tive entropy effect is more than counteracted by increased randomness or increased configurational entropy of the solubilized dye molecules. Several investigators, notably Frank and Evans (16) and Nemethy and Scheraga (17), have postulated water molecule structures partially surrounding nonpolar hydrocarbon molecules or groups, with van der Waals interactions lowering the energies of both hydrocarbon and water molecules. The breakup of this structure about surfactant monomers in the micellization process with consequent increased configurational entropy of the monomers in the micelle has been suggested as the cause of positive entropy changes in micellization by Schick (18) and by Goddard et al. (19). It is suggested now that the positive ΔH values of micellar solubilization may be attributed in part to similar water structure effects about the dye molecules.

The mean values of C_S, the dye concn in the micellar phase, for both surfactants give a possible clue to the cause of the negative entropy changes of the anionic SDBS in the 42.5–50C range. The maximum value of C_S for the nonionic OPE is 3.39×10^{-5} molecules Orange OT/Å^3 at 50C. This concn does not involve enough crowding to make the concomitant negative ΔS predominate over the positive entropy change effects previously mentioned. C_S values for SDBS are considerably larger, i.e., 6.05, 6.86 and 7.59×10^{-5} molecules Orange OT/ Å^3 at 35, 42.5 and 50C, respectively. One can speculate, therefore, that at a micellar packing of 6.86×10^{-5} dye molecules/Å^3 (ΔS negative), the negative entropy change due to restricted movement becomes larger than the positive entropy change effects involved. It is of interest to estimate the degree of packing at this point by determining the volume actually occupied by the micellized dye molecules. The molecular volume of Orange OT may be calculated from its mol wt and bulk density, as follows:

$$\text{Molecular volume, Orange OT} = \frac{10^{24} \times 262}{6.02 \times 10^{23} \times .54} = 810 \text{ Å}^3$$

The volume of (6.86×10^{-5}) Orange OT molecules is then 0.055 Å^3. Hence, it seems that the negative ΔS effect begins to predominate when solubilized dye molecules with a volume of 0.055 Å^3 are contained in a 1 Å^3 space.

It is of interest to note that the reversal of sign in ΔH and ΔS with increasing temp for the micellar solubilization of Orange OT by anionic SDBS duplicates similar sign reversals in the micellization of ionic surfactants as reported by Goddard and Benson (20) and Flockhart (21).

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ACKNOWLEDGMENTS

Most of the data used obtained by Troy Nichols and Allan Potter.

[Received October 1, 1964—Accepted November 27, 1964]

The Effect of Tallow-Based Detergents on Anaerobic Digestion[1]

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Abstract

Eight anionic detergents from three general classes (alcohol sulfates, α-sulfo fatty acid esters and alkylbenzenesulfonates were tested for biodegradability under anaerobic conditions of sludge digestion. The alcohol sulfates were found to be readily and completely degraded. The α-sulfo fatty acid esters did not degrade but had no adverse effect on bacteriological digestion while the alkylbenzenesulfonates used for control purposes did not degrade and disrupted the normal digestion process.

Preliminary lysimeter studies showed that sodium isopropyl α-sulfostearate is completely degraded, linear alkylbenzenesulfonate 83%, and ABS 35%.

Introduction

Recent studies by this laboratory have reported on the biodegradation of some tallow-based surface active agents in river water (9) and in activated sludge (1). The present study is concerned with the effect of tallow-based surfactants on the anaerobic digestion process. Two preliminary approaches have been made. First, the use of anaerobic sludge digesters and second, the use of lysimeters utilizing local soil.

The effect of detergents on the anaerobic biodegradation process is an important consideration in septic tank operation and seepage from a septic tank to saturated soil.

Experimental

Materials

The preparation of sodium isopropyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)_2$, disodium 2-sulfoethyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2C_2H_4SO_3Na$, sodium methyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH_3$, sodium 9,10-dichlorooctadecyl sulfate $C_8H_{17}CHClCHCl(CH_2)_7CH_2OSO_3Na$ and hydrogenated tallow alcohol sulfates (HTAS) has been

