Hydrophile-Lipophile Balance Values for O/W Emulsions Stabilized by Nonionic Surfactants. I. Hydrophile-Lipophile Balance Values of Nonionic Surfactants Determined by Emulsification

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Concerning the study of emulsifications or emulsions stabilized by any nonionic surfactants, there is the well-known concept of HLB (hydrophile-lipophile balance) suggested by Griffin[1].

Following this concept, Kawakami[2] has presented an equation to calculate the HLB value from the structure of the surfactant molecule, that is,

$$\mathrm{HLB}=7+11.7\log(M_w/M_o) \tag{1}$$

In this equation, M_w is the molecular weight of the hydrophilic group in the molecule and M_o, that of the lipophilic group.

In 1954, Griffin[3] also proposed another equation for this purpose, which enabled one to calculate the HLB value from both analytical and composition data. His second equation was,

$$\mathrm{HLB}=20(1-S/A) \tag{2}$$

where S is the saponification number of the ester and A, the acid number of fatty acid used for the preparation of the derivatives of polyhydric alcohols, such as sorbitan, glycerol, etc.* For the surfactants, which involve only the polyoxyethylene chain as a hydrophilic group, the following equation was said to be suitable:

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[1] W. C. Griffin, *J. Soc. Cosmetic Chemists*, **1**, 311 (1949).
[2] Y. Kawakami, *Kagaku*, **23**, 546 (1953).
[3] W. C. Griffin, *J. Soc. Cosmetic Chemists*, **5**, 249 (1954).

* The values calculated by Eq. 1 are not materially different from those calculated by Eq. 2; we used the latter equation, together with Eq. 3, in the present experiment.

$$\mathrm{HLB}=E/5 \tag{3}$$

where E is the weight percentage of oxyethylene content.

Furtheremore, Griffin assumed that the HLB of the surfactant mixture can be calculated by the following equation:

$$[\mathrm{HLB}]_{\mathrm{m}}=[\mathrm{HLB}]_{\mathrm{a}}x/100+[\mathrm{HLB}]_{\mathrm{b}}(100-x)/100 \tag{4}$$

where $[\mathrm{HLB}]_{\mathrm{m}}$, $[\mathrm{HLB}]_{\mathrm{a}}$ and $[\mathrm{HLB}]_{\mathrm{b}}$ are the HLB values for the mixture, surfactant "a" and surfactant "b" respectively, and x, the weight percentage of "a" in the mixture. By this equation, the HLB value of any mixture of two surfactants can be predicted.

The concept of HLB, though convenient in practice, still has some difficulties in its applications. Besides, Griffin did not give the details of his emulsification experiments which are required for the HLB calculation. To clarify these points, we took up those O/W emulsions stabilized by nonionic surfactants and studied the system in detail by a method of emulsification experiments similar as those proposed by Griffin.

Experimental

Materials.—*Nonionic Surfactants.*—Sorbitan fatty acid esters and their polyoxyethylene derivatives were selected as typical nonionic surfactants, polyethylene glycol stearates as the ester type, polyoxyethylene-lauryl ethers and -cetyl ethers as the ether type, and polyoxyethylene nonylphenyl ethers as the alkylphenyl ether type, as listed in Tables I to VI.

These were used without further purification, as we needed to know merely the exact HLB value of a given sample. The nonionic surfactants listed in Tables III, IV, V and VI were exclusively prepared in the author's laboratory.

Mineral Oil. — "Carnation white mineral oil", prepared by the Sonneborn Co., U.S.A., was used as the oil to be emulsified, its average viscosity being 70 cp.

TABLE I. SORBITAN FATTY ACID ESTERS

Abbr.	Chemical constitution	Trade name*
SML	Monolaurate	Span 20 or SL-10
SMP	Monopalmitate	Span 40 or SP-10
SMS	Monostearate	Arlacel 60 or SS-10
SMO	Monoöleate	Arlacel 80 or SO-10
SSO	Sesquioleate	Arlacel 83 or SO-15
STS	Tristearate	Arlacel 65 or SS-30
STO	Trioleate	Arlacel 85 or SO-30

* In Tables I and II, Spans, Arlacels and Tweens are commercial products of Atlas Powder Co., the others were prepared in our laboratory.

