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Some considerations about the hydrophilic–lipophilic balance system

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Abstract

The methods and results obtained by Griffin et al. in the determination of the hydrophilic–lipophilic balance (HLB) values of non-ionic surfactants and of required HLB values of oil mixtures are reviewed in the present work. HLB values published by Griffin were compared with those obtained by calculations from theoretic chemical formulas. Griffin HLB values of polyoxyethylene alkyl ethers, polyoxyethylene monoesters and propylene glycol monoesters coincide with those obtained from such theoretical chemical formulations. These results demonstrate that, for these surfactants, Griffin did not experimentally obtain their HLB values, but instead calculated them from theoretic formulae. For the calculation of the HLB values of glycerol monostearate, sorbitan fatty acid esters and polyoxyethylene sorbitan fatty acid esters, Griffin's assumptions were possibly based upon the mean saponification values of the ester and the acid of the fatty acid. It is concluded that the HLB values of non-ionic surfactants were not rigorously defined. Moreover, Griffin could not demonstrate the validity of the assumption that individual required HLB values can be added up to obtain the overall required HLB value of an oil mixture. The HLB and required HLB values published by Griffin should only be taken as approximate guidelines.
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Keywords: HLB; HLB system; Non-ionic surfactants; Required HLB

1. Introduction

The hydrophilic–lipophilic balance (HLB) for emulsifier classification and selection was first issued in 1948 in an Atlas Powder Company's brochure (Atlas, 1948). The following year, William Griffin, one of the company's chemists, formally presented the HLB concept at a meeting in Chicago for the first time and later on in an article published in the first volume of the Journal of the Society of Cosmetic Chemists (Griffin, 1949).

In this innovative paper, Griffin stated: "emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups and the balance of the size and strength of these two opposite groups is called HLB. For the purpose of convenience, the effective balance of these groups is assigned a numeric value". Griffin also explained some experimental details for the determination of the numerical HLB values of the emulsifiers and the required HLB for oils. In addition, Griffin stated that HLB values for emulsifier mixtures and required HLB values for oil mixtures were obtained by applying the additive property. In these calculations, the HLB values of standard emulsifiers were involved. Such values were established following arbitrary criteria. Nevertheless, Griffin neither stated which standards were used, nor the criteria implemented to establish the HLB values.

In accordance with Delgado Charro et al. (1997), Griffin arbitrary assigned the value of 1 to the HLB value of pure oleic acid and a value of 20 for that of sodium oleate. In these authors' view, Griffin used these two substances as HLB standards. However, in none of Griffin's consulted publications it is stated that these two substances were indeed used as standards. Moreover, in his 1949 paper, Griffin assigned an HLB value of 18, not 20, to sodium oleate. Additionally, he assigned oleic acid an approximate value of 1, which would contradict its use as a standard, since it is not an exact value.

In a later publication, Griffin (1954, 1955) gave the following, more accurate definition for the method of determining HLB values: "this method, called the HLB method from the term hydrophile–lipophile balance, is used on the bases that all surfactants combine hydrophilic and lipophilic groups in one molecule and that the proportion between the weight percentages of these two groups for non-ionic surfactants is an indication of the

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behavior that may be expected from that product”. Consequently, in order to calculate the HLB value of a non-ionic surfactant of known composition, the concept of hydrophilic group should be known first.

For the polyoxyethylene alkyl ethers and polyoxyethylene esters, Griffin considered the chain unities of ethylene oxide as the hydrophilic group. The HLB value of such surfactants, according to Griffin (1954), is equivalent to the mass (or weight) percentage of oxyethylene content (E) divided by 5.

$$\text{HLB} = \frac{E}{5} \tag{1}$$

For most polyhydric alcohol fatty acid esters, the HLB value can be calculated in an approximate way, according to Griffin (1954), by means of the following equation:

$$\text{HLB} = 20\left(1 - \frac{S}{A}\right) \tag{2}$$

where S is the saponification value of the ester and A is the acid value of the acid.

