Application of Infrared Spectroscopy to Surfactant Degradation Studies

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Abstract

Several IR spectroscopic methods are described for the determination and analysis of detergent actives in sewage, ground water and finished detergents. The methods include the determination of the ratio of straight-chain to tetrapropylene chain alkylbenzene sulfonate (ABS), the determination of level and polyethoxy chain length of alkyl and alkylphenyl ethers of polyethylene oxide condensates, and the type of alkyl group in detergent actives isolated from formulated detergents. Specific applications of these methods to study of the degradation of alkylbenzene sulfonate in sewage from controlled use areas, and in studies of the rate and mechanism of degradation of the alkylphenyl ethers and alkyl ethers are discussed.

Introduction

WHILE MANY METHODS have been reported for the determination of surfactants in sewage and ground waters, most of them use a single-valued physical or chemical property for measurement and are therefore of limited use for the examination of the structure of the materials being determined. Such methods include the methylene blue method (1) for ABS, the ammonium cobalt thiocyanate method (2) for the polyethoxylates, and the several methods based on physical properties such as surface tension (3) and foam height (4). Since the IR spectrum of a material is a multi-valued physical property which can provide information regarding structure as well as level, IR methods hold great promise for following the progress of surfactant degradation.

An IR method based on measurement of the absorption bands attributed to the sulfonate group has been reported for the determination of level of ABS in sewage and river water and is part of the Soap and Detergent Assoc. method (5). Extensions of this method to permit determination of relative amt of branched (tetrapropylene) and straight-chain LAS have also been reported (6,7). Comparable methods for the nonionics, alkylphenol polyethoxylate (ABE) and the alkyl polyethoxylate (AE) have not been reported.

The work reported herein has been carried out in an effort to develop satisfactory test procedures for the determination of residual ABE and AE in the river water die-away test (8), as well as to contribute to the knowledge of the rate and mechanism of biodegradation of these nonionics.

TABLE I

Analysis of Sewage in Controlled Test Area

Sample	ppm ABS	% tetrapropylene
Influent—1	3.7	27
Effluent—1	0.8	96
Influent—2	9.1	13
Effluent—2	0.9	98
Influent—3	11.2	15
Effluent—3	0.6	78

Experimental

Alkylbenzene Sulfonate (ABS)

Methods. In the IR spectra of ABS, characteristic bands appear at 1410 cm^{-1} for straight-chain isomers and at 1367 cm^{-1} for branched-chain (tetrapropylene) isomers. The use of these bands to determine the level of straight-chain and tetrapropylene-chain isomers in sewage and ground water has been reported previously (6,7).

For sewage and river water, isolation of the ABS is by the Soap and Detergent Assoc. (SDA) method (5,9). For detergent products, the isolation is simpler. The ABS is extracted directly from a water-ethanol solution of the product as the *n*-octylamine salt, and its tetrapropylene content determined using the calibration prepared for sewage. Significant amt of amide, soap, sulfated surfactants and nonionics cause interference and, if present, are removed by a preliminary acid hydrolysis-petroleum ether extraction step. Inorganics, hydrotropes, carboxymethyl cellulose and other hydrophylic materials do not interfere.

Procedure. Weigh 2 g of detergent into a 100-ml beaker, add 50 ml of 5N HCl, cover with a watch glass and heat on a steam bath for 3 hr. Evaporate to dryness and transfer to a 250-ml extraction cylinder with 70 ml of water. Add 30 ml of ethanol and extract three times with 50-ml portions of petroleum ether. Discard the extracts. Add 0.2 ml of 0.1% chlorophenol red indicator solution and neutralize with 10% NaOH to the endpoint (pH 6.8). (If the hydrolysis step is omitted, dissolve the sample in 100 ml of 70/30 water-ethanol, add the indicator and neutralize with HCl.) Add 25 ml of pH 6.8 phosphate buffer solution (6.8 g KH_2PO_4 in 1 liter of water, adjusted to pH 6.8 with NaOH), 0.3 ml of *n*-octylamine and extract once with 100 ml of petroleum ether. Evaporate the extract to dryness on a steam bath and dry at 80C for 30 min to remove excess amine. Dissolve in an amt of CCl_4 to make an approx 3% solution. Scan the IR spectrum and determine the ratio of tetrapropylene to straight chain ABS using the analytical conditions and calibration curve for sewage.

