# Nonionic Detergent Degradation. II. Thin-Layer Chromatography and Foaming Properties of Alkyl Phenol Polyethoxylates

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## Abstract

In Part I of this series (1) a study of the degradation of a number of commercially available alcohol polyethoxylates is described. This paper describes the application of the same procedures to the less degradable class of alkyl phenol polyethoxylates. It appears that, for these materials, the rate and extent of degradation is dependent on the environment in which the degradation occurs. Experiments are described that were carried out under neutral and high pH conditions, but it may well be that other variations in the environment could influence the degradation rate.

Slow degradation was observed under conditions comparable with those used for the alcohol polyethoxylates, for example, a common alkyl phenol 9-ethoxylate initially at a concentration of 5 mg per liter showed approximately 50% loss after six weeks. No degradation residues of the polyethylene glycol type and no additional acid degradation products of the types derived from the alcohol ethoxylates were observed. The only visual evidence of degradation was a retardation of the spots on the thin-layer plates, and it was most readily observed on chromatograms prepared so that they showed a resolved series of spots.

In the course of some of the degradation experiments using sewage effluent as the medium, an increase in pH value was observed. Under these conditions the degradation of the alkyl phenol ethoxylate was much more rapid and complete than usual, and the resolved trace on the thin-layer plate showed a predominance of ethoxy groups near the top of the chromatogram.

In this series of experiments, as in those described in Part I, the foaming capacity during degradation could be closely correlated with the results obtained by using the thin-layer chromatographic procedure.

## Introduction

RELEVANT LITERATURE references have for convenience been grouped with references to the alcohol ethoxylates in Part I of this series, but it is appropriate that the paper by Huddleston and Allred (2) should be mentioned again because it is important in relation to this work; these authors observed that the reduction in concentration of alkyl phenol ethoxylates during degradation, when determined chemically by using the cobaltothiocyanate colorimetric method (3,4), did not necessarily correlate with the loss of foaming capacity and surface-tension properties.

After passage through a sewage works, partial degradation of alkyl phenol ethoxylates might be expected to have occurred and, in fact, is demonstrated in the retardation of spots derived from sewage effluents, which is noted in the original papers describing the thin-layer chromatographic method (5,6); hence it is important that, when the content of residual "nonionic-detergent" in effluents and in river waters is determined by a chemical method, the result should be directly related to the foaming potential.

This paper describes degradation studies with a variety of commercially available alkyl phenol polyethoxylates from different sources, and foaming tests conducted on a representative selection of materials during the course of degradation. All the experiments are based on the laboratory die-away test described in our earlier paper, but a greater variety of experiments was conducted for confirmation that the degradations observed under the standard conditions were in fact true degradation; this was considered necessary because in these experiments the degradation of the nonionic detergent was not accompanied by the formation of clearly defined degradation products. Hence it could be possible to attribute any observed reduction in concentration to adsorption on suspended matter in the solution, and it was also important to confirm that any observed degradation was not proceeding at an abnormal rate because the bacteria were starved of other food.

## Procedures and Data

### Experimental Section

The Thin-layer Chromatographic Method and the Foaming Test are described in Part I of this series (1). The normal Biodegradation Test Method, in which moist air is blown over a solution of the detergent containing 30 mg per liter of air-dried activated sludge, is also described in Part I. The following variations on the normal method were introduced during the experiments described in this paper.

a) A medium containing an excess of organic material other than detergent was provided by using sewage effluent as the medium. The degradations were conducted in the effluents as received from the sewage works or after dilution with distilled water. Where special sewage effluent free from detergents was used, it was produced and supplied by the Water Pollution Research Laboratory, Stevenage. For some experiments the effluents were filtered initially through a No. 1 Whatman paper on a Buchner filter.

b) In one method of obtaining solutions free from visible particles, the dried activated sludge was removed by filtration through a Whatman No. 1 filter paper, after over-night aeration in B.O.D. water.

c) In a second method for obtaining solutions free from visible particles, a bacterial growth was prepared on a sterile agar slope containing alkyl phenol ethoxylate as the only added source of organic carbon. The slope was streaked with sewage effluent and incubated at room temperature for seven days; at the end of this period the colonies of microorganisms were washed off into 5 ml of sterile distilled water and added to the prepared B.O.D. water.

d) In an attempt to accelerate the degradation of an increased quantity of detergent, the proportion of dried activated sludge present in the medium was increased.

e) In media where a high initial pH was required, the pH of the medium was increased to 9.2 by the addition of 0.5 g of borate buffer to the test flask.