[1] Presented at the AOCS meeting, Chicago, 1964.
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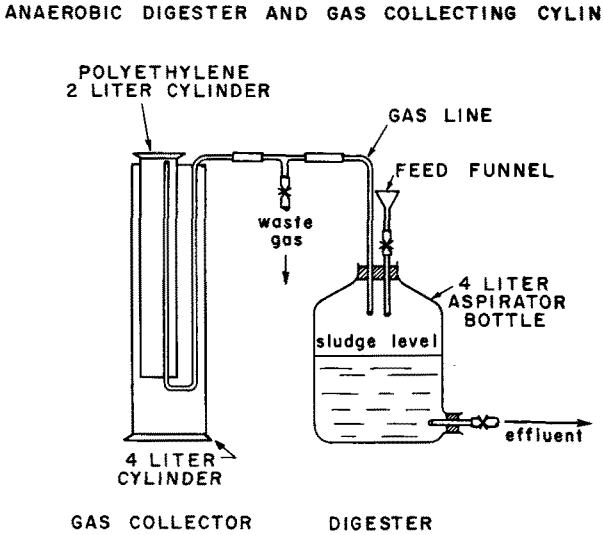

FIG. 1. Experimental apparatus used for anaerobic sludge.

described in previous publications (7,8,10). Three sodium alkylbenzenesulfonates were used for comparison: branched chain ABS, a standard sample supplied by the Soap and Detergent Association; straight chain LAS-I, a commercial sample; and a laboratory preparation LAS-II, from the aluminum chloride catalyzed reaction of 1-dodecene with benzene, followed by sulfonation with sulfuric acid.

Procedure

A. Sludge Digestion

The experimental apparatus and procedure were patterned after Johnson and Bloodgood (4) and Hernandez and Bloodgood (3). Figure 1 illustrates the apparatus used. Three liters of digesting sewage (volatile solids 57–58%) obtained from the anaerobic digester of a local sewage treatment plant, were placed in each digester and the 3-liter level marked. The digesters were then placed in an incubator at 35C for the duration of the test period. Gas was collected in 2-liter polyethylene cylinders inverted in 4-liter glass cylinders filled with tap water. Since the gas collection units were located outside the incubator they were subject to changes in room temp.

In the initial stage of operation the digesters were operated by shaking, reading the gas vol in the collection units, withdrawing 100 ml of sludge, adding 100 ml of primary sludge as feed and again shaking. Primary sludge is a mixture of settled raw sewage and insoluble solids from the activated sludge process. After 5 days the digesters were found to be operating uniformly as shown by nearly equal gas vol, pH and per cent volatile solids for each unit. One digester was then kept as a control and the remaining units used for testing the biodegradability of detergents.

Each unit was serviced daily (as previously described) for 31 days in a similar manner. The control digester was fed only primary sludge while the remaining units were fed primary sludge to which was added 90 mg of test detergent. The term "added detergent" should not be confused with "detergent" (calculated as ABS) naturally present in the primary sludge. No additional detergent was added to replace the amount removed by the daily withdrawal of 100 ml of digesting sludge; therefore the actual concn of each detergent decreased daily by the amount contained in the withdrawn sludge. This, of course, assumed that after shaking, a homogeneous mixture was removed each day. The accuracy of this assumption is illustrated graphically by Figure 2 which shows the plot of detergent added and daily analysis (excepting week-ends) of ABS (no degradation) and HTAS (complete degradation).

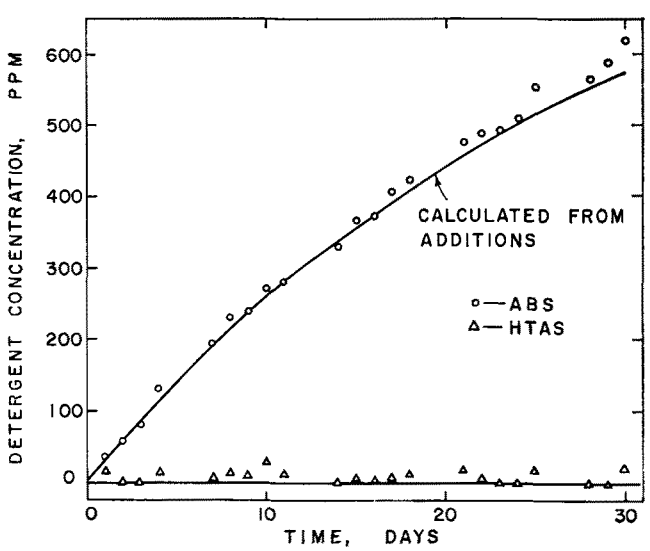

FIG. 2. Detergent analysis of anaerobic sludge. Solid line shows detergent concn calculated from daily additions; circles and triangles show the analysis for ABS and HTAS, respectively.

