Application of NMR for the Determination of HLB Values of Nonionic Surfactants

ABSTRACT

Hydrophilic lipophilic balance (HLB) values for various commercial nonionic surfactants have been determined by means of high resolution NMR. The results are in good agreement with given HLB values. The method is rapid, nondestructive and requires only small samples.

The hydrophilic lipophilic balance (HLB) (1) is one of the most important properties of a surfactant. The HLB value expresses the ratio of water soluble groups to oil soluble groups in the same molecule and thus determines the type of emulsion that is likely to be formed.

The HLB values of most nonionic surfactants can be calculated from the theoretical composition by weight of the molecule. Such a calculation, however, gives only an approximation. For most polyhydric alcohol esters of fatty acids, approximate HLB values can also be calculated from the saponification number of the ester and the acid number of the fatty acid (2).

One experimental method for HLB determination involves the preparation of a series of emulsions covering the entire range of HLB values (3). Both this technique and the method based upon polarity index (4) are quite time consuming. Recently gas chromatographic (5), titration (6) and surface tension (7) methods have also been published.

NMR has been utilized previously for end group analysis and number average molecular weight determinations of nonionic surfactants (8). Crutchfield et al. (9) have employed NMR for the structural determination of detergents. The technique has also found use in the measurement of ethylene oxide units in nonionic surfactants (10).

We have now employed NMR as a direct measure of HLB values utilizing the empirical relationship: $\text{HLB} = \frac{AH}{5\,(AH + BL)}$, where, A = 15, B = 10, H = relative integration value of hydrophilic protons and L = relative integration value of lipophilic protons. A and B may be considered constant for all nonionic surfactants examined.

Figure 1 shows the NMR spectrum of a typical polyoxyethylene alkyl aryl ether (Renex 697). The hydrophilic protons of the polyoxyethylene chain appear in the vicinity of 4.0 ppm. All other protons are considered as lipophilic.

Table I summarizes the results obtained using the above method for the determination of the HLB values of commercial Atlas surfactants. For comparison, the HLB values given by the manufacturer are included (11). All spectra were measured on a Varian Model T-60 NMR spectrometer, using 10% solutions of surfactant in deuterochloroform or carbon tetrachloride and TMS as internal standard.

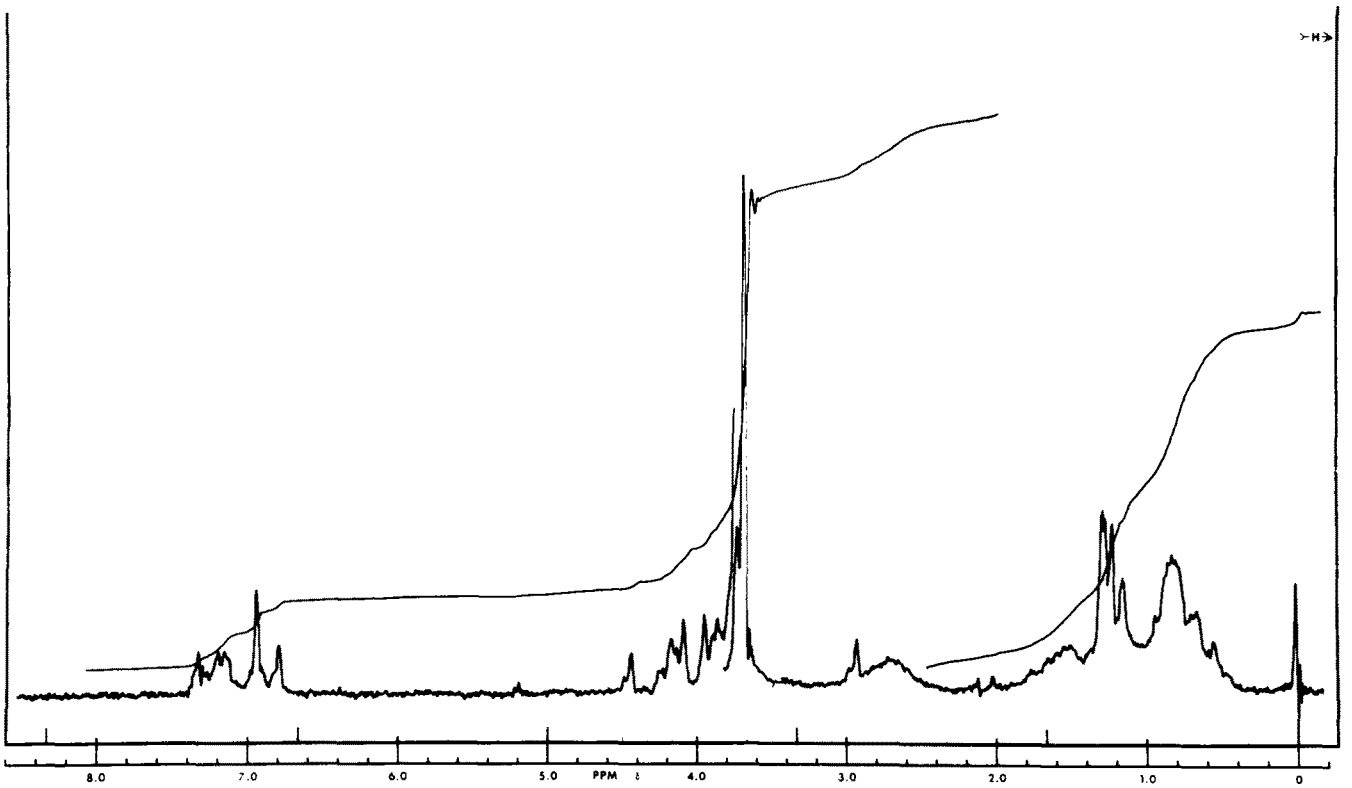

FIG. 1. NMR spectrum of a typical polyoxyethylene alkyl aryl ether (Renex 697).

TABLE I

HLB[a] Values of Commercial Nonionic Surfactants

Surfactant	HLB by NMR	HLB given
Renex 30	14.0	14.5
Renex 650	17.5	17.0
Renex 678	16.0	15.0
Renex 690	14.1	13.3
Renex 697	11.3	10.9
Span 80	4.6	4.3
Span 40	7.1	6.7
Myrj 45	11.6	11.1
Myrj 49	15.2	15.0
Myrj 52	17.5	16.9
Myrj 59	19.0	18.8
Tween 20	16.6	16.7
Tween 40	15.4	15.6
Tween 60	15.8	14.9
Tween 80	15.2	15.0
Tween 81	10.2	10.0
Tween 85	11.4	11.0
Brij 30	10.4	9.7
Brij 35	17.5	16.9
Brij 52	6.4	6.4
Brij 56	12.7	13.0
Brij 58	16.0	15.7
Brij 72	5.3	4.9

[a]HLB = hydrophilic lipophilic balance.

The HLB values given in Table I show good agreement with given values. NMR thus provides a convenient method for rapid HLB determination of polyethoxylated nonionic surfactants, even if no prior knowledge of sample composition is available.

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