### Degradation Results

Table I shows typical results obtained in the laboratory aeration test under a variety of conditions. The same nonionic material, a readily obtainable alkyl phenol 9-ethoxylate of British manufacture, was employed in Experiments 1 to 34, and the quantities present were assessed by the thin-layer chromatographic method as degradation proceeded by using the original undegraded material as the standard for assessment on the thin-layer plates. In Experiments 35 to 54, showing the comparison in rates of degradation of alkyl phenol ethoxylates of varying ethoxy chain-length and varying alkyl group structure, the results were in each case assessed by comparison with a series of standards of the corresponding material on the thin-layer plates.

The effluents were selected from sewage works in a variety of locations in the United Kingdom, some receiving mainly domestic effluent, others receiving a large proportion of industrial effluent. All could be considered to be acclimated to nonionic detergent.

In one effluent (Experiment 8) degradation appeared to be almost complete when it was received from the sewage works, and repeat samples gave the same result. One isolated batch of the detergent-free sewage effluent out of several batches supplied by the Water Pollution Research Laboratory unexpectedly gave rise to fast degradation.

In addition to the results listed in Table I, a series of experiments with the use of the standard medium was conducted in closed Winchester quart-bottles; samples were removed as necessary and the stoppers replaced. Slow degradation was observed, of the same order as the degradation in the aerated medium, accompanied by a fall in pH, but the results have not been tabulated because the conditions are not sufficiently reproducible and cannot be regarded as either aerobic or anaerobic.

### Foaming Results

Foaming tests were conducted along the same lines as the corresponding tests on alcohol ethoxylates described in Part I. The detergent content of a series of solutions undergoing degradation was measured at intervals during the degradation and the concentration was adjusted, by suitable dilution based on the thin-layer chromatographic assay, to provide four liters of solution containing 0.5 mg per liter of detergent for the foaming tests. The procedure was simpler than it had been for the alcohol ethoxylates because no polyglycol type of degradation products was formed from the alkyl phenol ethoxylates. The 10 mg per liter were considered to be the maximum practicable starting concentration for degrading this class of compounds under the laboratory conditions. Special precautions were taken in one series of experiments to provide solutions free from visible particles by using slope cultures prepared as described under (C) in the Experimental Section although no interference with the foaming procedure was experienced in the later experiments with an unfiltered medium even when a relatively large proportion or the whole of the solution under test in the foaming apparatus consisted of medium or detergent-free effluent.

Typical results obtained in the more important types of experiments are shown in Table II; many of the foaming measurements were made at weekly intervals, but the degradation observed from one week to the next was frequently barely significant hence only results obtained at more widely spaced intervals have been included. For convenience, the results have been grouped under material types; Experiments 1, 4, 9, 12, and 13 were the same series run at the same time and 2, 3, 5, 6, 10, and 11 constituted another series. Experiments 2, 5, and 10 were conducted at the normal pH of the medium and in 3, 6, and 11 the pH was adjusted initially to 9.2; the pH fell during these experiments and the degradation slowed up, but by starting at the higher pH it became possible to take the degradations from the 10-mg-per-liter level much farther than had previously been obtainable under the controlled conditions that were suitable for foaming experiments. It was found that the special detergent-free effluent could be used as a medium in the same manner as the synthetic medium used in the other experiments after it had "aged" for a day or two, but the effluents obtained from sewage works were not found to be suitable media for comparative tests.

