Polarity Index of Surface-Active Ethylene Oxide Adducts

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Abstract

The polarity indexes of surface-active ethylene oxide adducts with varying lipophilic parts and varying content of ethylene oxide have been studied. An interesting relationship has been found between the fraction of ether groups and polarity index, which gives a polarity index line for every type of ethylene oxide adduct. It permits the calculation of polarity indexes of all ethylene oxide adducts of known composition with known polarity index of the lipophilic part. It also gives valuable information for evaluating different lipophilic substances as raw materials for ethylene oxide adducts.

Introduction

A very important property of surface active agents is their hydrophilic-lipophilic balance. Griffin (2) has introduced the HLB-number for characterizing this balance. It is determined by studying the behavior of an emulsifier in different emulsion systems. The HLB-scale has been chosen so that a linear relationship is obtained between HLB-number and fractions of surface-active agent in mixtures of two surface-active agents. No details are given in the literature about the determination of the HLB-scale but it is said to be very time-consuming. A determination by comparison can be made by other laboratories if surface-active agents with known HLB-numbers are available. Even so the determination is very time-consuming. Lately a gas chromatographic method for determination of the HLB-number in the interval 2–17 has been published by Becher and Birkmeier (1). The method greatly simplifies the determination of the HLB-number but is, for certain substances, very sensitive to the column temperature used for the determination. Formulas for calculating the approximate HLB-number of certain types of surfactants have been published (3,4). For simple ethylene oxide adducts, where ethylene oxide is the only hydrophilic component Griffin suggests the calculation of the HLB-number as E/5, where E is the per cent fraction of ethylene oxide.

In 1963 a new unit for characterizing the hydrophilic-lipophilic balance was introduced by Huebner (5), namely, polarity index. It is determined from the carbon number, corresponding to methanol, when methanol and normal hydrocarbons are separated on a gas chromatographic column with the surfactant as the stationary phase. The determination is easily performed and is very insensitive to the practical gas chromatographic conditions. The chemical composition of the substance to be analyzed need not be known.

Huebner has shown that there is a linear relationship between polarity index and fractions of surfactant in mixtures of two surfactants. A linear relationship was also found between polarity index and HLB-number for four products, for which the HLB-numbers were available.

The possibilities of characterizing the hydrophilic-lipophilic balance of ethylene oxide adducts of different lipophilic substances by means of polarity index have been investigated in the work reported here. An attempt has also been made to determine numerically the difference in polarity index of an alkylamine ethylene oxide adduct in neutral and acidic medium.

Experimental Procedures

The ethylene oxide adducts were freed of polyglycols by extraction from a suspension in a 5M sodium chloride solution into ethyl acetate according to the method described by B. Weibull (7). The ethyl acetate solution was evaporated and the adducts separated from inorganic salt by dissolving the residue in ethanol-acetone 1:1 and filtering. The hydroxyl values of the pure adducts were then determined with acetic anhydride.

Gas chromatographic columns of the adducts, containing 75% acid-washed Chromosorb W and 25% of the adducts, were prepared by depositing the adducts on the Chromosorb from a methylene chloride solution. The columns were 1.8 m long and had a diameter of 4 mm. Gas chromatograms of 0.2 μliter of a mixture of equal parts of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane, together with 0.6 μliter methanol and 0.4 μliter air were run at 65 C on a Beckman GC-2A gas chromatograph. The helium carrier gas flow was adjusted so that the time of each run was 15–20 min. From the gas chromatograms the polarity indexes of the substances were determined.

Polarity indexes of some fatty amine ethylene oxide adducts were determined after transforming the amines into their sulfuric acid salts by adding an amount of sulfuric acid equivalent to the amine groups of the adducts.

The polarity index of Carbowax 20M, which is a polyethylene glycol with a molecular weight of 15.000–20.000, was also determined.

Calculations

The polarity indexes, P, have been calculated according to Huebner's formula,

$$P = 100 \cdot \log (C - 4.7) + 60 \qquad [1]$$

where C is the carbon number of the methanol, obtained from a graph of the logarithms of the hydrocarbon retention times against the number of carbon atoms in the hydrocarbons. Huebner has shown that there is a linear relationship between polarity index and amount of surfactant in mixtures of two surfactants. This relationship may be written

$$\gamma \cdot P_1 + \lambda \cdot P_2 = P_{1+2} \qquad [2]$$

where γ and λ are the amounts of the emulsifiers ($\gamma + \lambda = 1$), P_1 and P_2 their polarity indexes and P_{1+2} the polarity index of the mixture. The relationship has been adapted to single ethylene oxide adducts.

The formula for an ethylene oxide adduct can be written

$$L[\,'(CH_2OCH_2)_a{}'CH_2OH]_k$$

where L is the lipophilic part of the molecule; for instance $ROCH_2$–, $RCOOCH_2$– or –$CH_2N(R)CH_2$–, k is the number of ethylene oxide chains in the molecule and $a \cdot k$ the number of –CH_2OCH_2–groups.

