Biodegradation of Synthetic Detergents Evaluation by Community Trials: I. Linear Alkylbenzene Sulphonates

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ABSTRACT

The biodegradability of a number of linear alkylbenzene sulfonates (LAS) has been evaluated by field trials with a trickling filter sewage plant serving a small community. All the LAS material examined showed a satisfactory order of biodegradability. In all the LAS materials examined, aeration of the sewage effluent resulted in further biodegradation to a degree corresponding to 96% to 99% degradation of the LAS present in the settled sewage. The results of laboratory scale biodegradation tests are largely in agreement with those obtained in the field trials. However, with tests of the simple open bottle type, such as the test of the U.K. Standing Technical Committee on Synthetic Detergents, misleading indications of low biodegradability may sometimes be obtained on products of higher molecular weight. Such products do not appear to acclimatize sufficiently rapidly to bacteria under the conditions of the open-bottle test. Under practical sewage treatment conditions, or with tests which simulate these, a high order of biodegradation is obtained. There were only minor differences in biodegradability between an LAS derived from paraffins and those derived from cracked wax olefins.

INTRODUCTION

A variety of laboratory scale tests have been developed to assess the biodegradability of detergents. These range from the simple open-bottle die-way test to the continuous activated sludge test now employed in Germany by law. The object of the present work was to relate the results of laboratory scale evaluation to the results obtained under practical conditions of sewage treatment.

Part I of this paper deals with the biodegradability of linear alkylbenzene sulfonates (LAS). Part II will deal with primary alcohol and branched chain alkyl phenol ethoxylates, and Part III, with sulfates of natural and synthetic alcohols.

The LAS we wished to evaluate were the sodium sulfonates of the Shell "Dobane" series of alkylbenzenes (Throughout this paper the "Dobane" designation is intended to refer to the sodium sulfonate of the alkylbenzene.), which are based on cracked wax olefins. For comparative purposes, an LAS based on an alkylbenzene derived from paraffins was also included in the test series. The paraffin-derived LAS has been designated "PD".

The results obtained in various laboratory tests and in the pilot plant activated sludge test of the Water Pollution Research Laboratory (1) (WPRL) are shown in Table I.

All the LAS products showed a high order of biodegradability in most of the tests. However, in the simple open-bottle aeration test of the U.K. Standing Technical Committee (2) Dobane 055 showed variable performance. The results obtained when this test was applied by 10 laboratories of members of the Standing Technical Committee are shown in Table II. Low values for biodegradability were obtained in 7 tests with high values (>90%) in the remaining 12 tests. This test of the U.K. Standing Technical Committee gave very reproducible results in collaborative analysis on Dobane JN-X, a value of 88 ± 2% being obtained.

It was of interest, therefore, to discover if material, such as Dobane 055, which showed a variable performance in a simple bottle test, did in fact degrade satisfactorily under practical sewage treatment conditions.

EXPERIMENTAL PROCEDURES

Characterization of Alkylates Used

The parent alkylates, from which the sulfonates were prepared, were characterized, with respect to carbon number and isomer distribution, by the method of Carnes (4). The results obtained are shown in Table III. It is seen that Dobane 055 is distinguished from the other alkylates by possessing a higher average molecular weight, while Dobane 83 is distinguished by a lower average molecular weight.

Precise evaluation of the degree of linearity was not made. However, it may be deduced from the known quality of the olefins used in manufacture that Dobane JNQ is more linear than Dobane JNX, which again is more linear than Dobane JNB. Dobane JNB is now obsolescent.

Selected Community

We discussed our intention to carry out field trials with members of the WPRL. They suggested the use of a group of 31 houses in the village of Preston, Hertfordshire. These houses are connected to a small sewage works, of the trickling filter type, which receives no sewage other than from these houses. The WPRL had previously carried out some experimental work and had shown that this plant gave an effluent of about the same quality as that from larger

TABLE I

Biodegradation of Alkylbenzene Sulfonates by Different Methods, Per Cent Degraded

Product	German federal test	U.K. Standing Technical Committee	U.S. semi continuous activated sludge test (3)	Water Pollution Research Laboratory pilot plant	U.S. shake flask test (3)
Dobane JN-Q	96	95	98	96	91
PD	97	94	—	97	—
Dobane JN-X	93	88	95	92	85
Dobane 055	94	0 to 99[a]	95	92	88
Dobane 83	92	85	91	—	87
Dobane JN-B	90	77	88	—	71

[a]See Table II.

