Nonionic Detergent Degradation: III. Initial Mechanism of the Degradation

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Abstract

In Parts I and II of this series (1,2), degradation and foaming experiments on a number of commercially available alcohol polyethoxylates and alkyl phenol polyethoxylates are described. This paper describes an extension of the thin layer chromatographic work on which the experiments described earlier were based, supplemented by a variety of other chemical and physical tests to provide some insight into the initial mechanism of degradation of these materials before they disappear by the established oxidation and hydrolytic routes. In the case of the readily degradable alcohol ethoxylates, two distinct mechanisms are shown to proceed simultaneously: a fission of the molecule into hydrophobic and hydrophilic entities, and a rapid oxidation of the hydrophobic group. No fission occurs in the case of the alkyl phenol ethoxylates, the more usual route of degradation being slow oxidation and hydrolysis of the alkyl groups, the aromatic ring and the ethoxy chain simultaneously; occasionally, and at higher pH, the hydrolysis of the ethoxy chain proceeds at a considerably increased rate.

Introduction

Schick (3) has provided a review of recent literature on the degradation of polyethoxylated nonionic detergents; the influence of parameters such as the length of the ethoxy chain and the position of attachment of the hydrophobic group have been studied, but lack of a suitable method for identification of traces of these materials and their degradation products has hampered progress in elucidation of the actual mechanism by which the degradation occurs. It can, however, be concluded from the available literature that biodegradation of the hydrophobic group can occur in all nonionics except those having very highly branched chains, and follows an oxidation process of the type described by Swisher (4,5) in his study of the degradation of anionic detergents. A hydrolytic mechanism is considered to be responsible for the degradation of the ethoxy chain (6), although it has been suggested that alkyl phenol ethoxylates containing more than 10 ethylene oxide chains were nonbiodegradable (6,7) and that alcohol ethoxylates with long ethylene oxide chains were only very slowly degraded (8,9).

The two previous papers in this series (1,2) describe the application of the thin layer chromatographic method (TLC) to the assessment of the amount of degradation occurring during laboratory die-away tests on a large number of the commercial ethoxylated nonionics of the types used in detergent formulations. In these papers it is confirmed that the structure of the hydrophobe and the length of the ethoxy chain do influence the rate of degradation, although none of the materials examined was found to be completely undegradable. Photographs of thin layer chromatograms of alkyl phenol and alcohol polyethoxylates during degradation indicated that the TLC method should provide a valuable tool in the elucidation of the mechanism of biodegradation, but these papers were confined to experimental results and no attempt was made to enlarge on the significance of the observed shift in chromatographic patterns as degradation proceeded. In the present paper, the information contained in the two earlier papers is combined with extended application of TLC, and other techniques such as alumina column chromatography, solvent partition, UV, IR and NMR spectrometry, to provide confirmatory evidence for the theories put forward for the initial breakdown of the molecules prior to the established oxidation and hydrolytic routes by which they eventually disappear.

Experimental Procedures

The thin layer chromatographic method, the normal biodegradation test method and the foaming test are described in Part I of this series (1). The following additional techniques were employed during experiments described in this paper.

(a) Specially-Purified Silica Gel Thin Layer Plates

Prior to recovery of the required fractions from thin layer plates, the prepared plates were washed by the normal chromatographic running procedure in the single-spot solvent: ethylacetate 40, acetic acid 30, water 30, parts per volume, until the solvent front had travelled beyond the usual running distance. They were then dried, reactivated and similarly washed with chloroform, then dried and reactivated ready for use. For some experiments, extra-thick layers of 0.5 mm spreading thickness were prepared, to permit isolation of larger quantities of material.

(b) Isolation of Individual Zones from Thin Layer Chromatograms

A band of the chloroform solution of the material under investigation was streaked onto the starting line of the prepared thin layer plate; spots of the solution were placed on either side of the band to serve as markers, and after running the chromatogram the central zone was covered while the marker chromatograms were sprayed with Dragendorff reagent. The required bands were then scraped off the unsprayed central portion of the plate, placed in a small filter paper and extracted with a solvent mixture of chloroform-ethanol-water (50:45:5 v/v/v). The solvent was evaporated off, and the residue dissolved in a small quantity of chloroform; a little of this solution was then rechromatographed to confirm that the required portion had been extracted.

(c) MEK, Water Partition

The chloroform extract under investigation was taken to dryness on a water bath, then the residue was warmed with 50 ml of distilled water, and after cooling, this solution was extracted by shaking each extraction in 500 ml separating funnels for 2 min with 3 × 50 ml of methyl ethyl ketone (MEK). By this means, the less polar material was extracted into the MEK, leaving the more polar material in the water layer, and these fractions could then be isolated by evaporation of the solvents and re-solution

of the residue in chloroform. This procedure was of particular value in dealing with the alcohol ethoxylates, when undegraded nonionic detergent separated into the MEK layer.

