Effect of Substituents in the Aromatic Nucleus on the Biodegradation Behavior of Alkylaryl Sulfonates

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Abstract

Taking the results of methylene blue analysis as a yardstick for biodegradability, substituents in the benzene ring of linear alkylaryl sulfonates (CH_3, C_2H_5, OH) greatly deteriorate the aerobic biodegradation characteristics of these products: adaptation time, amount of hard residue, and, to a lesser extent, rate of biodegradation. Replacement of one long alkyl chain by two short ones of the same total length also retards biodegradation. When the benzene ring is replaced by a thiophene ring, adaptation is improved.

Introduction

THE RELATION BETWEEN the aerobic biodegradation of an anionic detergent and its structure has in recent years been studied intensively (1–5). The general conclusion is that biodegradation is slower as the hydrophobic part of the molecule is more branched and the hydrophilic group shifts from the end to the middle of the molecule. It is also affected by molecular weight.

Experiments with alkylbenzene sulfonates reported in the literature were restricted to variations in structure and size of the alkyl chain and position of the hydrophilic group. It was found that not only the aromatic nucleus itself has a retarding effect but also that branching of the alkyl chain affects biodegradation adversely.

Whether or not the influence of detergent structure on biodegradation can be established clearly depends on the test method which is employed. The influence of small structural differences will go undetected under severe test conditions but will become apparent when conditions are milder.

A mild test was used to study the influence on biodegradation of a) substituents in the benzene nucleus of alkylbenzene sulfonates and b) replacement of the benzene ring by a thiophene ring. The results are presented in this paper.

Test Methods

The literature describes a wide variety of methods in the study of the aerobic biodegradation of detergents in the laboratory. Three categories can be distinguished, viz., dynamic (6,7), semidynamic (8), and static procedures (9–12).

An example of the dynamic method is the legal German test. The detergent is fed continuously to the biodegradation system. After an arbitrary time of biodegradation the amount of residual detergent is determined. This operation is repeated several times, and the average percentage of residual detergent is regarded as a measure of biodegradability.

In a semidynamic test, detergent feeding is intermittent, but for the rest it resembles the dynamic method.

The static test method differs from the continuous techniques in that the detergent is added in one pass, and the degradation is followed as a function of time.

These procedures all have their merits and demerits. The continuous and semicontinuous techniques more or less simulate an activated-sludge sewage plant whereas a static method can be taken to represent the behavior of a detergent in public waters.

The dynamic method, which only measures the amount of residual detergent, gives no information on the rate of biodegradation and the biological behavior of the residual detergent. In consequence, it might not distinguish between two surfactant systems of which the one biodegrades at a medium rate and the other consists of a mixture of a soft material and a bioresistant detergent.

On the other hand, the static method offers the advantage that, in one test, data are obtained on adaptation time, biodegradation rate, and the amount of detergent degrading slowly or not at all (the hard residue). This is why a static die-away test was preferred in the investigation.

Analytical Methods

To evaluate the biodegradability of anionic detergents, various analytical techniques can in principle be used, viz., colorimetric analysis, Warburg manometry, BOD determination, GLC analysis after desulfonation, the radioactive-tracer technique, and surface-tension measurements. Although these methods may give valuable data, each has its distinct

TABLE I

Biodegradation of Various Types of Anionic Surfactants According to the River Die-away Test

Product	Percentage of active matter remaining after . . . . days												
	1	2	3	6	7	8	9	13	14	16	17	20	21
Dodecylbenzene sulfonate	95	96	94	76	31	0	....	....	....	....	....	....	....
Dodecylethylbenzene sulfonate	105	99	99	102	100	98	98	68	53	49	51	49	47
Dodecyl-p-xylene sulfonate	93	96	....	95	91	87	80	12	....	9	8	8	8
Dodecyl-m-xylene sulfonate	100	101	100	92	99	102	100	101	....	96	100	96	84
Dodecyl-o-xylene sulfonate	101	100	98	99	97	93	95	90	....	46	39	39	39
Dihexylbenzene sulfonate	101	98	99	100	98	91	95	93	89	85	82	81	78
Dodecylphenol sulfonate	106	106	107	108	102	102	96	103	....	66	42	16	14
Dodecylthiophene sulfonate	98	92	6	3	4	2	2	....	....	....	....	....	....
References													
Lauryl alcohol sulfate	0	....	....	....	....	....	....	....	....	....	....	....	....
Linear alkylbenzene sulfonate (ex-cracked wax olefins for ex-n-paraffins)	95	94	98	91	85	45	25	4	6	2	1	0	....
Branched alkylbenzene sulfonate (ex-propylene tetramer)	101	99	92	95	87	92	93	94	....	82	82	....	76

limitations, which often make the results difficult to interpret.

The method most utilized is the colorimetric method according to Longwell-Maniece (13,14). This technique is based on the capability of a cationic dyestuff to form a complex with the anionic surfactant. The dye is, in general, methylene blue. The complex is extracted with chloroform, and the color intensity is measured. The amount of nondegraded surfactant is reported. However partially bio-oxidized molecules (intermediate degradation products) do not show up (15). Thus no answer is obtained to the question of how far the bio-oxidation has progressed. For lack of a better method the colorimetric technique has been adopted internationally and in some countries even legally, which is the reason this procedure was utilized.

Experimental

The static test employed to compare the rate of biodegradation of anionic detergents with different structures was a river die-away test, in which the bacteria concentration is low. Degradation proceeds slowly, which ensures proper differentiation.