Feed

Standard detergent stock solutions containing 4500 mg/l were prepared; 20 ml of this stock solution (equivalent to 90 mg of detergent) was a convenient vol to add to the primary sludge which was obtained fresh every Monday, Wednesday, and Friday. By feeding a vol of primary sludge equivalent to 2 g of volatile solids (volatile at 600C) the daily gas production was maintained safely within the 2000 ml capacity of each collecting cylinder. The sewage plant from which this sludge was obtained normally feeds 1/15 to 1/30th of the vol of digesting sludge per day. Our rate was 1/30th of the vol. The actual vol of primary sludge equivalent to 2 g of volatile solids varied from 50 to 80 ml. Appropriate dilution to 100 ml was made with distilled water for the control unit but in the case of the test units, 20 ml of detergent solution was first added. Further dilution with water, if necessary, was then made to 100 ml. Prepared feed samples were refrigerated under anaerobic conditions at 4C until used.

B. Lysimeter Soil Percolation

The apparatus consisted of three 1-liter aspirator bottles. About 200 g of ½-in. washed stone was placed around each outlet, then 750 g of local soil (Califon Silt Loam) was poured in each bottle and tamped lightly with a glass rod. After saturating the soil with 500 ml of tap water, 20 ppm solutions of detergent were added continuously and the vol of percolated solution recorded each day for the duration of the tests (21–39 days). Analysis of effluents for detergent was made by the methylene blue method (2).

Analysis of Digested Sludge

Volatile Solids and Volatile Acids

Volatile solids and volatile acids were determined twice weekly following standard procedures for sew-

TABLE I

Gas Production of Anaerobic Digesters for 31 Days

Experiment Number	Digesters	Volume of gas produced	
		Total ml	Daily average, ml
1	Control	32,580	1053
	LAS-I (commercial)	14,980	.....
	Sodium isopropyl α-sulfostearate	33,930	1093
2	Control	32,060	1034
	ABS	14,830	.....
	Sodium methyl α-sulfostearate	31,550	1018
	Disodium-2-sulfoethyl α-sulfostearate	23,870	.....
	HTAS	36,410	1175
3	Control	32,340	1043
	LAS-II (laboratory preparation)	19,360	.....
	Sodium 9,10-dichlorooctadecyl sulfate	32,020	1033

age analysis (6). Volatile solids were found by evaporating 25 ml aliquot samples nearly to dryness on the steam bath, then for 1 hr at 100C in a convection oven, weighing, and ashing at 600C for 1 hr. The loss on ignition represents volatile solids.

Volatile acids were determined by slightly modifying the procedure outlined on page 422 of Standard Methods (6). The 100 ml sample required for steam distillation was obtained by centrifuging the unused vol of sludge removed on a given day, acidifying the 50 ml of the supernatant liquor with 5 ml of 1:1 sulfuric acid and refrigerating overnight. The following day a second 50 ml aliquot of liquor was obtained in a similar manner combined with the previous day's aliquot, steam distilled, and the distillate titrated with 0.1*N* sodium hydroxide. Volatile acids concn was calculated as mg/liter of acetic acid.

Detergent Concentration and pH

Detergent analyses and pH measurements were made daily excepting weekends. Detergent concn was determined by a method related to that of Roberts and Lawson (5) who found methanol to be the best solvent for continuous extraction of sewage sludge. We found 95% ethanol worked equally well with no difference in results. A 5 ml aliquot of sludge was weighed, diluted to 100 ml with 95% ethanol, shaken, let stand 1 hr, then filtered. (A control experiment showed that a single extraction recovered 95% of added detergent; further extractions did not improve the accuracy.) An appropriate vol of the filtrate was then analyzed by the methylene blue method.

Results and Discussion

Sludge Digestion

Three separate groups of experiments were conducted as follows: 1) control, LAS-I (commercial) and sodium isopropyl α-sulfostearate; 2) control, ABS, disodium 2-sulfoethyl α-sulfostearate, sodium methyl α-sulfostearate and hydrogenated tallow alcohol sulfates (HTAS); and 3) control, sodium dodecylbenzenesulfonate LAS-II (laboratory preparation) and sodium 9,10-dichlorooctadecyl sulfate.

Gas Production

It is significant that for the three groups of experiments the individual control digesters averaged nearly the same vol of gas, 1043 ml/day (1053, 1034, and 1043), confirming the reliability of the individual digester operations. Table I lists the total vol of gas produced by each of the digesters in the three experiments. The difference between max (32,580) and min (32,060) vols of gas produced equalled 529 ml, or an average daily difference of 17 ml in the control digesters. For practical purposes the ABS digester (14,830) equalled that of LAS-I (14,980) in gas production while the LAS-II digester (19,360) exceeded ABS and LAS-I digesters by about 4,500 ml. The disodium 2-sulfoethyl α-sulfostearate digester produced 23,870 ml. These vols, which are significantly less than those of the control digesters, indicate an adverse effect on the sludge digestion process, as will be pointed out in more detail later. The vol of gas produced by the HTAS is especially noteworthy since it exceeded that of the control by 4,350 ml, or by a daily average of 140 ml.