Experiment 8 illustrates the use of detergent-free effluent, in which it was possible to degrade 5 mg per liter of alkyl phenol ethoxylate down to 1 mg per liter; a bottle of the same batch of effluent was aerated at the same time to provide controls in the foaming experiments. In Experiment 7 a large volume of synthetic medium containing initially 0.5 mg per liter of alkyl phenol ethoxylate was held in a stoppered container alongside a control bottle of the medium held under similar conditions without detergent; four liters of the solutions were removed at intervals for the foaming experiments after determination of detergent content; by this means the detergent was degraded to a low level under conditions in which it could be demonstrated that the foaming capacity of the solution containing degraded detergent corresponded with a control to which a similar concentration of fresh detergent had been added down to a level at which the detergent content was virtually negligible. In a similar experiment a large batch of synthetic medium was aerated by bubbling air through it and evaporation losses were replaced periodically; results similar to those shown in Experiment 7 were obtained.

## Discussion

### Degradation

The results for degradation in aerated sewage effluent illustrate that the degradation of alkyl phenol ethoxylates has followed one of two routes: when the pH of the medium is increased, a relatively rapid degradation is observed; but at neutral pH the rate of degradation is much slower. No correlation appears to exist between the method of sewage treatment and the change of pH on aeration.

It will be observed (Experiments 7, 17, 18) that, when the effluent was diluted in the ratio of one part with nine parts of water in order to simulate a possible dilution of effluent after discharge to a river, both the degradation and the pH value followed the same route as in the undiluted effluent. The observed degradations under the conditions of the laboratory test are not necessarily indicative of the degradations that would occur under natural conditions; nevertheless, from the evidence obtained in these experiments, some relatively rapid degradation

TABLE I

Degradation of Alkyl Phenol Ethoxylates Under Simple Laboratory Conditions
All solutions continuously aerated at 20C in the dark; results expressed in mg per liter

