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Biodegradation of Nonionic Surfactants used by the Textile Industry

by
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Abstract

Biodegradation of the two largest classes of nonionic surfactants, alcohol ethoxylates and nonylphenol ethoxylates, has been studied under realistic summer and winter conditions. The use of double-radiolabeled surfactants facilitated obtaining ultimate biodegradation data and permitted a greater understanding of the mechanisms by which the surfactants biodegrade. The results of these studies show alcohol ethoxylates degrade to CO_2 and H_2O faster and more extensively than nonylphenol ethoxylates under both summer and winter conditions. In addition, sewage effluents contained greater quantities of biodegradation intermediates from nonylphenol ethoxylates than from alcohol ethoxylates. Under average winter conditions found in northern U. S., the biodegradation of nonylphenol ethoxylates was particularly poor and resulted in effluents having considerable foaming. In contrast, under these winter conditions the biodegradation of alcohol ethoxylates did not result in effluent foaming.

Introduction

Nonionic surfactants are used more extensively by the textile industry than any other type of surfactant. The two principal nonionic surfactants used are alcohol ethoxylates (AE), having essentially linear alkyl chains, and alkylphenol ethoxylates (APE), having highly branched alkyl chains.[1] These surfactants are used in such textile applications as wetting, scouring, dye leveling, emulsification, fiber lubrication and more recently in foam finishing[2,3,4] and foam mercerization.[5] Although generally applied at relatively low levels (0.1-0.2%), the newer foam end uses require much higher surfactant levels (2-3%). Figure 1 shows AE and APE structure.

Biodegradation of surfactants is important to the textile industry for several reasons. Firstly, surfactants generally show considerable surface active properties such as foaming and reduction of interfacial tension. Although these properties are useful in textile processing, their appearance in greige or finishing mill effluents is undesirable. The presence of foam, for example, interferes with effective oxygen transport in biotreating systems, prevents proper functioning of secondary clarifiers in waste treatment plants and is unsightly.[6] Biodegradation of the surfactant, such as can take place in sewage treatment plants, results in significant reduction in foaming and other surface active properties. Surfactants which are "hard" (biodegrade relatively slowly) will tend to exit intact from sewage treatment plants resulting in considerable foaming. The major thrust for the household detergent industry voluntarily switching its anionic workhorse surfactant, branched alkylbenzene sulfonates (ABS), to linear alkylbenzene sulfonates (LAS) in 1965 was the discovery that "hard" ABS was largely responsible for the extensive foaming which occurred in receiving waters during the 1950s and early 1960s. This foaming decreased significantly when the more biodegradable LAS replaced ABS.

A second reason for the importance of surfactant biodegradation to the textile industry is the relatively high aquatic toxicity of nonionic surfactants. Alcohol ethoxylates and alkylphenol ethoxylates generally have LC_{50} (concentration required to kill 50% of the total number of aquatic species) levels generally ranging from 1-10 ppm. Biodegradation of these surfactants significantly reduces their aquatic toxicity capabilities.

A third important reason for surfactant biodegradation is that current regulations for textile mills require a low plant effluent BOD (biochemical oxygen demand) and COD (chemical oxygen demand). The combined requirements of low effluent BOD and COD favor those surfactants which biodegrade more rapidly.

The reduction of foaming and interfacial tension lowering properties of surfactants are examples of methods used to determine their primary biodegradability. Primary biodegradation is defined as loss of a chemical or physical property of the surfactant as a result of microbial attack. BOD is a measurement of aerobic ultimate biodegradation defined as microbial oxidation of an organic substrate to produce CO_2 and H_2O utilizing oxygen present in the system. The ultimate biodegradation of an alcohol ethoxylate may be represented stoichiometrically as follows:

$$CH_3(CH_2)_{11}CH_2O(CH_2CH_2O)_9H + 42O_2 \xrightarrow{\text{bacteria}} 31CO_2 + 32H_2O$$

It is frequently possible to follow the ultimate biodegradation of a substrate under controlled conditions by measurement of loss of organic carbon, uptake of oxygen (BOD test), evolution of carbon dioxide or production of water.

In the past, surfactant biodegradation was measured most frequently using primary biodegradation criteria. More recently, the Environmental Protection Agency (EPA) have included ultimate biodegradation criteria in recommended tests for premanufacture notification under the Toxic Substances Act.[7] The inclusion of ultimate biodegradation criteria is prompted by the possibility of the formation of intermediate biodegradation products which resist further biodegradation and persist in the environment.

This paper reviews the biodegradation of AE and APE carried out over a number of years in our laboratories and those of associated companies in the

Figure 1/**Principle classes of nonionic surfactants**

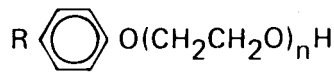
Alcohol Ethoxylates (AE)

$RO(CH_2CH_2O)_nH$

where R = Mixed predominantly linear alkyl groups in the C_8 to C_{18} range.

n = Average ethylene oxide groups per mole

Alkylphenol Ethoxylates (APE)



where R = Highly branched alkyl group, typically C_8 or C_9, such as 1,1,3,3-tetramethylbutyl or mixed isomers derived from propylene trimer.

n = Average ethylene oxide groups per mole

Netherlands and United Kingdom. Emphasis will be placed on biodegradation results which have an impact on foaming, aquatic toxicity and the ultimate biodegradation criteria defined in EPA recommended test guidelines. The use of a powerful radiochemical technique to follow the biodegradation pathway of nonionic surfactants will also be discussed.