Results. The use of this method for determining relative rates of degradation is illustrated in Table I, in which are listed analyses obtained on samples collected at a sewage treatment plant in a controlled test area. An increase in the relative amt of tetrapropylene ABS during the course of biodegradation is expected as a consequence of its slower rate of degradation, and this is clearly indicated by the data.

Alkyl Phenol Polyethoxylates (ABE)

Method. The IR spectrum of a commercial ABE containing an average of 9.5 moles of ethylene oxide (EO) and a branched alkyl group derived from propylene trimer is shown in Figure 1. The absorption bands at 1250 cm^{-1} and 1120 cm^{-1} are attributable to aromatic ether and to aliphatic ether. Since in an ABE containing *n* EO units there will be *n*-1 aliphatic

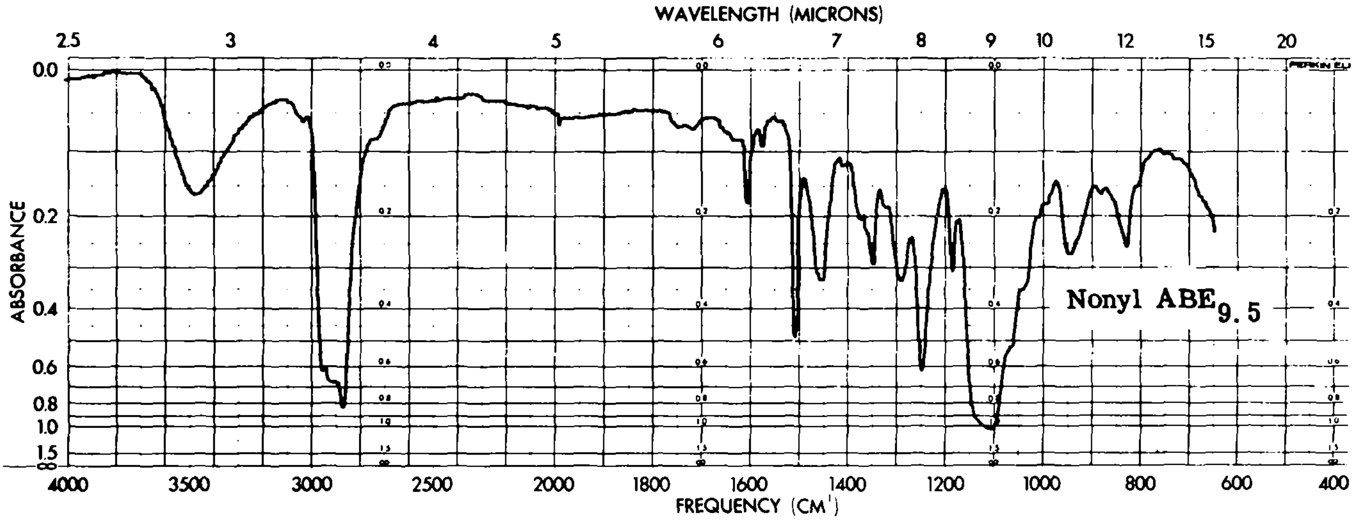

FIG. 1. IR spectrum of nonyl ABE$_{9.5}$.

ethers and one aromatic ether, the ratio of these two bands will be a measure of n, the EO chain length. The 1120 cm^{-1} band can be used to determine the concn of EO in solution and knowledge of the mol wt of the ABE will allow the calculation of concentration of nonionic. Visual inspection of the CH bands at 2900 cm^{-1} and the bands due to ethoxyl chain vibrations will be useful in determining whether changes have occurred in the alkyl chain.

