

or based upon synthesized straight chain materials exhibit the greatest degree of biodegradability in all tests run. Varying degrees of indicated degradation can be obtained from specific tests on products possessing unknown or doubtful degradation structures. Branched chain materials continue to show greatest resistance to degradation.

Attempts to develop acclimated microorganisms to specific structures (i.e., branched chain detergents) did not significantly change biodegradation rates. The acclimation time using two 72-hr transfers may not have been sufficient.

Ethylene oxide derivatives of amides and straight chain alcohols biodegraded to a substantial degree in all tests.

ACKNOWLEDGMENT

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Surfactants Containing Ethylene Oxide: Relationship of Structure to Biodegradability

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Abstract

Anionic ethoxy sulfate and nonionic ethoxylate surfactants were prepared from the following straight-chain hydrophobes: fatty or Ziegler primary alcohols, oxo alcohols derived from straight-chain olefins, secondary straight-chain alcohols and straight-chain alkylphenols. These were studied to relate biodegradability to the following elements of structure: the nature of the connecting link, its position of attachment to the hydrophobe, the chain length of the hydrophobe, and the length of the ethylene oxide chain used. Previously described methods were used to estimate both rate and completeness of degradation in river water as well as activated sludge environments.

Data are presented to support the following conclusions.

1) All surfactants derived from straight-chain primary and secondary alcohols are rapidly and completely degraded with loss of surfactant properties. The length of the ethylene oxide chain from zero up to ten units has no effect on the rate or the completeness of degradation. In such surfactants, the ethylene oxide chain is completely degraded.

2) In contrast, surfactants from straight-chain alkylphenols are not as rapidly or as completely degraded as those described above. The position of attachment of the phenol ring to the straight-chain has a large effect on degradability; normal or primary attachment leads to a faster rate of disappearance than secondary attachment. Nonionic surfactants from straight-chain alkylphenols containing ten to twelve moles of ethylene oxide are not completely degradable.

Introduction

WHEN THIS PROJECT was started several years ago, it appeared evident that surfactants which were not biodegradable were in for a siege of bad publicity

and poor reputation, deserved or not. The manufacturers of detergent products through the Soap and Detergent Assoc. had produced evidence that detergents were not a major pollution problem (1). Yet the sweep of bad publicity sustained by the presence of tell-tale foam has carried the country along the road toward restrictive legislation. After much effort, the manufacturers of alkylbenzene sulfonate are now able to offer a wide range of linear alkylate sulfonate (LAS) products at competitive prices to meet the needs of this pollution or foam problem.

Long Term Goal: Complete Biodegradability. During these years, suggested screening and legislative standards for biodegradability have often coned more on the elimination of foam than on proof of the complete biodegradability of the new products. It was a relatively simple matter to demonstrate the rate of disappearance of the LAS molecules and related foam and other surface active properties in river water die-away tests. It has taken more sophisticated methods to demonstrate that the molecule is completely biodegradable, for which we are indebted to the work of Swisher (2), Allred (3) and many others.

This progress with LAS biodegradability is encouraging. The long term goal of complete biodegradability for other new surfactants cannot be realized until these new products can also meet tests for completeness of biodegradation as well as tests to demonstrate rate of disappearance of the initial molecules.

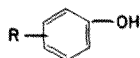
Short Term Goal: Loss of Surface Activity. Initial prospects for the preparation of completely biodegradable products did not appear favorable for the manufacturers of ethoxylated surfactants. The limited screening data available at that time indicated that the ethylene oxide chain itself was not biodegradable (4). Thus the manufacturer had to look not only for a biodegradable hydrophobe but also for a biodegradable water-solubilizing nonionic group to replace the versatile and inexpensive ethylene oxide chain.

The thought did occur, however, that a short-term goal for biodegradability might be readily obtained. Such a goal would be satisfied with degradation of

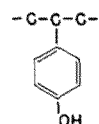
A. ETHOXYLATED SURFACTANTS



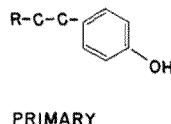
B. HYDROPHOBES SUITABLE FOR ETHOXYLATION



C. STRAIGHT-CHAIN ALKYLPHENOLS



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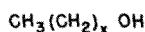


PRIMARY

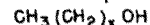
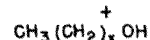
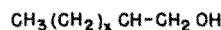
FIG. 1.