| No. of Experiment | Experiment | Time Elapsed | | | | | | | pH | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Initially | 1 week | 2 weeks | 3 weeks | 4 weeks | 5 weeks | 6 weeks | Initial | Final |
| | Widely-used nonyl phenol 9-ethoxylate | | | | | In sewage effluent | | | | |
| 1 | Effluent A, as received | 0.5 | 0.5 | 0.3 | 0.2 | 0.15 | | | 7.4 | 5.6 |
| 2 | Effluent A, + 0.5 mg per liter nonionic | 1.0 | 1.0 | 0.7 | 0.5 | 0.25 | | | 7.4 | 5.6 |
| 3 | Effluent A, filtered | 0.5 | | 0.3 | | 0.15 | | | 7.4 | 5.4 |
| 4 | Effluent A, filtered + 0.5 mg per liter nonionic | 1.0 | | 0.7 | | 0.25 | | | 7.4 | 5.6 |
| 5 | Effluent B, as received | 5.0 | 5.0 | 3.0 | 2.5 | 2.5(1) | | | 6.7 | 5.5 |
| 6 | Effluent B, + 5 mg per liter nonionic | 10.0 | 9.0 | 6.0 | 4.5 | 4.5(1) | | | 6.7 | 5.6 |
| 7 | Effluent B, diluted 1 in 10 v/v, + 0.5 mg per liter nonionic | 1.0 | 1.0 | 0.6 | 0.5 | 0.5(2) | | | 6.7 | 5.0 |
| 8 | Effluent C, as received | 0.05 | 0.05 | 0.05 | | | 0.05 | | 7.4 | 8.0 |
| 9 | Effluent C, + 0.5 mg per liter nonionic | 0.5 | 0.4 | 0.2 | 0.15 | | 0.05 | | 7.4 | 8.2 |
| 10 | Effluent C, + 5 mg per liter nonionic | 5.0 | 4.0 | 2.0 | 1.2 | | 0.4 | | 7.4 | 8.2 |
| 11 | Effluent C, filtered | 0.05 | 0.05 | | | | 0.05 | | 7.3 | 8.2 |
| 12 | Effluent C, filtered + 0.5 mg per liter nonionic | 0.5 | | | 0.15 | | 0.05 | | 7.4 | 8.2 |
| 13 | Effluent C, filtered + 5 mg per liter nonionic | 5.0 | 4.0 | | 1.2 | | 0.4 | | 7.4 | 8.2 |
| 14 | Effluent D, as received | 0.45 | 0.15 | 0.1 | 0.05 | 0.05 | | | 7.6 | 8.5 |
| 15 | Effluent D, + 1 mg per liter nonionic | 1.5 | 0.3 | 0.2 | 0.1 | 0.05 | | | 7.6 | 8.5 |
| 16 | Effluent D, + 5 mg per liter nonionic | 5.5 | 2.2 | 0.4 | 0.15 | 0.1 | | | 7.6 | 8.6 |
| 17 | Effluent D, diluted 1 in 10 v/v, + 0.5 mg per liter nonionic | 0.5 | 0.5 | 0.05 | 0.02 | <0.02 | | | 7.6 | 8.7 |
| 18 | Effluent D, diluted 1 in 10 v/v, + 0.1 mg per liter nonionic | 0.15 | 0.1 | 0.03 | <0.02 | | | | 7.6 | 8.7 |
| 19 | Detergent-free effluent, as received | 0 | | | | | | | | |
| 20 | Detergent-free effluent, + 0.5 mg per liter nonionic | 0.5 | 0.4 | 0.2 | 0.15 | | 0.15 | | 7.7 | 7.7 |
| 21 | Detergent-free effluent, + 5 mg per liter nonionic | 5.0 | 4.0 | 3.0 | 2.0 | | 1.5 | | 7.7 | 7.8 |
| 22 | Detergent-free effluent, filtered, + 0.5 mg per liter nonionic | 0.5 | | | 0.15 | | 0.05 | | 7.7 | 7.8 |
| 23 | Detergent-free effluent, filtered, + 5 mg per liter nonionic | 5.0 | | | 2.5 | | 1.0 | | 7.7 | 7.8 |
| | | | | | | In dried activated sludge medium | | | | |
| 24 | Blank on medium | 0 | | | | | | | 7.0 | 6.5 |
| 25 | 30 mg dried sludge per liter filtered + 0.5 mg per liter nonionic | 0.5 | 0.4 | 0.25 | 0.25 | 0.2 | | 0.15 | 7.0 | 6.5 |
| 26 | 30 mg dried sludge per liter filtered + 5 mg per liter nonionic | 5.0 | 4.5 | 4.5 | 4.0 | 3.5 | | 3(1) | 7.0 | 6.5 |
| 27 | 30 mg dried sludge per liter unfiltered + 0.5 mg per liter nonionic | 0.5 | 0.35 | 0.3 | 0.25 | 0.2 | | 0.2 | 7.0 | 6.5 |