Effects of surfactant structure on biodegradation

The primary biodegradibility of AE and APE has been investigated generally in separate studies for each of these surfactant classes. Where both AE and APE have been compared directly, AE having essentially linear alkyl chains biodegraded considerably faster than APE.[8-11] An example from recent laboratory shake flask studies[12] is shown in Figure 2. Here, the primary biodegradation criterion was CTAS (cobalt thiocyanate active substance) in which cobalt thicyanate forms a blue-colored complex with the ether linkages in the polyoxyethylene (POE) chain. The blue complex is extracted with a chlorocarbon solvent and determined spectrophotometrically. Biodegradation, which shortens the POE chain appreciably or cleaves it from the hydrophobic moeity, causes a decrease in the color intensity of the blue complex. Figure 2 shows the primary biodegradation of an essentially linear AE having a range of 12-15 carbon atoms in the alkyl chain and an average of 9 ethylene oxide (EO) units in the POE chain (C_{12-15} AE-9) compared to highly branched octylphenol ethoxylate (C_8 APE-9). The C_{12-15} AE-9 biodegraded considerably faster than the C_8 APE-9 as measured by CTAS.

The ultimate biodegradability of the C_{12-15} AE-9 is compared with that of C_8 APE-9 in Figure 3. The same shake flask test used in the CTAS evaluation described above was used to generate the ultimate biodegradation data based on CO_2 evolution. The results show CO_2 evolution was considerably faster and more extensive for C_{12-15} AE-9 than for C_8 APE-9. Glucose, a highly biodegradable substrate, was used as a positive biodegradation standard and, as shown, biodegraded to CO_2 at a slightly faster rate than the C_{12-15} AE-9.

The effect on biodegradability of varying hydrophobe structure for AE and APE has also been investigated. Sturm[13] has shown the ultimate biodegradability of detergent range (C_8-C_{17}) linear alcohol ethoxylates is not affected significantly by the length

Figure 2/**Primary biodegradation**

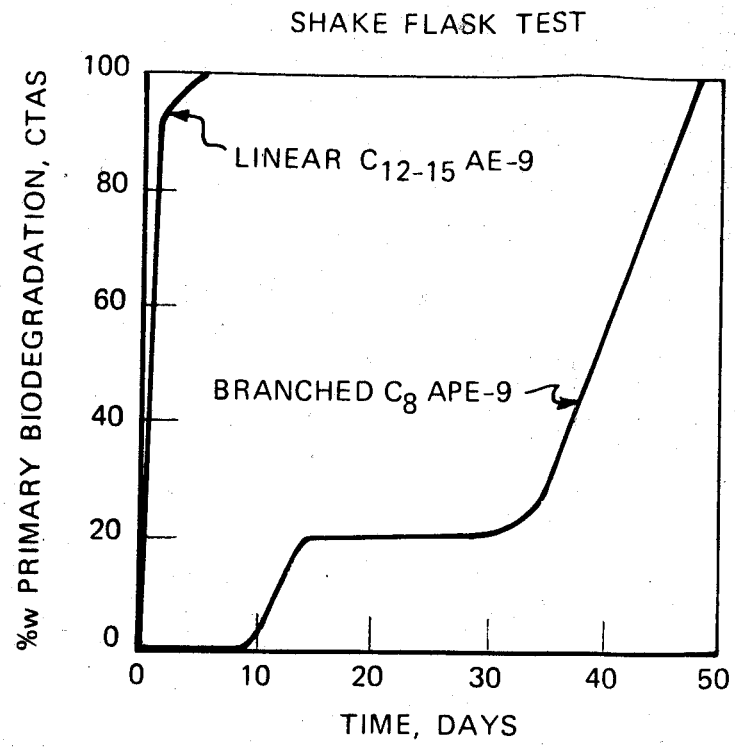
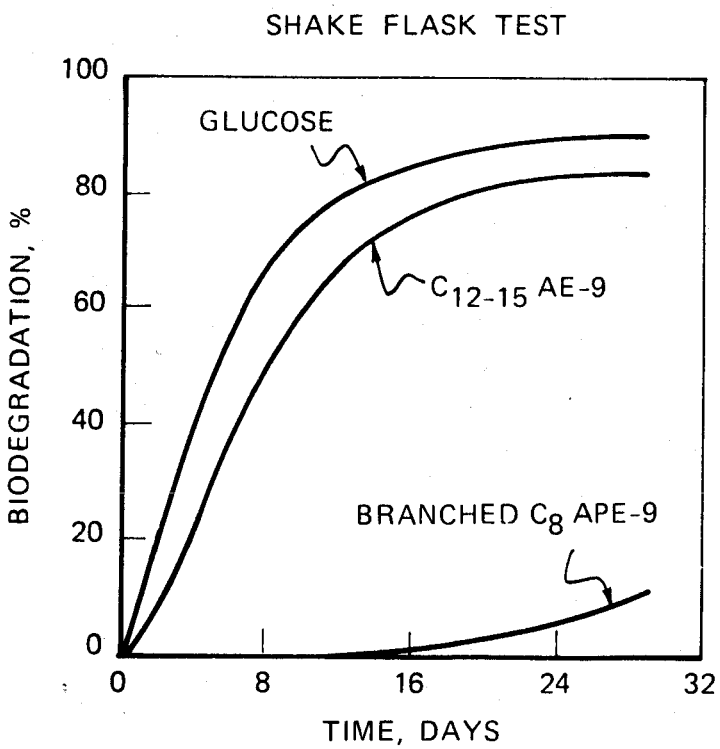


Figure 3/**Ultimate biodegradation**



of the alkyl chain.