Calibration. Prepare a series of CS$_2$ solutions of a known ABE ranging from 0.05–0.5% concn. (The ABE should be of the type being studied.) Prepare a second series of CS$_2$ solutions containing 0.4% of ABE's containing the same alkyl group but varying ethoxyl chain length. Scan the spectra of the solutions from 4000–950 cm^{-1} in a 1-mm cell vs. a 1-mm cell filled with CS$_2$. Measure the 1250 and 1120 cm^{-1} bands, subtracting the background absorbance at the valley near 975 cm^{-1}. Calculate the absorbance ratio of the 1250 to the 1120 cm^{-1} absorption bands. For each solution, calculate the "mg EO per ml,"

$$\text{mg EO/ml} = \text{mg ABE/ml} \times (44 \times n)/\text{MW of ABE}$$

where, n = moles EO/molecule.

Plot calibration curves of the absorbance of the 1120 cm^{-1} band vs. mg EO/ml for both series of solutions and plot absorbance ratio of the 1250/1120 bands vs. moles EO for the second series of solutions.

Isolation Procedures. Several basic procedures have been employed to isolate the ABE from river water die-away samples; namely, adsorption chromatography, chloroform extraction and foam stripping.

In the adsorption chromatographic method, 250–500 ml portions of the test solution were shaken with monobed ion exchange resin followed by adsorption of the nonionic surfactant on activated carbon from which it was eluted with methanol and chloroform.

