any applause from those who object to foam in their water supply! Rather than applause, you are being challenged to lick your problem because *you walk with sewage,* just as *sewage walks with your industry.*

You have the misfortune in your "between the devil and the deep blue sea" situation of reminding a cleanliness-loving people that we are caught in the web of our own weaving—that the foam we produce is symbolic of the wastes we produce, and that to admit it is to admit that we are guilty of fouling our own nest!

It is common for industrialized America to wave its banners and plead for free enterprise. Your industry, I am sure, pleads for the right to operate its practices in the best way it can do so, without interference in the normal operations of your business procedures. You must practice what you preach. If you plead for free enterprise, you should demonstrate your enterprise by producing formulations of detergent products which can eliminate your part of the nation's pollution problem.

I plead today for a further role for the American Oil Chemists' Society. In addition to cleaning up your "front door" problem, and in addition to carrying out the internal industrial operations of your profession in a way that will eliminate the "back door" industrial wastes pollution problem, I urge you to play a third important role in the problem of solving the nation's pollution problem.

It would be true justice if your Society would resolve to do even more. Since your foam has aroused all of the frenzy on the part of people who think *emotion* takes the place of *motion* . . . who are attacking the foam problem with more *heat* than *light* . . . you can do something about the pollution which walks with ABS. You could render a great national service by becoming a part of the great drive for licking the nation's pollution problem.

The sanitary engineering profession which I represent challenges your profession to help correct the conditions which caused the congregation to plead for forgiveness for the things we have done which we should not have done and the things we have not done which we should have done.

What is detergent's role in the nation's pollution problem? The story is told of a traveller who first saw the ocean from the rail of his steamer. He marveled over the vast expanse of water until a ship's officer said: "Yes, but that is only the top of it!" The detergent problem is only the "top" of the nation's water pollution problem, but it is the part the public can see. It is our task to clean up the "top," and, in so doing, to make certain that we lick the other wastes which "walk with ABS."

With your help, we can do both.

# The Chemistry of Surfactant Biodegradation

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THE PRIMARY incentives prompting study of the biodegradation of surfactants arise from the waste detergent situation, a situation which has by now been covered so thoroughly in the technical literature and the public press as to require no further elaboration here. A comprehensive review has recently been published by the Detergent Subcommittee of the Ohio River Valley Water Sanitation Commission (1). It provides a very useful entry to the literature on all aspects of the problem.

Biodegradation of surfactants in wastewaters, in treatment plants, and in the ultimate receiving bodies is primarily the result of bacterial action, just as is the case with the other organic components of the waste. The biochemical metabolic reactions involved appear to be much the same whether surfactant or not, although there are certain characteristic features exhibited in surfactant biodegradation which arise from the characteristic structure of surfactants themselves—strongly hydrophilic and strongly hydrophobic groups joined together in the same molecule.

Accordingly, as a preliminary to the discussion of surfactant biodegradation, the more common test methods and the more likely metabolic pathways will be reviewed.

To serve as a convenient point of reference, Figure 1 shows a typical biodegradation experiment applying the river water technique devised by Hammerton (2). Here a seven-milligram sample of surfactant was dissolved in a liter of river water and the solution was anaylzed every few days by the methylene blue method. Three different surfactants are shown, one which was readily attacked by the microorganisms present in the river water, one which was quite resistant, and one of intermediate character, the present day commercial product.

## Test Methods

Basically, biodegradation is measured by exposing the test compound to microorganisms and analyzing the system at intervals to determine such things as the disappearance of the test compound, the formation of degradation products or the uptake of oxygen. As will be evident, many combinations of microbiological environments with analytical methods have been used depending on the exact objectives of the work.

### 1. Microorganisms

The microorganisms chosen may be a pure strain or a mixture. Mixtures are ordinarily used, derived from such sources as river water (2), activated sludge (3), sewage (4), soil (5), or air (6). The general microbiological makeup of mixed cultures from these sources seems to be fairly constant, deriving from the characteristic species of common soil bacteria (4), and they should give a fairly realistic basis for extrapolation of performance from the laboratory to the field.

Pure cultures, on the other hand, should be of value in the detailed study of specific metabolic reactions, but are less suited for general screening of surfactants for biodegradability. It often happens that a specific strain of microorganism is unable to carry out some specific reaction in a metabolic sequence which a related strain can do quite readily. In a mixed culture, the species present can make up for each others' deficiencies. There is another reason

why a pure standard organism probably cannot be established for determination of biodegradability: It would have to be readapted or reacclimated to the specific chemical structures characteristic of each different surfactant, and after such acclimation it would no longer be quite the same as the original standard organism.

### 2. Analytical Procedures

The initial surfactant concentrations used in biodegradation studies are ordinarily below 10–20 parts per million, somewhat higher than commonly met in the field. A qualitative estimate of degradation can be made by observation of changes in surfactancy properties of the solution as the test goes on, for example the surface tension (7) or foaming tendency (8).

Quantitative analysis for anionic surfactants at or below this concentration level is readily accomplished by the widely used methylene blue method (9) or a variant thereof. This is fairly specific for anionic surfactants and modifications have been developed, for example by Longwell and Maniece (10), to make it even more so. Thus, even though a surfactant may disappear as monitored by methylene blue during biodegradation, this gives no information beyond the fact that it has been altered enough to destroy its surfactancy properties and its response to methylene blue; how far it has progressed toward complete conversion to $CO_2$, $H_2O$, $Na_2SO_4$ and microorganisms is left indeterminate.

Direct quantitative analysis for nonionics is much more difficult, and no method has yet appeared with ease and accuracy comparable to the methylene blue method. However, Huyser (11) has reported some data on biodegradation of nonionics using the analytical method of Stevenson (12).

Ryckman and Sawyer (13) verified the biodegradability of the primary and secondary alkylbenzene sulfonates by the disappearance of their characteristic infrared spectra.

