THE HLB NUMBER DETERMINATION OF POLYOXYETHYLENE SURFACTANTS

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The Hydrophile-Lipophile-Balance (HLB) numbers were evaluated on the basis of three different, commonly used methods of determination and calculation, in a series of lauric, resp. stearic acids and lauryl alcohol oxyethyenation products prepared by an alkali-catalyzed reaction in a similar scale of hydrophobe : ethylene oxide molar ratios. The results showed that, due to the different prirciples of the used methods, the HLB numbers were obtained with a great variance, limitirg their use as parameters for estimation of the application effectiveness of non-ionic surfactants of the polyoxyethylene type. The HLB concept was not found able to consider the complicated composition of the studied types of surfactants and to provide relevant information in the already mentioned sense.

The Hydrophile-Lipophile-Balance (HLB) number is one of the fundamental parameters used for the estimation of relations between the composition and properties of surface-active agents. Usually, when a surfactant, suitable for appropriate application is to be chosen, it is the first of the characteristics to be taken into account. Originally being established by Griffin[1] on the empirical basis, the HLB concept has become a theoretically well-founded, widely spread system, one of the attributes of surface-active agents. It has been largely extended, namely in the family of non--ionics, with regard to the substantially complicated composition of these products. From this point of view it represents one of the few relatively simple possibilities to be considered in respect to the composition parameters in relation to the required application property.

Based on the results of the original experimental testing, which was a work consuming procedure, a series of calculations has been suggested later, thus enabling the determination of the HLB numbers of some types of surfactants even on the basis of relatively scanty information on product composition. Griffin[2] suggested the following relation:

$$HLB = H/5 , \qquad\qquad (1)$$

where H is the content of bonded ethylene oxide (wt. %) in the surfactant. The

equation is being widely used for a number of types of polyoxyethylene surfactants. Another equation suggested by the same author is:

$$HLB = 20[1 - (S/A)],\qquad\qquad(2)$$

where S is the saponification number of the ester and A is the acid number of the esterified fatty acid. This relation can be used for homologous series of esters of polyvalent alcohols and fatty acids. Davies[3] established a method for the determination of HLB numbers considering the properties of each part of the molecule; e.g. polarity, hydration and electric charge were taken into account. The calculation of the HLB number is based on the molecular formula of the surfactant. This causes some problem with regard to the use of HLB numbers calculated in this way, since industrially produced surfactants are never completely pure, but are always composed of many homologous esters and various other components. Newly developed methods for the determination of HLB numbers employ, therefore, various modified instrumental procedures, for the treatment of results of which no further information is generally necessary.

Although it can be demonstrated that application properties of surfactants depend on a large number of physical-chemical factors, the determination of the HLB number remains a traditional basic estimation for the prediction of the application effectiveness. The aim of this paper is to demonstrate that the profound interpretation of HLB numbers depends usually on the extent of additional information about the tested product.

EXPERIMENTAL

Chemicals

Oxyethylenated fatty acids were prepared by the reaction of ethylene oxide (EO) (BASF, F.R.G.) with the corresponding acid (FA) under Na-methoxide catalysis (0·04 mole Na/mole FA) in the following EO/FA molar ratios: 3, 9, 12 and 20 moles EO/mole FA for lauric acid (HLa) and 6, 12, 17 and 24 moles/mole FA for stearic acid (HSt). The reactions were performed in Parr (U.S.A.) oxyethylenation autoclave (volume 600 cm^3), under nitrogene atmosphere, at 120°C. The reaction pressure was 0·4 MPa and reaction time was approx. 6 hours. Oxyethylenated lauryl alcohol (LaOH) products were prepared and provided by Dr Milan Paulovič (Research Department of W. Pieck Chemical Plant, Nováky). The other materials used were commonly of an analytical grade purity (Lachema, Czechoslovakia).

Methods

The composition of prepared oxyethylenation products was determined in the terms of the content of bonded EO (the Siggia method[4]) and the content of the unreacted fatty acid (FA), monoester (ME), diester (DE) and free polyethylene glycol (PEG) fractions (the HPLC method[5,6]). The HPLC method was used for the determination of unreacted LaOH, of the

adduct (ADD) and of PEG fractions in oxyethylenated LaOH products. In addition, the distribution of ME, ADD and PEG oligomers was evaluated; the distribution of the DE fractions could not be determined, but was considered to be the same as that of the ME fraction, owing to the fact that diesters are formed predominantly by the transesterification of monoesters. The mean oxyethylenation degree was calculated from the distribution curves on the one hand; the calculation based on mass balance of bonded EO was used on the other hand[7].