STRAIGHT-CHAIN HYDROPHOBES

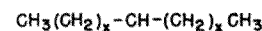
ALCOHOLS



PRIMARY

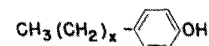


OXO PRIMARY

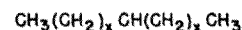


SECONDARY

ALKYLPHENOLS



PRIMARY



SECONDARY

FIG. 2.

the hydrophobe chain of the surfactant with a resulting loss of foam and surface active properties. It was assumed that the non-biodegradable ethylene oxide chain residues would be harmless and go unnoticed in the company of the vast amount of other residues in the streams.

In Figure 1A are illustrated the two major families of ethoxylated surfactants of interest: the short-chain ethoxy sulfates and the longer-chain nonionic surfactants. Turning attention to the straight-chain hydrophobe sources which might be commercially feasible, the nonionic manufacturer's plight was even here more complicated than that of the LAS producer. To make ethoxylates, a handle must be put on the ethylene oxide could be added. Two groups have been most generally used for this purpose: the hydroxyphenyl and the hydroxyl (Fig. 1B). The most economical grouping has been the secondary hydroxyphenyl group obtained by the alkylation of phenol with olefins; the synthesis of alcohols has usually been too expensive. Thus the polypropylene alkylphenols have been the largest volume hydrophobes to date for the preparation of ethoxylates.

Straight-Chain Alkylphenol Ethoxylates. The easiest solution to the problem appeared to be the production of straight-chain alkylphenols to replace the non-biodegradable branched-chain alkylphenols, such as LAS is to replace alkylbenzene sulfonate (ABS). Accordingly, many processes were examined for the production of straight-chain secondary alkylphenols with 9-12 carbons in the alkyl side chain. These were converted to ethoxysulfates and nonionics by commercial processes for testing. As a model of the least-branched alkylphenol ethoxylates possible, synthetic normal or primary alkylphenols were also prepared and converted to surfactants (Fig. 1C).

Straight-Chain Alcohol Ethoxylates. In more recent work, the objective has been to compare all of the potentially commercial straight-chain hydrophobes suitable for ethoxylate production. Figure 2 shows those which are of major interest: primary alcohols, oxo alcohols derived from alpha-olefins (primary with a small amount of branching), linear secondary alcohols (5) and the above-mentioned alkylphenols. For interfamily testing, the best secondary alkylphenol was chosen along with the model primary alkylphenol. In each family, at least two alkyl chain lengths were tested together with a commercial type of mixed chain length to estimate the effect of hydrophobe size over

the range of commercial interest. These comparisons relate empirically the effect on biodegradability of the following elements of structure: the connecting link, its position of attachment to the straight-chain hydrophobe, the size of the hydrophobe and the size of the ethylene oxide chain.

Experimental

Biodegradability Testing. C. A. Vath has reported recently on the methods used in this program to measure both rate and completeness of degradation (6).

Completeness of Biodegradation. For the measurement of completeness of degradation, the results of Warburg respirometer studies using acclimated activated sludge seed are reported. For poorly degradable compounds, 48-hr values of net oxygen uptake as a percentage of applied chemical oxygen demand (net BOD, percentage of COD) are reported. For more easily degraded compounds, values of net BOD, percentage of COD at the inflection point (approx 8-10 hr after start) are reported. A complete presentation of Warburg technique and interpretation of results is given by Vath (6). For present purposes, those compounds which do not reach a value of 35-40 net BOD, percentage of COD are not considered completely degradable.

Rate of Biodegradation. Results reported here for rates of degradation in river water die-away tests rely mainly on methylene blue analyses for anionics and cobalt thiocyanate analyses for nonionics. The latter is a method developed by N. T. Crabb which is being presented in this Symposium (7). Earlier work was handicapped by the lack of an analysis for nonionics, and during this period much use was made of surface tension data. Surface tension reduction is a function of the logarithm of concentration; but observed surface tension data do not allow this relationship to be established. A simple square relationship is used here as a model of the actual behavior. Instead of a record of surface tension reduction, percentage of first day, against time, the square of this percentage is recorded. This has given reasonable agreement with other measures of surfactant concn.