Gas chromatography has been very useful in the study of alkylbenzene sulfonate degradation (7,14). Even though the ABS itself is not volatile, the sulfonate group can be removed by boiling with concentrated phosphoric acid and the resulting alkylbenzenes determined.

The foregoing analytical methods give information on the amount of the original surfactant remaining in the test solution. It is also important to learn about the further course of the degradation reaction, since many intermediate stages must be passed through before complete conversion to $CO_2$ and $H_2O$.

Since the overall process is oxidative, measurement of the oxygen uptake of the system has long been used in estimating the extent. Hammerton (2) observed that the disappearance of the methylene blue response in his river samples was paralleled by the oxygen uptake in duplicate samples using the biochemical oxygen demand (BOD) technique. This technique is limited by the amount of dissolved oxygen which is originally present in the initial sample, a limitation which can be avoided by use of the Warburg respirometer and higher concentrations of bacteria than are ordinarily present in river water (3,8,13).

However, conclusions drawn from such oxygen measurements may be subject to considerable uncertainty. For example, the oxygen uptake of the surfactant culture in a Warburg test is usually corrected by subtraction of the oxygen uptake of a parallel blank culture fed no surfactant, with the attendant risk that the metabolism of the two cultures might be altered by the presence or absence of the surfactant. Furthermore, even when the culture is fed a completely degradable food such as a long chain fatty acid sodium salt, the oxygen uptake is usually far below the theoretical amount and may vary depending upon the exact conditions (8). In short, there are many microbiological reactions involved in the overall oxygen utilization by the culture. Calculation of the percent oxidation of the surfactant from such data is an indirect process, and is necessarily of limited accuracy.

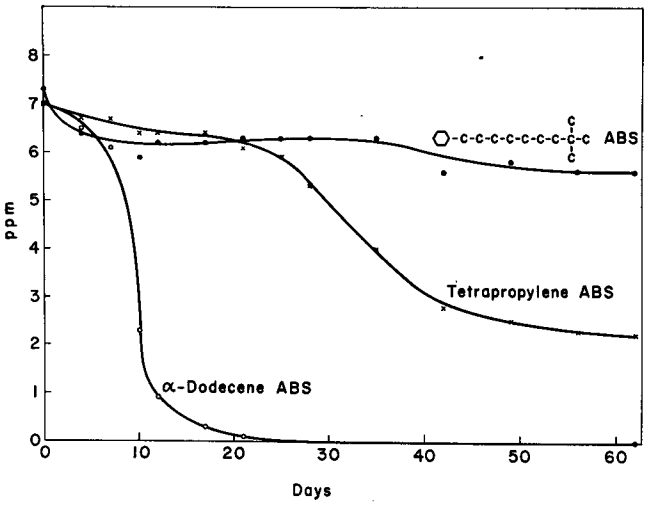



FIG. 1. River water degradation of three types of ABS (methylene blue analysis).

The overall progress of degradation may be estimated by an inverse of the oxygen uptake method, determination of the oxidizable organic compounds (chemical oxygen demand; COD) remaining in the solution (8). This direct approach eliminates much of the inference necessary in the interpretation of oxygen pickup data, but nevertheless it has its own share of uncertainties. The analysis is non-selective and would respond to any organic compounds desorbed from the protoplasm or sludge during the test, and of course would not detect any adsorbed surfactant or intermediate degradation products. Improvement of the COD determination itself would be desirable also, since the standard method is near the limit of its useful range at the low concentrations ordinarily used in surfactant biodegradation work (15).

Formation of inorganic sulfate is a good indication of complete destruction of a sulfonate type surfactant such as alkylbenzene sulfonate (ABS); several workers followed the progress of ABS degradation by sulfate analysis (13,17,18).

Gas chromatography has been useful in the study of intermediate degradation products (14,16).

Finally, radiotracer techniques are applicable to many of the analytical problems by appropriate labeling of the hydrogen, carbon (16), or sulfur (17,18).

## Biochemical Oxidation

Microorganisms are capable of degrading a wide variety of organic compounds, using them as food to provide for growth and energy requirements. The variety of biochemical mechanisms required for this job is considerably narrower since a given mechanism can be used by the organism for many related com-

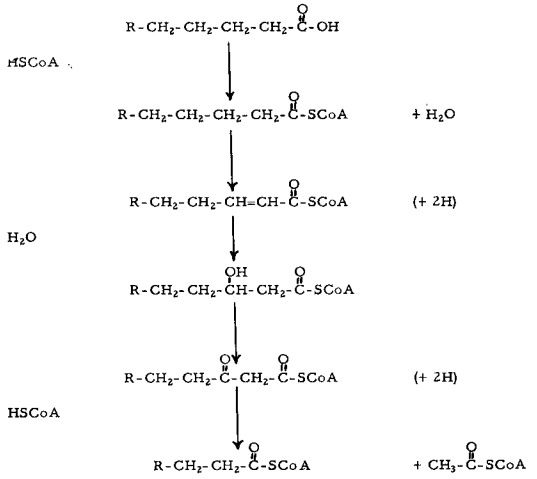


FIG. 2. Stages in beta oxidation (HSCoA = coenzyme A).

pounds and since many of the intermediate degradation products are the same. Surfactant degradation is brought about by these same reactions, although some minor modifications of the processes may arise from the peculiar molecular combination of hydrophobic and hydrophilic groups which makes a surfactant what it is. The three biochemical mechanisms outlined below are particularly applicable in surfactant biodegradation.

**1. Beta-Oxidation**

By this process fatty acids are degraded, and they may be synthesized by the reverse reactions. Fatty acids are a necessary part of all life processes, and the $\beta$-oxidation mechanism is used in all types of living cells: animal, plant, or microbial. The literature on it is voluminous and may be entered by way of recent reviews (19,20).