TABLE II. POLYOXYETHYLENE SORBITAN FATTY ACID ESTERS

Abbr.	Chemical constitution		Trade name*
	Esters	n**	
E-SML-20	SML	20	Tween 20 or TL-10
E-SMP-20	SMP	20	Tween 40 or TP-10
E-SMS-6	SMS	6	Tween 61 or TS-106
E-SMS-20	SMS	20	Tween 60 or TS-10
E-SMO-6	SMO	6	Tween 81 or TO-106
E-SMO-20	SMO	20	Tween 80 or TO-10
E-STS-20	STS	20	Tween 65 or TS-30
E-STO-20	STO	20	Tween 85 or TO-30

TABLE III. POLYETHYLENE GLYCOL STEARATES

Abbr.	Chemical constitution n**	Trade name
PEGS-2	2	MYS-2
PEGS-4	4	MYS-4
PEGS-10	10	MYS-10
PEGS-25	25	MYS-25
PEGS-45	45	MYS-45

TABLE IV. POLYOXYETHYLENE LAURYL ETHERS

Abbr.	Chemical constitution n**	Trade name
POEL-4.2	4.2	BL-4.2
POEL-5	5	BL-5
POEL-10	10	BL-10
POEL-20	20	BL-20
POEL-25	25	BL-25

TABLE V. POLYOXYETHYLENE CETYL ETHERS

Abbr.	Chemical constitution n**	Trade name
POEC-2	2	BC-2
POEC-3	3	BC-3
POEC-5.5	5.5	BC-5.5
POEC-7	7	BC-7
POEC-10	10	BC-10
POEC-15	15	BC-15
POEC-20	20	BC-20

TABLE VI. POLYOXYETHYLENE NONYLPHENYL ETHERS

Abbr.	Chemical constitution n**	Trade name
POENP-2	2	NP-2
POENP-7.5	7.5	NP-7.5
POENP-9	9	NP-9
POENP-10	10	NP-10
POENP-20	20	NP-20

** n, Average mol. number of ethylene oxide in molecule.

Emulsification.—In the present series of experiments, an "Emulsification by Inversion"[4], which involves phase inversion as an important process, was utilized to prepare the emulsions.

The standard composition of the emulsion for this series of experiments is shown in Table VII.

TABLE VII. COMPOSITION OF EMULSION

Mineral oil	40.0%
Mixture of emulsifiers	4.0%
Distilled water	56.0%

The emulsifications were carried out by the following procedure. A mixture of mineral oil and mixed surfactants was heated up to about 90°C. Into this mixed oil phase, water which had also been heated to about 90°C was added slowly with stirred. After adding all of the water, stirring was continued until the temperature of the emulsion fell to about 40°C. The emulsions thus obtained were used for studying their properties.

Estimation of the "Required HLB Value" of O/W Emulsion

Griffin suggested the HLB system, but there is no nonionic surfactant to use as the standard of the HLB value.

In our series of experiments, however, Arlacel 60 (HLB=4.7) and Tween 60 (HLB=14.9), i. e., SMS and E-SMS-20 in our case, were used as the standards of the HLB value. These two samples were selected as standard because they are easy to prepare as a series of homologues, they emulsify a wide variety of oils, and they are situated in appropriate positions in the HLB region.

The HLB value of an emulsion or the HLB value for an oil in making an emulsion can be estimated by means of an emulsification test following the concept of HLB. Griffin proposed the term "required HLB" for the oil phase used to emulsify. This required HLB value is considered to be equal to $[\mathrm{HLB}]_m$ in Eq. 4, calculated from the composition of a system when the mixture of two surfactants gives the most stable emulsion among a series of emulsions made with a given pair of agents under varying compositions, as is shown in Table VIII.