The extraction procedure was carried out by adding

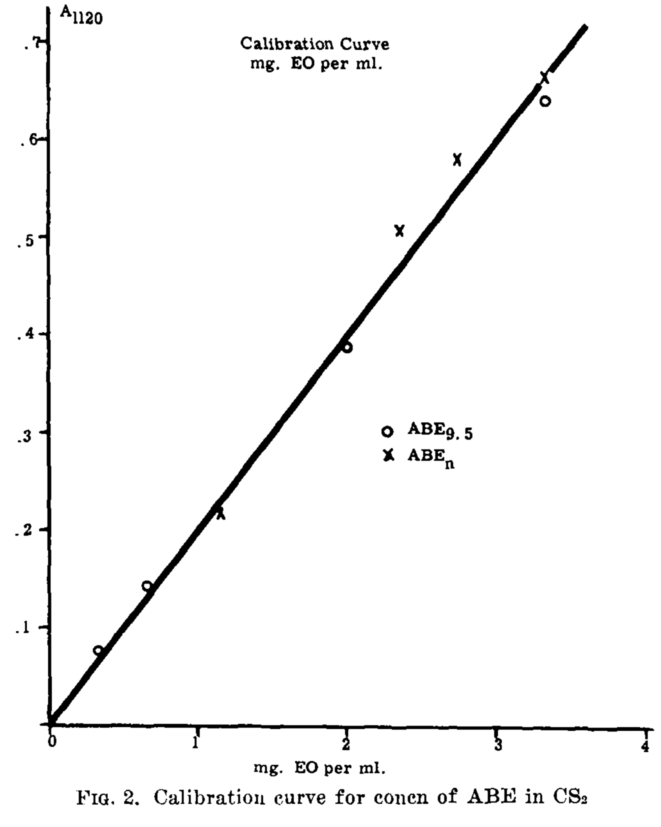

FIG. 2. Calibration curve for concn of ABE in CS$_2$

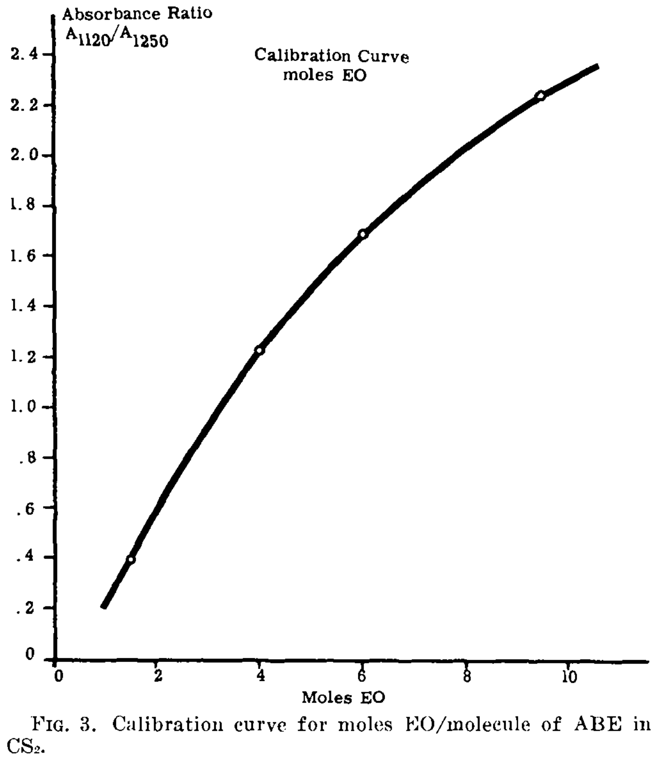

FIG. 3. Calibration curve for moles EO/molecule of ABE in CS$_2$.

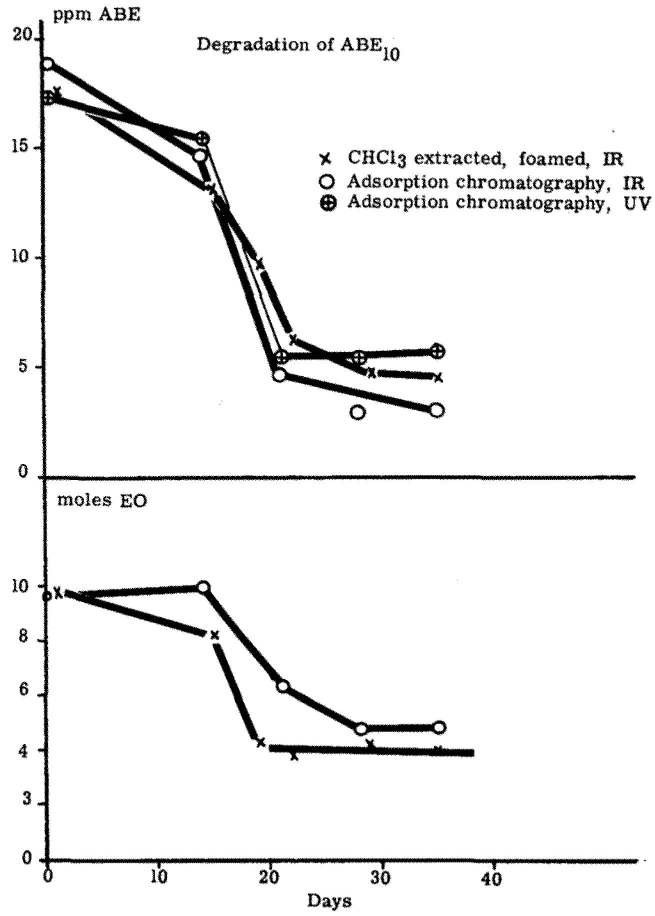

FIG. 4. Degradation of ABE$_{10}$ in river water die-away test.

sodium chloride to 250 or 500 ml of the test solution to give an 8% NaCl concn and extracting with three 100-ml portions of chloroform.

Foam stripping was accomplished by passing a stream of nitrogen through a gas dispersion tube in the bottom of a glass cylinder containing 100 ml of the test solution. The foam generated in this manner was removed through an overflow tube and collapsed with chloroform.

In all our work, the isolated ABE was diluted to a suitable volume with chloroform and the UV spectrum measured. The solvent was then removed and the residue examined using the IR procedure. The UV measurement gives a result related to the aromatic content of the sample and does not reflect changes in the hydrophobe or hydrophyl structures of the molecule.

