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Degradation of Linear Alkylate Sulfonates in Sewage

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Abstract

Residual linear alkylate sulfonates isolated from sewage effluents during a field test of biologically soft detergents reveal chain-length and phenyl isomer distributions similar to those in the influent stream. The data suggest no preferential degradation of linear alkylate sulfonate isomers under the field test conditions. The effluent is, however, characterized by apparent changes in branching content.

Introduction

AN INTENSIVE STUDY has been conducted in this laboratory of the alkyl benzene sulfonates isolated from sewage during a field test of the biodegradation of linear alkylate sulfonates in a sewage treatment plant located at Elm Farm Mobile Home Park community near Woodbridge, Virginia (1). At this locality the sanitary waste is treated in an extended aeration activated sludge system. Conditions for control of the test were particularly favorable at this site and the satisfactory analytical results obtained reflect this factor.

To complement the more extended study (1) information was sought regarding the nature of residual linear alkylate sulfonate species present in the effluent stream from the plant subsequent to introduction of products containing these materials. To obtain this additional information samples of raw sewage and treated effluent were taken periodically and the residual linear alkylate sulfonate species isolated as the methyl heptyl ammonium salts. These isolated materials were examined by infrared spectroscopy, then desulfonated and the alkylates analyzed by mass spectrometry to determine chain length distribution and phenyl position isomer distribution.

Experimental

Sewage samples were taken over a five-week period after the introduction of products containing linear alkylate sulfonate (LAS). Three raw sewage influent samples were taken during the study, one prior to the introduction of products containing LAS and two during the interval these were being used. The influent designated A in Table I was taken approximately one month after the introduction of LAS products and influent B one month later. The influent control sample shown in Table I was taken prior to the introduction of LAS material. Influent studies were made to monitor the changeover to linear material and to permit comparison with materials isolated from the treated effluent leaving the plant. The standard sample listed in Table I is the base linear alkylate sulfonate with which the test products were formulated.

A total of four treated waste samples were studied, the first (Effluent A, Table I) taken approximately six weeks after the introduction of LAS materials and the remaining three, namely B, C, and D, at successive weekly intervals. Details of the sampling methods are outlined elsewhere (1). All sewage samples in this work were preserved with formaldehyde and, as an additional precaution, maintained at a temperature of 4C or less, prior to analysis.

Methylene blue active species (MBAS) were determined by the method described in *Standard Methods for the Examination of Water and Waste Water*

TABLE I

Mass Spectrometric and Infrared Characterization of ABS Isolated from Sewage

Sample	Date taken	Na ABS ppm		Est. % branching		Mol. wt.	Est. % unsat.
		as MBAS	by IR	IR	m.s.		
Influent "Control"	8-26-63	27.0	14.0	90	88.2	250.0	21.5
Standard			....	0	3.1	256.0	4.9
Influent A	9-27-63	24.5	20.7	11	14.0	256.0	7.2
Influent B	10-28-63	28.0	17.6	2	6.4	257.2	10.6
Effluent A	10-14-63	3.7	3.8	51	34.5	258.3	22.9
Effluent B	10-21-63	2.4	2.4	79	62.9	255.6	32.6
Effluent C	10-28-63	1.1	0.85	53	22.5	261.5	35.2
Effluent D	11- 4-63	0.8	0.59	60	21.0	259.2	32.8

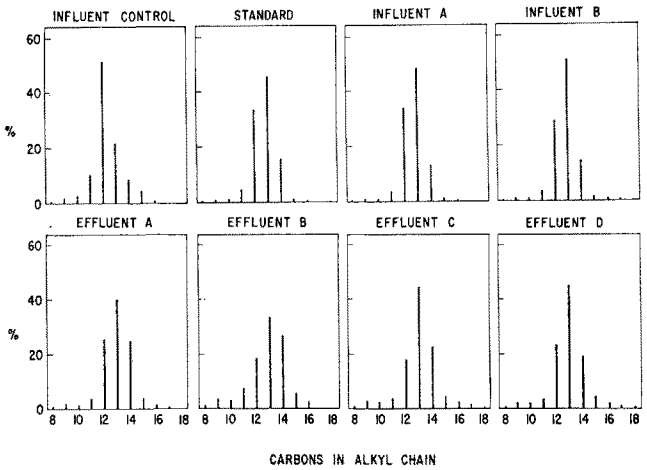

FIG. 1. Chain length distribution by mass spectrometry—desulfonated amine salts.