Briefly the reaction is an oxidation of the fatty acid chain two carbons at a time into a succession of acetyl groups which are used for energy or synthesis reactions by the cell.

Figure 2 shows a detailed picture. First the carboxyl group must be esterified with coenzyme A, a moderately complex organic mercaptan, and at least two steps are involved here. Next, two hydrogens are removed to give the $\alpha$-$\beta$ unsaturated derivative which is then hydrated to the $\beta$-hydroxy and dehydrogenated to the $\beta$-keto derivative. Finally, another molecule of coenzyme A adds between the $\alpha$- and $\beta$-carbons, splitting off acetyl coenzyme A and leaving a fatty acid coenzyme A ester two carbons shorter than the original, ready to engage in a similar sequence of reactions for still further degradation.

Each of the reactions indicated in Figure 2 it itself a sequence of reactions. Each is catalyzed by

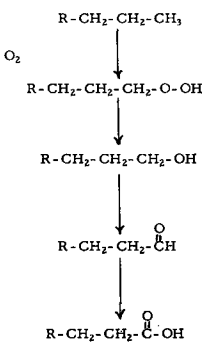


FIG. 3. Stages in biochemical oxidation of methyl group to carboxyl.

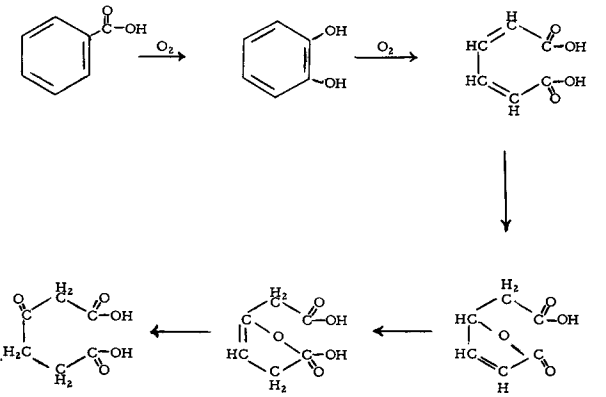


FIG. 4. Stages in biochemical oxidation of aromatic ring.

its own specific enzyme and activators and is reversible under the proper circumstances. The hydrogen does not actually appear as hydrogen atoms as indicated in Figure 2, but instead is plucked off by hydrogen transfer agents such as diphosphopyridine nucleotide or flavin adenine dinucleotide, which pass it on to other labile components of the cell. In aerobic systems the hydrogen may be ultimately accepted by atmospheric oxygen to form $H_2O$. Anaerobic degradation of fatty acids also proceeds by the $\beta$-oxidation sequence shown in Figure 2, but the ultimate hydrogen acceptor might be a carbon compound (forming $CH_4$), sulfate (forming $H_2S$) or the like, depending on the particular organism involved.

**2. Methyl Oxidation**

If the terminal methyl group of a surfactant hydrophobe can be oxidized to a carboxyl group, degradation should then proceed rapidly by the above $\beta$-oxidation mechanism found so universally in living systems. Evidence for such methyl group oxidation is found in the fact that many microorganisms have the ability to live on hydrocarbons as their sole source of food. This is amply attested in a recent comprehensive review by Fuhs (21), who states "Bacteria which attack higher hydrocarbons are everywhere on the earth's surface and are not dependent on the natural presence of these substrates."

The biochemistry of this oxidative process has not been investigated as fully as $\beta$-oxidation. Kallio and co-workers have shown that one important route involves an attack by oxygen to give a primary hydroperoxide (22). Subsequent reactions convert this intermediate to the primary alcohol, aldehyde, and carboxylic acid as outlined in Figure 3. Each step is catalyzed by appropriate enzyme systems. The first step differs significantly from the non-biochemical attack by oxygen, which occurs preferentially at secondary and tertiary hydrogens instead of the primary ones.

**3. Aromatic Oxidation**

The benzene ring occurs in all living systems, for example in several of the amino acids, and it is not surprising that metabolic mechanisms are available for the synthesis and degradation of aromatic compounds. Degradation has been recently summarized by Knox (23). One of the common routes is shown in Figure 4. Benzoic acid is illustrated as an example of a likely product formed by oxidation of an alkylbenzene, but the same sequence has been found for benzene itself, or phenol, or salicylic acid, or other derivatives. In each case, catechol is formed by an enzyme catalyzed oxidation with molecular oxygen

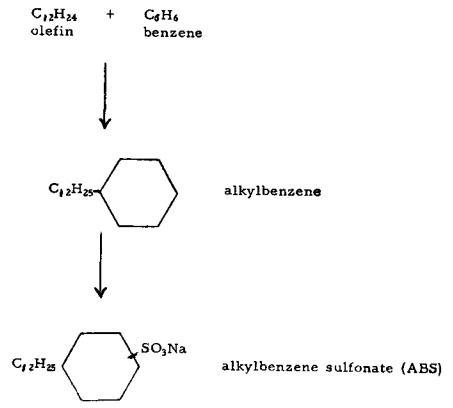



FIG. 5. Preparation of ABS.

and the ring is then split between the two hydroxyl groups to give a dicarboxylic acid. By three successive molecular rearrangements, this is converted into $\beta$-keto adipic acid which can then be split by the same means used in the $\beta$-oxidation process, giving acetate and succinate groups, both of which are components involved in the cell metabolic equilibria.