TABLE II

Degradation of Nonyl ABE$_4$ in River Water Test

Day	Method	ppm	moles EO
0	foam	20	4
10	foam	10.4	3.9
34	extraction	8.4	2.4

Operation. Transfer, quantitatively, the ABE isolated by one of the procedures described to a 2-ml volumetric flask. Depending on the amt of ABE expected, add 0.5–2 ml of CS$_2$ by pipet and dissolve the residue. Scan the spectrum from 4000 to 950 cm^{-1} in a 1-mm cell vs. a CS$_2$ blank. Measure the absorbance of the 1120 cm^{-1} band and read the mg of EO/ml from the calibration curve. Calculate the absorbance ratio of the 1250/1120 cm^{-1} bands and read the moles of EO from the calibration curve. From these values, calculate the level of ABE using the following formula:

$$\text{ppm ABE} = (1000 \times \text{mg EO/ml} \times \text{ml CS}_2/\text{volume of river water sample}) \times (220 + 44 \times \text{moles EO})/44 \times \text{moles of EO}$$

where; 220 is the MW of nonyl phenol and 44 is the MW of the ethoxyl unit.

The calibration curve for mg EO/ml is plotted in Figure 2. Data for the concn series of ABE$_9$ and the series ABE$_n$ are superimposable. The calibration curve for moles EO is plotted in Figure 3.

Results. In order to investigate the degradation of the ethoxyl chain, die-away tests were carried out on a branched chain (nonyl) ABE$_{10}$. The branched chain material was chosen to retard loss of the ABE by degradation of the alkyl chain and thus allow time for changes in the ethoxyl chain to occur. Isolation of residual surfactant was made using the adsorption chromatographic procedure and the chloroform extraction followed by foam stripping. Examination of the extracts was by the UV and the IR procedures. Results are shown in Figure 4.

Examination of these results shows the biodegradation of the ethylene oxide chain to have occurred to an appreciable extent between the second and third weeks of the test. IR spectra of the residual ABE isolated at 0 and 34 days (Fig. 5) clearly shows the loss in ethoxyl, and the 34-day isolate is substantially identical to ABE$_4$.

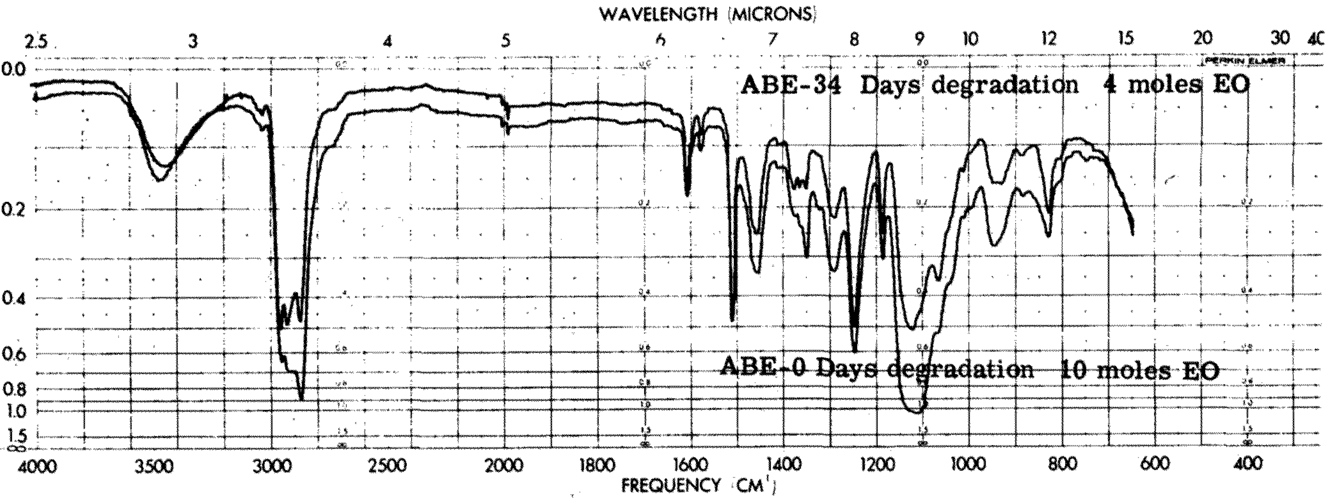

FIG. 5. IR spectra of ABE isolated from river water die-away test of ABE$_{10}$.