As for the surfactants that contain polyoxyethylene chains and polyhydric alcohols (as glycerol and sorbitol) as hydrophilic groups, Griffin (1954) proposed the following equation:

$$\text{HLB} = \frac{E + P}{5} \tag{3}$$

where P is the mass (or weight) percentage of polyhydric alcohol content.

According to Griffin, the proposed formulas are satisfactory for non-ionic surfactants of various types. However, non-ionic surfactants containing propylene oxide, butylene oxide, nitrogen or sulphur, exhibit a behavior which has not been related to their composition. For these products, an experimental method must be used. In order to calculate the HLB value for these surfactants it is found that HLB values are additive properties (Griffin, 1949).

$$\text{HLB} = \sum \text{HLB}_i \times f_i \tag{4}$$

where f_i is the mass (or weight) fraction of the surfactant i.

The required HLB for the emulsification of blended oils was calculated by Griffin (1949) with the following equation:

$$\text{HLB}_{\text{required}} = \sum \text{HLB}_{\text{required}_i} \times f_i \tag{5}$$

where f_i is the mass (or weight) fraction of the oil i.

Possibly, Griffin obtained Eq. (5) by analogy from Eq. (4), with neither theoretical nor experimental corroboration.

An important conclusion reached by Griffin (1949) is that, for certain emulsion components, the difference between the oily and emulsifier phases is not clear. This is the case of amphiphilic, weakly polar products, such as long chain alcohols, fatty acids, cholesterol and beeswax, that may serve a dual role.

The main motivation for our investigation was the absence of a rigorous definition for HLB values in any of Griffins papers, and how the author’s proposed formulas were deducted. The objectives of this paper are: (1) specify the requirements that a surfactant must meet in order to be assigned a reliable HLB value, (2) analyze the methodologies used by Griffin for HLB and required HLB value determinations and (3) analyze the results obtained by Griffin.

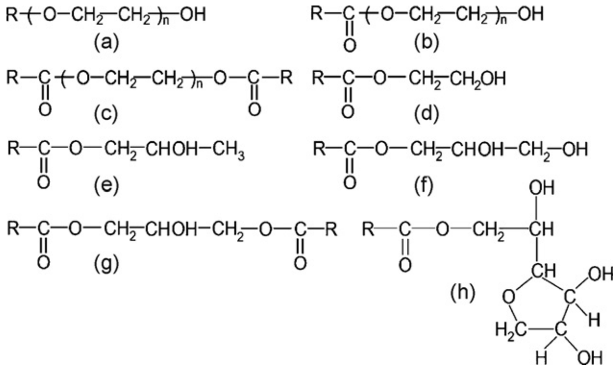

Fig. 1. Structure of the most common non-ionic surfactants: (a) polyoxyethylene alkyl ether, (b) polyoxyethylene monoester, (c) polyoxyethylene diester, (d) ethylene glycol monoester, (e) propylene glycol monoester, (f) a glycerol monoester, (g) a glycerol diester and (f) sorbitan monoester.

2. Methods

The HLB values of different surfactants (Fig. 1) were calculated as described below.

2.1. *HLB values of polyoxyethylene alkyl ethers*

If Mr(POE) is the relative molecular mass of the ethylene oxide chain unit and Mr is the relative molecular mass of the surfactant, the E value of polyoxyethylene alkyl ethers and polyoxyethylene esters, according to Griffin, is given by the following equation:

$$E = \frac{\text{Mr(POE)}}{\text{Mr}} \times 100 \tag{6}$$

However, Griffin did not take into account the polarity of the terminal hydroxyl group in the chain of ethylene oxide unities and did not include it in the E value. This omission leads to lower HLB values, especially in surfactants of low molecular masses.

