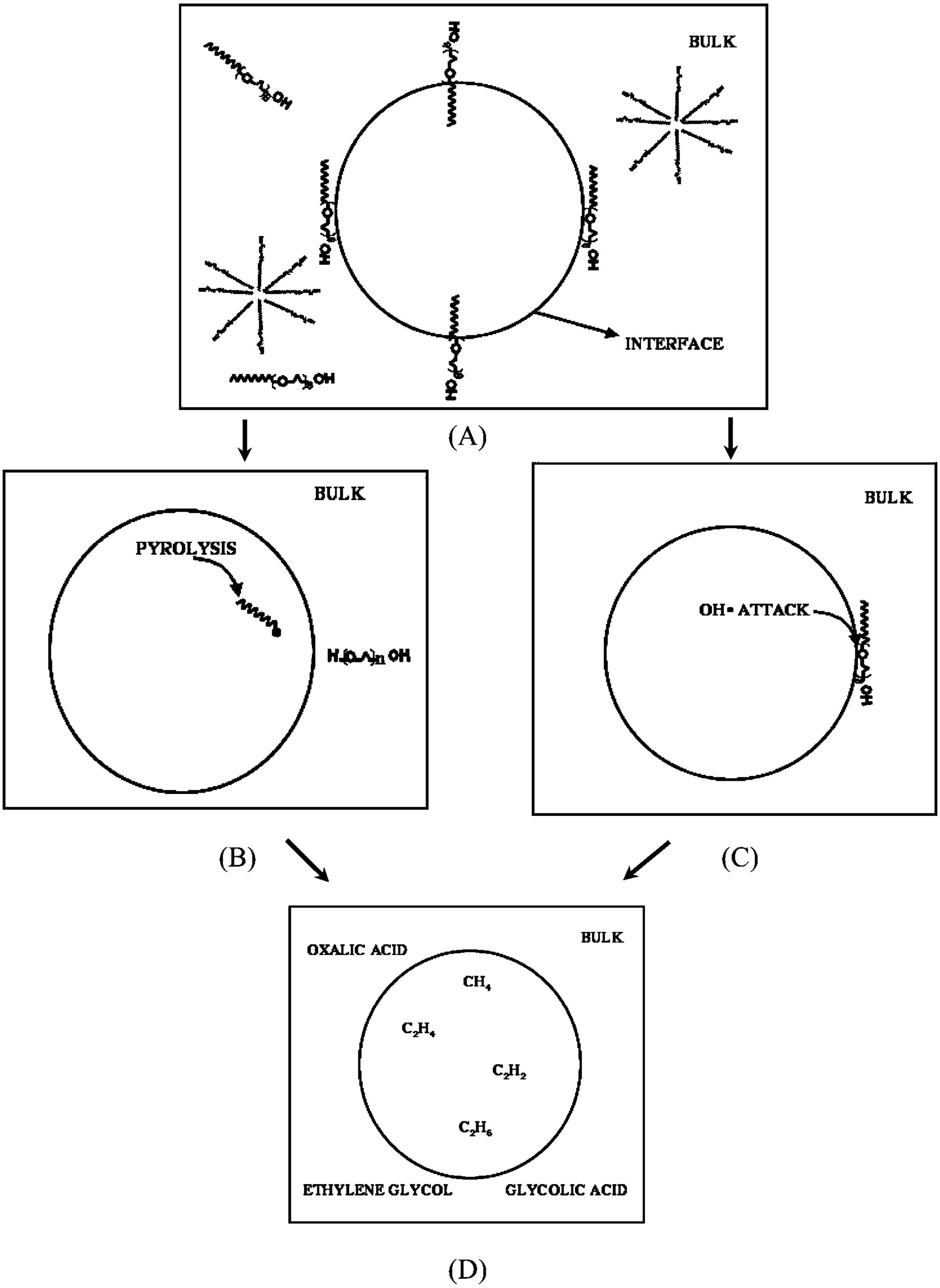
Alternatively, the observed decrease in $G_{SC}(H_2O_2)$ can also be due to a decrease in the cavitation bubble temperature, and hence OH yield, as a result of the formation and accumulation of pyrolytic decomposition products within the bubbles (see Scheme 1).[31,32] Rae et al.[17] and Tauber et al.[27] have shown that pyrolysis of alcohols within the cavitation bubble results in the formation of gaseous, low molecular weight hydrocarbons, and a lowering of the cavitation bubble temperature.