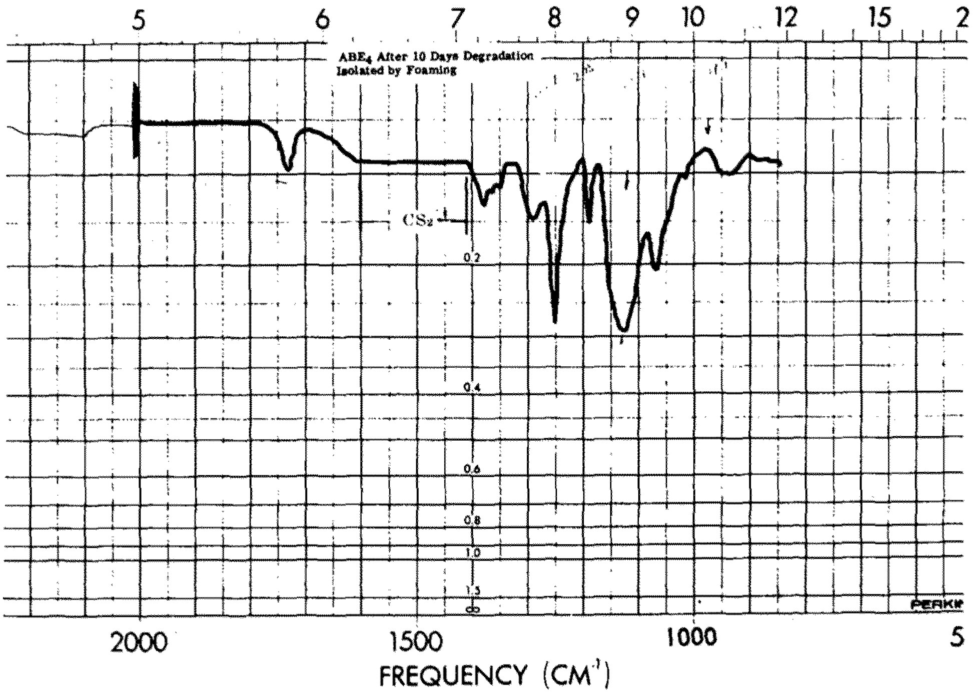

FIG. 6. IR spectrum of ABE isolated from river water die-away test of ABE$_4$.

In order to determine whether the ethylene oxide chain is degradable beyond the 4 moles indicated by these tests, a die-away test was conducted on a nonyl ABE$_4$. The results of this test, given in Table II, show the ether chain to be further degradable, but at a much slower rate.

In this study, it was shown that ABE with EO chain-length less than 3 is insoluble in water under conditions of the die-away test. This may account for the lack of further degradation of the EO chain.

The effect of biodegradation on the alkyl chain was investigated in an effort to confirm for this material the carboxylation mechanism proposed by Swisher (8) for ABS. The residual ABE was isolated from the ABE$_4$ die-away test at intervals by both foam stripping and chloroform extraction. The IR spectrum of the ABE isolated on the tenth day by foam stripping is shown in Figure 6. Little carboxylation is present in the foamed material as evidenced by lack of an absorption band in the carbonyl region. The chloroform extracted residue, however, shows a prominent carbonyl band at 1700 cm^{-1}.

After 34 days, all surface activity was lost as indicated by lack of foaming (although the solution still foamed, the foam was not sufficiently stable to carryover in the foam stripping procedure), and the chloro-