| 28 | 30 mg dried sludge per liter unfiltered + 5 mg per liter nonionic | 5.0 | 4.0 | 4.0 | 3.5 | 3.0 | | 2.5 | 7.0 | 6.5 |
| 29 | 30 mg dried sludge per liter unfiltered + 5 mg per liter nonionic (pH 9.2) | 5.0 | 3.0 | 2.5 | 1.5 | 1.0 | | 0.3 | 9.2 | 8.7 |
| 30 | 100 mg dried sludge per liter unfiltered + 10 mg per liter nonionic | 10.0 | 8.0 | 7.0 | 5.5 | 5.0 | | 4.5 | 7.0 | 6.9 |
| 31 | 100 mg dried sludge per liter unfiltered + 10 mg per liter nonionic (pH 9.2) | 10.0 | 6.0 | 4.0 | 3.0 | 2.5 | | 2.5 | 9.2 | 8.2 |
| 32 | 200 mg dried sludge per liter unfiltered + 5 mg per liter nonionic | 5.0 | 4.0 | 3.0 | 3.0 | 2.5 | | | 7.0 | 6.3 |
| 33 | 300 mg dried sludge per liter filtered + 5 mg per liter nonionic | 5.0 | 4.0 | 3.5 | 3.5 | 3.0 | | 2.5 | | |
| 34 | 300 mg dried sludge per liter unfiltered + 5 mg per liter nonionic | 5.0 | 4.0 | 3.5 | 3.0 | 2.5 | | 2.0 | | |
| | Comparative Tests on Various Alkyl Phenol Ethoxylates<br>Dried Activated Sludge Medium, 30 mg per liter unfiltered; the same batch of medium used for Experiments 35 → 50 | | | | | | | | | |
| 35 | Typical British alkyl phenol 4-ethoxylate | 5.0 | 4.0 | 4.0 | 3.5 | 3.0 | | 2.5 | | |
| 36 | | 0.5 | 0.4 | 0.3 | 0.3 | 0.25 | | 0.15 | | |
| 37 | Typical British alkyl phenol 9-ethoxylate, Source A | 5.0 | 4.5 | 4.0 | 3.5 | 3.0 | | 2.5 | | |
| 38 | | 0.5 | 0.4 | 0.3 | 0.2 | 0.2 | | 0.15 | | |
| 39 | Typical British alkyl phenol 9-ethoxylate, Source B | 5.0 | 4.0 | 4.0 | 3.5 | 3.0 | | 2.5 | | |
| 40 | | 0.5 | 0.35 | 0.3 | 0.25 | 0.25 | | 0.2 | | |
| 41 | Typical British alkyl phenol 9-ethoxylate, Source C | 5.0 | 4.5 | 4.0 | 3.0 | 2.5 | | 2.5 | | |
| 42 | | 0.5 | 0.4 | 0.35 | 0.25 | 0.2 | | 0.2 | | |
| 43 | Typical British alkyl phenol 16-ethoxylate | 5.0 | 4.5 | 4.5 | 4.0 | 3.5 | | 3.5 | | |
| 44 | | 0.5 | 0.45 | 0.4 | 0.35 | 0.3 | | 0.3 | | |
| 45 | German highly branched chain-alkyl phenol 4-ethoxylate | 5.0 | 4.0 | 3.5 | 3.0 | 2.5 | | 2.5 | | |
| 46 | | 0.5 | 0.4 | 0.3 | 0.3 | 0.25 | | 0.2 | | |
| 47 | German highly branched chain-alkyl phenol 9-ethoxylate | 5.0 | 4.5 | 4.5 | 4.5 | 4.0 | | 3.5 | | |
| 48 | | 0.5 | 0.4 | 0.4 | 0.35 | 0.3 | | 0.25 | | |
| 49 | British "straight chain"-alkyl phenol 9-ethoxylate | 5.0 | 3.5 | 3.0 | 2.5 | 2.0 | | 2.0 | | |
| 50 | | 0.5 | 0.3 | 0.25 | 0.15 | 0.1 | | 0.1 | | |
| | Dried Activated Sludge Medium, 300 mg per liter filtered; the same batch of medium used for Experiments 51 → 54 | | | | | | | | After 10 weeks (re-seeded at 6 weeks) | |
| 51 | Typical British alkyl phenol 4-ethoxylate | 10.0 | 7.0 | 6.5 | 6.0 | 6.0 | | 6.0 | 4.0 mg per liter | |
| 52 | Typical British alkyl phenol 9-ethoxylate | 10.0 | 8.0 | 7.0 | 6.0 | 5.5 | | 5.5 | 0.3 mg per liter | |
| 53 | Typical British alkyl phenol 16-ethoxylate | 10.0 | 8.0 | 6.5 | 6.0 | 5.5 | | 5.5 | 4.0 mg per liter | |
| 54 | German highly branched chain-alkyl phenol 9-ethoxylate | 10.0 | 8.0 | 7.0 | 6.0 | 6.0 | | 6.0 | 4.5 mg per liter | |