## Surfactant Biodegradation

### 1. Alkylbenzene Sulfonates

The foregoing discussion shows that metabolic processes are available to bacteria whereby they should be able to degrade surfactants. We shall now consider the biodegradation properties of alkylbenzene sulfonates, at present the most important class of surfactants, and see how well they fit into this framework.

a) *Chemical Nature.* The chemistry of ABS is summarized in Figure 5. The main commercial route involves alkylation of benzene with an olefin to give the alkylbenzene, followed by conversion to the sulfonate with sulfuric acid or oleum. A $C_{12}$ alkyl group is shown, somewhere near the middle of the useful detergent range, but it must be remembered that "ABS" is not a single chemical entity but rather is a large family. Calculations by Henze and Blair (26) show that as the number of carbons in the alkyl group of the alkylbenzene is increased, the number of possible structural isomers (not even counting the stereoisomers) increases enormously faster:

| Alkyl Carbons | Isomers |
|---|---|
| 10 | 507 |
| 11 | 1238 |
| 12 | 3057 |
| 13 | 7639 |
| 14 | 19241 |
| 15 | 48865 |

Thus, over 80,000 isomeric alkylbenzenes are possible in the range from $C_{10}$ to $C_{15}$.

The present commercial alkylbenzene is derived from tetrapropylene, a complex mixture of olefins averaging about $C_{12}H_{24}$. The alkylbenzene contains at least seventy-five or one hundred major components detectable by gas chromatography and probably several hundred minor components, and it is not too surprising that some of these components are more resistant to bacterial attack than others.

On the other hand, the alkylbenzene of the future will be derived from olefins which are predominantly straight chain. Figure 6 shows a typical

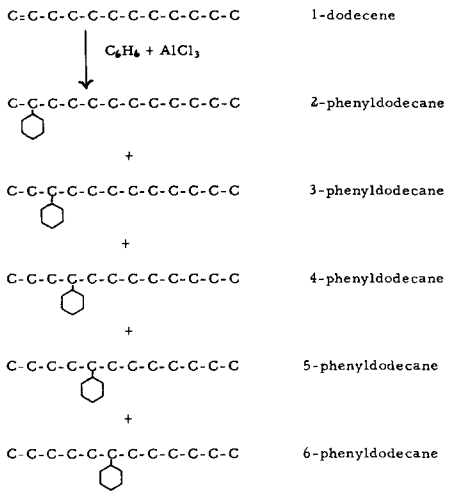



FIG. 6. Preparation of straight chain alkylbenzene.

representative of this class, $\alpha$-dodecene, and the reaction mixture obtained in the alkylation. A rearrangement occurs which gives a mixture of five isomers with the benzene attached anywhere along the chain except at the two end carbons.

b) *Biodegradation Responses.* Figure 1 shows the results of a river water test on these materials. The middle curve, tetrapropylene ABS, held constant for about three weeks near the initial value of 7 ppm, then dropped to around 2 ppm where it leveled off. The curve thus shows that some of the components are degraded by the bacteria in the river water, while others are more resistant. However, even the more resistant components of tetrapropylene ABS are degradable if given enough exposure to microorganisms, according to recent reports (18,27). This may even take place in river water. One can often find samples of river water which, because of more active bacteria or perhaps because of some other accident of environment, will do a much better job on tetrapropylene ABS than is shown in Figure 1—will degrade it both faster and further.

The straight chain ABS shown in Figure 1 held constant for about one week before it started to disappear, and it took a total of three weeks before it was all gone. Here again, with an active sample of river water the disappearance is much more

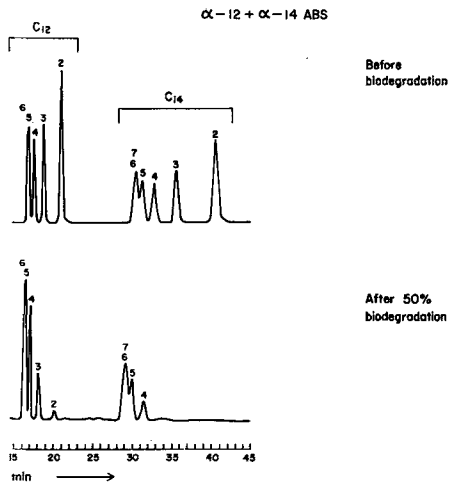



FIG. 7. River water degradation of $\alpha$-dodecene + tetradecene ABS. (Desulfonation, gas chromatography) (Initial concentration 5 ppm).

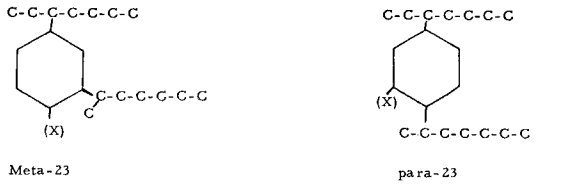



FIG. 8. Diheptylbenzene isomer nomenclature. (X) indicates most probable location of sulfonate group.

rapid, and, more often than not, this material will be gone in six or seven days—sometimes as little as four days. In a concentrated bacterial system such as activated sludge, it is degraded in a few hours.

At the other extreme is the ABS isomer shown in the top curve of Figure 1. This was synthesized as a model of a biologically resistant ABS by virtue of its quaternary carbon atom. The curve reflects the difficulty the microorganisms presumably experienced in forming a double bond at a carbon atom already joined to four other carbons, thus having no hydrogens available for dehydrogenation. But as will be shown below, this product also is degraded when it is exposed to a more active sample of river water.

Thus some varieties of ABS degrade much more rapidly than others. The difference in rate stems from size and shape of the side chain. In general, we can say that the degradation is easier the straighter the chain, the longer the chain, and the greater the distance between the sulfonate group and the end of the chain. This suggests that the sulfonate group of the surfactant molecule may become fixed on the oxidative enzyme at a location a certain distance away from the enzyme site at which oxidation of the side chain is initiated. The greater the distance betwen the sulfonate group and the end of the chain, the easier this distance on the enzyme can be spanned and the easier the degradation should be if other things are equal (14,25).

c) *Phenyl Position.* Figure 7 shows typical results obtained using the gas chromatographic technique in conjunction with river water biodegradation. The upper chromatogram gives the composition of a mixture of straight chain $C_{12}$ and $C_{14}$ ABS at time zero, immediately after dissolving in the river water. The numbers identifying the individual peaks show which carbon along the chain is attached to the phenyl group. The area under each peak is proportional to the amount of that component present in the mixture.