Indeed, gaseous products such as methane, ethane, acetylene, and ethylene were detected during the sonication of $C_{12}E_8$ aqueous solution as shown in Figure 4. However, the quantities produced, as can be seen, were relatively small, and therefore it is reasonable to conclude that the main reason for the decrease in the H_2O_2 yield with increasing amounts of $C_{12}E_8$ is due to the latter's ability to scavenge OH radicals.

Proposed Sonolytic Degradation Mechanism. The analyses of degradation intermediates and additional experimental work presented in this section allow for an identification of some of the individual reaction steps that occur in the complete degradation of the parent surfactant molecule.

Mass spectrometry (ESMS) analysis prior to sonication showed the base peak of $C_{12}E_8$ at *m/z* 561.7. This peak at *m/z* 561.7 indicates the addition of the Na^+ ion to the molecular weight of $C_{12}E_8$ (538.7 + 23) (see Figure 5). Mass spectrometry literature[33] shows that Na^+ ion has affinity for oxygen molecules present in ethylene oxide units. However, the source of Na^+ ions is uncertain. It is believed that Na^+ ions come from the

SCHEME 1: Illustration of Sonolytic Degradation of $C_{12}E_8$ Molecule at the Bubble/Solution Interface: (A) Orientation, $C_{12}E_8$ Molecule Hydrophobic Tail Perpendicular to the Surface of Bubble and $C_{12}E_8$ Molecule Lying at the Bubble/Solution Interface, (B) Scission of $C_{12}E_8$ Molecule and Pyrolysis of Hydrophobic Tail, (C) OH Attack of $C_{12}E_8$ Molecule, and (D) Formation and Accumulation of Degradation Products



leaching of ions from glass vials or glass column used during the preparation and injection of samples.[34]

An innate problem associated with ESMS analysis is that it is common that fragmentation of the parent molecule occurs in the instrument. To investigate the fragmentation of $C_{12}E_8$, the ESMS spectrum was analyzed simultaneously at three cone voltages of 30, 50, and 80 V (see Figure 5). At 80 V, a fragment at *m*/*z* 89 was detected. At 50 V, fragments at *m*/*z* 57, 89, 133.1, and 177.1 were detected. At 30 V, fragments at *m*/*z* 60, 74, and 130 were detected. These fragments may either be impurities present in the original sample or be generated during the electrospray ionization process. Considering that some of the fragments have been assigned to oxonium ions, it is unlikely that impurities are an issue. Therefore, the product analysis was considered bearing in mind machine-based fragmentation.

To analyze the various intermediates formed during the sonication, ESMS spectra of the sonicated solutions of $C_{12}E_8$

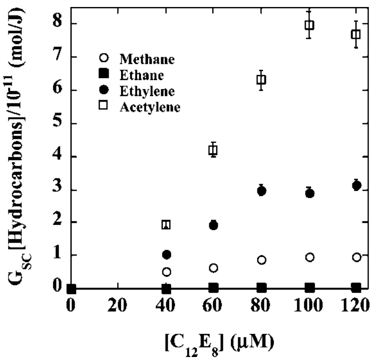


Figure 4. Amount of gaseous hydrocarbon products produced upon the sonication of various initial concentrations of $C_{12}E_8$ in aqueous solution. The aqueous solutions of $C_{12}E_8$ were sonicated for 15 min at an ultrasound frequency of 355 kHz.