TABLE II

Test of the U.K. Standing Technical Committee on Dobane 055

Laboratory	1, one test	2, two tests	3, two tests	4, one test	5, two tests	6, four tests	7, three tests	8, one test	9, one test	10, two tests
time for 50%	11	12-14	7-8	11-13	17	>31	1	>17	11-17	6-10
biodegradability,						>31	20			
days		8-9	7-8		12-14	>31	9-13			6-10
						>31				
time for maximum	16	16	11	18	>17	---	15	---	17	21
biodegradability,						---	>26			
days		18	14		17	---	15			21
per cent	96.5	91.5	94.5	91	0	14	98	27.5	92	96.4
biodegradability						19	65			
		95.4	95.8		98.9	8	94			96.8
						3				

sewage works in the U.K. This information was very pertinent to our trials, because we wished to assess the degree of biodegradation under the conditions of a typical sewage plant. A photograph of the Preston sewage plant is given in Figure 1. This shows the top of the settling tanks in front of the pump house with the trickling filters on either side.

The WPRL also kindly consented to set up the sampling schedule and carry out the routine analysis of sewage and effluent quality and also active matter analysis.

The sewage works consists of two small covered settling tanks of total capacity 1,856 U.K. gallons, two 4 ft 6 in. deep trickling filters and two humus tanks. The flow to the works is by gravity, the settled sewage being pumped to revolving distributors supplying the filters. The effluent from the humus tanks is discharged into a ditch and the contents of the primary settling tanks and humus tanks are removed every four weeks by a cesspool-emptying vehicle.

Organization of Trials

It was first necessary to formulate acceptable clothes and dishwashing products from the sodium sulfonates of the various alkylates. The clothes washing powder formulation contained 18% w active material (LAS) together with typical builders, foam promoter and optical bleach. The dishwashing liquids contained 12% w LAS, together with 9% w of a nonionic component added to obtain acceptable dishwashing performance.

Seven weeks before the beginning of the distribution of the selected formulations arrangements were made to collect sewage samples for analysis so that the efficiency of normal performance could be assessed.

Four automatic samplers were installed so that the settled sewage and final effluent could each be sampled every 2 hr, with and without the addition of mercuric chloride at a concentration of 50 ppm as preservative. Samples were taken for analysis on two consecutive 24 hr periods each week.

A tipping trough was placed to measure the flow of settled sewage applied to the trickling filters.

At the end of the seven-week initial survey the 31 housewives were approached and told about the impending trial. They were asked about the products which they had been using and they were persuaded to use only the materials supplied by us for the duration of the trial. They all agreed to cooperate in this.

After the preliminary survey the products containing the LAS under investigation were delivered to each house every week. The housewives were given as much detergent powder and washing up liquid as they requested so that there was no need for them to buy other detergents. At the end of each period of the trial, the housewives were asked to hand back any remaining detergent and to use only the new products (based on a different alkylate) for the next period of the trial.

Samples were taken for analysis during the trial periods in the same way as the initial survey.

Analytical Methods

The analytical methods were those generally used in sewage works to measure the "strength" of sewage and the efficiency of sewage purification.

The methods for anionic surface active material, five days biochemical oxygen demand (BOD) and 4 hr permanganate value were the classical methods given in the handbook of methods for sewage analysis (5). The analysis for anionic surface active material was performed automatically using an "Auto-analyzer".

Ammonia and oxidized nitrogen were estimated colorimetrically by "Auto-analyzer" (6)—the former using the

TABLE III

Characterization of Alkylates, Total Percentages of Component Types

Component	Totals of each carbon number								Totals of each phenyl isomer							
Sample	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	Average C	2	3	4	5	5+6	6	6+7	7
Dobane JNQ	nil	13.8	30.0	27.6	21.5	7.1	nil	11.8	22.4	18.8	18.8	15.7	9.9	7.0	6.0	1.4
PD	nil	11.3	37.7	29.9	20.8	0.3	nil	11.6	31.8	18.6	17.2	11.2	11.0	5.3	4.9	nil
Dobane JN-X	nil	13.3	29.6	27.1	23.9	6.1	nil	11.8	20.4	20.1	19.6	15.8	10.2	6.7	6.3	0.9
Dobane 055	nil	9.6	19.5	16.6	14.3	21.4	18.6	12.7	21.6	17.1	16.2	14.9	7.0	3.5	11.8	7.9[a]
Dobane 83	18.7	25.7	21.4	17.2	12.7	4.3	nil	10.9	21.8	20.0	21.1	19.3	8.3	4.8	3.8	0.9
Dobane JN-B	nil	22.6	23.7	26.5	20.5	6.7	nil	11.6	22.6	20.5	19.1	17.0	7.1	7.3	5.5	0.9

[a]Value includes some 6-phenyl and 8-phenyl isomer.