Note. (1) 5 mg per liter alcohol ethoxylate added at end of experiment, degraded normally.
Note. (2) 0.5 mg per liter alcohol ethoxylate added at end of experiment, degraded normally.

TABLE II

Alkyl Phenol Ethoxylates, Correlation of Foaming Capacity with Degradation[a]

| No. of Experiment | Material | Medium | Time | pH | | Concentration mg per liter | | Foam Height, cm | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Control | Total | After dilution for foaming | Alone | | +0.5 mg per liter anionic | |
| | | | | | | | | Initial | 2 min later | Initial | 2 min later |
| 1 | Typical British alkyl phenol-4-ethoxylate | Agar slope culture | Initially | 7.0 | | 10 | 0.5 | 0.2 | 0.1 | 1.4 | 1.1 |
| | | | after 2 weeks | | | 6 | 0.5 | 0.1 | 0.1 | 1.2 | 1.0 |
| | | | after 4 weeks | | | 5 | 0.5 | 0.2 | 0.1 | 1.3 | 1.0 |
| 2 | Typical British alkyl phenol-4-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 7.0 | 7.0 | 10 | 0.5 | 0.2 | 0.1 | 1.4 | 1.1 |
| | | | after 4 weeks | 6.3 | 6.4 | 4 | 0.5 | 0.2 | 0.1 | 1.3 | 1.1 |
| | | | after 9 weeks | 5.4 | | 3 | 0.5 | 0.2 | 0.1 | 1.4 | 1.2 |
| 3 | Typical British alkyl phenol-4-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 9.2 | 9.2 | 10 | 0.5 | 0.2 | 0.1 | 1.4 | 1.1 |
| | | | after 4 weeks | 8.5 | 8.4 | 2.5 | 0.5 | 0.2 | 0.1 | 1.4 | 1.2 |
| | | | after 9 weeks | 8.2 | 8.0 | 2 | 0.5 | 0.2 | 0.1 | 1.3 | 1.1 |
| 4 | Typical British alkyl phenol 9-ethoxylate | Agar slope culture | Initially | 7.0 | | 10 | 0.5 | 1.3 | 0.9 | 2.2 | 1.9 |
| | | | after 2 weeks | | | 7 | 0.5 | 1.4 | 1.0 | 2.5 | 2.2 |
| | | | after 4 weeks | | | 5 | 0.5 | 1.3 | 1.0 | 2.7 | 2.4 |
| 5 | Typical British alkyl phenol 9-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 7.0 | | 10 | 0.5 | 1.3 | 1.0 | 2.2 | 1.9 |
| | | | after 4 weeks | 7.3 | | 5 | 0.5 | 1.4 | 1.0 | 2.4 | 2.1 |
| | | | after 9 weeks | 5.8 | | 4 | 0.5 | 1.2 | 1.0 | 2.6 | 2.1 |
| 6 | Typical British alkyl phenol 9-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 9.2 | | 10 | 0.5 | 1.3 | 1.0 | 2.4 | 2.0 |
| | | | after 4 weeks | 8.4 | | 2.5 | 0.5 | 1.3 | 1.0 | 2.4 | 2.0 |
| | | | after 9 weeks | 8.2 | | 2 | 0.5 | 1.4 | 1.0 | 2.4 | 2.0 |
| 7 | Typical British alkyl phenol 9-ethoxylate | Dried activated sludge, 30 mg per liter filtered (unaerated) | Initially | 7.0 | | 0.5 | not diluted | 1.3 | 1.0 | 2.3 | 2.0 |
| | | | after 4 weeks | 6.5 | | 0.2 | not diluted | 0.2 (0.2) | 0.1 (0.1) | 0.4 (0.3) | 0.3 (0.2) |
| | | | after 7 weeks | | | 0.08 | not diluted | 0.0 (0.1) | | 0.0 (0.1) | |
| 8 | Typical British alkyl phenol 9-ethoxylate | Detergent-free sewage effluent | Initially | 8.2 | | 5 | 0.5 | 1.2 (1.4) | 0.9 (1.0) | 2.3 (2.4) | 2.0 (2.0) |
| | | | after 5 weeks | 8.0 | | 1 | 0.5 | 1.1 | 0.8 | 2.4 | 2.0 |
| | | | after 9 weeks | 7.9 | | 1 | 0.5 | 1.3 (1.4) | 0.9 (1.0) | 2.4 (2.4) | 2.0 (2.0) |
| 9 | Typical British alkyl phenol 16-ethoxylate | Agar slope culture | Initially | 7.0 | | 10 | 0.5 | 1.0 | 0.6 | 3.5 | 2.7 |
| | | | after 2 weeks | | | 7 | 0.5 | 0.9 | 0.5 | 3.2 | 2.7 |
| | | | after 4 weeks | | | 6 | 0.5 | 0.9 | 0.6 | 3.2 | 2.6 |
| 10 | Typical British alkyl phenol 16-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 7.0 | | 10 | 0.5 | 1.1 | 0.6 | 3.6 | 2.7 |
| | | | after 4 weeks | 7.4 | | 5 | 0.5 | 1.2 | 0.7 | 3.4 | 2.6 |
| | | | after 9 weeks | 7.2 | | 4 | 0.5 | 1.0 | 0.5 | 3.3 | 2.5 |
| 11 | Typical British alkyl phenol 16-ethoxylate | Dried activated sludge, 100 mg per liter unfiltered | Initially | 9.2 | | 10 | 0.5 | 1.1 | 0.6 | 3.6 | 2.7 |
| | | | after 4 weeks | 8.6 | | 3 | 0.5 | 1.1 | 0.6 | 3.7 | 2.7 |
| | | | after 9 weeks | 8.2 | | 2.5 | 0.5 | 1.2 | 0.7 | 3.6 | 2.7 |
| 12 | British "straight chain" alkyl phenol 9-ethoxylate | Agar slope culture | Initially | 7.0 | | 10 | 0.5 | 0.9 | 0.8 | 2.2 | 2.0 |
| | | | after 2 weeks | | | 5.5 | 0.5 | 0.8 | 0.6 | 2.3 | 2.0 |
| | | | after 4 weeks | | | 3.5 | 0.5 | 0.9 | 0.8 | 2.1 | 1.9 |
| 13 | German highly branched-chain alkyl phenol 9-ethoxylate | Agar slope culture | Initially | 7.0 | | 10 | 0.5 | 1.5 | 1.2 | 2.7 | 2.4 |
| | | | after 2 weeks | | | 7 | 0.5 | 1.3 | 1.0 | 2.6 | 2.4 |
| | | | after 4 weeks | | | 6 | 0.5 | 1.4 | 1.0 | 2.7 | 2.4 |