Figure 4 shows the effect of hydrophobe branching on the ultimate biodegradation rates of AE as determined by CO_2 evolution. Up to 55% branching in the alkyl chain was found to have a marginal negative effect on the ultimate biodegradation rates of primary alcohol ethoxylates[12] at 25°C. A slight decrease occurred in the initial rate of CO_2 evolution for a 55% 2-alkyl branched primary AE-9 compared to a 25% 2-alkyl branched primary AE-9. A 100% linear secondary AE having approximately the same alkyl and POE chain length degraded at a slightly slower rate than the primary AE products.

The effect of varying POE chain length on the ultimate biodegradabilities of linear primary AE containing averages of 7, 18, 30 and 100 EO units/mole of alcohol is shown in Figure 5 using CO_2 evolution as the biodegradation criterion.[14] The results of this study indicate a significantly lower level of biodegradation only for the AE containing 100 EO units/mole of alcohol.

Branched octyl (OPE) and nonylphenol (NPE) ethoxylates are currently the only alkylphenol ethoxylates of commercial importance. Bruschweiler recently has reported[15] that the biodegradabilities of OPE and NPE were not significantly different. Replacing the branched nonyl chain of commercial nonylphenol ethoxylate (NPE) with a linear nonyl chain was found to increase the extent of biodegradation somewhat.[13] The branched NPE had biodegraded to 5% of the theoretical CO_2 evolution whereas the linear NPE evolved 40% of the theoretical quantity of CO_2. A 75% linear C_{12-15} AE having essentially equivalent oxyethylene content yielded greater than 65% of the theoretical CO_2 evolution in equivalent tests. These results indicate that both the alkyl chain branching and aromatic structure of alkylphenol ethoxylates retard their rates of biodegradation.

Primary biodegradation and fish toxicity

Many of the widely used anionic and nonionic surfactants of commerce are relatively toxic to fish. Although aquatic toxicity data for nonionic surfactants have been reported, for example in the work of Macek and Krzeminski,[16] the question of key concern in a practical context is whether toxic effects persist during and after biodegradation.

Figure 6 shows a comparison of AE and APE in a laboratory river dieaway test carried out by our UK associates.[17] The residual nonionic concentration was estimated during biodegradation by chemical analysis as bismuth iodide active substance (BiAS), and by a fish bioassay procedure. The bioassays were carried out by exposing rainbow trout *(Salmo gairdneri)* to the biodegrading liquor and comparing