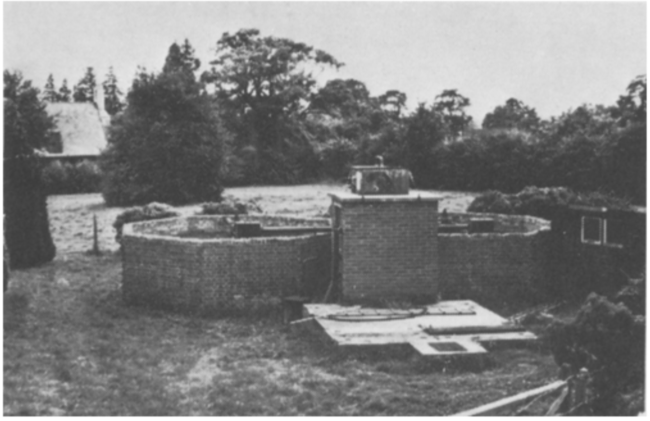

FIG. 1. Preston sewage plant.

color formed by ammonia with sodium phenate and sodium hypochlorite and the latter the color formed by nitrates with 1-napthylamine-7-sulfonic acid and sulfanilic acid. Nitrates were reduced to nitrites with hydrazine before the color reaction so that the oxidized nitrogen analysis measured the sum of nitric plus nitrous nitrogen.

Suspended solids were measured by filtering the samples through glass fiber filter paper, drying at 105 C and weighing.

BOD was measured on the samples containing no preservative but all other analyses were carried out on the samples preserved with mercuric chloride.

RESULTS AND DISCUSSION

WPRL Test Data

We wished to ascertain whether the results obtained in duplicate trials were in good agreement and whether trials carried out at different times of the year gave significantly different results due to temperature changes. With the first three samples tested, duplicate trials each of two months duration were carried out at different times of the year. A summary of the average values of the tests carried out in each period for the three products, Dobane JN-X, Dobane JN-Q and PD, is given in Table IV. The data obtained in the initial survey are also included.

Single trials were carried out on the remaining three samples, Dobane 055, Dobane JN-B and Dobane 83. The data obtained in these trials are given in Table V.

Order of Biodegradation

It is seen that all these LAS materials degrade well and consistently under practical sewage treatment conditions giving average values in the 86-95% region with low standard deviations. Duplicate trials gave similar results. There is some difference between the biodegradation values of the various Dobanes which is in line with the degree of linearity. The same order of biodegradability is shown by Dobane JN-Q, Dobane 055 and PD, this result is at variance with the observation of Renn et al. (7,8) that PD LAS showed markedly superior biodegradability to LAS based on cracked wax olefins.

Effect of Temperature

It is seen from Table IV that the value for per cent biodegradation of each LAS is slightly higher in the trial at the higher temperature. A statistical evaluation on the daily data obtained provided the linear regression curves relating temperature to per cent biodegradability shown in Figure 2. These curves show a small but distinct temperature influence on biodegradation. They also indicate the difference in biodegradability between PD and Dobane JN-Q to be of the order of 1%. The data indicates the linear correlation between biodegradation and temperature to be highly significant (99%) for Dobane JN-Q and PD but not significant (>90%) for Dobane JN-X.

Relationship to Laboratory Tests

Comparison of the results given in Table I with the values for biodegradation given in Tables IV and V shows that the degree of biodegradability indicated by most of the laboratory tests is of the same order as indicated by practical sewage treatment in a trickling filter.

With the simple open-bottle test of the U.K. Standing Technical Committee, however, the low values obtained on Dobane 055 by some laboratories (Table II) are not found in practice. The higher values found by the majority of the laboratories by the open-bottle test (ca. 95%) are confirmed by the results of practical sewage treatment.