The Weibull method[8] was used for the separation of the adduct and free PEG fractions; separated adduct fractions of tested oxyethylenation products were analysed and treated identically as the original samples.

Using three different methods, the HLB numbers were evaluated. The first one was the simple calculation from Griffin's equation (1); the ^{1}H NMR method, established by Ben-Et and Tatarsky[9], was used as a second one. Finally, the calculation based on Davies'group numbers[3] was used, completed with the composition data of the tested samples. Thus, the HLB numbers of the individual components of fatty acids and fatty alcohols oxyethylenation products can be evaluated as:

$$HLB_{FA} = 9.575 - 0.475n_C \tag{3}$$

$$HLB_{ME} = 11.775 - 0.475n_C + 0.33n \tag{4}$$

$$HLB_{DE} = 14.03 - 0.95n_C + 0.33n \tag{5}$$

$$HLB_{ADD} = 8.9 - 0.475n_C + 0.33n \tag{6}$$

$$HLB_{PEG} = 9.52 + 0.33n \tag{7}$$

where n_C is the number of carbon atoms in the molecule of an initial hydrophobe and n is the mean oxyethylenation degree. Equation (6) can be used for the calculation of the HLB number of the unreacted alcohol; in such a case n has the value of zero.

The HLB number of the whole product was calculated on the basis of HLB molar additivity:

$$HLB = x_{FA} HLB_{FA} + x_{ME} HLB_{ME} + x_{DE} HLB_{DE} + x_{PEG} HLB_{PEG} \tag{8}$$

for oxyethylenated fatty acids or

$$HLB = x_{LaOH} HLB_{LaOH} + x_{ADD} HLB_{ADD} + x_{PEG} HLB_{PEG} \tag{9}$$

for oxyethylenated LaOH
where x is the corresponding mole fraction of the individual component in the product. The content of the unidentified component X, mentioned in our earlier paper[6] was added to that of the free PEG fraction in the cases of the original samples; while treating the adduct fractions, the content of X was neglected.

RESULTS AND DISCUSSION

The survey of results is given in Figs 1=6. HLB numbers of original samples are plotted against the content of the bonded EO (Figs 1=3), with regard to the fact, that the products are mixtures of at least two oligomers fractions, the distributions of which may not be identical. In the case of oxyethylenated fatty acids, however, the presumption of the identical oxyethylenation degree of ME, DE and free PEG fractions is often being made, according to reaction mechanism. Although some

deviations from this rule have been sustained, their extent seemed not to be large. This can be demonstrated on the presented results of the HLB numbers, calculated
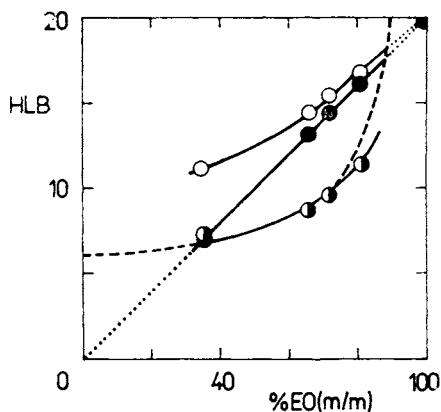

FIG. 1

HLB numbers of lauric acid oxyethylenation products, calculated from Griffin's formula (●), ^{1}H NMR record (○), and Davies' group number system (◑) vs content of bonded ethylene oxide (EO)
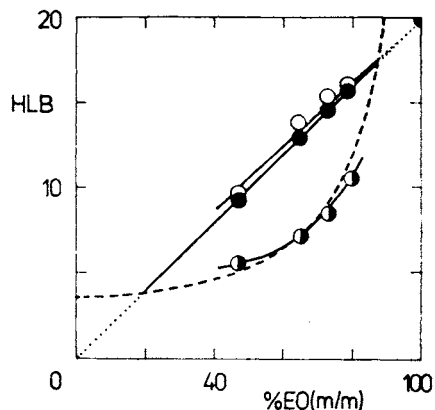

FIG. 2

HLB numbers of stearic acid oxyethylenation products vs content of bonded EO. For methods of calculation see Fig. 1
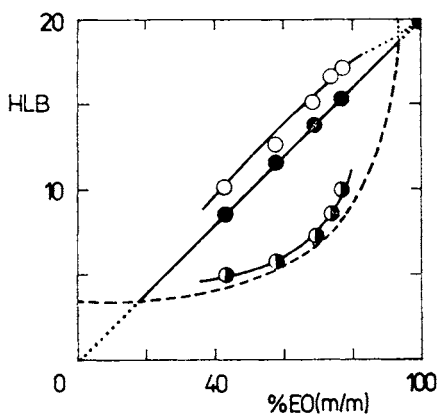