Test Procedure

Twenty liters of river-water (IJ-water) were sampled and filtered through cotton wool to remove solid particles. To 990 ml of filtered water 10 ml of a 1000-ppm detergent solution were added so the resultant mixture had an initial detergent concentration of 10 ppm. The solution was stored in the dark at ambient temperature (approximately 20C) in open bottles to allow oxygen uptake. At suitable intervals samples were taken, and the content of nondegraded detergent was determined according to the methylene blue method (12,13).

Products Tested

Biodegradation studies, known from the literature, refer generally to the effect of substituents in the alkyl moiety of the alkylbenzene sulfonate molecule. This study however was to determine whether the presence of extra substituents (CH_3, C_2H_5, OH) in the benzene ring of an alkylbenzene sulfonate has any influence on its biological behavior. Also investigated was the effect of replacement of one long alkyl chain by two short ones of the same total length and that of replacement of the benzene ring by a thiophene ring.

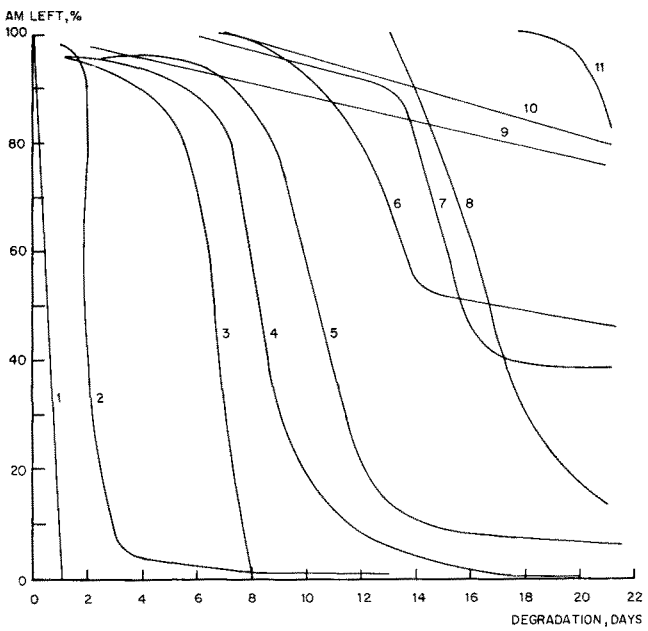

FIG. 1. Biodegradation of various types of anionic detergents according to the y-water storage test: 1. lauryl alcohol sulfate, 2. dodecylthiophene sulfonate, 3. dodecylbenzene sulfonate (ex-n-dodecene), 4. linear alkylbenzene sulfonate (ex-cracked wax olefins or ex-n-paraffins), 5. dodecyl-p-xylene sulfonate, 6. dodecylethylbenzene sulfonate, 7. dodecyl-o-xylene sulfonate, 8. dodecylphenol sulfonate, 9. branched alkylbenzene sulfonate (ex propylene tetramer), 10. dihexylbenzene sulfonate (ex-n-hexene), 11. dodecyl-m-xylene sulfonate.

Table I lists the various products which were examined. All substances, except for dihexylbenzene sulfonate, contained a C_{12} alkyl chain that was introduced into the benzene ring by alkylation, using concentrated H_2SO_4 as the catalyst (for the thiophene derivative, BF_3 etherate was the catalyst) and n-dodecene-1 as the olefinic base material. Dihexylbenzene was alkylated with n-hexene and $AlCl_3$ as the catalyst.

During alkylation, isomerization of the olefinic double bond takes place so the resultant product consists of a mixture of position isomers. The alkyl chain can be introduced at any position (*ortho, para,* or *meta*) with regard to the substituent already present. It is known that, under mild conditions, the entering group tends to become oriented in the *ortho* or *para* positions whereas under severe alkylation conditions *meta*-substitution predominates. In this study the ratio of *ortho, meta,* and *para*-substitution was not determined, but it may be assumed that all types were present. The alkylate was sulfonated with oleum that contained 20% SO_3. If the position is free, mainly *para*-substitution will occur. Obviously the ultimate product is a complicated mixture of position isomers.

Results

Experimental results (Figure 1 and Table I) were evaluated on three points: adaptation time,[1] hard residue, and rate of degradation. The products showed large differences in adaptation time and hard residue; with a few exceptions the differences in biodegradation rate were small.

Adaptation time varied from less than one day for lauryl alcohol sulfate to 20 days for dodecyl-m-xylene sulfonate. Intermediate values, ranging from 10 to 14 days, were observed for dodecylethylbenzene sulfonate, dodecyl-o-xylene sulfonate, dodecylphenol sulfonate, and dihexylbenzene sulfonate. Lower values, between two and ten days, were found for dodecylbenzene sulfonate, linear alkylbenzene sulfonate, dodecyl-p-xylene sulfonate, and branched alkylbenzene sulfonate. Dodecylthiophene sulfonate had an adaptation time of about two days.

The amounts of hard residue found were between zero and 80%. The best products in this respect were lauryl alcohol sulfate, dodecylbenzene sulfonate, and linear alkylbenzene sulfonate (hard residue zero), closely followed by dodecylthiophene sulfonate. Somewhat harder (approximately 10% residue) were dodecyl-p-xylene sulfonate and dodecylphenol sulfonate. A 40% level was found for dodecyl-o-xylene sulfonate, dodecylethylbenzene sulfonate, and heavily branched alkylbenzene sulfonate; dihexylbenzene sulfonate and dodecyl-m-xylene sulfonate showed up even worse.

The rate of biodegradation of the branched alkylbenzene sulfonate and dihexylbenzene sulfonate was low; the highest rate was found for lauryl alcohol sulfate and dodecylthiophene sulfonate. In all other

[1] The adaptation period was assumed to be terminated when 10% of the detergent had degraded.

cases degradation was somewhat slower than in the latter two products but much faster than in the two former ones.

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