The reason for this anomalous behavior of Dobane 055 may relate to the fact that some components of this product have alkyl chains slightly longer than the alkyl chains in the other products. Dobane 055 sulfonate has an average molecular weight of 358 in comparison with 345 for Dobane JN-Q sulfonate. The work of Ciattoni and Scardigno (9) and that of Setzkorn et al. (10), does much to explain this. These workers have shown that LAS with long alkyl chains are toxic to bacteria. Acclimatization can readily develop, however, and when acclimatization does occur the work of Swisher (11,12) would indicate that the long chain LAS would degrade faster than the short chain LAS.

In certain of the bottle tests, therefore, it would appear that acclimatization has not taken place. This may be associated with lack of nutriment in the bottle test (13). Under practical sewage treatment conditions, where an excess of nutrient would be present, acclimatization takes place readily.

This is in line with the general experience in the United Kingdom, where Dobane 055 has been widely used. Waldmeyer (14) has reviewed the synthetic detergent content of U.K. sewage plants and rivers during the period 1956 to 1966. A dramatic drop in the detergent content of sewage effluents and rivers occurred during this period: this would not have happened if Dobane 055 had not been a readily biodegradable material, under practical sewage treatment conditions.

BOD and LAS Removal

The reduction in the BOD value across the trickling filters, expressed as a percentage of the BOD value of the settled sewage, is shown for each trial in Tables IV and V. The average value for BOD removal over all the trials was 93.8% in comparison with a value of 91.7% for the overall LAS removal. The data show, therefore, that the LAS is removed very nearly as rapidly as the naturally occurring organic material.

Biodegradation on Further Aeration

Spot samples of sewage effluent were taken during each of the trials and air was passed through them for several days. Daily determinations of active material were carried out and the final concentration in the aerated effluents compared with the concentration in the settled sewage. The final biodegradation values expressed as a percentage of the active matter in the settled sewage are shown in Table VI.

Thus it would appear that the LAS in the typical sewage effluent should eventually biodegrade in a reasonably well aerated river to leave no more than a small percentage of the active material originally present in the settled sewage.

It should be noted that the small differences observed between Dobane JN-Q, Dobane 055 and PD, across the trickling filter, disappear on further aeration.

TABLE IV

Dobane JN-X, Dobane JN-Q and PD, Two Test Periods

Analysis	Initial survey, period, spring		First Dobane JN-X period, summer		First Dobane JN-Q period, autumn		First PD period, winter		Second Dobane JN-X period, winter		Second Dobane JN-Q period winter-spring		Second PD period spring-summer	
	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent
Estimate of sewage temperature, C[a]	15	---	17	---	15	---	10	---	9	---	9	---	12	---
Flow UK gal/day	2182	---	1931	---	1838	---	1798	---	1875	---	1910	---	1840	---
Anionie active material, mg/liter[b]	31.3	2.88	36.4	3.46	40.1	2.5	40.4	2.7	39.1	4.1	42.1	3.2	44.1	2.6
Percentage removal of anionic active material	---	90.8 (σ = 0.94)	--- ---	90.5 (σ = 1.27)	---	93.7 (σ = 0.72)	---	93.3 (σ = 1.15)	---	89.5 (σ = 1.32)	---	92.3 (σ = 0.83)	---	94.1 (σ = 0.94)
5 day BOD[c] mg/liter	444	15.3	300	11	358	18	384	24	377	34	360	30	404	23
Per cent BOD removed	---	96.5	---	96.3	---	95.0	---	93.7	---	91.0	---	91.6	---	94.3
Permanganate value, mg/liter	73	17.9	57	14	58	16	68	19	64	22	64	21	64	21
Ammonia, mg /Nliter	73.8	5.8	61.1	4.6	67	5.3	68	11.6	66.7	11.8	64.6	8.9	64.8	6.8
Oxidised nitrogen, mg N/liter	---	53.1	---	50.3	---	58.4	---	54.6	---	55.6	---	56	---	57.5
Suspended solids, mg/liter	---	---	181	30	190	31	190	36	180	63	197	58	189	36

[a]No facilities were available for the continuous recording of sewage temperatures at Preston and so the temperatures given are for a neighboring sewage works (Stevenage). They are intended only as an indication of the probable effect of climate changes on the temperature of Preston sewage.