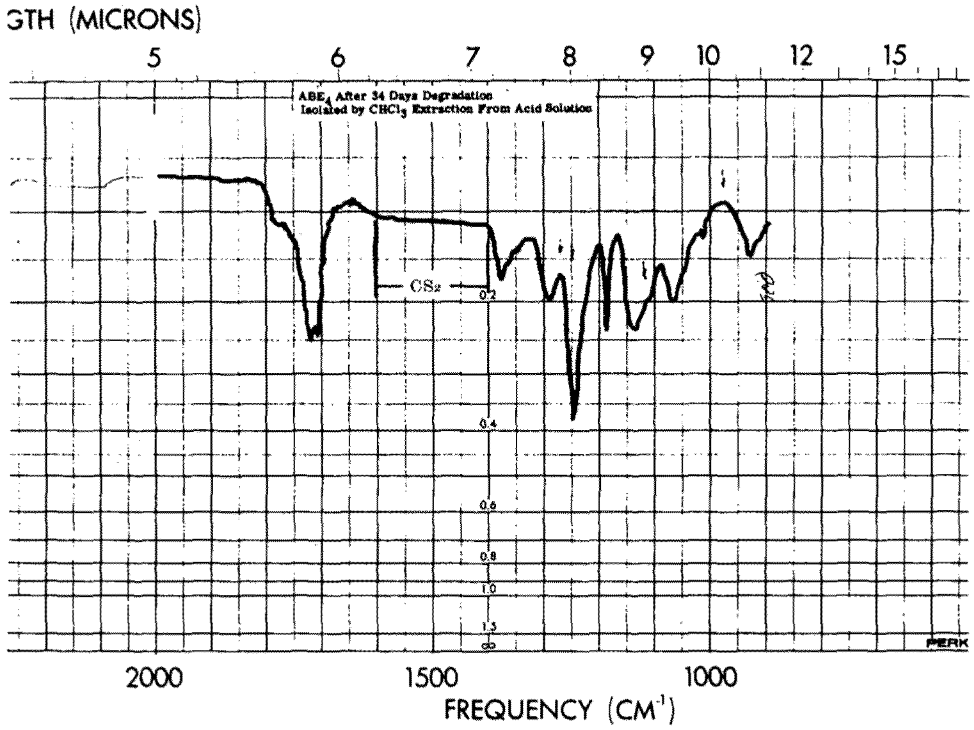

FIG. 7. IR spectrum of ABE isolated from river water die-away test of ABE$_4$.

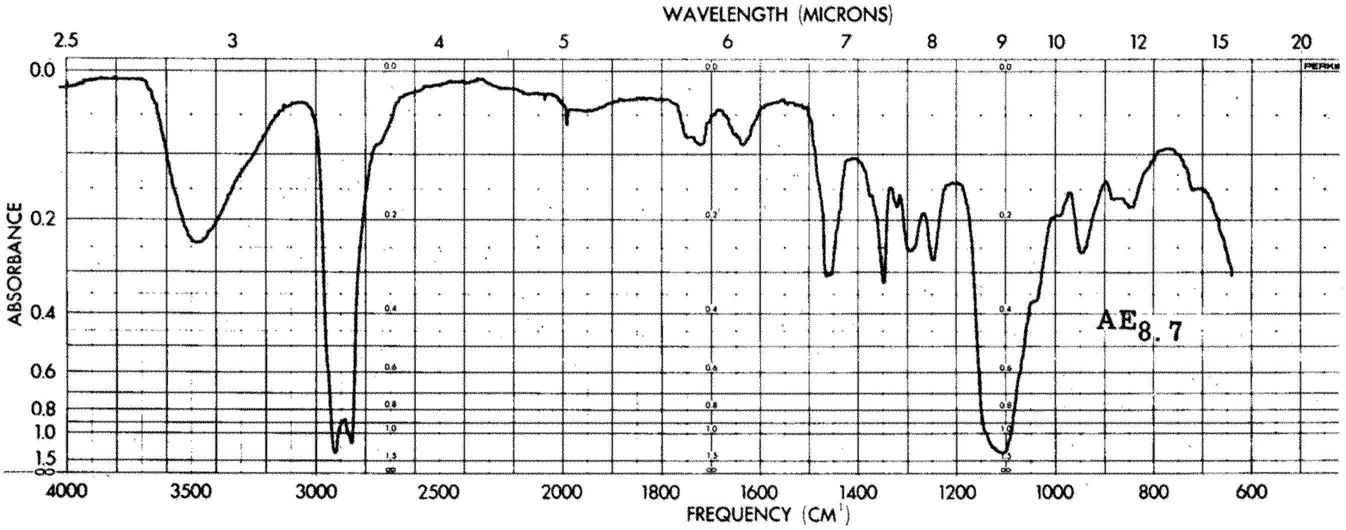

FIG. 8. IR spectrum of $AE_{8.7}$.

form extractable ABE amounted to ca. 60% of the initial level. Extraction made from strongly acid solution yielded ca. 75% of the initial concentration of material and this extract was strongly carboxylated, as shown in Figure 7.

