Determination of Ethylene Oxide Content in *n*-Alcohol Ethoxylates by Proton Nuclear Magnetic Resonance Spectroscopy[1]

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Proton Fourier transform nuclear magnetic resonance spectral data were collected on *n*-alcohol ethoxylates and used to calculate the percent ethylene oxide (EO) content of the *n*-alcohol ethoxylate without an internal or external standard. The accuracy and precision of the method were determined from ten repetitive analyses of hexaethylene glycol mono *n*-dodecyl ether. The standard deviation was 0.23 wt% EO with a relative standard deviation of 0.40%. The method had a relative error of +0.55% and an absolute error of +0.32% EO.

KEY WORDS: Ethylene oxide, *n*-alcohol ethoxylate analysis, NMR.

The classical method for determining wt% ethylene oxide (EO) in an *n*-alcohol ethoxylate is by the hydroiodic acid (HI) cleavage method (1,2). In this method, the sample is refluxed with 57% aqueous HI under a blanket of CO_2 for 1.5 h. The HI cleaves the EO units and forms diiodoethane, which is then quenched with water to form iodine. The iodine is titrated with standardized sodium thiosulfate solution, and wt% EO is calculated. This method takes several hours to complete. In comparison, determination of EO content by proton nuclear magnetic resonance (NMR) spectroscopy takes about 15 min.

The NMR method to determine wt% EO is by no means new (3–6). However, this is the first validation of proton data from a Fourier transform NMR spectrometer. This method is considered nonclassical because there are no internal or external standards. It is fast, automatable and only uses twenty micrograms of material.

EXPERIMENTAL PROCEDURES

A Bruker AMX 300 spectrometer (Burlington, Ontario, Canada) was used in this study. One drop of *n*-alcohol ethoxylate, CH_3-$(CH_2)_n$-$C_\beta H_2$-$C_\alpha H_2$-$(O$-CH_2-$CH_2)_m$-OH, is added to an NMR tube containing 0.5 mL of deuterated chloroform and shaken well. Care should be taken not to use excess ethoxylate to prevent spectral line broadening. The key parameters for running a proton spectrum are: time domain, 16k; number of scans, 16; proton pulse width, 30°; acquisition and delay times, 9 s; line broadening, 0.1 Hz; receiver gain, maximized.

In setting up the parameters data collection, the T_1 values were determined by the inversion recovery method. The T_1 values will vary, depending on sample concentration and impurities. We found T_1 values in a typical sample to be as follows (seconds): EO (OCH_2), 0.77; $C_\alpha H_2$, 0.84; $C_\beta H_2$, 0.85; $(CH_2)_n$, 1.11; CH_3, 2.50. It is important to avoid saturation of the methyl resonances are the basis of the quantitation.

The free induction decay collection time is about 3 min. All chemical shifts are in parts per million and referenced to the protio impurity in the deuterated chloroform solvent. A typical spectrum is shown in Figure 1.

The integral area is divided into three separate regions (Fig. 1). Region 1 is the methyl (CH_3) resonance from 0.50 to 0.93 ppm. This region is normalized to a value of 3, to represent three methyl protons from the alcohol ethoxylate. Region 2 represents the methylene chain $(CH_2)_n$ resonances from 0.93 to 1.70 ppm. Region 3 shows the methylene next to oxygen (OCH_2) resonances from 3.1 to 4.0 ppm. The integral values from the three integrated regions are used to calculate the % EO.

The calculation is outlined below with several intermediate steps. To determine the average number of carbons in the precursor *n*-alcohol, divide the area of Region 2 by 2 for the two protons in the methylene. Add two carbon atoms for the terminal methyl and the α carbon:

$$\text{average carbon chainlength of precursor ROH} = [(\text{Region 2})/2] + 2 \quad [1]$$

To calculate the average molecular weight (MW) of the *n*-alcohol, divide Region 2 by 2 for the two protons in the methylene. Multiply by 14, the MW of a methylene unit. Add 46, the MW of the terminal methyl, the α methylene and the hydroxyl group:

$$\text{average MW of precursor ROH} = [(\text{Region 2})/2 \cdot 14] + 46 \quad [2]$$

The number of EO groups attached is calculated by subtracting 2, for the α methylene protons, from Region 3, and then dividing by 4, the number of protons in EO:

$$\text{average moles EO per ethoxylate} = [(\text{Region 3}) - 2]/4 \quad [3]$$

The MW of the *n*-alcohol ethoxylate EO chain is obtained by multiplying the number (#) of EO units in the chain by 44, the MW of EO:

$$\text{average MW of the EO chain} = (\#\ \text{EO}) \cdot 44 \quad [4]$$

The average MW of the *n*-alcohol ethoxylate is obtained by adding the MW of the EO chain to the average MW of the initial alcohol:

$$\text{average MW of ethoxylate} = [(\text{MW EO}) + (\text{MW ROH})] \quad [5]$$

The % EO by weight is obtained by dividing the EO chain MW by the total average MW and multiply by 100:

$$\%\ \text{EO by weight} = [(\text{MW EO})/(\text{MW ethoxylate}) \cdot 100 \quad [6]$$

As a trial calculation, the % EO is calculated for the spectrum in Figure 1. The result is 39.84% EO.