[a] All solutions (except Experiments 7 and 8) are in standard B.O.D. water, aerated, at 20C in the dark. The foam heights of standard material added to a medium control are in parentheses.

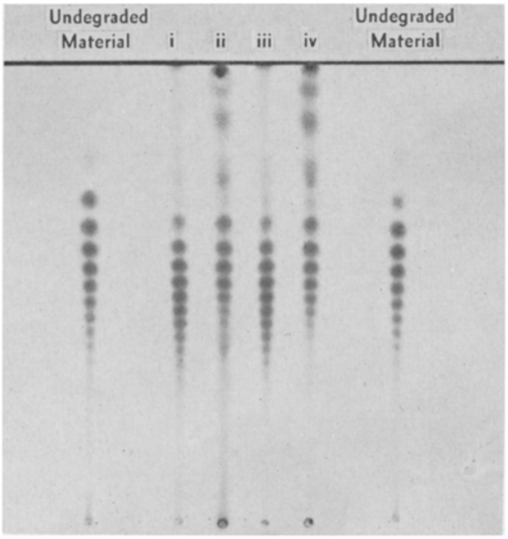

FIG. 1. Thin-layer plate, showing typical alkyl phenol 9-ethoxylate during degradation: (i) and (iii) by the slower route, (ii) and (iv) by the faster route.

of alkyl phenol ethoxylates might occasionally be expected to take place in rivers.