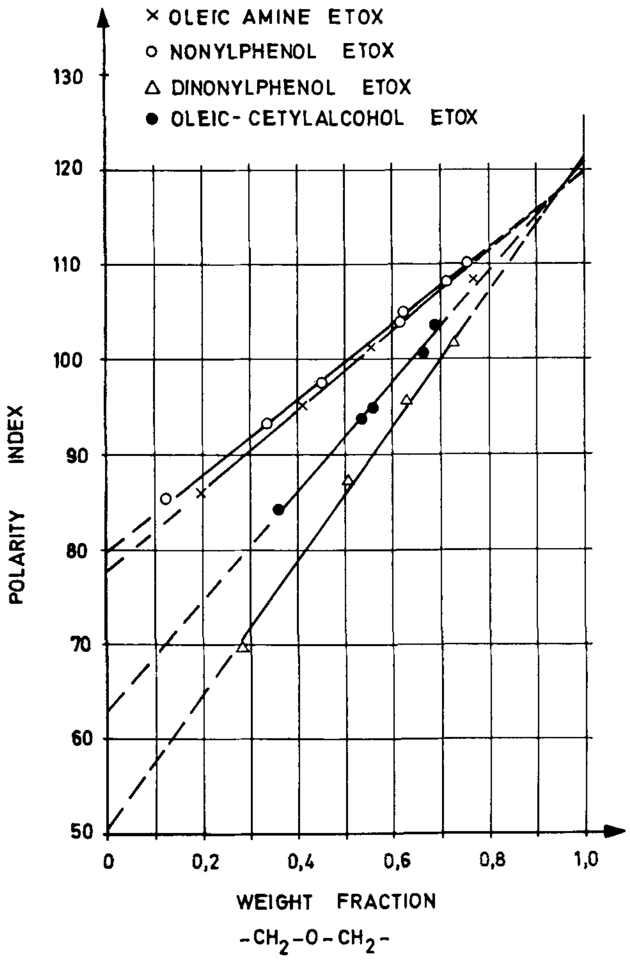

FIG. 1. Plot of polarity indexes of ethylene oxide adducts with differing lipophilic parts against weight fraction of ether units in adducts.

These groups will be called ether units in spite of the fact that, for example, in fatty alcohol adducts, the ethylene oxide is coupled to the alcohol by an ether unit not included above.

If the molecule is divided at the ′–marks as shown above, i.e., along unpolar carbon-carbon bonds, one obtains three units, L–, $-CH_2OH$ and the ether unit. The relationship between L– and $-CH_2OH$ is constant for every type of ethylene oxide adduct and they can be regarded as one unit, d, with constant polarity index P_d, the other being the ether unit, e, with the polarity index P_e.

Equation 2 for an ethylene oxide adduct, ed, with the polarity index P_{ed} can thus be written

$$f \cdot P_e + (1\text{-}f) \cdot P_d = P_{ed} \quad [3]$$

or

$$P_{ed} = (P_e - P_d) \cdot f + P_d$$

where f is the weight fraction of ether units, i.e.,

$$f = 44\ (n\text{-}k)/M_{ed} \quad [4]$$

M_{ed} is the molecular weight of the adduct and n the average number of ethylene oxide units added to form one molecule of the adduct.

For ethylene oxide adducts with the same lipophilic part, $(P_e - P_d)$ and P_d are constants. If the relationship in equation 3 is valid, a straight line should be obtained when plotting P_{ed} against 44 $(n\text{-}k)/M_{ed}$. The value when extrapolating the line to the y axis should be P_d and the slope of the line $P_e - P_d$.

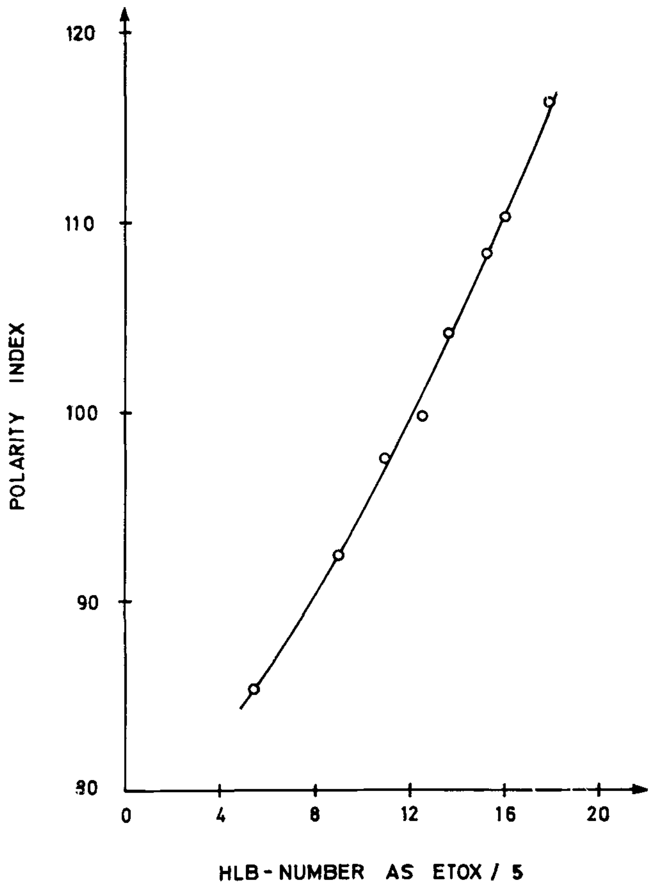

FIG. 2. Plot of polarity index against HLB-number calculated as one fifth of the per cent fraction of ethylene oxide for nonylphenol adducts.