TABLE II

Detergent Concentration, Milligrams Per Liter (ppm) for Each Digester, After 30 Additions of Detergent

Digester	Added	Found	Corrected
Control	.....	229[a]	0
LAS I	563	842	613
Na isopropyl α-sulfostearate	563	815	586
Control	.	265[a]	0
ABS	563	852	587
Na methyl α-sulfostearate	563	804	539
Naa 2-sulfoethyl α-sulfostearate	563	890	625[b]
HTAS	563	265	0
Control	..	280[a]	0
LAS II	575[c]	853	573
Na 9,10-dichlorooctadecyl sulfate	575[c]	301	21

[a] Calculated as ABS.
[b] High value because of di-ionic nature of disodium 2-sulfoethyl α-sulfostearate.
[c] Milligrams per liter added for 31 days. Because stored samples gave very erratic results the addition of detergent was extended here so that analysis could be made on a work day.

Figure 3 illustrates this same data graphically for the alkylbenzenesulfonates and the 2-sulfoethyl ester, showing how ABS, LAS-II and the 2-sulfoethyl ester adversely affect the gas production. The curves for ABS and LAS-I (not shown) follow an almost identical line. Gas production started to decrease steadily with LAS-I at the 214 ppm added detergent level, with ABS at the 280 ppm level and with LAS-II at the 259 ppm level. However, with LAS-II the drop was more gradual, as evidenced by the larger vol of gas produced. In the case of the 2-sulfoethyl ester gas production started to gradually decline at the 427 ppm level.

pH

In general, the pH for normal operation of the digesters ranged from 7.0–7.25, excepting those containing ABS, LAS-I, LAS-II and disodium 2-sulfoethyl α-sulfostearate. During the last week of operation the pH of these digesters dropped to 6.85, 6.75, 6.90, and 6.85, respectively, corresponding with a large increase in volatile acids content. Because the sludge is so well buffered the pH does not register as

TABLE III

Biodegradation of Five Tallow-Based Detergents and Three Alkylbenzenesulfonates in Activated Sludge and in River Water

Detergent	Activated sludge			River water time for 80% degradation hr
	Av. analysis ppm	High value ppm	% Time > 1 ppm	
HTAS	0.4	1.3	3	56
Sodium 9,10-dichlorooctadecyl sulfate	0.2	1.0	0	82
Sodium methyl α-sulfostearate	0.3	1.8	10	93
Sodium isopropyl α-sulfostearate	0.5	1.4	6	117
Disodium 2-sulfoethyl α-sulfostearate	0.7	5.1	17	123
ABS	11.0	17.0	100	> 700
LAS-I (comm'l)	7.3	12.2	100	88
LAS-II (lab prep'n)	3.5	7.4	74	130

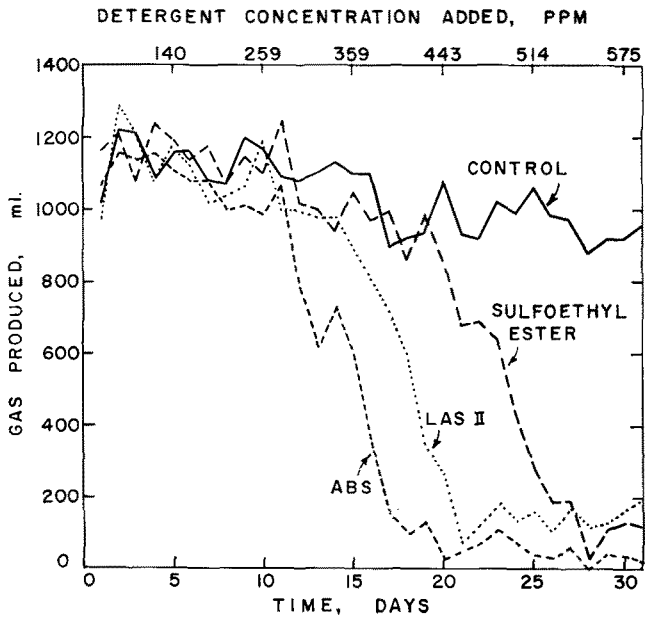

FIG. 3. Effect of test detergents on daily gas production.

acid until long after the digesting sludge has been adversely affected, as evidenced by decreased gas production, high values for volatile acids and volatile solids, separation and floating of sludge, gray color of digester liquor and disagreeable odor of the digesters.