(d) Alumina, Column Separation Procedure

An alumina column was prepared from 10 g of aluminium oxide for chromatographic adsorption (Brockmann Grade 2) stirred into a slurry with a mixture of chloroform-ethanol-water (50:47.5:2.5 v/v/v), and poured into a small glass chromatographic column about 2 cm diameter plugged with absorbent cotton wool. The sample for separation on the column was applied to the top of the column as a solution in a small volume of the solvent mixture then 50 ml of the same solvent were passed through the column to give the first column extract. The column was then eluted with 50 ml of a more polar mixture consisting of chloroform-ethanol-water (50:42.5:7.5 v/v/v) to give the second column extract. This separation technique proved valuable as a means of separating alkyl phenol nonionic materials from more polar degradation products.

Results and Discussion

Alcohol Polyethoxylates

General formula:

$$CH_3(CH_2)_x CH_2O(CH_2CH_2O)_n CH_2CH_2OH$$

Figure 2 of Part I of this series (1) indicates the starting-point of the investigation; this photograph shows the degradation products from a cetyl stearyl 9-ethoxylate visible on a thin layer chromatogram, and the relative quantities obtained under the experimental conditions described are illustrated graphically in Figure 3 (ii) of the same paper. The significance of the terms normal extract and acid extract is also explained in the accompanying text.

Normal Streak Material. A solution containing a high initial concentration of 300 mg per 1 cetyl stearyl 9-ethoxylate and 300 mg per 1 dried activated sludge was allowed to degrade for two weeks; at the end of this time the concentration of starting material determined by the thin layer chromatographic method had fallen to 10 mg per 1. Initially, the normal chloroform extract of this degraded solution was chromatographed in bulk on a thick silica-gel plate specially purified, as described in (a) and (b) of the Experimental section, using the single-spot solvent consisting of ethyl acetate-acetic acid-water (40:30:30 v/v/v). After extraction from the central band of the chromatographic plate, a further separation according to polarity was obtained by partition between MEK and water as described in the Experimental section (c); a confirmatory thin layer chromatogram showed that the water fraction contained all the streak material (y of Part I, Fig. 2) while the chromatogram of the MEK fraction showed undegraded nonionic detergent.

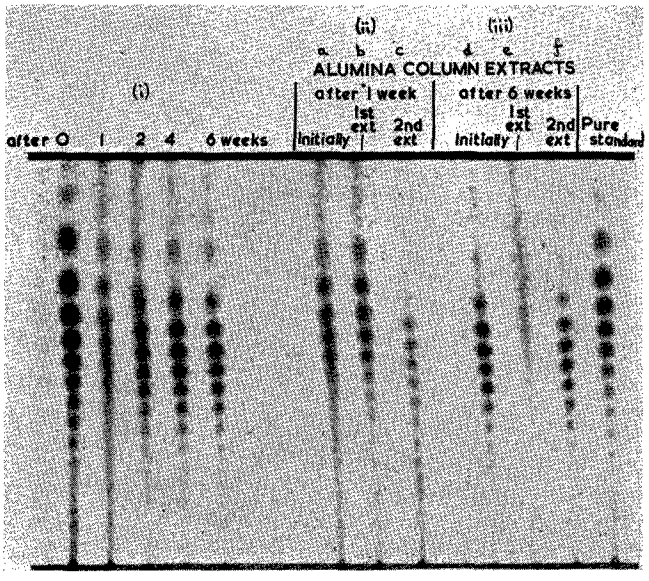


FIG. 1. Thin layer plate showing changes in resolved pattern of alkyl phenol 9-ethoxylate as degradation proceeds. (i) Total extract, (ii) and (iii) first and sixth week extracts separated by polarity on an alumina column. Solvent: ethyl acetate-glacial acetic acid-water (70:16:15 v/v/v).

IR and NMR examination of these fractions showed that the more polar degradation streak (water fraction) contained polyglycol-type material of molecular weight approximately 400, accompanied by some carbonyl grouping indicative of oxidation; alkyl chain material was absent. The MEK fraction contained some ethoxy and carbonyl groupings and a substantial amount of alkyl chain material, some of which could be attributed to unchanged original nonionic, but the ratio of alkyl material to ethoxy material was greater than in the undegraded original. Thus there is a clear indication that during degradation a hydrolytic fission has occurred between the alkyl and ethoxy portions of the molecule.