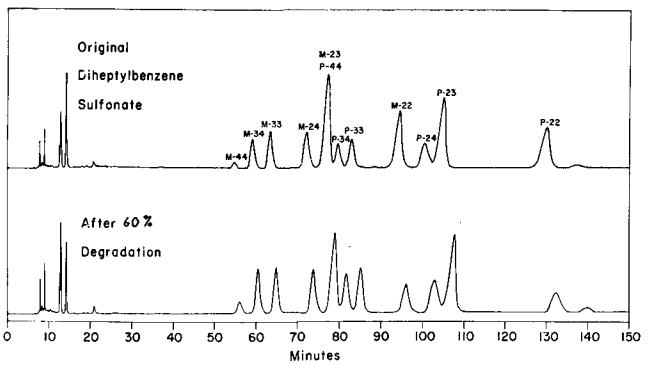



FIG. 9. Activated sludge degradation of α-heptene DABS. (Desulfonation, gas chromatography) (Initial concentration 25 ppm).

The lower chromatogram shows this river water solution fifteen days later, at which time the methylene blue analysis had dropped from the initial 5 ppm to 2.5 ppm. The 2- and 3-phenyl isomers have obviously disappeared more rapidly than those with the phenyl group nearer the center of the chain. Quantitative comparison based on peak areas shows a progressive decrease in speed for each successive isomer from the 2-phenyl inward. Straight chain ABS of all chain lengths from $C_{10}$ through $C_{15}$ show similar results (14). Likewise for even chain lengths from $C_6$ through $C_{12}$ (16); odd chain lengths have not been examined in this range, but would unquestionably give similar results.

The twelve component mixture of straight chain diheptylbenzene sulfonates illustrates the effect of phenyl position very well (25). The mixture contains the six meta isomers and six para isomers, typical examples shown in Figure 8. There is the possibility of six orthos also, but actually the alkylation reaction gives only the metas and paras as indicated in the chromatogram at the top of Figure 9. When this mixture is fed to an activated sludge unit at 25 parts per million, along with ordinary food, about 60% disappears in 24 hr. The bottom chromatogram shows the composition of the remaining 40%. From the areas of the peaks is calculated the amount of each of the twelve isomers which has degraded and the percent remaining. In Figure 10 these are plotted against the structure of the isomers, and the regularity found is in good agreement with the results on the monoalkyl derivatives discussed previously.

The dotted line at 40% shows the average of the whole mixture remaining. The bottom curve shows the three meta isomers in which one of the chains is attached at the 2-position, the other at the 2-, 3-, or 4- as indicated by the scale at the bottom. The meta-22 isomer, lower left, shows only 18% remaining—82% has been degraded in the 24 hr. There is 32% of the meta-23 remaining and 46% of the meta-24. Thus the degradation is slower as the linkage to the second heptyl group is brought nearer to the center of the chain—in other words as the sulfonate is brought closer to the end of the chain.

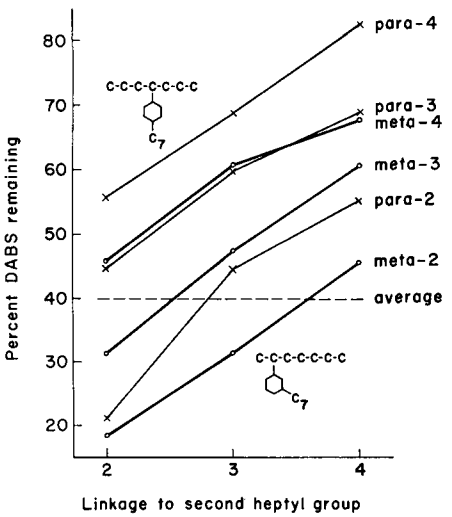



FIG. 10. Biodegradation rates of diheptylbenzene sulfonate isomers. (Amount of each isomer remaining in 24 hr activated sludge effluent expressed as percent of the amount in the feed solution).

Next above is the corresponding para family, somewhat slower, and so on—the meta-3's, the para-3's, and meta-4's, and finally the para-4's. The most resistant isomer is the para-44 at the upper right, with about 85% left after the 24 hr exposure. Each family shows the same result from bringing the phenyl group toward the center of the chain.

d) *Chain Length.* The chromatograms in Figure 7 also give information on chain length effects. In the 50% degraded mixture, each individual $C_{14}$ isomer has disappeared to a greater extent than its $C_{12}$ homolog—the 2-14 and 3-14 have already disappeared, while some of the 2- and 3- twelves remain. The sum total of the $C_{14}$ remaining is only 40% of the original amount present, compared to 60% for the $C_{12}$. In other words, the $C_{14}$ is degrading faster than the $C_{12}$. With a $C_{10\text{-}15}$ mixture the same effect is observed—the longer the chain, the greater the distance from the sulfonate group to the end of the chain, the speedier the degradation (14). Similar results have been reported in the $C_{6\text{-}12}$ range (16).

Comparison of degradation rates of the straight chain homologs has also been made by determination of their methylene blue disappearance curves when dissolved separately in river water. Progressive increase in speed was observed for each carbon number for $C_6$ through $C_{12}$. Beyond $C_{12}$, however, acclimation and inhibitory effects characteristic of the longer straight chain ABS preclude comparison of rates in unacclimated river water from one solution to another (14).

The results of Ryckman and Sawyer (13) show somewhat the same general correlation with chain length. They used oxygen uptake (BOD and Warburg) and sulfate ion formation as measures of biodegradation and found that the secondary butyl and amyl alkylbenzene sulfonates were significantly slower than the octyl, decyl, and tetradecyl. However, they found little difference between the primary ABS homologs from $C_1$ to $C_{12}$.

e) *Sulfonate Position.* For straight chain primary ABS (in which the phenyl group is attached to the end of the chain) the para sulfonate isomer disappears more rapidly in the river water test than does the ortho sulfonate (11,14). A similar effect has been noted for the straight chain secondary ABS (11). This suggests that the distance between the sulfonate group and the end of the chain may be the important factor governing the degradation rate rather than the position of the phenyl along the chain.