RESULTS AND DISCUSSION

Alcohol ethoxylates are named by designating the carbon number of the alcohol first, followed by the wt% EO. For

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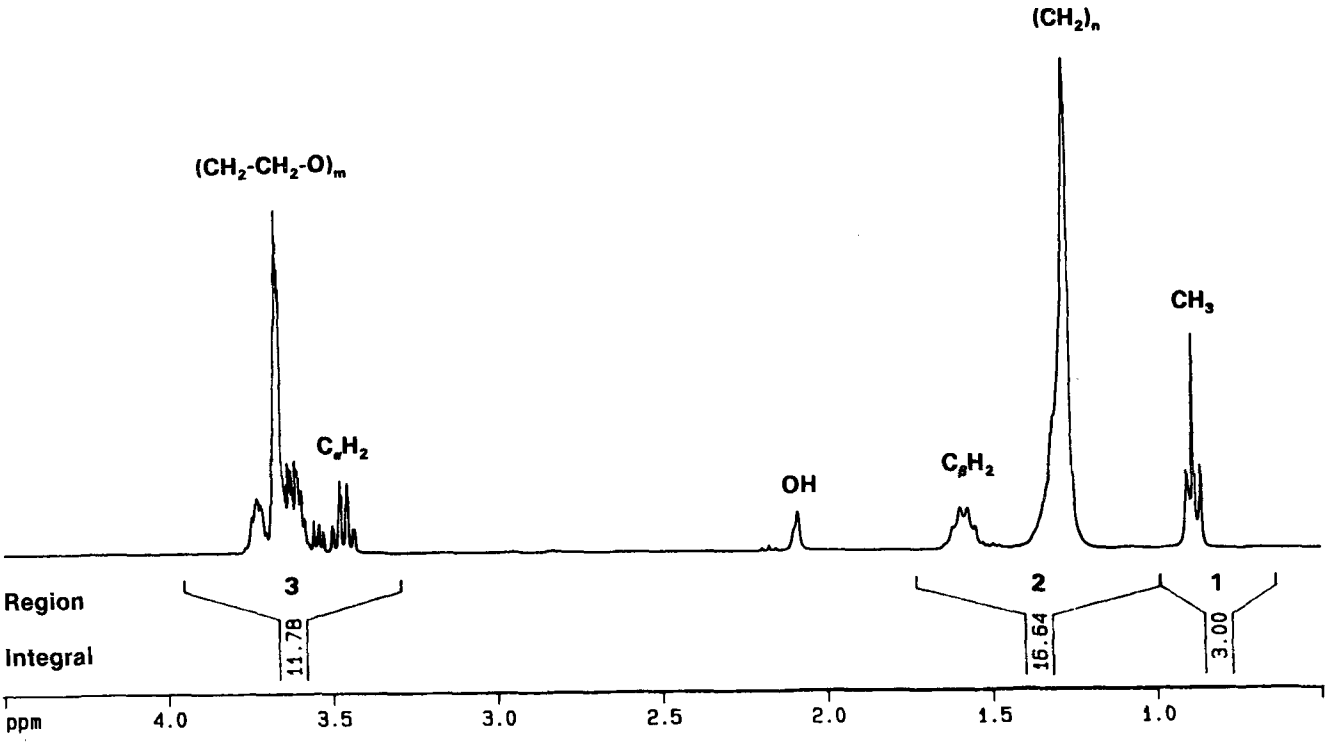

FIG. 1. Proton spectrum of alcohol ethoxylate HO-$(CH_2$-CH_2-$O)_m$-$C_\alpha H_2$-$C_\beta H_2$-$(CH_2)_n$-CH_3.

example, hexaethylene glycol mono *n*-dodecyl ether is named 12-59.

The accuracy and prevision was tested with hexaethylene glycol mono *n*-dodecyl ether ($C_{12}EO_6$) purchased from Nikko Chemical Co. Ltd., Tokyo, Japan. The purity of the standard was checked. Gas-chromatographic analysis showed 97.7% $C_{12}EO_6$. Impurities were less than 0.1% dodecanol and 2.2% dodecyl ethoxylate molecules containing one to ten EO units. Liquid chromatography found 58.40% EO, which was used as the true value of % EO in calculation of accuracy.

The standard was analyzed ten times (in % EO: 58.20, 58.83, 58.82, 58.77, 58.75, 58.84, 58.67, 58.81, 58.45 and 59.04) by the NMR method with no more than three replicates per day. The average wt% EO was 58.72 with an SD of 0.23 and an absolute error of +0.32%. The 99% confidence level of the mean was calculated to be 58.72 ± 0.24% EO. Thus, there is a 99% probability that the measured average is ± 0.24% EO off the real mean.