A concentrated band of water fraction streak material derived from the three-week degraded cetyl stearyl 9-ethoxylate was then isolated on a thin layer plate and examined in greater detail. Horizontal cuts were made across the band on a thin layer plate to produce four separate zones which were individually removed from the plate, solvent extracted and submitted to IR examination. Proceeding downwards from the top of the streak, a gradual fall in the proportion of ethoxy relative to carbonyl grouping was observed; thus the more polar end of the streak contained the more highly oxidised material. The experiment was repeated after the degradation had been allowed to proceed for six weeks when TLC and IR examination both indicated an appreciable fall in the quantity of ethoxy material present. The MEK fractions were also examined at the three- and six-week stages; alkyl chain material was observed to persist into the six week extract, but the presence of carbonyl absorption indicated that some oxidative attack was proceeding.

The experiments were repeated with the alcohol 22-ethoxylate for which the degradation is illustrated at Figure 8 of Part I (1). IR examination again showed that undegraded nonionic and alkyl chain material, were concentrated in the less polar MEK fractions, while material closely resembling PEG 1000 was concentrated in the water fractions and was still present in appreciable quantity at the six-week stage, although the original nonionic had virtually disappeared at the three-week stage. Carbonyl absorption was again observed in all the fractions examined.

The three-week stage in this series of experiments was selected for confirmatory foaming tests, since PEG 1000 has a characteristic and appreciable foaming capacity. In accordance with the central cleavage hypothesis, the bulk of the ethoxy material to which the foaming is attributable should be present in the water fraction after MEK-water partition and should have the foaming characteristics of PEG

TABLE I
Foaming of PEG 1000 Isolated From Water Fraction of Three-Week Degradation of Alcohol 22-Ethoxylate

Expt.	Degradation material	Foam height, cm	Expt.	Control material	Foam height, cm
1	1 mg/l PEG 1000 from nonionic	0.8	1a	1 mg/l PEG 1000	0.9
2	2 mg/l PEG 1000 from nonionic	0.9	2a	2 mg/l PEG 1000	1.0
3	3 mg/l PEG 1000 from nonionic	0.9	3a	3 mg/l PEG 1000	1.0
4	4 mg/l PEG 1000 from nonionic	1.0	4a	4 mg/l PEG 1000	1.0
5	5 mg/l PEG 1000 from nonionic	1.2	5a	5 mg/l PEG 1000	1.0
6	1 mg/l PEG 1000 + 1 mg/l nonionic detergent	4.8	6a	1 mg/l PEG 1000 + 1 mg/l nonionic detergent	5.0
7	1 mg/l PEG 1000 from nonionic + 1 mg/l nonionic detergent + 1 mg/l anionic detergent	9.8	7a	1 mg/l PEG 1000 + 1 mg/l nonionic detergent + 1 mg/l anionic detergent	10.2
8	5 mg/l PEG 1000 from nonionic + 1 mg/l nonionic detergent + 1 mg/l anionic detergent	10.2	8a	5 mg/l PEG 1000 + 1 mg/l nonionic detergent + 1 mg/l anionic detergent	10.2

1000; the MEK fraction containing only a trace of undegraded original nonionic and nonfoaming alkyl group material should have a negligible foaming capacity. The ethoxylated material isolated from the water fraction was quantitatively estimated by TLC comparison against standards of PEG 1000 then dissolved in four liters of distilled water. Foaming tests as described in Part I of this series (1) were carried out over a range of concentrations corresponding to 1 to 5 mg per l of PEG 1000, then in admixture with nonionic detergent (alkyl phenol 9-ethoxylate) and finally in admixture with nonionic detergent and anionic detergent (alkyl benzene sulphonate); a parallel series of tests was then conducted replacing the nonionic-derived PEG 1000 with authentic PEG 1000. The results are given in Table I. The whole of the corresponding MEK fraction, after removal of the solvent, was dissolved in 4 liters of distilled water and subjected to foaming tests alone and in admixture with nonionic and anionic detergents. The results are given in Table II. The tables show that foaming capacity was absent from the MEK extract, and that the water extract exhibited the typical foaming characteristics of a higher molecular weight polyglycol and not of a nonionic detergent; the foam itself also had the typical polyglycol appearance, small well-packed bubble formation. Finally, the foams produced in Experiments 7 and 8, and 7a and 8a of Table I were collected and analyzed; the compositions were found to be similar in both series of experiments.

Thus there appears to be little doubt that hydrolytic fission of the molecule to produce an alcohol and a polyglycol rapidly occurs during degradation of linear primary alcohol ethoxylates prior to the oxidation and hydrolytic processes (4,6) by which the material ultimately disappears.