If we take into account that the hydroxyl value (N_{OH}) of an alcohol is inversely proportional to its relative molecular mass, the HLB value of certain polyoxyethylene alkyls could be obtained using Eq. (7), where $N_{\text{OH tensioactive}}$ is the hydroxyl value of the polyoxyethylene alkyl ether and $N_{\text{OH alcohol}}$ the hydroxyl value of the alcohol from which it derives.

$$\text{HLB} = 20\left(1 - \frac{N_{\text{OH tensioactive}}}{N_{\text{OH alcohol}}}\right) \tag{7}$$

2.2. *HLB values of polyoxyethylene esters*

The relative molecular mass of polyoxyethylene monoesters minus the relative molecular mass of the fatty acid is equal to the relative molecular mass of the oxyethylene units.

$$\begin{aligned}\text{Mr(POE)} &= n \cdot \text{Mr}(\text{O} - \text{CH}_2 - \text{CH}_2)\\ &= \text{Mr(monoester)} - \text{Mr(acid)}\end{aligned} \tag{8}$$

Thus, the HLB value of a polyoxyethylene monoester is given by the following equation:

$$\mathrm{HLB}_{\mathrm{monoester}} = \frac{[\mathrm{Mr(monoester)} - \mathrm{Mr(acid)}] \times 20}{\mathrm{Mr(monoester)}} \tag{9}$$

Taking into account that the relative molecular mass of a pure monoester is inversely proportional to its saponification value, and that the relative molecular mass of a fatty acid is inversely proportional to its acid value, Eq. (2) is valid for polyoxyethylene monoesters. This equation was proposed by Griffin for the polyhydric alcohol fatty acid esters.

The HLB value for the polyoxyethylene diesters can be calculated from the relative molecular mass of the diester [Mr(diester)] and the fatty acid (Eq. (10)) or from the saponification value of the diester (*S*) and the acid value of the fatty acid (*A*) (Eq. (11)). For these surfactants, Eq. (2) is not valid. In Eq. (11), Mr(KOH) is the relative molecular mass of potassium hydroxide and Mr(H_2O) the relative molecular mass of water.

$$\mathrm{HLB}_{\mathrm{diester}} = \frac{[\mathrm{Mr(diester)} + \mathrm{Mr(H_2O)} - 2\mathrm{Mr(acid)}] \times 20}{\mathrm{Mr(diester)}} \tag{10}$$

$$\mathrm{HLB}_{\mathrm{diester}} = 20\left(1 + \frac{\mathrm{Mr(H_2O)} \times S}{2000 \times \mathrm{Mr(KOH)}} - \frac{S}{A}\right) \tag{11}$$

The above premises, that allow for the calculation the HLB values of pure polyoxyethylene esters, are not described in any of Griffin's papers.

2.3. HLB values of polyhydric alcohol fatty acid esters

For the non-ionic surfactants formed from the fatty acid esters and polyols, Griffin (1954) proposed Eq. (2) for the approximate calculation of the HLB values.

If the definitions of the saponification value and the acid value are taken into account, Eq. (2) can be re-written for the pure monoesters, from the relative molecular mass of the ester (Eq. (9)). In this equation, Mr(ester) – Mr(acid) represents the relative molecular mass of the polyol [Mr(polyol)] minus the relative molecular mass of water [Mr(water)], which at the same time is equal to the relative mass of hydrogen, that is replaced by the acid group, plus that of the hydroxyl group. Again, Griffin did not take into account the hydroxyl group of the hydrophilic group in the calculation of *E*. According to Griffin, the hydrophilic groups of polyoxyethylene, ethylene glycol, propylene glycol, glycerol and sorbitan monoesters, would be those shown in Fig. 2.

If Eq. (2) is applied to polyhydric alcohol fatty acid diesters, Eq. (12) is obtained.

$$\mathrm{HLB}_{\mathrm{diester}} = \frac{[\mathrm{Mr(diester)} - 2\mathrm{Mr(acid)}] \times 20}{\mathrm{Mr(diester)}} \tag{12}$$

However,

$$\begin{aligned}\mathrm{Mr(diester)} - 2\mathrm{Mr(acid)} &= \mathrm{Mr(hydrophilic\ group)}\\ &= \mathrm{Mr(polyol)} - 2\mathrm{Mr(H_2O)}\end{aligned} \tag{13}$$