Figure 4/**Ultimate biodegradation of AE**

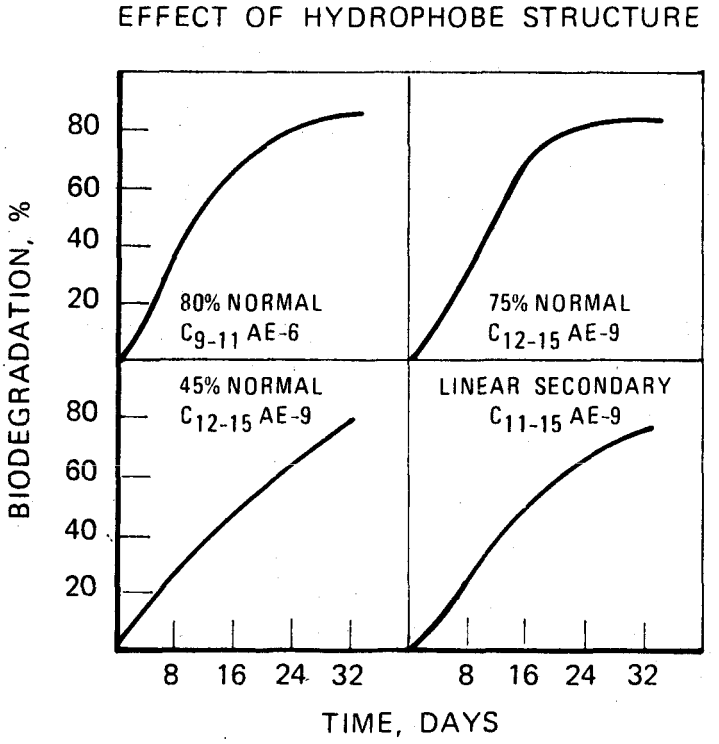


Figure 5/**Ultimate biodegradation of AE**

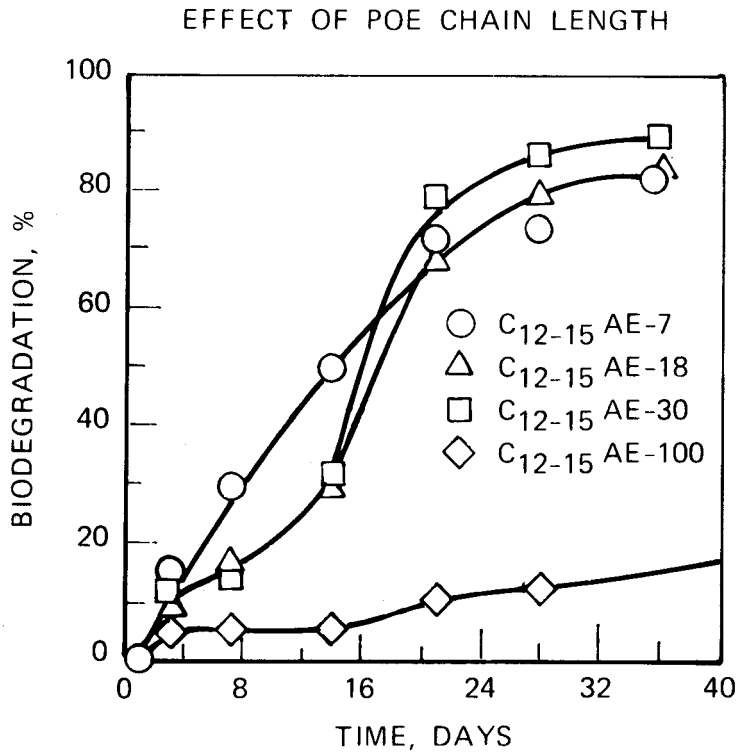
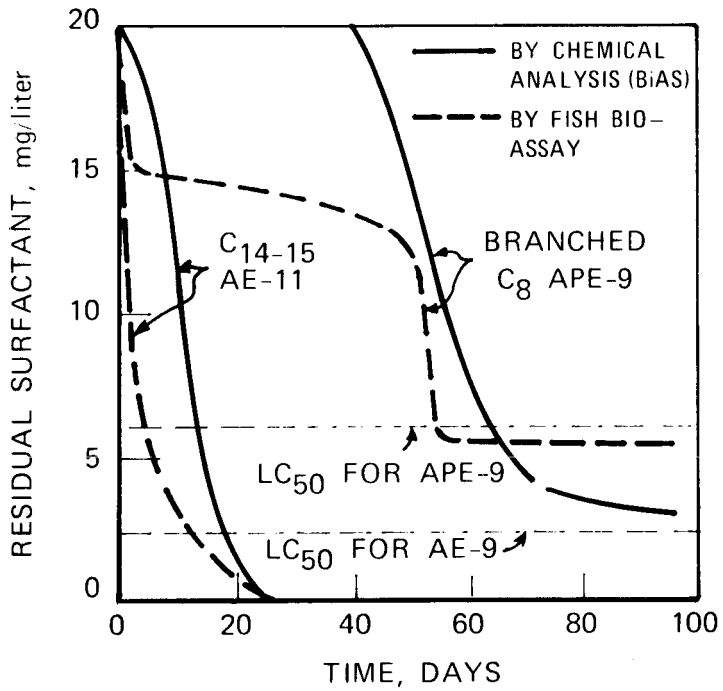


Figure 6/**Effect of primary biodegradation on acute fish toxicity**



their survival times with those in known concentrations of the starting materials. The results show that at a high initial loading of 20 mg/l the AE lost toxicity to rainbow trout in 10-14 days in spite of an absence of adapted organisms. However, under these conditions the APE required 10-11 weeks to be rendered non-toxic to trout. Another important conclusion was that the intermediate products of biodegradation appeared to be less toxic than the starting AE or APE.

Acclimation

The capability of bacteria in sewage treatment plants to acclimate rapidly to chemicals entering the plant is important. All sewage treatment plants experience periodic episodes of upset, generally initiated by toxification of bacteria from inadvertent discharge of toxic waste into the plant or by storm runoff which can remove appreciable levels of bacteria from activated sludge units. Under these conditions, rapid readaptation or reacclimation of the existing bacterial systems to the normal organic loadings of the plant is required in order to prevent discharge of high levels of undergraded chemicals into streams, rivers and other receiving waters. In the case of nonionic surfactants like AE and APE, this would cause considerable foaming and possibly fish kills in the receiving waters. The data in Table 1 list results obtained in a river die-away test[17] using AE and APE. These results show the APE tested was slower to adapt than two AE surfactants and slower in primary biodegradation after adaptation. Others have commented on the importance of adequate acclimation for biodegradation of APE.[18] These tests imply that readaptation and recovery of a practical effluent treatment plant after a period of upset may be slower with APE than AE.

Field tests

The primary biodegradation of AE and APE has been compared under realistic conditions in an extensive field trial carried out in a small U.S. community[19] under summer and winter seasons. The results are summarized in Figure 7 and show the sharp decrease in biodegradation of nonionic surfactant when AE was replaced by APE during the first winter period. Although the biodegradation levels for APE increased in the warmer summer months, they never consistently reached those of AE. The level of biodegradation declined again for APE with the onset of cooler winter weather, but rose sharply when APE was replaced by a second AE material. In addition, the poor biodegradation of the APE during winter was accompanied by significant foaming in the effluent. Foaming was not observed in the effluent during winter when either of the AE products was used. The poorer biodegradation of nonylphenol and octylphenol ethoxylates under winter conditions has been reported by Stiff and Rootham[20] in laboratory tests.