TABLE VIII. ESTIMATION OF THE HLB VALUE BY EMULSIFICATION TESTS

No.	Composition of emulsifier SMS %	E-SMS-20 %	Stability of emulsion
1	52.5	47.5	+
2	50.0	50.0	++
3	47.5	52.5	+++
4	45.0	55.0	+++
5	42.5	57.5	++
6	40.0	60.0	++

We can see in Table VIII that the emulsions of Nos. 3 and 4 are the most stable, and the HLB, $[\mathrm{HLB}]_m$, required for a mineral oil to be emulsified with a pair of SMS and E-SMS-20 is estimated as 10.2 by Eq. 4. In later sections, we adopt this value as the standard of the required HLB. Thus, by these experiments, the required HLB of mineral oil may be determined for every pair of emulsifiers. To make the comparison simple, one of the emulsifiers taken as the standard is always kept as a fixed component in any pair of surfactants in the emulsification tests.

Results and Discussion

Applicability of Eq. 4.—The results of sorbitan fatty acid esters and their polyoxyethylene derivatives are shown in Table IX. In this table, the required HLB values of mineral oil, $[\mathrm{HLB}]_m$, which are shown in the 4th column, were calculated by Eq. 4, using the HLB value of the combined component surfactant, $[\mathrm{HLB}]_{\mathrm{calcd}}$, shown in the 2nd column, and the HLB value of the fixed component surfactant.

TABLE IX. HLB VALUES FOR SORBITAN DERIVATIVES

Combined emulsifier	$[\mathrm{HLB}]_{\mathrm{calcd}}$	Fixed emulsifier	$[\mathrm{HLB}]_m$	$[\mathrm{HLB}]_a$
SML	8.6	E-SMS-20	11.6	5.8
SMP	6.7	E-SMS-20	11.2	4.4
SMS	4.7	E-SMS-20	10.2	4.7
STS	2.1	E-SMS-20	(7.8)	(6.5)
SMO	4.3	E-SMS-20	9.8	5.1
SSO	3.7	E-SMS-20	9.4	5.2
STO	1.8	E-SMS-20	(4.4)	(9.0)
E-SML-20	16.7	SMS	9.9	17.3
E-SMP-20	15.6	SMS	10.2	15.6
E-SMS-6	9.6	E-SMS-20	10.4	9.4
E-SMS-20	14.9	SMS	10.2	14.9
E-SMO-6	10.0	E-SMS-20	11.0	9.0
E-SMO-20	15.0	SMS	10.2	15.0
E-STS-20	10.5	SMS	10.2	10.5
E-STO-20	11.0	E-SMS-20	11.6	9.3
			Average 10.5±1.1	

The required HLB value of mineral oil is

$$[\mathrm{HLB}]_m = 10.5 \pm 1.1 \tag{5}$$

excepting the values for STO and STS, which are not considered to fall into the category of O/W emulsifiers. Within the range of this error, it may be said that the concept of the HLB system is applicable in emulsion systems with nonionic surfactants.

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[4] Presented at the 12th Symposium of Colloid Chemistry, Hiroshima, 1959.

For the rest of the types of nonionic surfactants, the required HLB values of mineral oil were calculated by the same procedure as in Table IX; the results obtained are:

$$\text{PEGS,} \quad [\text{HLB}]_m = 10.2 \pm 0.3 \qquad (6)$$

$$\text{POEL,} \quad [\text{HLB}]_m = 9.7 \pm 1.6 \qquad (7)$$

$$\text{POEC,} \quad [\text{HLB}]_m = 9.0 \pm 0.6 \qquad (8)$$

$$\text{POENP,} \quad [\text{HLB}]_m = 8.9 \pm 0.8 \qquad (9)$$

From these results, it may be concluded that the allowance of an obtained $[\text{HLB}]_m$ is in the range of ±1, excepting the case of POEL. However, we must draw attention to the fact that the mean value of the HLB itself fluctuates according to the pair of surfactants used. This fact has a very important implication concerning the concept of the HLB, which becomes the starting point for the further study of these phenomena.

HLB Values of Nonionic Surfactants.—If the additivity expressed in Eq. 4 is assumed to be correct, we can calculate $[\text{HLB}]_a$ from the values of $[\text{HLB}]_m$ and $[\text{HLB}]_b$ according to the following equation:

$$[\text{HLB}]_a = \{[\text{HLB}]_m - [\text{HLB}]_b(100-x)/100\}100/x \qquad (10)$$

Thus, using these $[\text{HLB}]_m$ and $[\text{HLB}]_b$ values;

$[\text{HLB}]_m$: 10.2, determined with the standard emulsifiers, SMS and E-SMS-20,

$[\text{HLB}]_b$: 4.7 for SMS, and 14.9 for E-SMS-20,

x: percentage content of emulsifier "a" in the mixed emulsifier,

the HLB value of any nonionic surfactant can be estimated from the emulsification experiments. The results are shown in the last column of Table IX.