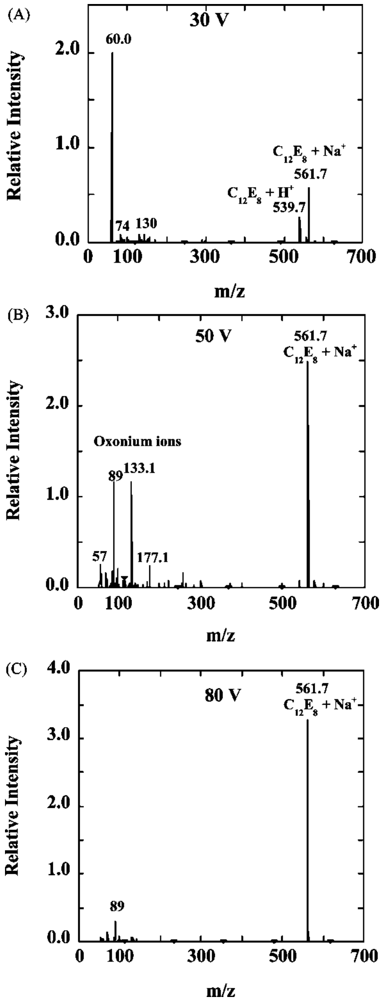


Figure 5. ESMS spectrum of $C_{12}E_8$ aqueous solution (40 μM) before sonication at (A) 30 V, (B) 50 V, and (C) 80 V.

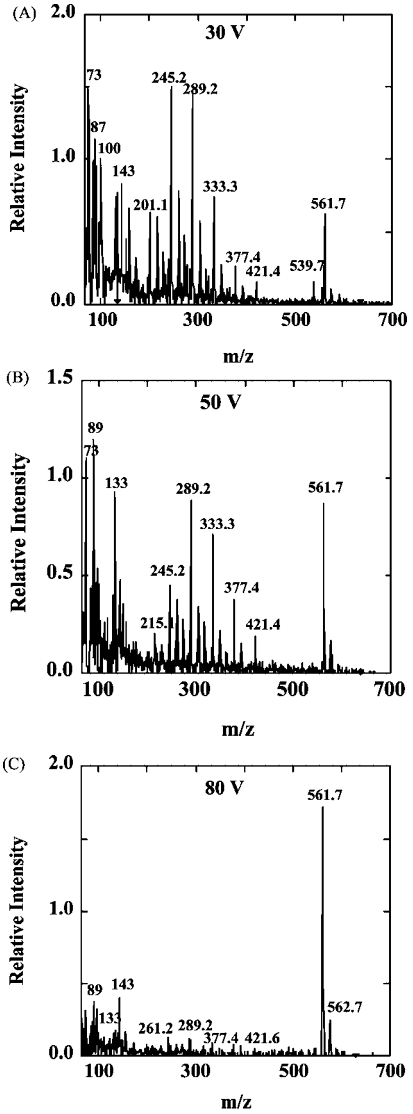


Figure 6. ESMS spectrum of $C_{12}E_8$ aqueous solution (40 μM) after 60 min of sonication at (A) 30 V, (B) 50 V, and (C) 80 V.

TABLE 1: Sum of the Relative Amount % of $C_{12}E_8$ (40 μM, 80 V) and Its Degradation Products Detected after 60 min of Sonication Time at 355 kHz

	relative amount of $C_{12}E_8$ and its degradation products, %	
m/z	sonication time = 0 min	sonication time = 60 min
561.6 ($C_{12}E_8$)	100	52.0
562.7		8.0
421.6		1.7
377.4		2.5
333.3		3.0
289.2		3.0
261.2		2.4
245.0		2.1
201.0		2.0
143.0		12.2
133.0		5.5
89.0		11.0
total relative amount, %	100	~100

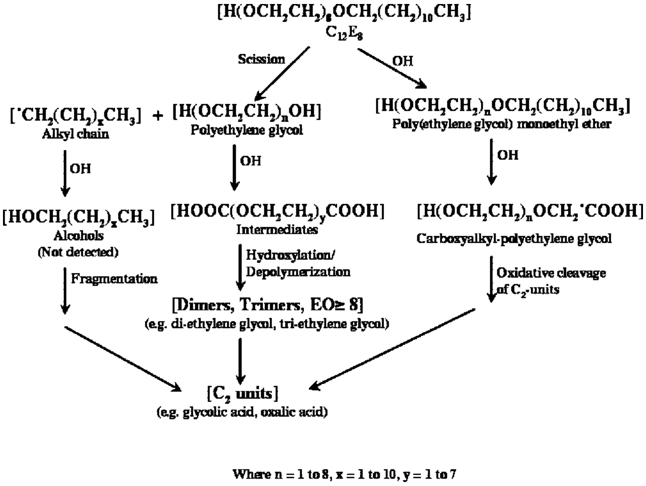
were analyzed at regular intervals over the sonication period of 15−120 min. It was observed during this sonication period that the base peak of $C_{12}E_8$ + Na^+ decreased in intensity while new peaks appeared and increased in intensity (see Figure 6).

