Determination of The Degree of Ethoxylation of Nonionic Surfactants by Elemental Analysis

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This report presents a fast, accurate analytical method for the determination of the degree of ethoxylation of nonionic ethoxylated surfactants based on the indirect determination of the oxygen content of the surfactant using a C,H,N elemental analyzer. The weight percent oxygen is then easily translated into ethylene oxide (EO) content. This method was found to be fairly accurate in determining the EO content of surfactants containing up to 20 mol EO, which is equivalent to about 80% EO content in most common nonionic surfactant ethoxylates. A comparison of the results obtained with this procedure versus hydroxyl value and HI cleavage methods is also presented in this paper.

The determination of the degree of ethoxylation of alkylphenol ethoxylates and fatty alcohol ethoxylates is a common task in the surfactant industry. The classical methodologies for this analysis are cloud point (1), hydroxyl value (2) and hydrogen iodide cleavage (3), which are tedious and very time consuming.

A more modern approach for determining the degree of ethoxylation is by high performance liquid chromatography (HPLC). HPLC has been used successfully to determine the EO content of a variety of nonionic and anionic surfactants (4, 5). However, this method can also be time consuming, with the average analysis time between 30 and 40 min/sample. This does not include sample preparation, which can be complex and time consuming when surfactants need to be derivatized to make them UV detectable.

A new approach using microprocessor controlled elemental analysis offers advantages in time, accuracy, precision and ease of determination of EO content.

Nonionic ethoxylated surfactants are prepared by the addition of ethylene oxide to a hydrophobic compound containing active hydrogen atoms. Their general structure is $R(CH_2CH_2O)_ROH$, where R represents the hydrophobic group (normally alkylphenol or fatty alcohol) and n represents the number of mol EO. As the number of EO units increases in the molecule, the weight percent of elemental oxygen increases proportionally. As a result of this, the degree of ethoxylation can be related to the weight percent of oxygen according to:

$$\% \text{ EO} = \frac{(n + 1) \times 1}{R + (n \times 44)} \times 100 \qquad [1]$$

where R is the molecular weight of the hydrophobe and n is the number of mol EO.

Use of a C,H,N determinator provides a precise and fast measurement of the total carbon, hydrogen and nitrogen content in a compound. The weight percent oxygen of the ethoxylates can then be easily determined in the elemental composition of the compound and translated into the degree of ethoxylation of the molecule using relationship [1].

This paper presents the results obtained in the measurement of the ethylene oxide content of several commercial nonionic surfactants using C,H,N determinator. The results are compared to those obtained using the classical hydroxyl number and HI cleavage methods.

EXPERIMENTAL

A Leco CHN-600 elemental analyzer was used in this work. The CHN-600 uses a combustion technique for the simultaneous determination of carbon, hydrogen and nitrogen content of organic compounds.

The samples are combusted in a pure oxygen atmosphere at 950 C, where carbon dioxide, water, nitrogen, nitrogen oxides and sulphur oxides are produced. The sulphur oxides are removed by calcium oxide. For nitrogen determination, an aliquot of gas is taken and carried by helium through various reagents and catalysts for the removal of CO_2, H_2O and reduction of NO_x to N_2; the N_2 is measured by a thermal conductivity detector. Simultaneously, the level of CO_2 and H_2O are selectively measured by infrared detection for the determination of carbon and hydrogen.

In this experimental work, the instrument was calibrated using a lab-prepared sample of nonylphenol ethoxylate containing precisely 64.1% of ethylene oxide by weight, which constitutes an elemental composition of 64.3% carbon, 9.7% hydrogen, 0% nitrogen and 26.2% oxygen. Liquid samples were weighed directly into a tared tin capsule, and solid samples were heated until completely liquid prior to analysis. Sample size was ca. 100 mg of material. Total analysis time, including sample preparation, for each sample is ca. six min. The analyzer generates a report listing the content of carbon, hydrogen and nitrogen; the weight percent oxygen is calculated by difference.

All samples analyzed were sulphur- and nitrogen-free.

RESULTS AND DISCUSSION

Table 1 shows the relationship between weight percent oxygen and degree of ethoxylation, expressed in terms of weight ethylene oxide and number of moles of ethylene oxide. The table corresponds to the values of nonylphenol ethoxylates; similar relationships can be obtained for ethoxylates based on octylphenol, fatty alcohols, etc. In fact, because the molecular weight of these compounds is in the range of 190 to 220, the relationships are of a similar order of magnitude.

The accuracy of the weight percent oxygen in this study with the C,H,N Determinator is about 0.2. Consequently, the determination of the degree of ethoxylation of surfactants containing up to 80% ethylene oxide can be carried out with a good degree of accuracy. Above this level of ethoxylation, the results obtained with this method are subjected to an error of about one to two

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TABLE 1

Relationship Between Percent Oxygen and Degree of Ethoxylation[a]

Oxygen (%)	E.O. (Moles)	E.O. (%)
12.1	1	16.6
15.6	2	28.6
18.2	3	37.5
20.2	4	44.4
21.8	5	50.0
23.1	6	54.5
24.2	7	58.3
25.2	8	61.5
25.9	9	64.3
26.6	10	66.7
27.3	11	68.7
27.8	12	70.6
28.3	13	72.2
28.7	14	73.7
29.1	15	75.0
29.4	16	76.2
29.7	17	77.3
30.0	18	78.3
30.3	19	79.2
30.5	20	80.0
–	–	–
32.2	30	85.7

[a]Expressed as moles of ethylene oxide and percent ethylene oxide in nonylphenol ethoxylates.

moles E.O. This, in our opinion, is acceptable for a high degree of ethoxylation.

Table 2 presents the results obtained in several commercial ethoxylated nonionic surfactants based on nonylphenol and fatty alcohols. The table includes the nominal content of ethylene oxide as reported by the manufacturer and the values obtained using the elemental analyzer, the hydroxyl value method and the HI cleavage technique. The results show a good correlation between the nominal degree of ethoxylation and the experimental values.

TABLE 2

Determination of the Degree of Ethoxylation Using Elemental Analysis, Hydroxyl Number and HI Cleavage

	Weight percent E.O.			
Hydrophobe	Nominal	Elemental analyzer	Hydroxyl value	HI cleavage
Nonylphenol	22.6	21.8	23.6	21.0
Nonylphenol	64.0	63.9	65.1	63.0
Nonylphenol	74.8	75.1	75.2	73.6
Nonylphenol	85.6	86.4	87.4	85.0
Lauryl alcohol	32.5	32.2	32.3	31.9
Tridecyl alcohol	47.4	47.0	47.6	46.5
Neodol 25	61.1	62.3	63.4	61.2
Alfol 810	83.8	85.4	85.1	82.0

The major advantage of the elemental analyzer is its ability to generate results in minutes as compared to classical methods which require about two hr.

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