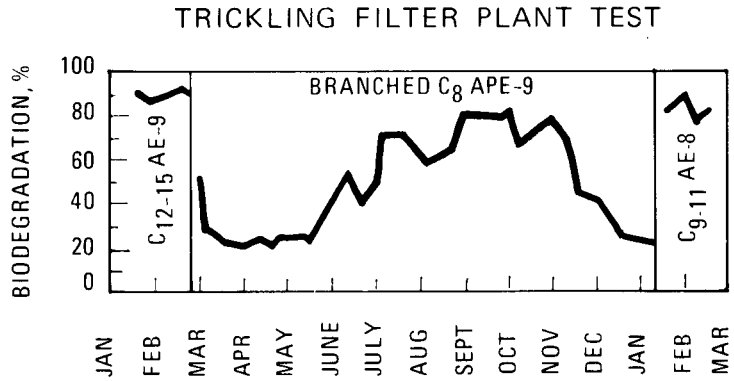
The results of a field test on the effect of an AE on the operation of an activated sludge treatment plant in Ohio recently have been reported.[21,22] In this test, the plant influent was dosed with 10mg/l of the AE under both summer and winter conditions. Plant performance was followed by sampling specific locations throughout the treatment facility before, during and after dosing. Results of analyses for such parameters as surfactant concentration, 5-day BOD, COD, sludge volume index and sludge retention time indicated that the AE was 90% removed and its presence had no adverse effects on plant performance or on aquatic life in receiving stream.

Until recently, the ultimate biodegradability of AE and APE under realistic sewage conditions had not been studied. This is due to the difficulty of deter-

Table 1/**Primary biodegradation**

	RIVER WATER DIE-AWAY TEST			
	NONIONIC SURFACTANT			
CLASS	ALKYL GROUP	EO GROUPS/MOLE	APPROXIMATE ADAPTATION TIME, DAYS	HALF-LIFE AFTER ADAPTATION, DAYS
AE	C_{14-15} HIGHLY LINEAR	7	2	8.7
AE	C_{14-15} HIGHLY LINEAR	11	2	7.0
APE	C_8 HIGHLY BRANCHED	9	42	22.5

Figure 7/**Primary biodegradation**



mining CO_2 evolution or organic carbon which results from surfactants, since in sewage plants there is generally a much higher loading of other organic materials which "swamp out" the contribution of the surfactants. This problem has been overcome recently by the use of radiolabeled AE and NPE In an extensive study under realistic sewage treatment plant conditions.[23] The AE and NPE were each doubled-labeled with tritium in the hydrophobes and carbon-14 in the hydrophiles. Figure 8 shows the positions of labeling of these surfactants. Radiolabeled glucose was also included as a positive biodegradation standard. To perform the study, a portable laboratory adjacent to a domestic waste treatment plant in Houston, Texas, was outfitted with closed bench scale activated sludge units. A slipstream of the plant influent was then fed with the surfactants into the bench scale units containing activated sludge from the plant. After an acclimation period of 14 days in which unlabeled surfactants were used, the radiolabeled surfactants were fed to the bench scale units for 14 days followed by an additional 12 day period in which unlabeled surfactants were again used and the radiochemical die-away determined. Figure 9 is a schematic of one of the four bench scale units used in the study.

Figure 10 shows the formation of ^3H_2O from the hydrophobes of AE 25-9 and NPE-9. As shown, AE 25-9 released approximately 90% of its tritium as ^3H_2O within one day. This level of ^3H_2O release remained essentially constant throughout the course of the radiolabeled feed phase. In contrast, release of tritium as tritiated water was considerably slower and less extensive for NPE-9, indicating its hydrophobe was more resistant to ultimate biodegradation than AE 25-9. The relatively large variations in ^3H_2O formations from NPE-9 during this phase may be due to slight variable inhibiting effects from the influent which might have more of an effect on slower biodegrading substrates.

Figure 11 shows that evolution of CO_2 from the POE chain of AE 25-9 was only slightly greater than for NPE-9 during he radiolabeled feed phase.

The release of soluble ^3H-labeled biodegradation intermediates from AE 25-9 and NPE-9 into effluent is plotted in Figure 12. These results indicate 35-50% of the hydrophobe of NPE-9 is discharged into the plant effluent while less than 5% of the hydrophobe of AE 25-9 appears in the effluent.

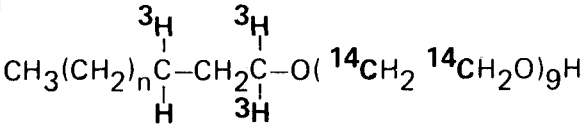
Figure 13 shows the release of soluble ^{14}C-labeled biodegradation intermediates into effluent. As shown, 8-14% of the hydrophile of NPE-9 is discharged to effluent while less than 2% of AE 25-9 is discharged.

The data in Table 2 show the ratio of EO/alkyl chain during NPE-9 biodegradation based on radiochemical analysis. These results indicate the NPE-9 degraded to an NPE with approximately 2 EO units. The NPE-2 appears to resist further biodegradation. Biodegradation of nonylphenol ethoxylates to NPE-2 which resists further biodegradation has also been reported by other workers.[24,25]

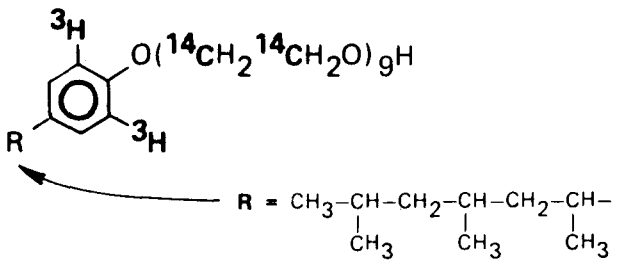
The distribution of radioactivity to the ultimate biodegradation products CO_2 and H_2O, to soluble ^3H- and ^{14}C-products and to ^3H- and ^{14}C-products found in cellular material obtained from activated sludge is listed in Table 3 for AE 25-9, NPE-9 and glucose. The data in this table indicated greater levels of ultimate biodegradability for the hydrophobe and the hydrophile of AE 25-9 compared to NPE-9, with greater discharge of metabolites from NPE-9 into effluent. Unexpectedly, larger quantities of ^3H and ^{14}C were found incorporated into cellular material from NPE-9 than from AE 25-9. It is interesting to note that $^{14}CO_2$ evolution from glucose was less than for AE 25-9 or NPE-9. However, more of the remaining ^{14}C activity was found in cellular material for glucose than for AE 25-9 or NPE-9.