[b]Expressed as "Manoxol" OT (sodium di-octyl sulfosuccinate).

[c]Biochemical oxygen demand.

TABLE V

Dobane 055, Dobane JN-B and Dobane 83, Single Test Period

Analysis	Dobane 055, summer period		Dobane JN-B summer-autumn period		Dobane 83, autumn period	
	Settled sewage	Effluent	Settled sewage	Effluent	Settled sewage	Effluent
Estimate of sewage temperature, C	17		19		15	
Flow, UK gal/day	1851		1771		1664	
Anionic active materials[b] mg/liter	35.3	1.8	37.9	5.2	46.8	4.5
Per cent removal of anionic active material	---	94.9 (σ = 0.7)	---	86.2 (σ = 0.9)	---	90.5 (σ = 1.9)
5 Day BOD[a] mg/liter	345	20	364	23	359	17
Per cent BOD removal	---	94.2	---	93.7	---	95.3
Permanganate value, mg/liter	60	19	61	17	66	18
Ammonia, mg N/liter	67.1	3.9	73.9	5.2	69.6	6.4
Oxidised nitrogen, mg N/liter	---	55.5	---	48.5	---	54.5
Suspended solids, mg/liter	166	34	159	24	178	23

[a]Biochemical oxygen demand.
[b]Expressed as "Manoxol" OT (sodium di-octyl sulfosuccinate).

Biodegradation of Individual Components

It was of interest to determine the relative biodegradation during the trials of the various components present in commercial LAS products. This involved separation of the LAS from the settled sewage and effluent so that analysis for isomers and homologs could be carried out.

This was done by the method of Hughes et al. (15) which employs a separation procedure based on ion exchange. Several liters of the sewage stream are passed through an anion exchange resin bed. The LAS is absorbed and is isolated by desorption with methanolic hydrochloric acid.

Hughes et al. (15) subsequently analyzed the LAS by IR spectroscopy and, after desulfonation, analyzed the recovered alkylbenzene by gas liquid chromatography. We employed the same analytical procedures. We showed that the carbon number and isomer distribution of the parent alkylate was similar to that of the alkylate recovered by desulfonation.

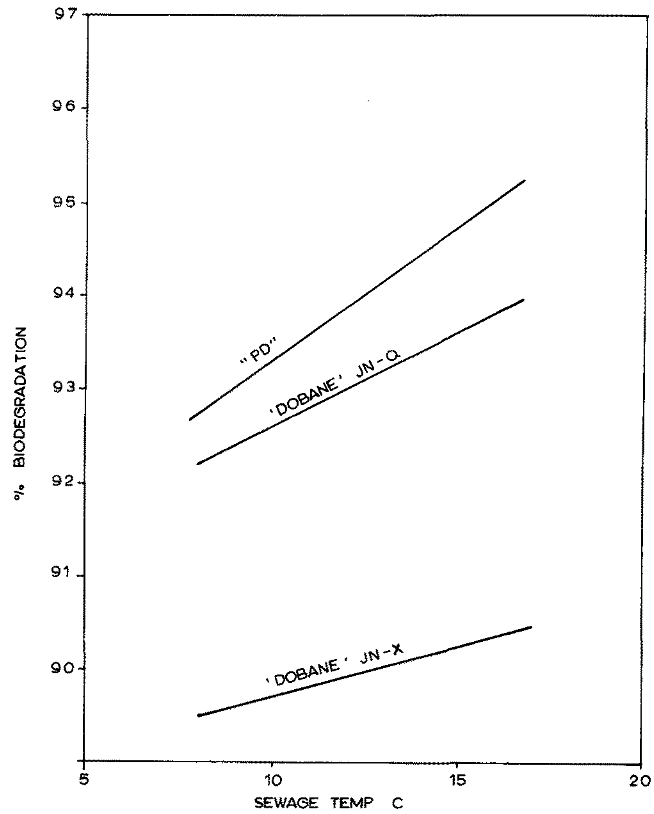

FIG. 2. Reduction in linear alkylbenzene sulfonates concentration (biodegradation) across the trickling filter at various sewage temperatures.

IR Analysis

The IR examination of the isolated alkylbenzene sulfonate was undertaken to determine the fate of any branched-chain alkylbenzene sulfonates which may have been present as an impurity in the linear material. The settled sewage influent contained an undetectable quantity of branched-chain material, that is, below the detectable limit of 3%.