Making the assumption that the intensity of each peak is directly proportional to the concentration of the corresponding $C_{12}E_8$ and its intermediates in the solution, an approximate mass balance of the system can be made. Table 1 shows that the percentage of $C_{12}E_8$ degraded and degradation products detected after 60 min of sonication approximately equals the initial amount of $C_{12}E_8$. This indicates that almost all of the decomposition products are detected by the ESMS. Also to note is

TABLE 2: Various Intermediates Detected during Sonolytic Degradation of $C_{12}E_8$ with Mass Spectrometry and HPLC

analytical technique	*m/z*	degradation products
	421.6, 377.4, 333.3, 289.2, 245.2, 201.1,	$HO(CH_2CH_2O)_xCH_2CH_3 + Na^+$, where $x = 3-8$ (poly(ethylene glycol) monoethyl ethers)
	305.0, 261.2, 217.2, 173.0	$H(OCH_2CH_2)_xOH + Na^+$, where $x = 3-6$ (polyethylene glycols)
	177.0, 133.0, 89.0	$(OCH_2CH_2)_x + H^+$, where $x = 2-4$ (oxonium ions)
HPLC		oxalic acid, malic acid, and maleic acid

SCHEME 2: Proposed Sonolytic Degradation Pathways of $C_{12}E_8$ and Its Intermediates

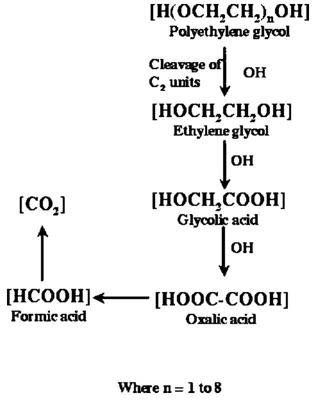


the multitude of products formed and all at relatively low percentages. This is indicative of multiple fragmentation steps.

The intermediates detected during the sonolytic degradation of $C_{12}E_8$ can divided into four main categories (see Table 2). The first category of degradation intermediates, that is, poly(ethylene glycol) monoethyl ether, contains sequential oligomers with *m/z* difference of 44. This indicates the removal of an ethylene oxide unit from each oligomer. The detection of oligomers suggests that the OH radical attacks the surfactant molecule at different parts of the ethylene oxide chain. The OH radical attack is suspected to take place with the same probability on the ethylene oxide chain except for the 1 and 2 positions because degradation intermediates mono- and di(ethylene glycol) monoethyl ether were not observed. This suggests that for unknown reasons the 1 and 2 positions of ethylene oxide chain are less likely to undergo OH radical attack to give rise to carboxyalkyl−polyethylene glycols. The oxidation of carboxyalkyl−polyethylene glycol may lead to the oxidative cleavage of C_2 (ethylene oxide) units to give rise to various shorter carboxyalkyl−polyethylene glycol intermediates, as shown in Scheme 2. It is also interesting to note that the fragmentation of the hydrocarbon chain occurs on the third carbon away from the ethylene oxide chain. As already mentioned, it is probably the case that once the alkyl radical is formed at the air/bubble interface, thermolysis is then responsible for breaking off the hydrocarbon moiety.