The relatively slower degradation of the secondary alcohol ethoxylates illustrated in Figure 5 of Part I of this series (1) could then be explained by a somewhat slower rate of hydrolytic fission due to the presence of the secondary alcohol grouping. An extreme example of inhibition of the fission is provided by the highly-branched iso-tridecyl alcohol ethoxylate illustrated in Figure 6 (ii) of Part I. The experiments illustrated in Part I also show that although the lengths of the ethoxy chains influence the persistence of the degradation products, the initial degradation of all the linear primary alcohol ethoxylates investigated is invariably rapid.

Acid Streak Material. The experiments on the acid streak material were a continuation of the cetyl-stearyl 9-ethoxylate degradation experiments described above. The aqueous degradation solution was acidified and additional material extracted into chloroform after the normal chloroform extract had been removed. The procedure is described in detail in Part I of the series (1) and a photograph of the acid streak is shown in Figure 2 (ii) of that paper. After isolation from the chloroform this material was separated by partition between MEK and water, and TLC showed that effectively all the ethoxylated material was present in the water fraction, confirming that a second degradation product had been isolated

TABLE II
Foaming of MEK Fraction From Three Week Degradation of Alcohol 22-Ethoxylate

Degradation material	Foam height, cm	Control material	Foam height, cm
MEK fraction, alone	0		
MEK fraction + 1 mg/l nonionic detergent	2.0	1 mg/l nonionic detergent	2.2
MEK fraction + 1 mg/l nonionic detergent + 1 mg/l anionic detergent	2.6	1 mg/l nonionic detergent + 1 mg/l anionic detergent	2.7

TABLE III

Degradation of Normal and Acid Streak Material From Primary Alcohol 9-Ethoxylate

Time	Normal streak Concentration, mg/l		Acid streak Concentration, mg/l	
	Normal	Acid	Normal	Acid
Initially	5.0	0	0	3.3
after 1 day	5.0	0	0	3.3
after 2 days	5.0	0	0	3.0
after 3 days	5.0	0	0	2.7
after 7 days	3.5	0	0	1.7
after 2 weeks	1.0	0	0	0.1
after 4 weeks	0	0	0	0

of greater polarity than the original nonionic material. This material was isolated at successive stages from its initial formation to its disappearance, and the thin layer chromatogram of these stages run in the resolving solvent showed that initially some resolution into separate spots was obtained. But at later stages of the degradation, only a streak was visible, indicating the presence initially of material of alkyl ethoxylate type giving a resolved chromatogram of the nonionic detergent type, degrading to predominantly ethoxy material giving the unresolved streak observed with polyglycols.

These observations were confirmed by IR examination; the water fraction from MEK-water partition contained carboxyl and ethoxylated material and these groups were also shown to be present by NMR examination which established that a single CH_2 group was alpha to the carboxyl. IR examination of the MEK fraction gave evidence of heavily oxidized alkyl chain material.

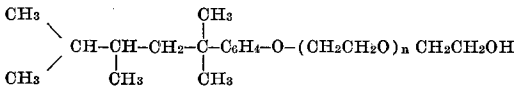
The experiment was repeated using the linear C_{11}–C_{15} secondary alcohol 9-ethoxylate for which the degradation is illustrated in Part I, Figure 5 (1). IR showed that in this case the alkyl group material was somewhat more persistent, indicative of a slower oxidation process which was confirmed by the higher R_f value, i.e., lower polarity, shown by the streak on a thin layer chromatogram.

In order to confirm that the two types of degradation depicted by normal and acid streaks proceeded independently, and were not interchangeable during degradation, some normal and acid streak material from the primary alcohol 9-ethoxylate was isolated and used as the starting material in independent degradation experiments. At intervals during the degradation, the normal and acid extracts were obtained from aliquots of the solutions, and estimated by TLC against PEG 450 standards; the results are shown in Table III, and illustrate that the two types of streak are not interchangeable, which is in agreement with the theory that two independent mechanisms are involved during degradation of the alcohol ethoxylates.

It thus appears that in the degradation causing the initial formation of the acid streak, a terminal –COOH eventually replaces the $CH_3(CH_2)_x$ of the hydrophobe prior to the usual oxidation and hydrolytic processes which lead to its disappearance.