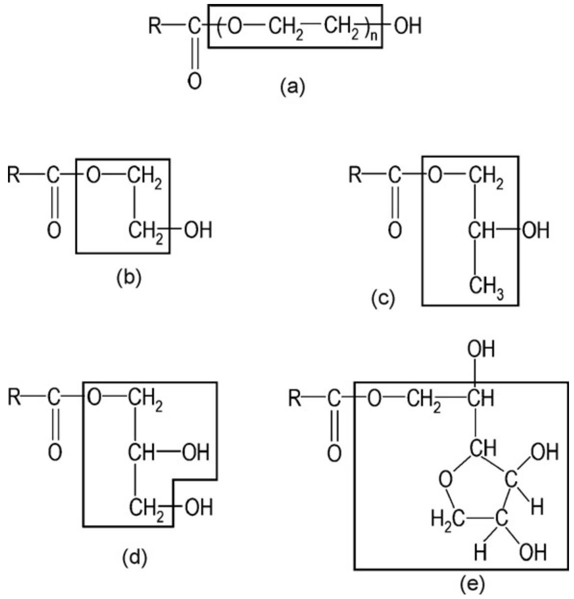

Fig. 2. Hydrophilic groups (inside each square), according to Griffin, in: (a) polyoxyethylene monoesters, (b) ethylene glycol monoesters, (c) propylene glycol monoesters, (d) glycerol monoesters and (e) sorbitan monoesters.

Thus, if Eq. (2) is considered valid, it must be admitted that for the polyhydric alcohol fatty acid diesters, the hydrophilic group of a polyol is equal to its molecule minus four hydrogen atoms and two oxygen atoms. In Fig. 3, the hydrophilic group is represented, as from this assumption, for the diesters of glycerol.

The HLB values of sorbitan fatty acid esters and polyoxyethylene sorbitan fatty acid esters can be approximately calculated by Eqs. (9) (monoesters), (14) (sesqui-esters) and (15) (triesters), which can be deduced from Eq. (2).

$$\mathrm{HLB}_{\mathrm{sesquiester}} = \frac{[\mathrm{Mr(sesquiester)} - 1.5\mathrm{Mr(acid)}] \times 20}{\mathrm{Mr(sesquiester)}} \tag{14}$$

$$\mathrm{HLB}_{\mathrm{triester}} = \frac{[\mathrm{Mr(triester)} - 3\mathrm{Mr(acid)}] \times 20}{\mathrm{Mr(triester)}} \tag{15}$$

2.4. HLB value of emulsifier mixtures

Griffin did not state in his papers how Eq. (4) was defined. This equation can be deduced from the balance of the hydrophilic group and the surfactants masses.

$$m_{\mathrm{H}} = \frac{E}{100} m = \sum \frac{E_i}{100} m_i \tag{16}$$

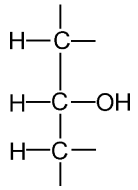

Fig. 3. Hydrophilic group of a glycerol diester (if Eq. (2) is admitted as valid).

Table 1
HLB values of polyoxyethylene alkyl ethers published by Griffin (1965) and the respective calculated ones from their theoretic chemical formulas

Commercial name	Alcohol from which derives	Ethylene oxide units	Published HLB (Griffin, 1965)	HLB calculated by authors from their theoretical chemical formulas
Brij 72	Stearyl alcohol	2	4.9	4.9
Brij 92	Oleyl alcohol	2	4.9	4.9
Brij 52	Cetyl alcohol	2	5.3	5.3
Brij 30	Lauryl alcohol	4	9.7	9.7
Renex 36	Tridecyl alcohol	6	11.4	11.4
Brij 76	Stearyl alcohol	10	12.4	12.4
Brij 96	Oleyl alcohol	10	12.4	12.4
Brij 56	Cetyl alcohol	10	12.9	12.9
Renex 30	Tridecyl alcohol	12	14.5	14.5
Brij 78	Stearyl alcohol	20	15.3	15.3
Brij 98	Oleyl alcohol	20	15.3	15.3
Renex 31	Tridecyl alcohol	15	15.4	15.4
Brij 58	Cetyl alcohol	20	15.7	15.7
Brij 35	Lauryl alcohol	23	16.9	16.9

where m_H is the total mass of the hydrophilic groups, m the emulsifiers mass and m_i is the emulsifiers i mass.