Of course, in this case, it is assumed as an important condition that the required HLB of mineral oil takes a fixed value.

$[\text{HLB}]_{\text{calcd}}$ and $[\text{HLB}]_a$. — To make a comparison between the values, $[\text{HLB}]_{\text{calcd}}$, calculated by Eq. 2 or 3 and $[\text{HLB}]_a$, those obtained experimentally, $[\text{HLB}]_{\text{calcd}}$ vs. $[\text{HLB}]_a$ diagrams are plotted in Figs. 1 and 2 for each type of nonionic surfactant. In these figures we should expect the plot to fall on the bisector of the angle between two coordinate axes.

In Fig. 1, for sorbitan derivatives, ○, an interesting curve is obtained. Their polyoxyethylene derivatives showed a coincidence between two values; however, sorbitan fatty acid esters deviated remarkably from the bisector, and this deviation seemed to follow a definite function of the HLB values. As a result, the values of $[\text{HLB}]_a$ for STO, STS, SSO and SMO are higher than the corresponding $[\text{HLB}]_{\text{calcd}}$ drawn from Eq. 2, while those for

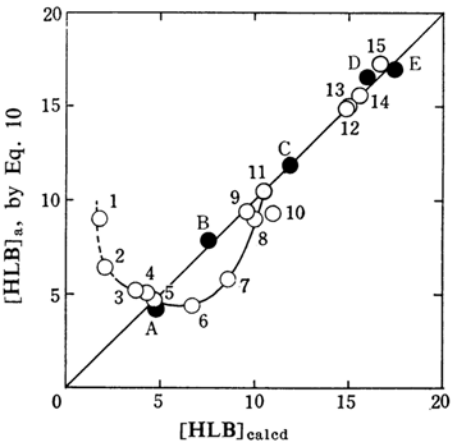

Fig. 1. $[\text{HLB}]_{\text{calcd}}$ vs. $[\text{HLB}]_a$ diagram for sorbitan derivatives: ○,

1, STO	2, STS	3, SSO
4, SMO	5, SMS	6, SMP
7, SML	8, E-SMO-6	9, E-SMS-6
10, E-STO-20	11, E-STS-20	12, E-SMS-20
13, E-SMO-20	14, E-SMP-20	15, E-SML-20;

and for polyethylene glycol stearates: ●,

A, PEGS-2	B, PEGS-4	C, PEGS-10
D, PEGS-25	E, PEGS-45	

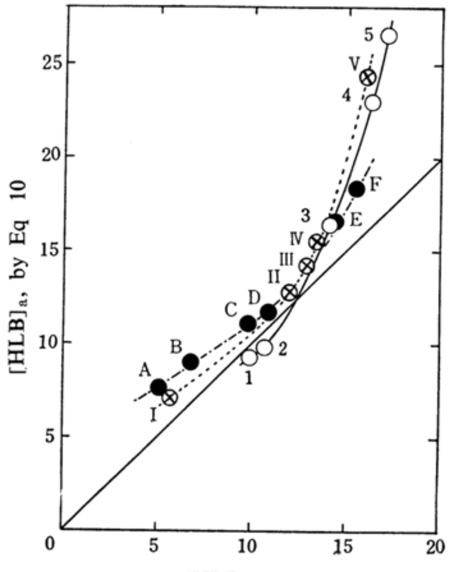

Fig. 2. $[\text{HLB}]_{\text{calcd}}$ vs. $[\text{HLB}]_a$ diagram for polyoxyethylene lauryl ethers: ○,

1, POEL-4.2	2, POEL-5	3, POEL-10
4, POEL-20	5, POEL-25;	

for polyoxyethylene cetyl ethers: ●,

A, POEC-2	B, POEC-3	C, POEC-5.5
D, POEC-7	E, POEC-15	F, POEC-20

and for polyoxyethylene nonylphenyl ethers: ⊗,

I, POENP-2	II, POENP-7.5	III, POENP-9
IV, POENP-10	V, POENP-20	

SMP and SML are lower than the corresponding $[\mathrm{HLB}]_{\mathrm{calcd}}$.