The rates of the diheptyl isomers shown in Figure 10 substantiate this concept. Each para dialkyl isomer is a little slower than the corresponding meta isomer. The distance from the sulfonate group to the most remote chain end is greater in a meta diheptyl isomer than in the corresponding para, as can be seen by reference to Figure 8.

f) *Methyl Branching.* Introduction of a single methyl group into the side chain has only a very slight effect on the biodegradation rate, as shown by a comparison of the three pure compounds shown in Figure 11, each having an effective chain length of eleven carbons (14). In four days time the methylene blue value of the mixture had dropped to 30% of its initial 7.4 ppm. About 23% of the original 1-phenylundecane sulfonate (compound 1) remained, compared to about 36% each for the other two. Thus the methyl group in the chain does retard the degradation rate very slightly, but it makes little difference whether it is at the near end of the chain or at the far end.

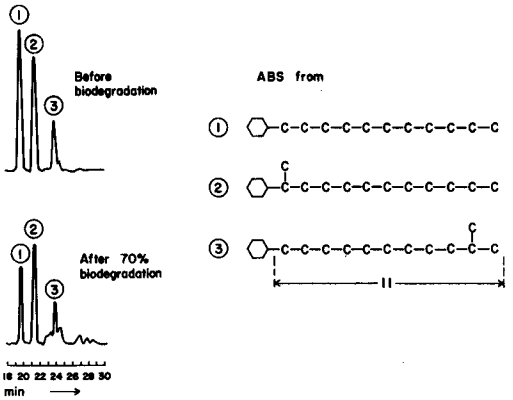



FIG. 11. River water degradation of $C_{11}$ effective chain length ABS (Desulfonation, gas chromatography) (Initial concentration 7.4 ppm).

g) *Quaternary Carbons.* As indicated earlier in Figure 1, a quaternary carbon at the far end of the chain does interfere seriously with the biodegradation. However, under suitable conditions, this compound does disappear after four or five weeks in the river water as determined by methylene blue response or by gas chromatography, and its next higher homolog (1-phenyl-9, 9-dimethyldecane sodium sulfonate) is somewhat faster (14). Obviously the degradation must involve some metabolic route in addition to those discussed previously, since the double bond characteristic of the $\beta$-oxidation process cannot be formed at a quaternary carbon atom. The initial attack might be at some intermediate methylene group along the straight chain; this seems reasonable since cyclohexane, made up entirely of methylene groups, is readily attacked by bacteria (21). Alternatively, the degradation might involve initial oxidation of one of the terminal methyl groups to carboxyl, subsequently proceeding along a route such as discussed by Mohanrao and McKinney (28) for quaternary carboxylic acids. In either case the more rapid attack observed for the longer homolog fits in with the picture developed above for the open ended chains—that the sulfonate group of the molecule may become attached to the enzyme at a point some distance removed from the enzyme site at which oxidation is initiated.

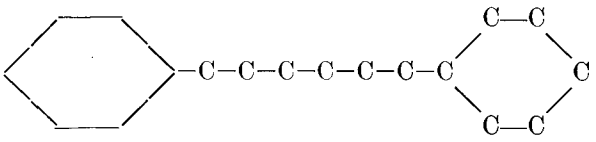
Several other terminal quaternary ABS compounds of known structure have also been reported as more resistant to biodegradation than the straight chain derivatives (8,11,29).

However, the mere presence of a quaternary carbon in the ABS does not necessarily mean slow disappearance in biodegradation; the presence of an open end chain of sufficient length in the molecule, will provide an easy point of attack. For example, the sulfonate of 2-phenyl-2-methylundecane is readily degraded (8,29). A terminal quaternary derivative, the sulfonate of 4-phenyl-2,2,3-trimethylnonane, was found to degrade at a rate not much slower than 6-phenyldodecane sulfonate (14). This difference in rate would be expected on statistical grounds since the latter compound has two open

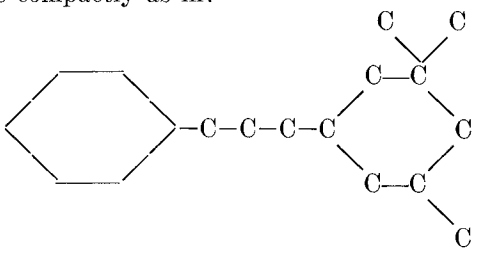
chains available for ready attack compared to only one in the quaternary derivative.

h) *Highly Branched Chains.* Aside from the above quaternary derivatives, there is little information in the literature on highly branched ABS of known structure. There can be little doubt, however, but that for a given carbon number the degradation will be slower with increased branching because of the shorter effective chain length. Terminal quaternary branching will of course introduce further resistance, as indicated in the preceding section. Possibly, even in the absence of the quaternary group, the bunching of several branches on adjacent carbons of the chain might result in slower degradation than would be predicted simply on the basis of the effective chain length. On the other hand, it seems equally possible that the bunching of several branches would have no such added effect, no more than the introduction of a single methyl group into the $C_{11}$ side chain noted in a preceding section.

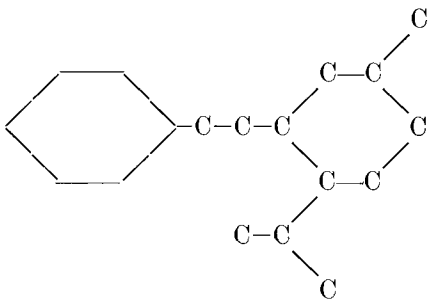
i) *Cyclic Groups.* Data on alkylbenzenes having cyclic structures in the side chain again bring out the importance of effective chain length. The sulfonate of 1-phenyl-6-cyclohexylhexane



is reported to degrade in river water quite satisfactorily, although slower than straight chain ABS (11). If the twelve alkyl carbons are arranged more compactly as in:



or



the degradation as tested in activated sludge appears to be much more difficult (8).