For the calculation of the HLB value of a mixture of mono and diesters of one polyol, we propose that Eq. (2) can be used in two different ways:

1. From the saponification value of the mixture.
2. From the saponification value of the monoester ($S_{\text{monoester}}$) and the saponification value of the diester (S_{diester}): the saponification value of the mixture (S) is calculated from Eq. (17), which can be deduced admitting the validity of Eq. (4) or from the balance of KOH, in moles, required for the saponification.

$$S = S_{\text{monoester}} \times f_{\text{monoester}} + S_{\text{diester}} \times f_{\text{diester}} \tag{17}$$

where $f_{\text{monoester}}$ is the mass fraction of the monoester and f_{diester} is the mass fraction of the diester.

2.5. Required HLB for the emulsification of a particular oil into o/w emulsion

The technique for the experimental determination of required HLB values of oils was explained by Griffin (1949) and Griffin et al. (1966). The use of Eq. (5) in the calculation of such values has no theoretical support.

3. Results and discussion

3.1. HLB values of polyoxyethylene alkyl ethers

In a study on emulsifiers, Griffin (1965) presented a table where 14 polyoxyethylene alkyl ethers (Table 1) were included. All of the included values agreed with those obtained from their theoretical chemical formulas. These results demonstrate that for these surfactants Griffin did not determine their HLB values experimentally, but from calculations.

3.2. HLB values of polyoxyethylene esters

Practically, all HLB values of polyoxyethylene monoesters (Table 2) published by Griffin (1954, 1965) agree with those calculated from their theoretical chemical formulas. Griffin (1949, 1954, 1965) did not publish HLB values of polyoxyethylene diesters.

3.3. HLB values of propylene glycol monoesters

All of the HLB values of propylene glycol monoesters (Table 3) published by Griffin en 1954 are in accordance with the ones obtained from calculations using theoretic chemical formulas.

3.4. HLB values of glycerol monostearate

The values published by Griffin for the HLB of glycerol monostearate from different sources are similar between them, and lower than the ones obtained from their theoretical chemical formulas. The coincidence in the values given by Griffin suggest the they were obtained by calculation using Eq. (2), possibly from average values of the ester's saponification value and the acid value of the fatty acid, as he showed as an example in his 1954 publication. It is interesting to note that "pure" glycerol monostearate has the same HLB value, as per Griffin, than its commercial analogues (Table 4).

Griffin (1954) used the calculation of the HLB value of glycerol monostearate as an example of the use of Eq. (2). He used 161 mg of KOH/g as the saponification value, and 198 mg of KOH/g as the acid value of the acid used in the esterification. From the latter it comes out that the relative molecular mass of the acid is 283 (this value corresponds to a mixture of 95.2% of stearic acid and 4.8% of palmitic acid), the molecular mass of the monoester is 357 and the diesters' is 622. If Eqs. (9) and (12) are applied, the conclusion is that the HLB values of glycerol monostearate and glycerol distearate are, respectively, 4.15 (the

Table 2
HLB values of polyoxyethylene monoesters published by Griffin, and those calculated from their theoretic chemical formulas

