Analysis of Alkyl Ethoxylates by NMR

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ABSTRACT

Complete identification of an unknown sample of alkyl ethoxylate cannot presently be accomplished without some resort to "wet" chemistry. A new, fast, simple technique is presented, which allows complete characterization of alkyl ethoxylates in terms of average chain length of the alkyl portion and degree of polymerization.

INTRODUCTION

The analytical chemistry of nonionic surfactants is reviewed in a recent book (1). Gravimetric methods are tedious and require extreme care for accurate results with small quantities; furthermore they are not suited to quality control work. Instrumental methods appear to offer advantages, and IR and UV methods are discussed at length in Reference 1.

DISCUSSION

We were interested in determining the average alkyl chain length and average number of ethylene oxide units ($-CH_2-CH_2-O-$) per molecule in alkyl ethoxylates. NMR spectroscopy appeared to be the instrumental method of choice. Alkylphenol ethoxylates were investigated by Greff and Flanagan (2). By using the phenyl moiety as a 5H reference, they were able to establish average alkyl chain length and average degree of polymerization. Further examples of this method were described by Crutchfield et al. (3). While it is theoretically possible to extend this basic method to alkyl ethoxylates by using the -O-$\underline{H}$ resonance as an internal reference, variability of this resonance and interference by water or ethanol render the method of dubious value. In order to overcome this difficulty, Page and Bresler (4) used pyridine as solvent; this resulted in the shift of the CH_2-OH resonance to lower field, out of the -O-CH_2-CH_2-O envelope. However the degree of separation is variable and it is frequently difficult to tell where the signals merge. Furthermore interference by the -O-$\underline{H}$ resonance in the integral is still possible.

In recent years, trimethylsilylation of hydroxylated compounds has been used with increasing frequency (5). The reaction is rapid and quantitative and results in the conversion of -O-H to -O-Si$(CH_3)_3$. In the NMR spectrum of the trisilylated compounds the O-Si$(CH_3)_3$ resonance