Figure 8/**Substrates in slipstream study (fed continuously at rate = 5 mg/l)**

- AE 25-9



- NPE-9



- GLUCOSE

  (UNIFORMLY LABELED WITH ^{14}C)

- BLANK

Figure 9/**Closed continuous bench-scale biotreater**

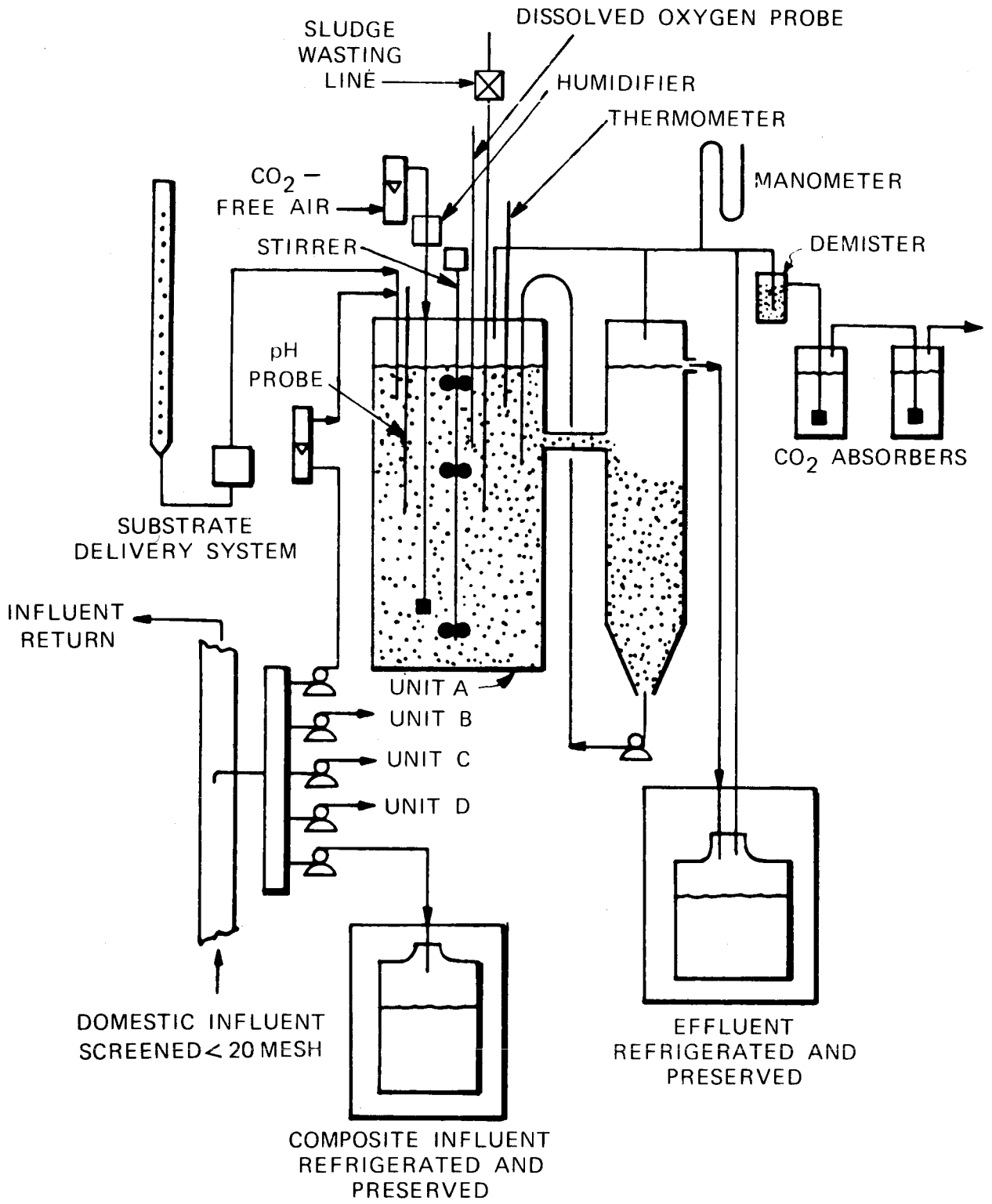


Figure 10/**Formation of $^{3}H_2O$ from AE 25-9 and NPE-9**

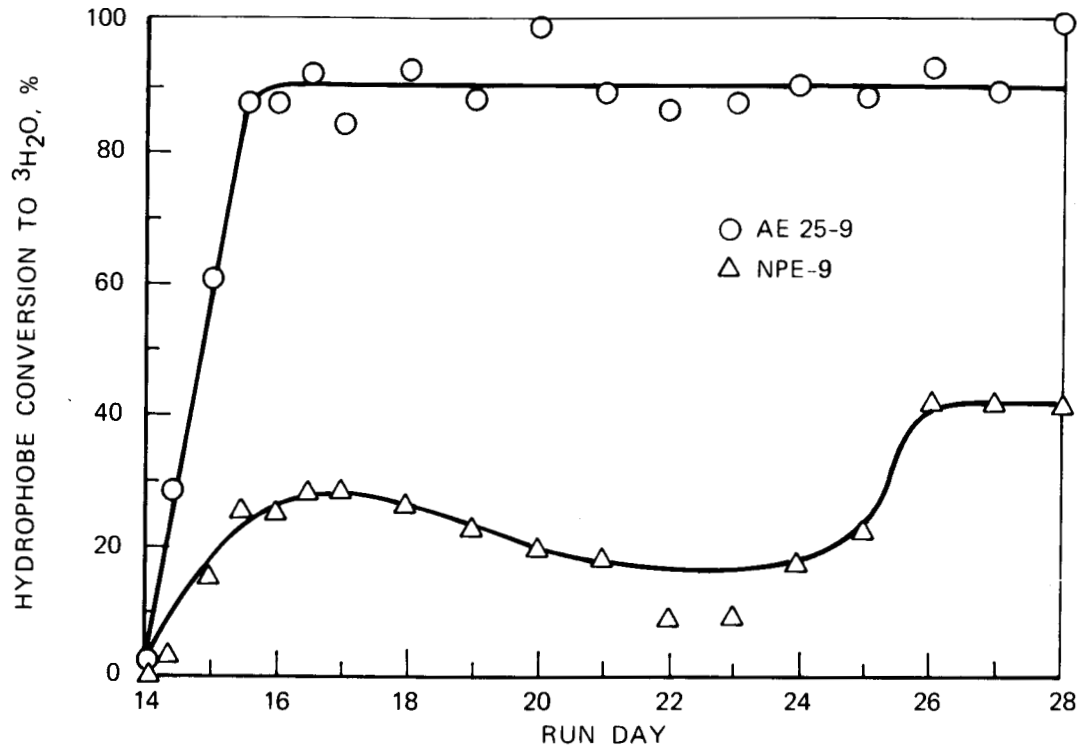


Figure 11/**Evolution of $^{14}CO_2$ from radiolabeled AE 25-9 and NPE-9**

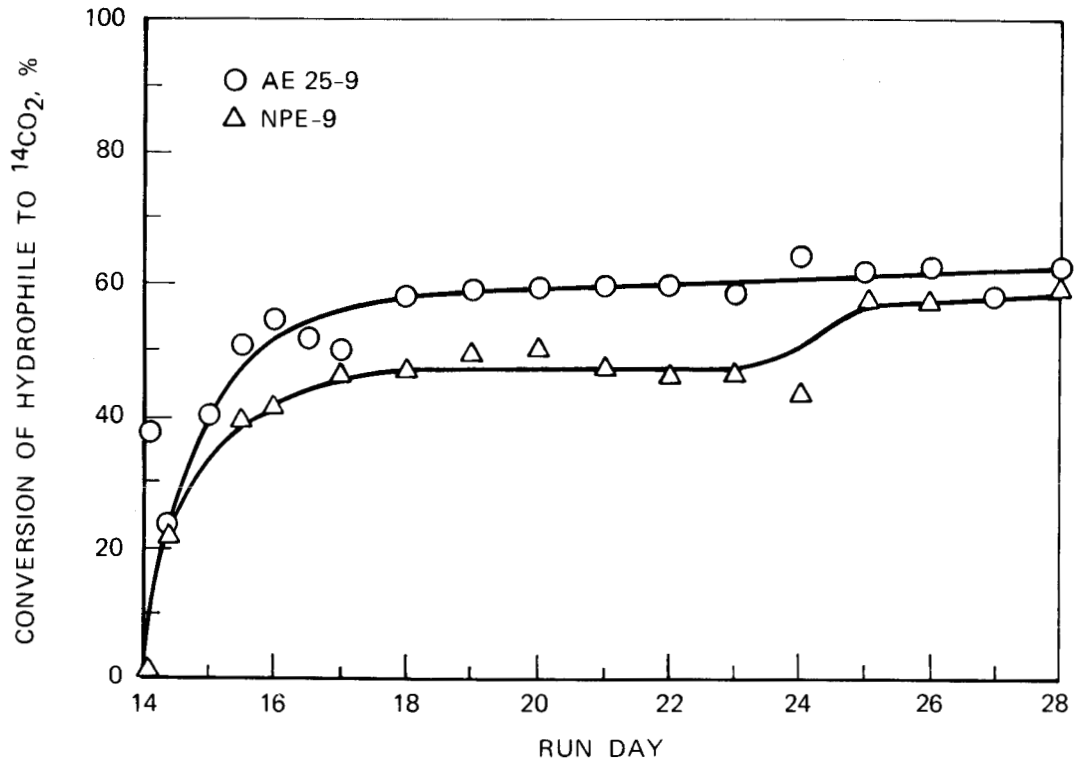
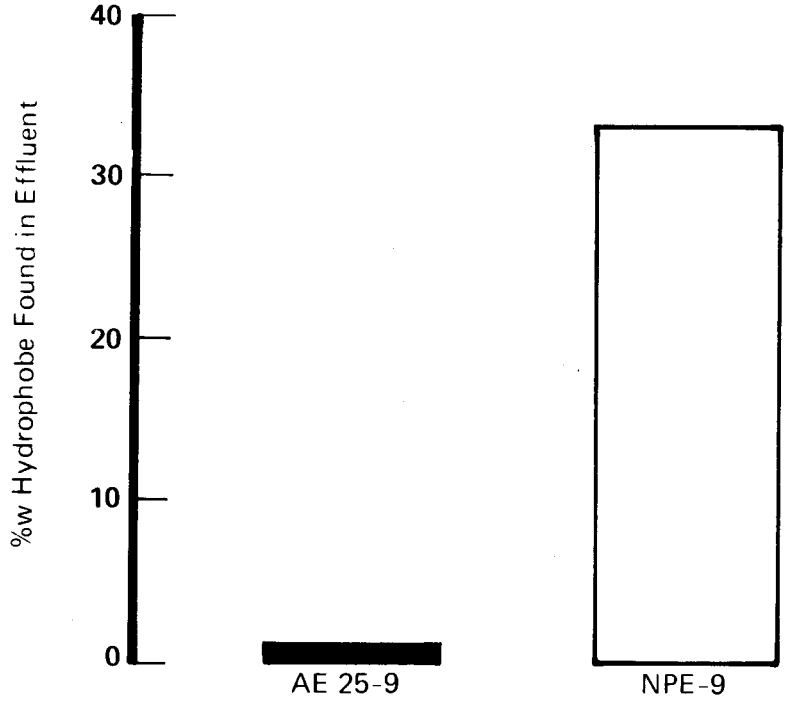
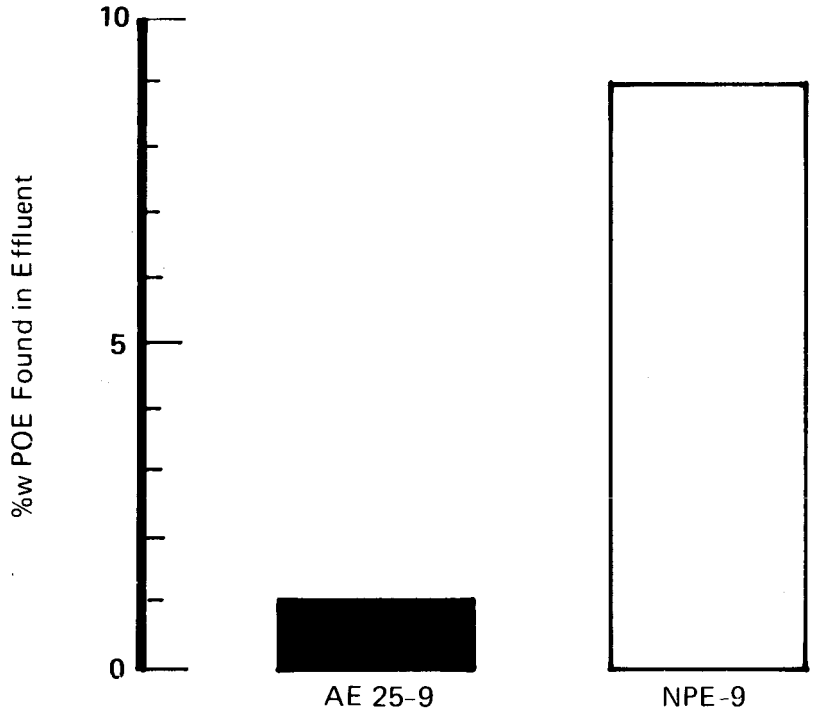


Figure 12/**Effluent metabolites from hydrophobe***



*Basis ^{3}H Analysis: Calculated as Intact Hydrophobe