Volatile Acids

The volatile acids concn normally ranged about 200–300 mg/l as acetic acid. Corresponding with the decrease in gas production was a gradual increase in volatile acids concn to 1200–1300 mg/l. For this reason volatile acids concn provided more direct evidence than did pH that disruption of the normal digestion processes was occurring in the ABS, LAS-I, LAS-II and 2-sulfoethyl ester digesters.

Volatile Solids

Volatile solids ranged normally between 58–59% for all of the digesters. However, in the presence of ABS, LAS-I, LAS-II, and disodium 2-sulfoethyl α-sulfostearate there was a gradual increase of volatile solids to 65%, indicating the feed was not being digested.

Biodegradation

Degradation was immediate and complete by methylene blue analysis for the hydrogenated tallow alcohol sulfates and sodium 9-10-dichlorooctadecyl sulfate. The other tallow based detergents did not degrade and had no evident adverse effect on the bacteriological system, except for the 2-sulfoethyl ester. The three alkylbenzenesulfonates, on the other hand, did not degrade and adversely affected the digestive processes. Figure 2 illustrates the course of analysis for ABS and HTAS. ABS analysis closely follows the curve for the calculated daily additions of detergent (as previously mentioned) while HTAS analysis closely follows the base or zero concentration line. By plotting the concn of LAS-I, LAS-II and the α-sulfo esters there is close correspondence (with minor variations) to the ABS plot in Figure 2. Likewise the plot of sodium 9-10-dichlorooctadecyl sulfate follows that for HTAS. Table 2 lists the final analysis for each

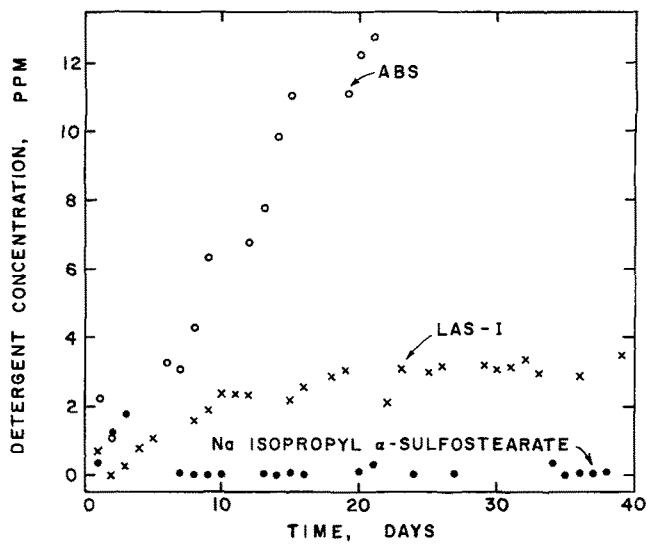

FIG. 4. Detergent analysis of lysimeter effluents.

of the detergents tested. The exceptionally high value for disodium 2-sulfoethyl α-sulfostearate can be attributed to its di-ionic character. The value of 21 ppm for sodium 9,10-dichlorooctadecyl sulfate can be explained by the minor fluctuations in analysis; in only 4 out of 21 analyses did the concn exceed 0.

Lysimeter Biodegradation

Figure 4 shows the course of analysis of the lysimeter effluent for ABS, LAS-I and sodium isopropyl α-sulfostearate. In 21 days the ABS degraded to the extent of 35%; in 39 days LAS-I degraded 83%; and in 38 days sodium isopropyl α-sulfostearate degraded 100% continuously with minor variations of less than 0.5 ppm. Desorption of the soil, after use in the lysimeter, with either 1*N* HCl or methanol recovered only a small portion of the ABS and none of the sodium isopropyl α-sulfostearate. Failure of detergent to appear in the effluent is therefore primarily due to biodegradation.

Activated Sludge and River Water Biodegradation

For comparison results of activated sludge (1) and river water biodegradation (9) of the detergents used in the present study are summarized in Table 3. The river water used in these tests came from the Schuylkill River at Fairmount Park in Philadelphia and the activated sludge from a local sewage disposal plant.

ACKNOWLEDGMENT

R. M. Bolenius and his staff of the Abington, Pa., Sewage Disposal Plant supplied samples of sewage.

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[Received November 17, 1964—Accepted January 22, 1965]