To save space, the standard die-away curve is represented by a first-order reaction rate constant from which a fair approximation of the complete curve might be reconstructed. Recorded values indicate the time at which 90% of the original concn has degraded and 10% remains; this value is labeled $t_{0.9}$. Use of

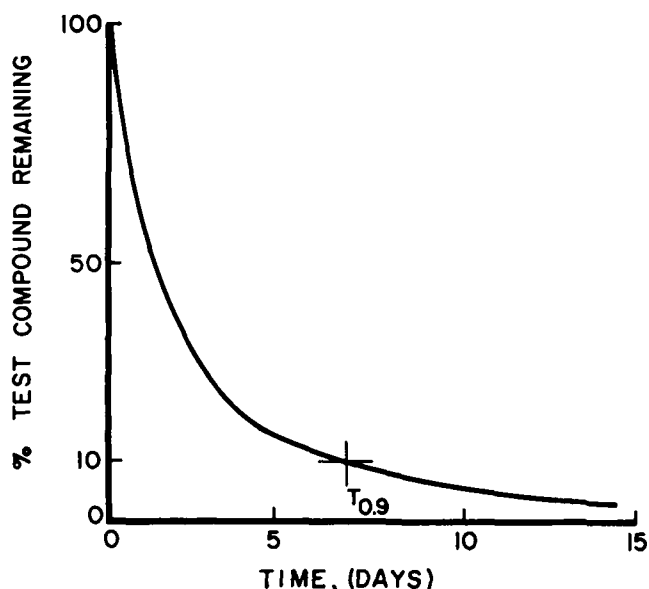


Fig. 3. Typical die-away curve.

these numbers allows many die-away results to be put in families of points on one graph. Figure 3 shows a typical die-away curve. Where the test compound is readily degraded, the $t_{0.9}$ will be taken directly from the curve. In reporting many of the variations of alkylphenol surfactants, methods of testing varied and many of the curves had lag periods and never reached 90% degradation. For these, the rate constant was calculated from the steepest rate of descent in the curve; such results give $t_{0.9}$ which are somewhat artificially small but adequate for comparison within the alkylphenol family.

Preparation of Surfactants. Commercially operated processes were used for the preparation of the hydrophobes, ethoxylates and sulfates, with the exception of the synthetic normal alkylphenols. The nine- and twelve-carbon normal side chain alkylphenols were prepared from pelargonyl and lauroyl chlorides, respectively. First the ketophenol was prepared through aluminum chloride catalyzed alkylation of the phenol with the acid chloride. Then the alkylphenol was

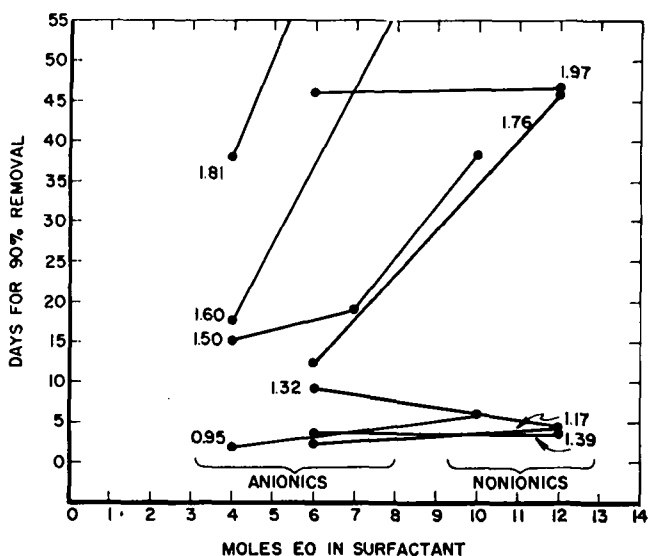


Fig. 4. Rate of degradation of surfactants from alkylphenols (NMR methyl numbers indicated). Surface tension data.

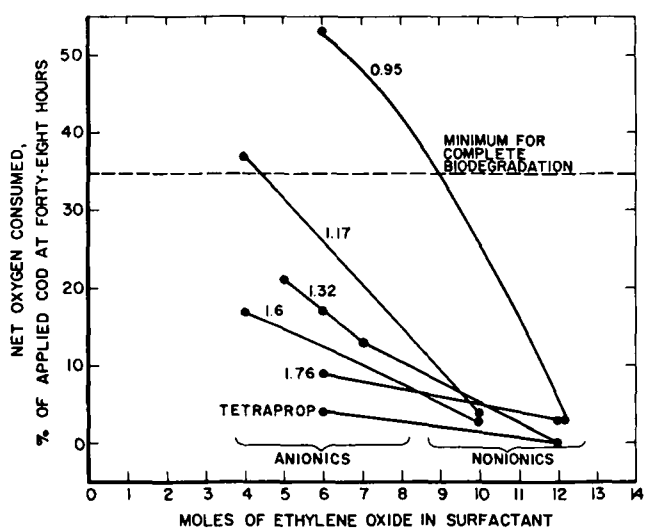


Fig. 5. Completeness of degradation of surfactants from alkylphenols (NMR methyl numbers indicated). Warburg respirometer data.