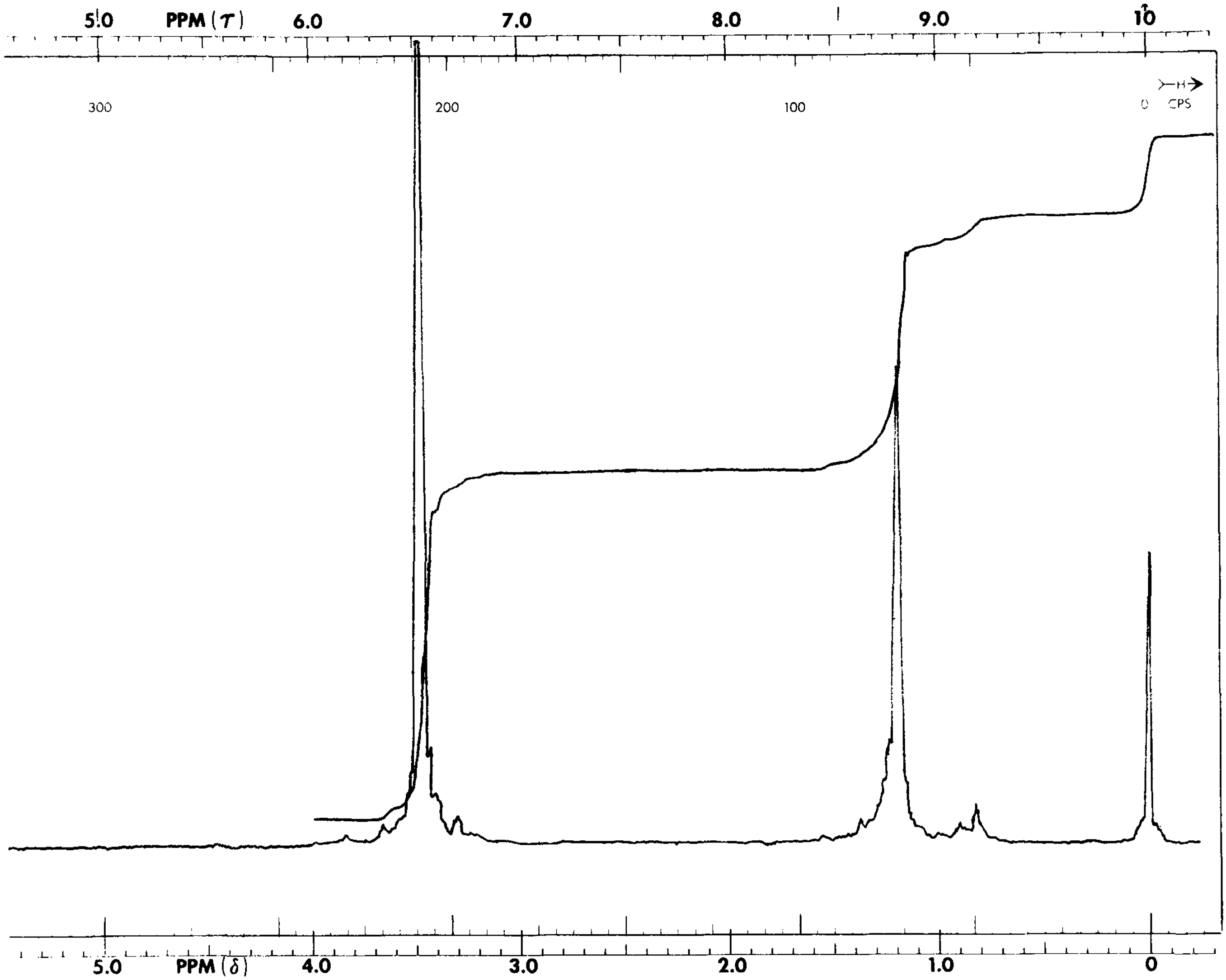

FIG. 1. Typical spectrum of trimethylsilylated alkyl ethoxylate.

TABLE I

Analyses of Commercial Alkyl Ethoxylates

	Average alkyl chain[a]		Average ethylene oxide units	
Sample	Stated	Found	Stated	Found
1	12-14	14	15	14.7
2	16-18	15.9	11	10
3	12-14	13	10	9.1
4	12-14	13	3	3.1

[a]Carbon units.

occurs close to 0 ppm, far removed from most other H resonances. Those facts suggested a novel approach to the average structure determination of alkyl ethoxylates. By trimethylsilylating the terminal -OH of an alkyl ethoxylate a sharp, distinct internal standard is obtained, i.e., nine hydrogens per molecule: $CH_3(CH_2)_m\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H \rightarrow CH_3(CH_2)_m\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}Si(CH_3)_3$. Thus the number of hydrogens responsible for the resonances at 0.7-1.5 and 3.0-3.9 ppm may be calculated and, consequently, the average alkyl chain length and average number of ethylene oxide units.

There are several advantages to this method over all other methods. In common with the other NMR methods, determinations are rapid, but in this case manipulation of HCl gas is avoided. The resonance of the $O\text{-}Si(CH_3)_3$ is always well separated from other resonances in the spectrum. Water and ethanol do not interfere as they are removed in the reaction. An increase in sensitivity of an order of magnitude is obtained in comparison with the method using the -O-H resonance as the internal standard (2,3); there is also an increase of 4.5-fold over the solvent shift method (4).

Clearly this method may be extended to the analysis of other hydroxylated compounds and, by analogy, to amines and thiols.

EXPERIMENTAL PROCEDURES

The trimethylsilyl derivatives of the alkyl ethoxylates were prepared by adding 0.2 ml hexamethyldisilazane and 0.1 ml trimethyl chlorosilane to a solution of ca. 50 mg alkyl ethoxylate in 1 ml dry pyridine in a 50 ml round bottom flask. The flask was closed and the contents mixed well for 30 sec. The reaction mixture was allowed to stand at room temperature for 5 min after which the solvent and excess reagent were removed under vacuum on a rotary evaporator at room temperature. The resulting oil and ammonium chloride mixture was taken up in ca. 0.4 ml deutero-chloroform and transferred to a NMR tube. The presence of ammonium chloride had no effect on the spectrum. The spectrometer employed in this work was a Varian A-60.

RESULTS

Figure 1 shows the clear separations of the resonance signals that were obtained. In order to calculate the original alkyl ethoxylate composition, the integral of the signal near 0 ppm is assigned to nine hydrogens of the $(CH_3)_3\text{-}Si$ on the terminal -OH. The integral at 0.7 to 1.5 ppm represents the hydrogens on the alkyl portion of the alkyl ethoxylates less the terminal $\text{-}CH_2\text{-}$, since it is connected to oxygen and will appear with the ethoxy portion of the spectrum at 3.0-3.9 ppm. Therefore, to calculate the average chain length of the alkyl portion, one must determine the number of hydrogens in the 0.7-1.5 ppm region and divide by two. One carbon must be added to allow for the oxygenated end of the chain. To calculate the number of ethylene oxide units, determine the number of hydrogens in the 3.0-3.9 ppm region, subtract two and divide by four.

The results obtained for several commercial alkyl ethoxylates by this method are presented in Table I. A comparison of the average composition, as stated by the manufacturer, with that determined spectrometrically shows good agreement.

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REFERENCES

1. "Nonionic Surfactants," Edited by M.J. Schick, Marcel Dekker, Inc., New York, 1967.
2. Greff, R.A., Jr., and P.W. Flanagan, JAOCS 40:118 (1963).
3. Crutchfield, M.M., R.R. Irami and J.T. Yoder, Ibid. 41:129 (1964).
4. Page, T.F., Jr., and W.E. Bresler, Anal. Chem. 36:1981 (1964).
5. Pierce, A.E., "Silylation of Organic Compounds," Pierce Organics, Inc.

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