Commercial name	Fatty acid from which derives	Ethylene oxide units	Published HLB (Griffin, 1954)	HLB calculated by authors from their theoretical chemical formulas
Emcol EO-50	Oleic acid	1	2.7	2.7
Emcol ES-50	Stearic acid	1	2.7	2.7
Emcol EL-50	Lauric acid	1	3.6	3.6
Atlas G-2139	Oleic acid	2	4.7	4.7
Emcol DO-50	Oleic acid	2	4.7	4.7
Emcol DS-50	Stearic acid	2	4.7	4.7
Emcol DP-50	Palmitic acid	2	5.1	5.1
Emcol DM-50	Miristic acid	2	5.6	5.6
Atlas G-2124	Lauric acid	2	6.1	6.1
Glaurin	Lauric acid	2	6.5	6.1
Emcol DL-50	Lauric acid	2	6.1	6.1
Atlas G-2147	Stearic acid	4	7.7	7.7
Atlas G-2140	Oleic acid	4	7.7	7.7
Atlas G-2125	Lauric acid	4	9.4	9.4
Atlas 2154	Stearic acid	6	9.6	9.6
Atlas G-2142	Oleic acid	8?	11.1	11.1
Myrj 45	Stearic acid	8?	11.1	11.1
Atlas G-2141	Oleic acid	8.67?	11.4	11.5
PEG 400 monoleate	Oleic acid	8.67	11.4	11.5
Atlas G-2076	Palmitic acid	8?	11.6	11.6
S-541	Stearic acid	8.67?	11.6	11.5
PEG 400 monostearate	Stearic acid	8.67	11.6	11.5
Atlas G-2127	Lauric acid	8?	12.8	12.8
S-307	Lauric acid	8.67?	13.1	13.1
PEG 400 monolaurate	Lauric acid	8.67	13.1	13.1
Myrj 49	Stearic acid	20?	15.0	15.1
Atlas G-2144	Oleic acid	20?	15.1	15.1
Atlas G-2079	Palmitic acid	20?	15.5	15.5
Myrj 51	Stearic acid	26?	16.0	16.0
Atlas G-2129	Lauric acid	20?	16.3	16.3
Myrj 52	Stearic acid	35?	16.9	16.9
Myrj 53	Stearic acid	55?	17.9	17.9
Atlas G-2159	Stearic acid	100?	18.8	18.8

The sign "?" indicates that the value of ethylene oxide units has been estimated by the authors of this paper based upon published HLB values by Griffin (1954).

theoretical value is 4.13) and 1.80 (the theoretical value is 1.79). Taking into account that the HLB value published by Griffin is 3.8, it can be estimated by applying Eq. (4), that this product was formed by a mixture of 85% of monostearate and 15% of distearate.

3.5. HLB values of sorbitan fatty acid esters

The differences between the HLB values of sorbitan fatty acid esters published by Griffin (1954, 1965) and the ones calculated by the authors, are within a 30.9% (defect) and 2.4% (excess).

Table 3
HLB values of propylene glycol monoesters published by Griffin and those calculated from their theoretic chemical formulas

Commercial name	Acid from which it derives	Published HLB (Griffin, 1954)	HLB calculated by authors from their theoretical chemical formulas
Emcol PO-50	Oleic acid	3.4	3.4
Atlas G-922	Stearic acid	3.4	3.4
"Pure"	Stearic acid	3.4	3.4
Atlas G-2158	Stearic acid	3.4	3.4
Emcol PS-50	Stearic acid	3.4	3.4
Emcol PP-50	Palmitic acid	3.7	3.7
Emcol PM-50	Miristic acid	4.1	4.1
Atlas G-917	Lauric acid	4.5	4.5
Atlas G-3851	Lauric acid	4.5	4.5
Emcol PL-50	Lauric acid	4.5	4.5

Table 4
HLB values of glycerol monostearates published by Griffin and those calculated from their theoretical chemical formulas

Commercial name	Acid from which it derives	Published HLB (Griffin, 1954, 1965)	HLB calculated by authors from their theoretical chemical formulas
Atmul 67	Stearic acid	3.8	4.1
Atmul 84	Stearic acid	3.8	4.1
Tegin 515	Stearic acid	3.8	4.1
Aldo 33	Stearic acid	3.8	4.1
“Pure”	Stearic acid	3.8	4.1

These differences could possibly be due to Griffin’s use of the mean saponification values of the ester and the acid value of the fatty acid of each surfactant (Table 5).

3.6. HLB values of polyoxyethylene sorbitan fatty acid esters

For the polyoxyethylene sorbitan fatty acid esters, the differences between the HLB values published by Griffin (1954, 1965) and the ones calculated, are between 11.5% defect and 8.1% excess. In his 1954 publication, Griffin calculates the HLB value of Tween 20 by applying Eq. (2) and the mean saponification value of the ester and the acid value of the fatty acid (Table 6).