prepared by reduction of the keto group using the Wolff-Kischner procedure. Gas chromatographic scans of the ketophenols indicated that little or no fatty acid chloride was present. Gas chromatographic scans of the alkylphenols indicated disappearance of the ketophenols. IR analyses confirmed these conclusions. Finally, nuclear magnetic resonance (NMR) evaluation of these alkylphenols indicated the approx correct mol wt for the alkylphenol and the expected number of methyl groups.

Results and Discussion

Alkylphenols; Rate of Degradation. These results of screening show that all of the straight-chain products were more rapidly degraded than the branched-chain alkylphenol products. Fastest were the synthetic normal alkylphenols. A method of classifying the surfactants was found in a methyl number count for the alkylphenol obtained by NMR; lower numbers indicate less branching. In Figure 4 are shown rates of degradation for ethoxy sulfates and nonionics from

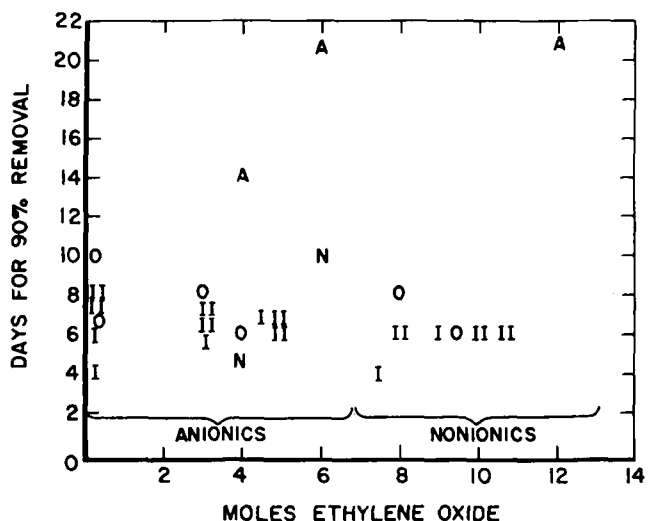


Fig. 6. Rate of degradation of surfactants by hydrophobe families. Analyses: nonionics by cobalt thiocyanate, anionics by methylene blue. A = II° alkylphenol, N = I° alkylphenol, O = oxo alcohol, II = II° alcohol, I = I° alcohol.

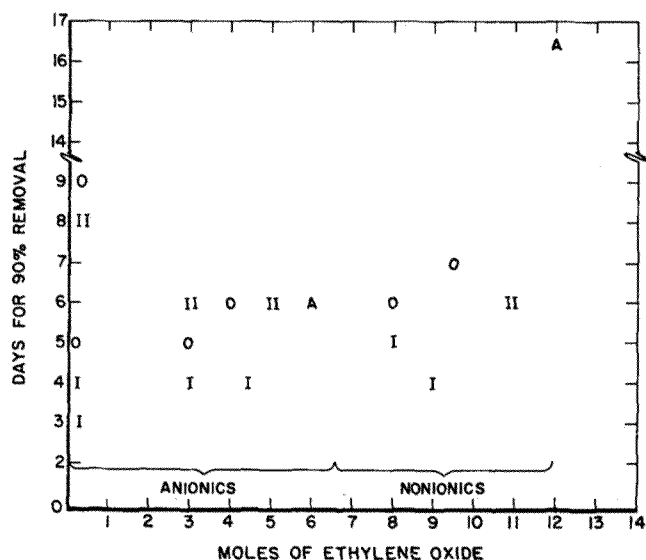


Fig. 7. Rate of degradation of surfactants by hydrophobe families. Analyses by surface tension. A = II° alkylphenol, O = oxo alcohol, II = II° alcohol, I = I° alcohol.

several alkylphenols, as determined by surface tension measurements. The $t_{0.9}$ is plotted against the moles of ethylene oxide in the surfactant; the lower ethylene oxide products are sulfates and the higher are nonionics. The NMR methyl number of the alkylphenol hydrophobe is indicated by each line. Two facts are apparent. First, in general, the lower the number of methyl groups, the faster the rate of degradation. Second, it appears that longer ethylene oxide chains lead to slower rates of degradation. In these curves, the product with an NMR methyl number of 1.39 was chosen as the best secondary alkylphenol product for further testing.