Brand et al.[10] in their study of alkylphenol ethoxylates proposed a similar mechanism for the degradation of the ethoxylate chain. They proposed that the attack of **OH** radicals on the ethoxylate chain resulted in the formation of alkoxy radicals and subsequent scission of C−O bond and C−C bond within the chain, thus leading to the formation of alkylphenol ethoxylates. Brand et al.[10] further indicated that O_2 in solution was able to react with the surfactant radicals ($R^\bullet$) to produce peroxy radicals ($ROO^\bullet$) that also, subsequently, played a role in the decomposition of the parent surfactant. Similarly, Vinodgopal et al.[14] suggested that the attack on the ethoxylate chain resulted in the chain shortening to produce low molecular weight polyethylene glycol as a byproduct.

SCHEME 3: Proposed Pathway for the Oxidation of the Polyethylene Glycol Chain



In our study, polyethylene glycols represent the second main category of byproducts. However, in this study, the detection of a range of polyethylene glycols provides evidence for the existence of an additional primary degradation mechanism, the scission of the surfactant molecule into alkyl chain and polyethylene glycol chain (see Schemes 1 and 2).

Polyethylene glycols react quite rapidly with OH radicals.[35] Therefore, it is proposed that the degradation of the polyethylene glycol chain proceeds oxidatively. The chain may be depolymerized by oxidation of either the terminal or the sub terminal carbon, which is followed by cleavage of the ether bond leaving an ethylene oxide chain shortened by one oxidized C_2 (ethylene oxide) unit. The successive cleavage of monomeric C_2 units seems to be the most probable mechanism because the mass spectrum peaks represent in each case a homologous series of polyethylene glycol units, ranging from the monomers to the corresponding polymers with ethylene oxide numbers ≤8. Several other degradation studies[1,9] on polyethylene glycol and the corresponding oligomers have suggested this type of chain shortening.

Further depolymerization/oxidation of the polyethylene glycol chain can produce end products such as ethylene glycol, glycolic acid, oxalic acid, malic acid, and formic acid (see Scheme 3). The formation of low molecular weight carboxylic acids was detected by HPLC (see Figure 7 and Table 2). These end products are simple metabolites that can undergo complete degradation. For example, ethylene glycol is oxidized to glycolic acid, and glycolic acid may subsequently be oxidized to oxalic acid and malic acid and then to formic acid, as shown in Scheme 3.

Destaillats et al.[13] also detected short-chain carboxylic products during the study of the nonionic surfactant Triton X-100. In addition to the formation of carboxylic acids, Destaillats et al.[13] and Brand et al.[10] also proposed the formation of formates and aldehydes, albeit in small amounts. However, in our study, no such intermediates were detected.

The possibility of the oxidation of the alkyl chain to produce an alcohol introduces another category of intermediates that may be formed. Destaillats et al.[13] in their study proposed that the alkyl chain was the most reactive part of the surfactant molecule, yielding polyethoxylated phenols. Brand et al.[10] also proposed

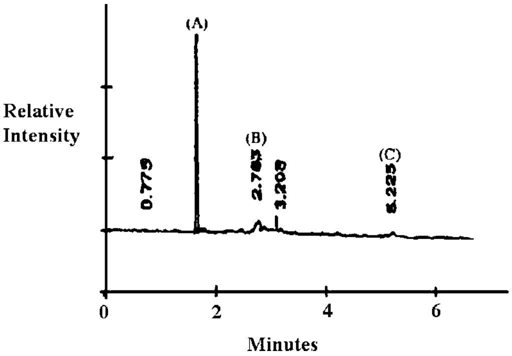


Figure 7. HPLC chromatogram of $C_{12}E_8$ aqueous solution after 60 min of sonication, and various peaks were identified as (A) oxalic acid, (B) malic acid, and (C) maleic acid.

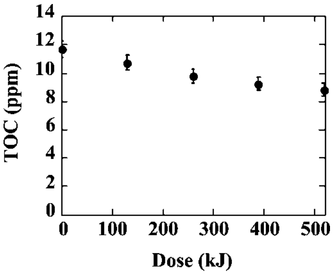


Figure 8. The change in total carbon content of $C_{12}E_8$ aqueous solution (40 μM) sonicated at 355 kHz as a function of dose.

the formation of octylphenol as one of the intermediates during their study on nonionics surfactants. However, in our study, we did not observe any alcohol byproducts.