FIG. 3

HLB numbers of lauryl alcohol oxyethylenation products vs content of bonded EO. For methods of calculation see Fig. 1
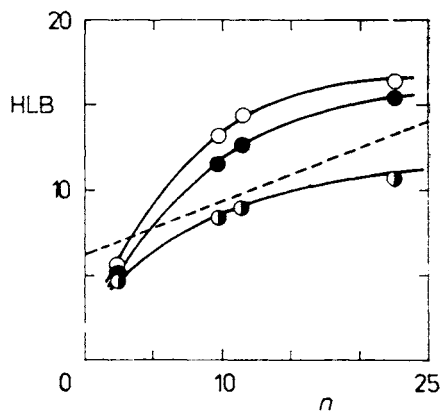

FIG. 4

HLB numbers of oxyethylenated lauric acid adduct fractions vs oxyethylenation degree. For methods of calculation see Fig. 1

from Davies' group numbers, which are only imperceptibly different from the theoretical course (dashed line) of the dependence of HLB numbers, calculated for pure monoester, or, identically, for a mixture of ME, DE and PEG in the state of transesterification equilibrium, i.e. in molar ratio 2 : 1 : 1. Corresponding deviations are much larger in the case of oxyethylenated LaOH products (Fig. 3) and are caused by an increment of HLB number, which is a result of the free PEG inclusion into a calculation.

The course of HLB dependence, calculated using Griffin's formula (1), is linear in the used plot, limited by the value of 20, which corresponds with the bonded EO content of 100 wt. %. The same limitation can be indicated in the case of ^{1}H NMR HLB values dependence, the course of which is similar to that given by Griffin's formula. A relatively great difference between ^{1}H NMR and Griffin's HLB values is observed in the case of the lowest HLa oxyethylenation product (Fig. 1) and can be explained as follows: the value of bonded EO content, determined by the Siggia method may be substantially lower, owing to the fact, that free PEG fractions of low FA oxyethylenation products may contain a considerable amount of ethylene glycol, which escapes the used determination, but is a source of a portion of hydrophile proton signals of ^{1}H NMR records. This influence evidently weakens with growth of the oxyethylenation degree. Generally, HLB numbers, calculated from ^{1}H NMR records must be at least imperceptibly higher than those evaluated from Griffin's formula, owing to the fact, that the content of the hydrophile part H in equation (1) is represented only by the amount of bonded EO, while proton signals of the
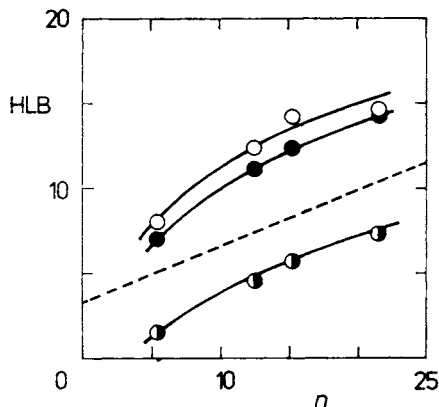

FIG. 5

HLB numbers of oxyethylenated stearic acid adduct fractions vs oxyethylenation degree. For methods of calculation see Fig. 1
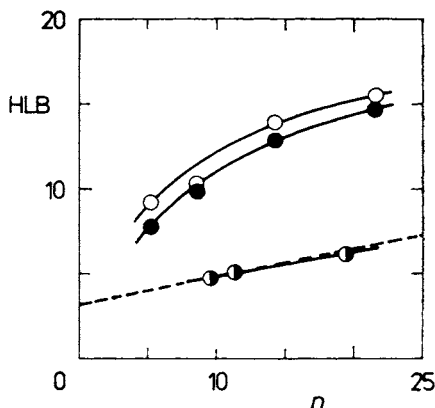
FIG. 6

HLB numbers of oxyethylenated lauryl alcohol adduct fractions vs oxyethylenation degree. For methods of calculation see Fig. 1

CH$_2$ group, neighbouring to ester bond of adducts are, in addition, comprehended to the hydrophile signals of ^{1}H NMR spectra.