The effluent, after biodegradation, gave values in the region of 6% to 12%; this would not appear to be due to contamination by the use of hard sulfonates but to the presence of small quantities of branched-chain alkylbenzene sulfonates in the original linear product. As the biodegradation obtained was of the order of 90% this value of 6% to 12% of hard material present in the effluent would represent only 0.6% to 1.2% of branched-chain alkylbenzene sulfonates present in the original product.

GLC Analysis

The LAS materials employed in the trials were prepared

TABLE VI

Biodegradation After Further Aeration

Product	Original biodegradability, %	Final biodegradability, %
Dobane JN-Q	93.7, 92.3	99
PD	93.3, 94.1	99
Dobane JN-X	90.5, 89.5	98
Dobane 055	94.9	99
Dobane 83	90.5	96
Dobane JN-B	86.2	94

TABLE VII

Percentages of the Alkylbenzene Components in Dobane JN-Q

Component	C_{10}				C_{11}				C_{12}					C_{13}					C_{14}					
	5	4	3	2	6+5	4	3	2	6	5	4	3	2	7+6	5	4	3	2	7	6	5	4	3	2
Sample	Phenyl isomer				Phenyl isomer				Phenyl isomer					Phenyl isomer					Phenyl isomer					
Alkylbenzene	3.2	3.5	3.2	3.9	9.9	6.2	6.7	7.2	5.1	6.6	5.1	4.7	6.1	6.0	4.5	3.2	3.4	4.4	1.4	1.9	1.4	0.8	0.8	0.8
Settled sewage influent	5.2	4.8	4.6	5.4	13.6	7.6	7.2	8.2	5.6	6.0	4.4	4.1	5.7	4.9	3.2	2.2	2.4	2.8	0.5	0.5	0.4	0.4	0.3	0.1
Sewage effluent	10.3	7.0	4.5	4.6	19.1	8.3	6.3	4.4	6.3	6.8	4.7	1.8	2.7	4.6	3.1	1.2	1.3	1.4	0.6	0.4	0.3	0.2	0.1	<0.1

TABLE VIII

Total Percentages of Component Types in Dobane JN-Q

Component sample	Totals of each carbon number					Totals of each Isomer							
	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	2	3	4	5	5+6	6	6+7	7
Alkylbenzene	13.8	30.0	27.6	21.5	7.1	22.4	18.8	18.8	15.7	9.9	7.0	6.0	1.4
Settled sewage	20.0	36.5	25.8	15.5	2.2	22.2	18.6	19.3	14.8	13.6	6.1	4.9	0.5
Sewage effluent	26.4	38.1	22.3	11.6	1.6	13.1	14.0	21.4	20.5	19.1	6.7	4.6	0.6

by sulfonation of the alkylbenzenes, and samples of the parent alkylbenzenes were available. We analyzed the parent alkylbenzenes by GLC, together with the alkylbenzenes recovered from the settled sewage and effluent. The results obtained on samples taken during the second trial period using Dobane JN-Q are shown in Table VII and VIII. Table VIII shows more clearly the influence of molecular structure on the rate of biodegradation of the various components. It is seen that during settling and in the later sewage treatment biodegradation takes place to alter the relative distribution. The longer alkyl chains degrade more rapidly so that the proportion of the components with carbon chain length of 12 to 14 carbons decreases, while that with 10 to 11 carbons increase.

With respect to the relative rate of biodegradation associated with the point of phenyl attachment to the alkyl chain it is seen that the 2-phenyl isomer degrades more rapidly than the 3-phenyl isomer which again degrades more rapidly than those isomers where the point of attachment of the phenyl groups is further from the end of the alkyl chain. Both these conclusions are in agreement with the work of Swisher (11,12) who compared the biodegradation rates of several pure alkylbenzene sulfonates. It was of considerable interest, however, to confirm these findings using a conventional material consisting of a complex mixture of homologs and isomers.

It is notable that some change in isomer distribution is seen between the results obtained on the original alkylbenzene and those obtained on the settled sewage. This indicates that some biodegradation had taken place during passage through the sewers or in the settling tank, which means that an even higher overall biodegradation has occurred than the values given in Tables IV and V. Such degradation has been observed by Spohn et al. (16) and Tschaekert (17).

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