The residual anionic detergent was also measured at the start and finish of the experiments. There did not appear to be any correlation between the decrease in anionic detergent content and change in pH value; in those effluents which showed an increase in pH value during the experiments, the relative decrease in anionic detergent content was much less than that of the nonionic detergent.

Degradations which were carried out by the standard method with dried activated sludge in B.O.D. water invariably followed the slower route and gave results which could be anticipated from the fact that the pH decreased during aeration of the medium and which were comparable with the results obtained in sewage effluents when a decrease in pH was observed. The degradation could be accelerated by raising the pH of the medium initially, as shown in Experiments 29 and 31.

Under the standard conditions a persistent undegradable residue was obtained from an initial concentration as low as 5 mg per liter even when the proportion of dried activated sludge present in the medium was considerably increased. In only one isolated instance (Experiment 52) the degradation proceeded almost to completion from a starting concentration of 10 mg per liter; this appeared to happen almost fortuitously in one of a series of solutions re-seeded with dried activated sludge after six weeks of aeration. No significant differences in degradation rates were observed in solutions filtered in order to remove visible particles which might be considered to adsorb detergent, and no detergent was extracted from the walls of vessels refluxed with chloroform after completion of some of the experiments. At the end of Experiments 5, 6, 7, and 26 (Table I) a readily degradable alcohol ethoxylate was added and the aeration was continued; it degraded normally, indicating that bacteria capable of degrading nonionic detergents were present in the solution.

When the degradations of the various branched-chain alkyl phenol ethoxylates recorded in Experiments 35 to 48 and 51 to 54 are compared, a slightly decreased degradation rate is possibly discernible as the length of the ethoxy chain is increased and increased branching in the alkyl chain possibly decreases the rate slightly, but these effects are much less pronounced than in the case of the alcohol ethoxylates described in Part 1 of this series (1). The "straight chain" alkyl phenol 9-ethoxylate showed a slightly increased rate of degradation; it was supplied by a British manufacturer but is not available commercially, and the results are inserted because of their interest in comparison with the others.

The two types of degradation are clearly distinguished on the resolved chromatogram on a thin-layer plate. Fig. 1 shows at (i) the depressed pattern of the slow degradation obtained in sewage effluent A, and at (ii) the upward shift obtained in the later stages of degradation in effluent D; the spots near the top of the chromatogram could be owing to an increase in the proportion of material present containing short ethoxy chains. The extracts from Experiments 28 and 29 are illustrated at (iii) and (iv), demonstrating that the rapid degradation route has been induced by raising the pH to 9.2 in a "standard" test. The two outside marker patterns are the original undegraded material.

Although the faster degradation has been induced in sewage effluents in the laboratory and is demonstrable on the thin-layer plates, it is not considered to be the usual mode of degradation effected during treatment in a sewage works. This conclusion is based on the examination of a large number of effluents in this laboratory (6) when only one elevated resolved pattern (Experiment 8 of Table I) was observed, indicating rapid degradation in the effluent at the time of sampling; some effluents showed a resolved pattern in alignment with that of the standard material and the majority showed a depressed pattern. In considering river waters the position is not so clear; it has been observed (7) that the ratio of residual nonionic to anionic detergent tends to be lower in river waters than in sewage effluents, but during the examination of a number of river waters (8) only the depressed pattern was observed on the resolving chromatogram; this could however be attributed to the disappearance of rapidly degradable material before sampling.

**Foaming**

In the later stages of degradation the nonionic detergent content, determined by the thin-layer chromatographic method, would include a high proportion of partially-degraded material, but the results in Table II demonstrate that in every experiment the foaming capacity could be correlated with the nonionic detergent content. The slower degradation route would appear to be of greater importance than the faster route in considering foaming capacity since it is the persistent residues that can be expected in practice to give rise to foaming troubles.

ACKNOWLEDGMENT

D. Burns of the Scientific Adviser's Division, Greater London Council, suggested and prepared the agar slope cultures.

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[Received November 27, 1967]