Of course the cyclohexyl group is not intrinsically resistant to bacterial attack; the parent compound, cyclohexane, is readily degraded (21).

j) *Intermediate Degradation Products.* The data presented so far are mainly concerned with the first step in the biodegradation reaction—the initial attack on the ABS molecule which makes it disappear so far as detection by foaming, surfactancy or methylene blue analysis are concerned. Tracing the further course of the reaction is hampered because of analytical difficulties.

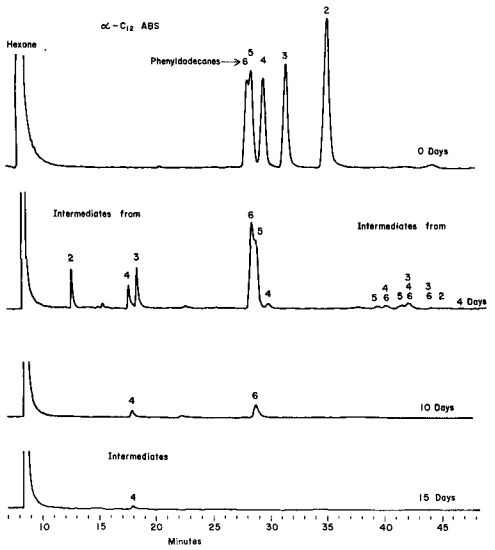


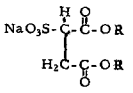

FIG. 12. River water degradation of α-dodecene ABS. (Desulfonation, gas chromatography) (Initial concentration 5 ppm).

Ryckman and Sawyer (13) concluded that straight chain ABS, both primary (attachment of the phenyl at the end of the chain) and secondary (non-terminal), were completely degraded by activated sludge on the basis of a) quantitative liberation of the sulfonate group as free sulfate ion, b) oxygen pickup approaching the theoretical in BOD and Warburg tests, and c) a final infrared spectrum substantially identical with that of the blank control which was fed only nutrient, and showing none of the initial characteristic absorption bands of the ABS. In contrast, "tertiary" ABS, e.g. tetrapropylene ABS, showed none of these features in parallel experiments.

Ryckman (30) has proposed a mechanism for the biodegradation of straight chain secondary ABS involving oxidative attack at the end of the chain, β-oxidation down the chain and degradation of the ring. There was some evidence for temporary resistance at an intermediate stage when the carboxyl group is at the first or second carbon next to the ring.

More recently, the technique of desulfonation has been applied to convert the nonvolatile intermediates to products more easily detected and identified. The gas chromatograms in Figure 12 show successive stages in the river water degradation of straight chain secondary $C_{12}$ ABS. As the initial alkylbenzene peaks disappeared, new peaks arising from intermediate degradation products showed up; these also subsequently disappeared as the degradation proceeded. (The large hexane peaks were from the solvent used.) The three prominent transient peaks were shown to arise from the β-oxidation products in which the carboxyl group is at the second or third carbon from the ring (24). Presence of earlier β-oxidation products has been demonstrated in the degradation of 2-phenyldodecane sulfonate in a more concentrated bacterial culture—small amounts of phenyldodecanoic and pheyldecanoic acids, larger amounts of the $C_8$ and $C_6$ acids (16).

Thus there seems little doebt but that the ordi-



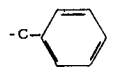
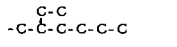
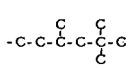
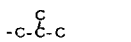
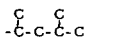
| | R Group | Degradation Time, days |
|---|---|---|
| A |  | 5 |
| B |  | 6 |
| C |  | 11 |
| D |  | 11+ |
| E |  | 24+ |
| F |  | * |
| G |  | * |

FIG. 13. River water biodegradation of dialkyl sulfosuccinates. * indicates no degradation in 28 days.

nary metabolic routes of the bacterial are used in the biodegradation of these surfactants.

**2. Other Surfactants**

a) *General.* Although the biodegradability of many other surfactant types has been studied, the data are quite fragmentary and include little of the detailed comparison of known isomers and homologs which has clarified the alkylbenzene sulfonate picture. The pioneer work of Hammerton (2,31) and of Sawyer and co-workers (3,13,32,33) still provides most of the information available today on biodegradation of non-ABS surfactants. At that time, the basic principle had already become evident: straight chain hydrophobes are more readily degradable than branch chains. There is little reason to doubt that the degradation proceeds along the same biochemical pathways described for ABS.

b) *Alkyl Sulfates.* Most of the alkyl sulfates commercially used are straight chain derivatives and readily degradable (2,3,11,13,31,32,33). However, Hammerton (2,31) early pointed out that this was not necessarily a characteristic of alkyl sulfates in general, and gave an example of a branched alkyl sulfate which was quite resistant. This was further confirmed by him (31) and by Huyser (11) for several other branched alkyl sulfates. Thus it seems that, contrary to what might be expected, the sulfate group is not readily hydrolyzed by the bacteria under usual conditions. If hydrolysis did occur, the solution would lose its response to methylene blue whether the hydrophobe was degraded or not.

c) *Alkane Sulfonates.* Primary and secondary alkane sulfonates, straight chain, are readily degradable (2,11,31). No studies on branch chain derivatives seem to have been reported.

d) *Ester, Amide Sulfonates.* Surfactants of this type which have been reported are for the most part straight chain derivatives, and these have degraded readily. For example, Sawyer et al. report that fatty acyl taurides and isethionates show oxygen absorption approaching the theoretical amount in BOD and Warburg tests; the ready degradability was interpreted as initial hydrolysis to the fatty acid which was then rapidly oxidized (3,13,32,33).