While the courses of ^{1}H NMR and Griffin's HLB dependences are limited by the value of 20, as mentioned above, no limitation is observed in the case of the dependence of HLB numbers, calculated using Davies' group numbers system, which runs asymptotically to infinity. The discrepancy occurs in the whole course of the mentioned dependences, but may have a special interpretation at their beginning and at their end. The Griffin's formula, evidently, does not give correct results in the case of a very low oxyethylenation degree, as it is not able to provide correct information on the HLB number of a pure hydrophobe. Increasing the content of bonded EO over the value of 95 wt. % (corresponding with the oxyethylenation degree values of 80, 86 and 123 for oxyethylenated LaOH, HLa and HSt, resp.), a rapid growth of HLB numbers calculated from Davies' group number system occurs, in contrary to an asymptotic termination of ^{1}H NMR and Griffin's HLB curves, thus enabling to distinguish e.g. the HLB numbers of free PEG of different molecular weights. The influence of these compounds on the application properties of polyoxyethylene surfactants has been proved, so they should also have effect on the HLB values. On the other hand, the concept of the unlimited growth of polarity does not correspond with the reality.

HLB numbers of adduct fractions separated by the Weibull method, are plotted against the oxyethylenation degree on Figs 4–6. These dependences could be discussed in the context presented for the original samples. The discrepancy between the theoretical (linear in this plot, dashed line) course of group numbers HLB dependences and experimental curves is a consequence of the inclusion of the values of unreacted FA and low polar DE contents into a calculation, together with the fact, that the content of DE is relatively high in FA oxyethylenation product (even greater than the theoretical value, derived from transesterification equilibrium, has been found in lower oxyethylenated products). In the case of oxyethylenated LaOH products only an imperceptible difference occurs, as the content of unreacted alcohol is low and only negligible amounts of dialkyl- derivatives were found in the prepared samples.

Finally, ^{1}H NMR dependences of original samples and adduct fractions HLB numbers are surveyed on Figs 7 and 8, resp., showing the mutual relations of HLB values of the studied oxyethylenation products. It should be mentioned that other courses would be obtained if based on the results of another method.

Several conclusions were arrived at based on results of the presented study, which may be expressed as follows:

All three methods, used for the evaluation of HLB numbers of studied oxyethylenation products provide different results. The differences are not caused by the variance or by the low accuracy of the used methods, but issue from the principles of calculation.

The method of HLB calculation, using Davies' group number system is substantially different from both of the other used methods and will provide identical results only as a consequence of a contingency.

Based on correct analytical data, the HLB calculation from the Davies' group numbers is able to distinguish the oxyethylenation products that have a similar composition, even if the composition differences are small.

The complete composition of studied products (or their adduct fractions) was taken into account, calculating the HLB numbers from the results of all three methods. Evidently, all the product components, either displaying surface activity or not, are probably participating in an application. The question is, whether the HLB numbers, as commonly used, should include the effect of compounds having non-typical or none surface activity (free PEG, DE, unreacted hydrophobe, extra low and extra high oxyethylenated products) or not. The authors of this contribution incline to the first approach.

The above mentioned facts limit, to a considerable extent, the use of the HLB numbers, determined by the used methods, as parameters of application properties and application effectiveness of surfactants. The correlation between application properties and HLB numbers can thus be estimated only with a particular limitation, depending, among others, on the procedure of HLB numbers calculation. From this point of view, the limitation may be potentially sizable, as was shown.
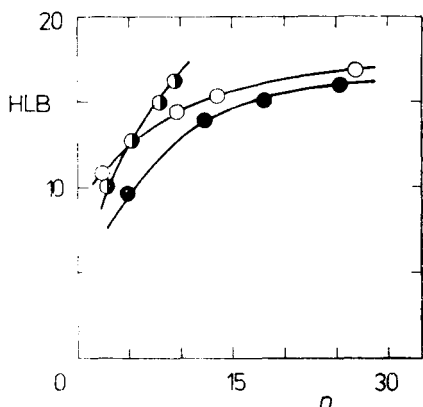

FIG. 7

HLB numbers calculated from ^{1}H NMR record for lauric acid (○), stearic acid (●) and lauryl alcohol (◑) oxyethylenation products vs oxyethylenation degree
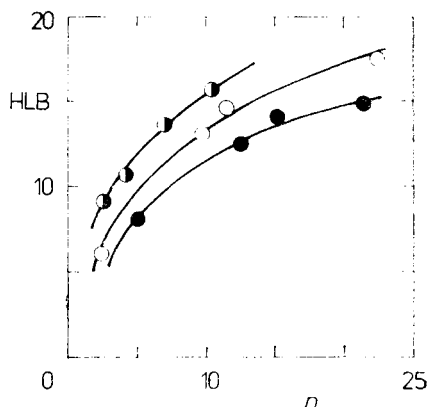

FIG. 8

HLB numbers calculated from ^{1}H NMR record for oxyethylenated lauric acid (○), stearic acid (●) and lauryl alcohol (◑) adduct fractions vs oxyethylenation degree

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