The last category of ions that may be identified are classed as oxonium fragments, that is, protonated ethoxy fragments. These are most likely byproducts of decomposition species in the ESMS itself. These fragments would be in keeping with the type of more stable intermediates produced by the degradation of the parent compound sonochemically.

In essence, results of this degradation study demonstrate the simultaneous action of two distinct primary degradation processes for linear alcohol ethoxylates: (a) scission of the surfactant molecule and (b) hydroxylation/oxidation of the surfactant molecule (see Scheme 2). This suggests that several processes affect the complete degradation process of the surfactant molecule. Moreover, it should be kept in mind that not all of the spectral peaks could be identified, and some of the species suggested by other researchers may be included in these minor product yields.

Mineralization. Total organic carbon (TOC) analysis is a method that has been used widely to determine quantitatively the complete mineralization of an organic compound. The TOC content of $C_{12}E_8$ was observed to decrease at a slower rate than the initial degradation process. Sonication of $C_{12}E_8$ solutions (40 μM) resulted in a decrease in the TOC content of about 20% (see Figure 8).

Even though $C_{12}E_8$ was completely degraded into intermediates, mineralization was typically less than 10% for most of the concentrations examined over typical sonication times. This suggests that despite complete degradation of $C_{12}E_8$, 90% of the initial carbon remained as water-soluble intermediates.

It is obvious from the degradation results that complete mineralization of pollutant is difficult to achieve at reasonable rates using ultrasound. The reason is that in sonolysis effective degradation is limited to the inside of the collapsing cavitation bubble and to the interface of the bubble. Molecules that are hydrophobic or volatile are effectively degraded through pyrolysis-type reactions because they can enter the hydrophobic interior of the bubbles and can also react with OH radicals at the bubble/solution interface.[36,37] Conversely, highly hydrophilic compounds that are dispersed in the bulk solution such as low molecular weight carboxylic acids degrade at extremely slow rates, due to a lack of OH activity in the bulk solution.

During the sonolytic degradation study of the herbicide 2,4-D, Peller et al.[36] observed that oxalic acid was an end product. They too suggested that the accumulation of oxalic acid in the bulk solution was the reason behind the relatively slow mineralization of the herbicide. They stated that the accumulation of oxalic acid might arise as a consequence of either the lack of reactivity of oxalic acid toward OH radicals or its inability to accumulate at the bubble (air/water) interface. The extremely high polarity of oxalic acid makes its adsorption at the bubble interface low. As most of the hydroxyl radical attack occurs at the bubble/solution interface, little chemical transformation of oxalic acid would therefore be expected to occur. These studies,[36,38] as well as those showing the difference in reactivity of protonated and deprotonated forms of other compounds, lead us to conclude that the extent of hydroxyl radical attack in the bulk solution is extremely small as compared to that of the reaction pathways at the bubble interface. Thus, it is not surprising that the mineralization of hydrophilic organic compounds by sonolysis is, in general, a slow process.

Conclusions

The sonolytic degradation rate of $C_{12}E_8$ is affected by both thermal and radical reactions due to its chemical structure. The evidence for this is provided from GC, hydrogen peroxide yield. In addition, the detected intermediates and the proposed degradation pathways support the argument that the degradation of the surfactant molecule occurs by both OH radical attack and thermolysis.

The absence of alcohols as an intermediate indicates that the alkyl chain undergoes rapid degradation, probably to low molecular weight carboxylic acids, as compared to the polyethylene glycol chain. The detection of C_2 intermediates such as ethylene glycol, glycolic acid, oxalic acid, and malic acid indicates that polyethylene glycol chain is also completely degradable through either depolymerization or hydroxylation. Furthermore, the other intermediates detected during the sonolytic degradation provide additional evidence for the complete degradation of the parent $C_{12}E_8$ molecule through either intramolecular scission or hydroxylation.

In conclusion, degradation of $C_{12}E_8$ by sonolytic degradation offers effective means for the degradation of nonionics surfactants in the environment. However, complete mineralization of the hydrophilic intermediates formed during the oxidation reactions of the surfactant molecule is difficult to achieve at reasonable rates.

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