It is postulated that carboxylated ABE is not very soluble by reason of its neutralization with calcium and other cations in neutral and basic solution and that hydrolysis to the soluble acids is responsible for their increased extractability from acid solution. This is supported by the finding that extraction from an alkaline solution yields uncarboxylated ABE in an amt equivalent to that obtained by foam stripping. This is illustrated in Table III.

Alkyl Polyethoxylates (AE)

Method. The IR spectrum of a commercial straight-chain (tetradecyl) alkyl polyethoxylate (AE) is shown in Figure 8. Absorption bands of interest include the aliphatic ether band at 1120 cm^{-1}, the CH bands at 2900 cm^{-1} and the primary OH at 1040 cm^{-1}. Our studies with AE degradation have been solely with the straight chain types which degrade so rapidly (as far as surface activity is concerned) that degradation in the EO chain need not be considered a factor. The 1120 cm^{-1} ether band may therefore be related to total residual AE.

Calibration. Prepare a series of CCl_4 solutions of a known AE ranging from 0.05–0.4%. Prepare a second series of CCl_4 solutions containing 0.3% of AE's containing the same alkyl group but varying ethoxyl chain length. Scan the spectra of the solutions from 4000–950 cm^{-1} in a 1-mm cell vs. a 1-mm cell filled with CCl_4. Measure the 1120 and 2900 cm^{-1} bands using tangent baselines. Calculate the absorbance ratio of the 1120–2900 cm^{-1} band. For each solution, calculate the mg EO/ml,

$$\text{mg EO/ml} = \text{mg AE/ml} \times (44 \times n)/\text{MW AE}$$

where, n = moles EO/molecule.

Plot calibration curves of the absorbance at 1120 cm^{-1} vs. mg EO/ml and the ratio of absorbance of the 1120–2900 bands vs. moles EO/molecule.

Procedure. Quantitatively transfer the AE isolated by foam stripping to a 2-ml volumetric flask and add 0.5 ml CCl_4. Scan the spectrum of the solution from 4000–950 cm^{-1} in a 1-mm cell using a 1-mm cell filled with CCl_4 as blank. Determine the absorbance at 1120 and 2900 cm^{-1}, calculate the ratio and determine the mg EO/ml and moles EO from the calibration curves. From these values, the level of AE can be calculated as follows:

$$\text{ppm AE} = \text{ml solution} \times \text{mg EO/ml} \times (n \times 44)/\text{MW of AE} \times 1000/\text{vol}$$

where, n = moles EO/molecule.

Results. At this time, only limited amt of work with AE materials has been done. Results of one test with a tetradecyl $AE_{8.3}$ are given in Table IV.

On the fifth day, the sample was extracted with chloroform and 5.7 ppm of unalkylated polyethylene glycol (PEG) recovered. The increase in moles of EO/mole AE through this test is apparently caused by carry-over during the foam fractionation procedure of the PEG produced on degradation. Such carry-over has been demonstrated on synthetic mixtures of AE and PEG.

TABLE III

Recovery of ABE from River Water Samples

Method	ppm ABE 20 days	23 days	34 days
Foam stripping	5.5	5.6	0
$CHCl_3$ extraction, basic	6.0	6.0	......
$CHCl_3$ extraction, acid	15.1	14.1	14.8

TABLE IV

Degradation of $AE_{8.3}$ in River Water Die-Away Test

Day	ppm AE[a]	mol EO/mol AE in extract
0	19.0	8.3
3	7.5	10.9
4	1.5	23.0
5	0	

[a] Corrected for PEG carry-over.

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