Alkylphenols; Completeness of Degradation. As a simple indication of completeness of degradation, the net BOD, percentage of COD for two days' time was taken. This, of course, could only be 100% if all of the test compound were converted through respiration to CO_2 and water. A value of 35–40 at least is required for complete biodegradation; otherwise, not enough energy is generated by respiration to use all of the food in biological growth. In Figure 5 we see the same alkylphenol-derived surfactants, with moles of ethylene oxide plotted against net BOD, percentage of COD, and the NMR methyl number recorded. It must be concluded that less branching leads to greater degradation, and that increased ethylene oxide content decreases the extent of degradation. Unfortunately, the longer ethylene oxide chains were not biodegradable, not even for the synthetic primary compounds with methyl contents around one.

One may conclude that the alkylphenol nonionics made thus far, including the model primary compound, are not completely biodegradable. By destruction of the side chain, they may usually lose surface active properties, but an ethylene oxide chain residue must be left. They may meet a short term goal but not a long term goal.

Alcohols vs. Alkylphenols; Rate Studies. River water die-away curves were taken for all of the straight-chain alcohol-derived surfactants previously outlined and compared with the best representatives of the secondary and primary alkylphenol-derived surfactants in a simultaneous run using the same river water. The results are indicated in Figure 6, where time for 90% removal is plotted against the moles of

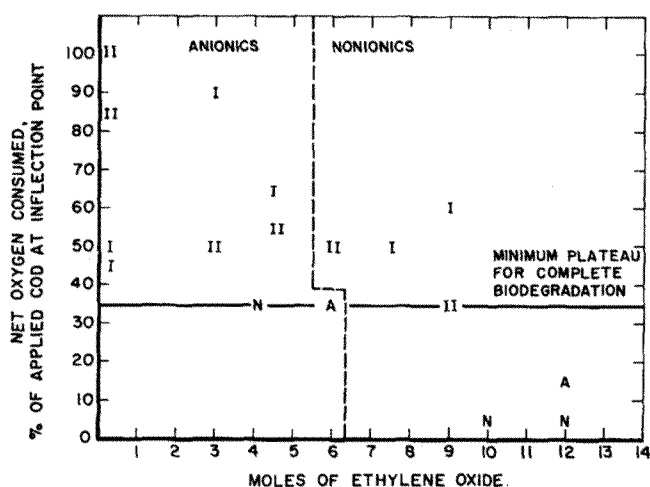


Fig. 8. Completeness of degradation of surfactants by hydrophobe families. Warburg respirometer data. A = II° alkylphenol, N = I° alkylphenol, II = II° alcohol, I = I° alcohol.

ethylene oxide in the surfactants of each family. Here, methylene blue was used to monitor anionics and cobalt thiocyanate was used for the nonionics. This summary shows all of the surfactants derived from straight-chain alcohols degrading rapidly in ten days or less. In contrast, the alkylphenols appear to take somewhat longer, especially for the nonionics. An interesting aspect is that the alcohol ethoxylates do not appear to be affected by the length of the ethylene oxide chain, the nonionic degrading as rapidly as the alcohol sulfate and ethoxy sulfate. Many other test results and methods of monitoring rate of disappearance show that the alcohol ethoxylates are always at least as fast and in many cases faster than the alkylphenols. Similar results are shown in Figure 7 where surface tension data were used to monitor rate of disappearance.

Alcohols vs. Alkylphenols; Completeness of Degradation. Figure 8 shows the results of testing the above surfactants for completeness of biodegradability. It will be noticed that the best of the alkylphenols still yield nonionic surfactants of incomplete degradability. On the other hand, the alcohol ethoxylates yield nonionics which meet the requirements for complete degradability, regardless of ethylene oxide content.

These data indicate that the choice of available linear alcohol ethoxylates may be made from primary, secondary and oxo primary on the basis of cost performance with confidence that these products will meet long-range standards of complete biodegradability.

ACKNOWLEDGMENTS

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