3.7. HLB value of emulsifier mixtures

Eq. (4) is easily justified from Eq. (16) as follows:

$$\mathrm{HLB} = 20\frac{m_{\mathrm{H}}}{m} = \sum 20 \times \frac{E_i}{100}\frac{m_i}{m} = \sum \mathrm{HLB}_i \times f_i$$

Griffin did not publish experimental results that would confirm the validity of Eq. (4). The different retention times of two liquids, one being polar and the other non-polar, allows for the measurement of the HLB value of a surfactant or a mixture of surfactants, if used as a substrate, via gas–liquid chromatography. The results obtained by Becher and Birkmeier (1964), using this technique, suggest that Eq. (4) is not fully confirmed.

Therefore, the use of Eq. (4) introduces an error in the calculations of the HLB value of an emulsifier, as from experimental results. This error will depend on both the surfactant of known HLB value, as well as on the one for which the HLB value is to be determined.

3.8. Required HLB for the emulsification of a particular oil into o/w emulsion

Griffin (1949) detailed a list of required HLB values that included solid products such as cetyl alcohol, beeswax, carnauba wax, candelilla wax and stearic acid. The experiments for the determination of the required HLB values of these solids were conducted at 60–70 °C. The HLB values of the non-ionic surfactants used by Griffin in these experiments are temperature dependent, which introduces an error in such determinations. This source of error could have been avoided by using a solution at room temperature as the oily phase, made up of the solid product in an oily liquid of known required HLB value. The required HLB value obtained by this method would be applicable to the o/w emulsions where the solid product is soluble in the oily phase. If the solid product is not soluble or has a low

Table 5
HLB values of sorbitan fatty acid esters published by Griffin and those calculated from their theoretical chemical formulas

Commercial name	Acid from which it derives	Published HLB (Griffin, 1954, 1965)	HLB calculated by authors from their theoretical chemical formulas
Span 85	Oleic acid (tri)	1.8	2.3
Arlacel 85	Oleic acid (tri)	1.8	2.3
Span 65	Stearic acid (tri)	2.1	2.3
Arlacel 65	Stearic acid (tri)	2.1	2.3
Arlacel C	Oleic acid (sesqui)	3.7	4.9
Arlacel 83	Oleic acid (sesqui)	3.7	4.9
Span 80	Oleic acid (mono)	4.3	6.8
Arlacel 80	Oleic acid (mono)	4.3	6.8
Span 60	Stearic acid (mono)	4.7	6.8
Arlacel 60	Stearic acid (mono)	4.7	6.8
Span 40	Palmitic acid (mono)	6.7	7.3
Arlacel 40	Palmitic acid (mono)	6.7	7.3
Span 20	Lauric acid (mono)	8.6	8.4
Arlacel 20	Lauric acid (mono)	8.6	8.4

Table 6
HLB values of polyoxyethylene sorbitan fatty acid esters published by Griffin and those calculated from their theoretical chemical formulas

Commercial name	Acid from which it derives	Ethylene oxide units	Published HLB (Griffin, 1954, 1965)	HLB calculated by authors from their theoretical chemical formulas
Tween 61	Stearic acid (mono)	4	9.6	10.6
Tween 81	Oleic acid (mono)	5	10.0	11.3
Tween 65	Stearic acid (tri)	20	10.5	10.7
Tween 85	Oleic acid (tri)	20	11.0	10.8
Tween 21	Lauric acid (mono)	4	13.3	12.3
Tween 60	Stearic acid (mono)	20	14.9	15.7
Tween 80	Oleic acid (mono)	20	15.0	15.7
Tween 40	Palmitic acid (mono)	20	15.6	16.0
Tween 20	Lauric acid (mono)	20	16.7	16.7

solubility, as it happens with the cetyl alcohol in a mineral oil in water emulsion, the wax is separated as a solid substance and a system made of an emulsion and a suspension is obtained, for which the required HLB value lacks of meaning.