Figure 13/**Effluent metabolites from poe chain***



*Basis ^{14}C Analysis

Table 2/**Ratio EO/hydrophobe during biodegradation of NPE-9**

TIME (DAYS)	RATIO, EO/HYDROPHOBE*
0.08 (2 HOURS)	5.4
0.33 (8 HOURS)	2.4
1	2.2
18	2.4
24	2.7
28	2.2

* BASIS, $^{14}C/^{3}H$ ACTIVITY IN EFFLUENT

Table 3/**Distribution of radioactivity***

	% CONVERSION TO . . .		% CONVERSION TO SOLUBLE . . .		FOUND IN CELLULAR PRODUCTS, %
HYDROPHOBE					
AE 25-9	90	$^{3}H_2O$	1	^{3}H PRODUCTS	5
NPE-9	25		33		33
HYDROPHILE					
AE 25-9	57	$^{14}CO_2$	1	^{14}C PRODUCTS	27
NPE-9	47		9		34
GLUCOSE	40		1		64

*AT COMPLETION OF RADIOLABELED FEED PHASE

Conclusions

Laboratory studies of the primary and ultimate biodegradation of commercial grade alcohol ethoxylates (AE) and alkylphenol ethoxylates (APE) show AE to biodegrade faster and more extensively than APE. Under realistic summer field conditions, both AE and APE appear to undergo adequate primary biodegradation while AE undergoes more extensive ultimate biodegradation than APE. Biodegradation of AE also permits lower levels of biodegradation intermediate to enter receiving waters compared to APE. Under conditions of plant stress, such as cold winter conditions or plant upset, the primary biodegradability of APE, but not AE decreases significantly and can permit undergraded APE to enter receiving waters and cause foaming.

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