To further test the precision, a sample matrix was selected that spanned the typical ranges of alcohol and ethoxylate chainlengths normally observed in our laboratory. Each was analyzed five or more times by independent replicate measurement for % EO. No more than three replicates per day were analyzed. Results are listed in Table 1. When tabulated by moles of EO attached to the alcohol, one notices that the relative standard deviation (RSD) decreases as the number of moles increases (see Table 2).

NMR and HI cleavage data have been collected over a typical range of samples. A scatter plot of the % EO determined by NMR and the HI cleavage methods is given in Figure 2. Applying linear regression to the data shows that there is a 99.9% correlation of the data. A slope of one would indicate that the methods are identical. The slope is 0.94. The NMR method has lower results for low EO percentages and higher results for high EO percentages as compared to the HI cleavage method.

TABLE 1

Percent Ethylene Oxide (EO) in *n*-Alcohol Ethoxylates by Proton Nuclear Magnetic Resonance Spectroscopy

Sample	810-40[a] (% EO)	1412-40 (% EO)	1214-20 (% EO)
	40.34	40.92	19.48
	40.87	40.97	19.38
	41.14	41.22	19.89
	40.78	40.79	19.97
	41.20	40.99	19.95
	40.67		19.65
	40.56		19.95
XBar	40.79	40.98	19.74
RSD	0.75	0.38	1.21

[a]The samples are identified with the first numbers representative of the number of carbons in the starting alcohol. The hyphen separates a second number representing the % EO. RSD, relative standard deviation.

Application of the *t*-test to the averages shows that the two processes are operating at the same average within a 95% probability. The SDs have a 99% probability that they are not significantly different. Individual differences show there is greater than 99% probability that the methods are systematically different.

This method applies to linear alcohol ethoxylates. Branched alcohol ethoxylates will introduce error in the %

TABLE 2

Relative Standard Deviations Tabulated by Moles of EO Attached to the Alcohol[a]

Sample	Moles EO	Analyses	RSD %
1214-20	1.1	7	1.20
810-40	2.3	7	0.75
1412-40	3.2	5	0.38
810-60	4.7	20	0.42
12-59	6	10	0.40

[a]See Table 1 for abbreviations.

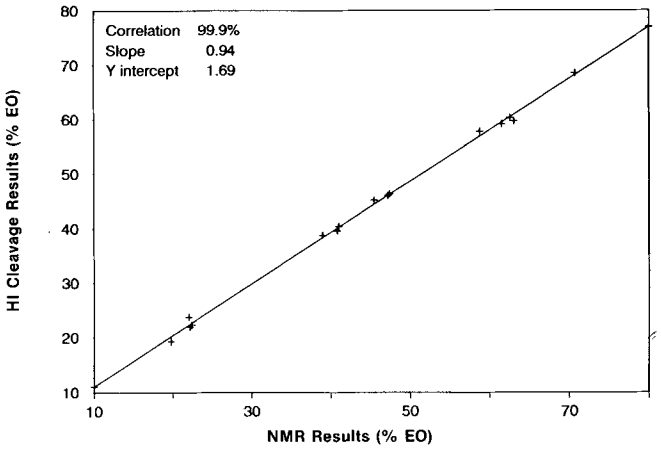

FIG. 2. Scatter plot of nuclear magnetic resonance (NMR) results *vs.* hydroiodic acid (HI) cleavage results. EO, ethylene oxide.

EO. A branched methyl at the α carbon position will be counted as a methylene. This has little effect on the results. However, if the branching occurs elsewhere in the chain, the methyl branch will be counted in the methyl region. This increases the methyl integral, decreases the calculated MW of the alcohol and results in increased % EO. The more branching, the greater the error.

Poly(ethylene glycol) (PEG) is a by-product formed during ethoxylation processes and is contained in the ethoxylation product. Theoretically, the NMR method takes into account the EO units contained in the PEG. However, it does not take into account the hydroxyl units attached to the PEG. This introduces a small amount of error based on the MW of the PEG (the higher the MW, the less error) and the percentage concentration of PEG (the higher the concentration of PEG, the more error). A preliminary investigation showed that spiking a sample with PEG resulted in the qualitatively expected increase in % EO as measured by the NMR method.

The hydroxyl resonance should be identified in every sample. Water will coalesce with the hydroxyl resonances. This may cause a broadening of the hydroxyl resonance or a shifting under Region 3. In either case, the amount of EO detected would be higher in these scenarios.

Alcohol ethoxylates are hygroscopic. Care should be given to keeping and preparing dry samples. This may include making the analysis samples fresh with dried deuterated chloroform.

When the hydroxyl resonance interferes with integration of the areas under consideration, it may be replaced with deuterium. This is accomplished by shaking the sample in $CDCl_3$ with D_2O and centrifuging the sample. The process also places PEG in the water layer. The $CDCl_3$ will be the bottom layer. The spectrum can then be reacquired. This procedure may be repeated more than once. A salt solution of D_2O might be required to prevent the formation of an emulsion.

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