(2). Methyl heptyl ammonium salts of alkyl benzene sulfonate were isolated by the procedure described by Foote et al. (3), modified in two respects. Filtration was carried out using a medium-fine sintered glass filter supporting a disc of Whatman No. 2 filter paper to facilitate slurrying the Celite cake and quantitative infrared measurements were made at the 9.6 μ band only. Infrared spectroscopy was utilized to estimate the relative amounts of branched and straight chain isomers according to the method of Frazee and Crisler (4). After infrared study the amine salts were microdesulfonated as described by Swisher (5) and the isolated alkylates examined by mass spectrometry.

Mass spectra were obtained on a Consolidated Electrodynamics Corporation Spectrometer, Model 21-103C, equipped with a heated inlet (150C). The desulfonated samples were frozen with dry ice and introduced into the instrument in the solid state employing a technique similar to that described by Biemann (6). Analysis of the spectra for molar distribution of the alkyl benzenes followed routine procedures paralleling those described by Brown et al. (7) and Boyer et al. (8).

The branching by mass spectrometry was estimated by the phenyl position analysis technique. The unsaturated species (indanes, tetralins and other hydrogen deficient alkyl benzenes) were determined relative to the normal alkyl benzenes.

Qualitative spot checks of a number of selected samples of desulfonated alkylate were also made by gas chromatography.

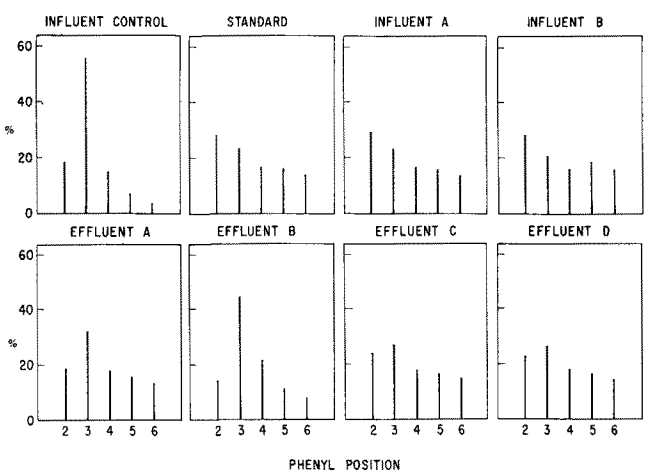

FIG. 2. Phenyl position analysis by mass spectrometry—desulfonated amine salts.

Discussion

Data obtained in the present investigation are summarized in Table I, and the distribution of chain length and phenyl position obtained by mass spectrometry are illustrated in Figures 1 and 2.

Examination of the data in Table I indicates that the quantitative results from the methylene blue and infrared methods of analysis correlate satisfactorily for the effluents but that the infrared results are consistently lower than the methylene blue results in the influents. A possible cause of these discrepancies could be loss of certain methylene blue active components during purification preparatory to infrared examination. The quantitative data for the effluents show methylene blue active species decreasing from 3.7 to less than 1 ppm in the three-week interval between sampling effluents A and D. The infrared results correlate with those from MBAS with both indicating about 85 to 95% degradation.

The branching estimates shown in Table I were obtained from infrared measurements and reflect relative differences. Infrared results on isolates derived from influent sewage distinctly mark the changeover to straight chain product by the sudden drop in branched content. Comparison of the effluent with influent A and B shows a marked increase in branched content. Obvious impurities as evidenced by color and strong carbonyl absorption in the infrared are present in the isolates, and it is not known whether these contribute significantly to the measured branched content. The differences shown by infrared study with respect to evidence for branched content are qualitatively paralleled by the results from mass spectrometric analysis shown in Table I. In addition, mass analysis of the influent sewage clearly shows an increase in molecular weight to a value equal to that of the standard after changeover to LAS products. Simultaneously, a marked drop in unsaturated species is observed. Conversely, the effluents exhibit a marked rise in unsaturated species over that found for the initial polypropylene benzene sulfonate control sample. It is postulated that these species show a markedly slower rate of degradation than normal alkyl benzenes. That they do biodegrade, however, is indicated by a study of mixed C_9-indanes and C_8-tetralins (9).

Chain length and phenyl position isomer distribution for the influents A and B (Figs. 1 and 2, respectively) resemble the standard very closely. The effluents, although exhibiting some differences from the standard, also show the presence of all phenyl isomers and the chains characteristic of the LAS being introduced. This is particularly true of effluent samples designated C and D, which were the last two taken and which exhibited the lowest concentration of MBAS. These samples represent materials which had biodegraded to a greater extent than effluent A or B and appear to most closely approximate the patterns exhibited by isolates from the influent. The presence of all chain lengths and phenyl isomers was qualitatively substantiated by gas chromatography.