Results

In Figure 1 experimentally determined polarity indexes of nonylphenol, dinonylphenol, oleic amine and oleic-cetyl alcohol ethylene oxide adducts are shown as a function of the fraction of ether units in the molecule. Straight lines are obtained which shows that the relationship in equation 3 is valid. The coefficients of correlation for the lines are 0.999, 0.999, 0.997 and 0.997, thus very close to 1.000. The polarity indexes of the lipophilic parts are obtained at the crossing of the extrapolated lines and the y axis. All lines converge to one point where the ether units are equal to 100% which is the limiting value of all ethylene oxide adducts and gives the polarity index of the ether unit as 121. The standard deviations of the scatter of the polarity index values about the regression line are for the nonylphenol, dinonylphenol, oleic amine and oleic-cetyl alcohol ethylene oxide adducts 0.415, 0.843, 0.915 and 0.713.

In Figure 2 experimentally determined polarity indexes for nonylphenol adducts are plotted against

TABLE I
Polarity Index of the Nonionic and Cationic Forms of Some Ethylene Oxide Adducts Containing Basic Nitrogen

Type of surfactant	Polarity index	
	Cationic form	Nonionic form
Lauric monoamine with 15 moles ethylene oxide	127	112
Lauric diamine with 10 moles ethylene oxide	128	102
Oleic amine with 30 moles ethylene oxide	124	110
Fatty acid amide amine with 10 moles ethylene oxide	124	119

the Griffin HLB-number, calculated as one fifth of the per cent fraction of ethylene oxide in the products. The function can be approximated by a straight line in the HLB-number interval 8–18.

Table I shows the difference in polarity index of some ethylene oxide adducts with basic nitrogen groups, in their nonionic and in their cationic form in sulfuric acid medium.

The polarity index obtained for Carbowax 20 M, i.e., a molecule containing more than 99% ether units, is 126.

Discussion

The results show that the polarity index is a good means of characterizing the hydrophilic-lipophilic balance of ethylene oxide adducts. The values are easily determined with a gas chromatograph and the chemical composition need not be known. When, on the other hand, the chemical composition of an adduct is known, the polarity index of the adduct can be calculated from the polarity index of the lipophilic part of the substance and its ether unit content.

The polarity index lines of different ethylene oxide adducts show the polarity indexes over the whole ethylene oxide range and give valuable information when evaluating different lipophilic substances as raw materials for surface-active ethylene oxide adducts. The amount of ether units necessary for obtaining a certain polarity index with a certain lipophilic part is easily obtained from the graph. The validity of the polarity index lines also at higher weight fractions of ethylene oxide than the ones studied is strengthened by the determination of the polarity index of Carbowax 20 M as 126, which is close to the polarity index value 121, obtained for the ether unit by extrapolation in Figure 1. The slight difference in the values is probably due to Carbowax 20 M being in a solid state at the analysis temperature.

On investigating a limited number of surfactants, Huebner showed that there is a linear relationship between polarity index and HLB-number. No further studies of this relationship have been made. However, the almost straight line obtained for nonylphenol adducts, when plotting polarity index against HLB-number, calculated as one fifth of the per cent fraction of ethylene oxide (4) indicates a linear correlation between HLB-number and polarity index.

The possibility of determining the polarity indexes of ethylene oxide adducts which are cationic in acids, in their cationic form, is of interest for comparison of different viscose and spin aids. An interesting relationship between polarity index and dissolution of viscose aids in acid medium has been found (6).

ACKNOWLEDGMENTS

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REFERENCES

1. Becher, P., and R. L. Birkmeier, JAOCS *41*, 169 (1964).
2. Griffin, W. C., J. Soc. Cosmetic Chemists *1*, 311–26 (1949).
3. Griffin, W. C., Ibid. *5*, 249–56 (1954).
4. Griffin, W. C., Am. Perfumer, May 26, (1955).
5. Huebner, V. R., Anal. Chem. *34*, 488 (1962).
6. Kolosh, F., and W. Söderberg, Proc. from Second Int. Symp. on Viscose Technical Questions, Stockholm 1967, p. 10.
7. Weibull, B., "Determination of Polyethyleneglycol in Surface Active, Ethylene Oxide Condensates," III Int. Congress on Surface Active Agents, Cologne 1960, III C, 121–124.

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