When Griffin (1949) referred to the amphiphilic oily products he stated: "the dividing line between ingredients and emulsifiers is often not clear". This resulted in assigning the oleic acid an HLB value of approximately 1, considering it as an emulsifier (Griffin, 1949) and a required HLB of 16, considering it as part of the oily phase (Griffin et al., 1966). For this type of oils, Eqs. (4) and (5) should be simultaneously verified. Thus, for instance, for an emulsion made up of an oily phase that contains 5 g of oleic acid and 10 g of mineral oil of required HLB = 10.5, and that was stabilized with 5 g of an emulsifier mixture made of polyoxyl 4 lauryl ether (HLB = 9.7) and polyoxyl 23 lauryl ether (HLB = 16.9), the required HLB for this oily phase would be 12.3, assuming Eq. (5) is valid. This HLB value is obtained from a mixture of 3.17 g of polyoxyl 4 lauryl ether and 1.83 g of polyoxyl 23 lauryl ether. Moreover, if a mixture of 5 g of oleic acid with 3.17 g of polyoxyl 4 lauryl ether and 1.83 g of polyoxyl 23 is taken as the emulsifier, by applying Eq. (4) the obtained required HLB value of the mineral oil would be 6.7 instead of 10.5. Griffin assumed that most of the amphiphilic oily product forms the bulk of the oil phase, but portions of the amphiphilic oily product are present as emulsifier. However, and though accepting that Griffin assumptions are probably correct, – in the latter example – if Eq. (5) is used for the mixture of oleic acid and mineral oil and Eq. (4) for the emulsifiers mixture, the conclusion is that the HLB of the emulsifiers mixture is equal to the required HLB only when the amount of oleic acid is equal to zero. This result indicates that the acceptance of Eqs. (4) and (5) is incompatible with the idea that the amphiphilic oily product can be divided into an oily phase and the interphase, as Griffin assumed.

4. Conclusions

The HLB value is a property that has not been rigorously defined. If Eq. (1) is assumed to define the HLB value, the only surfactants that would have accurately defined HLB values would be the polyoxyethylene diesters, as they do not have a hydroxyl group that modifies the hydrophilic properties given by the polyoxyethylene chain.

Eq. (3) assigns, without any theoretical or empirical support, the same importance to both the polyhydric alcohols and the polyoxyethylene chains with regards to the hydrophilic properties of the surfactants molecules. Moreover, in the calculations of the mass percentage of polyhydric alcohol content, it is not specified whether the entire polyol molecule or just a part of it should be taken into account.

Griffin did not specify which surfactants were used as standards for the experimental determination of HLB values. In order for a non-ionic surfactant to be used as a standard for the determination of HLB values or required HLB values, it should have a well-known chemical composition, and a polyoxyethylene chain as a unique hydrophilic group. For this reason, the polyhydric alcohol fatty acid esters and the polyoxyethylene sorbitan fatty acid esters should be disregarded. Pure polyoxyethylene diesters would be the most appropriate surfactants to be used as standards for HLB, as they have a polyoxyethylene chain as a unique hydrophilic group. However, polyoxyethylene diesters could have some disadvantages such as the presence of monoesters, free fatty acids, variable quantities of carbon atoms in the hydrocarbon chains of the alcohols and the fatty acids, as well as variable quantities of polyoxyethylene units. Other attractive candidates could be the polyoxyethylene alkyl ethers, as they offer an extra supply of hydrophilic properties from the terminal hydroxyl group of the polyoxyethylene chain.

It must be taken into account that most of the HLB values used at present are those published by Griffin (1954), most of which were calculated from theoretical chemical formulas or from manufacturers' specifications. These values should only be taken as orientative ones. When higher accuracies are needed, HLB values should be calculated from the chemical composition or be experimentally determined by using standard surfactants of well-known HLB values.

The HLB value is not a characteristic of a certain type of surfactants, but of a particular batch. It should be advisable that manufacturers inform of the calculated HLB value of each specific batch in their analysis protocol, including some of the proposed equations by Griffin. The values thus obtained would be much more precise than those published by Griffin.

Finally, Eq. (5) has no theoretical support. Values of the required HLB of each of the components of the oily phase as well as the calculation of the required HLB of the oily phase are affected by a noticeable error. For this reason, the results obtained in the calculation should be used as a first approach; the definite required HLB should be determined experimentally.

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