It was anticipated that linear alkylate sulfonate species shown to be more readily degraded in laboratory river water tests (5,10) would have been substantially reduced in the effluents. In Figure 2, for example, the relative amounts of 2 and 3 phenyl isomers do not appear to be appreciably reduced with

respect to the 4, 5 and 6 isomers as might be predicted (5). Also, from a consideration of the relative amounts of C_{12} and C_{14} chain lengths compared to C_{13}, as shown in Figure 1, an increasing rate of degradation with chain length should effect a decrease in the C_{14} to C_{13} ratio. The plotted data indicates that this is not occurring.

These divergences from results which would normally be anticipated from a knowledge of river water laboratory tests are not too surprising since the field conditions represent an open system and present a considerably different environment than a river water. Indeed, this possibility was pointed out by Swisher (10) and substantiated by the work of Sweeney (11) on a laboratory scale continuous sewage unit utilizing activated sludge. The work with activated sludge showed that the effects of molecular weight and phenyl position were smaller than in unacclimatized river water tests. It is important to emphasize that the mass spectral data and gas chromatographic data, particularly in respect to the effluents, are based on extremely small amounts of material. In the case of the latter two effluents this was less than one part per million of the total effluent.

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Dimensional Analysis Applied to Detergency

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Abstract

Six fundamental soil and surfactant variables of the detergency process have been combined by dimensional analysis into a complete and valid set of three dimensionless products which represent the mechanism by a diagram comprising a family of curves of two of the products at fixed values of the third. Five soils and six surfactants have been combined into eighteen soil-surfactant systems to validate the dimensional analysis. The dependent parameter of soil removal, normally viewed as dimensionless, was assigned the dimensions of mass times length following more subtle considerations of the mechanism. This means of representing the detergency process is a considerable improvement over the previously established transcendental relationships of selected groups of soil-surfactant systems (2).

Introduction

DETERGENCY RESEARCH at this laboratory has been oriented towards the development of a detergency function that could be utilized for the scientific selection of surfactants for specific soil removal applications. From the beginning of the program (1), it has been felt that attainment of the objective involved the correlation of detergency with specific physiochemical factors of the detergency mechanism. Tending to confirm this premise have been our developments of linear detergency-micellar solubilization functions in the practical 90–100% soil removal range and relationships between the linearity constants of such functions and soil dipole moment, surfactant HLB, and soil-surfactant interfacial energy (2). While this was an advance in the field, reservations have been entertained concerning its pragmatic value because many of the functions were transcendental. It seemed logical at

TABLE I

Surfactant and Soil Data

Surfactants

Compound	Symbol	CMC–Molar		Surface tension at CMC	
		Commercial	Pure	Commercial	Pure
Polyoxyethylene–20–nonylphenol	NPEGE	0.000155 (9)	0.000140	32.6	39.0
Polyoxyethylene–30–nonylphenol	NPTGE	0.000275 (9)	0.000185	37.7	41.3
Polyoxyethylene–40–nonylphenol	NPTTGE	0.000450 (9)	0.000233	41.0	44.0
Polyoxyethylene–50–nonylphenol	NP50E	0.000788 (9)	0.000280	43.2	45.6
Sodium dodecyl benzene sulphonate	SDBS		0.00353		32.5
Sodium lauryl sulphate	SDS		0.0081		35.5 (14)

Notes: (a) Nomenclature of nonionics indicates average number of ethylene oxide units condensed with hydrophobe for commercial surfactants.
(b) SDBS is a branched chain ABS.
(c) CMC data at 25C.
Literature references for CMC given.

Soils

Name	Absolute viscosity, cp	Surface tension, dynes/cm	Dipole moment, debyes
Palmitic acid	5.517	—	0.79 (13)
Octadecylamine	2.868	21.7	1.3 (11)
Lauryl alcohol	2.758	28.3	1.7 (11)
Oleic acid	5.294	31.5	1.009 (12)
Linoleic acid	4.780	—	1.208 (20)

Notes: (a) Dipole moment literature references are given.
(b) Lauryl alcohol contains 58.7% 12–C plus varying amounts of 8–18C alcohols. 98% lauryl alcohol = 2.480 cp.
(c) Oleic acid is USP grade.
(d) Viscosity at 185F.