Hammerton shows data for oleyl p-anisidide sulfonate in river water (31). The methylene blue value dropped to zero in two days, whereas the oxygen pickup had barely started by that time. He interpreted this as splitting of the molecule at a very early stage in the degradation.

In contrast, Hammerton's study of seven dialkyl sulfosuccinate esters summarized in Figure 13 shows a marked influence of alkyl group structure on the speed of degradation (31). He points out that "since two of the compounds show great stability and the others varying rates of disappearance, it can be concluded that the ester linkage is not a direct point of bacterial attack." Study of Figure 13 provides two surprises. Hydrophobe D, with a terminal quaternary, degrades at a rate comparable to the open end compound C; hydrophobe F is much more resistant than the shorter hydrophobe E. If the degradation rates of D and F were interchanged, the results would be in good agreement with the picture that has been developed for the alkylbenzenes.

As the results stand, however, Figure 13 shows two secondary esters resistant, five primary esters degradable, with the benzyl ester A the most rapid of all. This suggests that possibly the ester group may be involved in some manner after all.

e) *Nonionics.* The work of Sawyer, Bogan, and Simpson (3,32,33) established that nonionic surfactants were no exception to the generalities drawn for the other classes. Using the BOD and Warburg techniques, they found that straight chain polyglycol esters and amides were readily degradable, while the branch chain alkyl phenol derivatives were more resistant. They also found that for a given hydrophobe, lengthening the polyglycol ether hydrophilic group resulted in poorer degradation. Similar results were obtained with the polyglycol ethers themselves (33). They concluded that the higher polyglycol groups interfered with the diffusion of the molecule through the cell membrane, slowing down the degradation.

Huyser (11) investigated straight chain polyglycol ethers and branch chain alkylphenol derivatives with similar results. He reported that resistance increases with the number of ethylene oxide units and with the degree of branching.

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# Effects of Detergents on Surface and Ground Water Problems

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THE PURPOSE of this paper is to provide a brief picture of how synthetic detergents affect surface water and ground water on the basis of what is known today and what might be expected tomorrow. This subject is so complex that it is not easily or completely covered in a single paper. For those that are concerned with water quality at national, state, municipal or local levels, the Soap and Detergent Association has published a booklet, "Synthetic Detergents in Perspective" (1) that is very helpful. In addition, a report, "Components of Synthetic Detergents in Water and Sewage," prepared by ORSANCO detergent subcommittee and approved by the ORSANCO commission, is published in the March 1963 Journal of the AWWA (2). Because of the availability of the above, the effect of detergents as they are known today will be only briefly summarized here.

## Present Status

The most widely used surface active agent or surfactant in household detergents today is propylene tetramer alkyl benzene sulfonate, commonly known as ABS. Since World War II the usage of ABS in the U.S. has grown to approximately 560 million lb per year. Concurrent with increased use of ABS detergents, we have had a remarkable growth in automatic washers and concomitant frequency of washing. Therefore, more water and more surfactant are now being used than was ever used in the days of laundry soap. What has been the effect of this material on the quality of surface water and ground water?

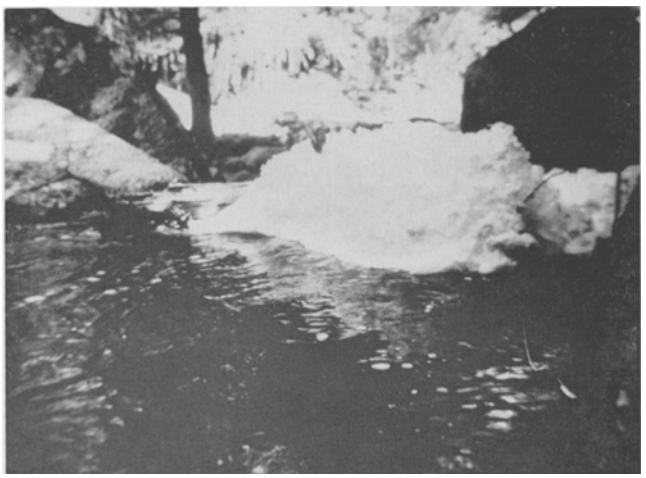

FIG. 1. Natural foam in the pristine waters below Vernal Falls in Yosemite National Park in spring of 1962.

By *surface water* we refer to streams and rivers that receive the discharge of sewage treatment plants. The first evidence of ABS is the appearance of froth or foam in waste treatment plants in the aeration stage and/or in the effluent. Prior to widespread use of ABS, sewage treatment plants often experienced frothing and foaming. This was due to other organic and protein compounds which exhibit a lowering of the surface tension much like any detergent. Thus ABS is not the only foamer in the waste, but can be a significant contributor.

Contrary to the opinion held by some, ABS is attacked by bacteria, as evidenced by the fact that approximately 60% of the material is degraded by primary and secondary treatment processes. Nevertheless, this degradation is slow to occur and consequently, measurable amounts, that is, parts per million, are present in treatment plant effluents and will enter surface waters. Appearance of foam on some surface waters that receive untreated sewage or the effluent of sewage treatment plants is usually ascribed to detergents, though other foamers may be present.

Monitoring of the ABS content of the Mississippi River at New Orleans and the Ohio River at Cincinnati, however, has not shown any build up of ABS over a two-year period, indicating that perhaps insofar as these rivers are concerned the concentration of ABS has reached an average level of about 0.05 ppm in the Mississippi and 0.16 ppm in the Ohio and is not increasing.

By *ground water* we mean deposits of water in sand and/or gravel strata at varying depths beneath the surface of the ground. In certain areas of the country, contamination of ground water by ABS and other pollutants has occurred to the extent that in a few cases the water from individual shallow wells will tend to froth when drawn from the household tap.