Alkyl Phenol Polyethoxylates

The investigation of the degradation of this group of nonionics is complicated in comparison with the alcohol ethoxylates by the relative slowness of their degradation and the lack of visible degradation products. In Part II of this series (2), two rates of degradation are described, the predominant type depending on the pH of the environment; but two simultaneous mechanisms comparable with those described above for the alcohol ethoxylates were not observed. All the experiments described in this section are based on the normal chloroform extract; no additional ethoxylated material was extracted when the aqueous solution remaining after the normal chloroform extraction of a degraded 9 mole ethylene oxide adduct of nonylphenol



was acidified to the usual concentration of 2N with sulfuric acid, or when this concentration was increased to 4N. The aqueous solution after removal of the normal extract was also re-extracted with MEK, but no additional polyethoxylated degradation product was extracted by the more polar solvent.

The more usual slow type of degradation was first investigated. A solution containing 20 mg per 1 of nonyl phenol 9-ethoxylate and 100 mg/1 dried activated sludge in the medium at pH 7.0 degraded to a concentration of 9 mg per 1 after six weeks determined by TLC. For this group of compounds, TLC using the resolving solvent was more informative than the single spot solvent. Figure 1 shows at (i) the typical appearance of the chromatographic pattern as degradation proceeds, an initial blurring being followed by retardation of the spots. The alumina column technique described in Experimental Procedures (d), also proved extremely useful in separating the more polar highly-degraded material. Figure 1 (ii) shows the one-week degraded material at a, and after passage through an alumina column the first and second column extracts are shown at b and c. The six-week degraded material in the same experiment is shown at (iii) d, and the first and second column extracts at e and f; at this stage 90% of the total material present was recovered from the second column extract.

The persistence of the resolved spot pattern, accompanied by increased polarity, suggests that although the nonionic detergent structure is being modified during degradation there is no fission of the molecule as in the case of the alcohol-ethoxylates. Increasing polarity would lower the R_f value, while decrease in the length of ethoxy chains would cause an increase in R_f. The patterns after six weeks suggest the presence of only a trace of ethoxy material, of much decreased chain length, remaining in the first column extract, and partially-degraded material, possibly of shorter ethoxy chain length, in the second column extract. IR examination of the first column extract confirmed the diminution in ethoxy chain and by the sixth week the aromatic group also showed some modification. The second column extract, showing significantly less aromatic grouping, and strong carbonyl and carboxyl absorption, evidently contained the more polar material resulting from end-chain attack on the alkyl grouping and slow hydrolysis of the ethoxy chain. UV analysis confirmed that the proportion of aromatic grouping was relatively greater in the first than in the second column extracts, both at the one- and six-week stages. The difference in the initial route of degradation of this class of nonionics compared with the linear primary alcohol ethoxylates would thus appear to be attributable to the presence of the aromatic ring and the alkyl chain branching preventing fast hydrolytic fission of the molecule or fast oxidative attack along the alkyl chain.

Examples of the relatively rapid degradation which

occurred occasionally in sewage effluents and could be artificially induced at pH 9.2 are given in Table I of part II of this series (2). IR examination of material obtained after such a degradation from 10 mg per 1 to 0.3 mg per 1 showed evidence of the presence of alkyl phenol ethoxylate in which the ethoxy chain was much reduced in length. Thus under more alkaline conditions there would appear to be an increase in the rate of degradation of the ethylene oxide chain, as demonstrated also by the thin layer chromatographic pattern shown at (ii) and (iv) of Figure 1 in Part II of the series.

A series of degradations of alkyl phenol 4-ethoxylate, 9-ethoxylate and 16-ethoxylate were conducted over 9 weeks from a starting concentration of 10 mg per 1 at normal and alkaline pH. Foaming tests carried out during these degradations at concentrations based on the thin layer chromatographic estimation of the quantity present are included in Table II of part II of this series. In all cases the foaming corresponded with that of undegraded starting material at the same concentration, providing additional confirmation that a single compound of similar character to the original nonionic persisted throughout the degradation.

REFERENCES

1. Patterson, S. J., C. C. Scott and K. B. E. Tucker, JAOCS *44*, 407–412 (1967).
2. Patterson, S. J., C. C. Scott and K. B. E. Tucker, Ibid. *45*, 528–532 (1968).
3. Schick, M. J., Edward Arnold Publishers London, p. 971–996. "Surfactants Science Series," Vol. 1, 1967.
4. Swisher, R. D., JAOCS *40*, 648–656 (1963).
5. Swisher, R. D., Soap Chem. Specialties *39*(2), 58–62 (1963).
6. Osburn, Q. W. and J. H. Benedict, JAOCS *43*, 141–146 (1966).
7. Steinle, E. C., R. C. Myerly and C. A. Vath, Ibid. *41*, 804–807 (1964).
8. Blankenship, F. A. and V. M. Piccolini, Soap Chem. Specialties *39*(12), 75–78 (1963).
9. Ruschenberg, E., Vom Wasser *30*, 232–248 (1963).

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