As the sorbitan group is a complicated hydrophilic group compared with those of polyoxyethylenes, there is some question as to the calculation of the HLB value according to Eq. 2 or 3, which merely involve the percentage content of the hydrophilic group in the molecule.

STS and STO, having little hydrophilic property, show too high a $[\mathrm{HLB}]_{\mathrm{a}}$ compared with their $[\mathrm{HLB}]_{\mathrm{calcd}}$. This means that the amount of emulsifiers, x, necessary for optimum emulsification is larger than that calculated from its $[\mathrm{HLB}]_{\mathrm{calcd}}$. Further, they do not produce fine emulsions. Thus, the behavior of a poorly hydrophilic emulsifier is quite different from the more hydrophilic one.

Polyethylene glycol stearates, as shown in Fig. 1, ●, showed only a slight deviation in plot from the bisector; i. e., Eqs. 2 and 10 give nearly equal results for this type of nonionic surfactants.

In this case, the emulsifiers used are all stearic acid esters, and an agreement is obtained between the values of $[\mathrm{HLB}]_{\mathrm{calcd}}$ and $[\mathrm{HLB}]_{\mathrm{a}}$. From this fact, together with the fact that the two components of the emulsifier have a stearate radical in common, we are inclined to the opinion that the mutual interaction between hydrophilic emulsifier and oleophilic one is due largely to this oleophilic stearate group in the molecule.

In Fig. 2, POELs, ○, POECs ●, and POENPs ⊗, show remarkable difference between their two values. POENP shows nearly the same deviation as POEL; that is, nonylphenol behaves quite similarly to lauryl alcohol in the emulsification of mineral oil, although the carbon number 15 for nonylphenol is different from the carbon number 12 for lauryl alcohol. As a whole, this difference between their two values is greater at a higher HLB and smaller at a lower HLB range. In other words, the difference between $[\mathrm{HLB}]_{\mathrm{a}}$ and $[\mathrm{HLB}]_{\mathrm{calcd}}$ for these types of nonionic surfactants becomes greater at a higher mole number of the ethylene oxide unit in the molecule, and the difference increases in the following order:

$$\mathrm{PEGS} < \mathrm{POEC} < \mathrm{POEL} \leqslant \mathrm{POENP}$$

The difference is due perhaps to the emulsifier having a different oleophilic group.

HLB Value by Emulsifications. — In HLB systems, the additivity of HLB values between two components was assumed as an important basis. Generally, in many cases of the two-component system their physicochemical properties show some deviation from an algebraic additivity as a result of their component properties.

To investigate the value of $[\mathrm{HLB}]_{\mathrm{m}}$ in Eq. 4 is merely to discuss its deviation from the value which is calculated by interpolation using two emulsifiers obtained by Eq. 2 or 3.

On the other hand, to examine the values of $[\mathrm{HLB}]_{\mathrm{a}}$ in Eq. 10 is to study its deviation, adopting the value calculated by extrapolation using the fixed $[\mathrm{HLB}]_{\mathrm{m}}$ and $[\mathrm{HLB}]_{\mathrm{b}}$ from $[\mathrm{HLB}]_{\mathrm{calcd}}$, which is calculated only by the percentage content of the hydrophilic group in the molecule. By this latter procedure, the difference between $[\mathrm{HLB}]_{\mathrm{calcd}}$ and $[\mathrm{HLB}]_{\mathrm{a}}$ naturally becomes larger, and this makes the discussion rather easy.

The above results and discussions lead us to the conclusion that it is possible to illustrate and study more details of the HLB systems or the HLB values for several nonionic surfactants in the emulsifications of mineral oil when we refer them to the properly assigned standards.

Summary

The HLB values of several types of nonionic surfactants were determined by experiments in emulsification according to the concept of HLB suggested by Griffin.

The HLB values required to emulsify the mineral oil do not show a consistent value, although the values are limited within a narrow range.

The HLB values calculated according to the law of the additivity for the surfactant mixture, $[\mathrm{HLB}]_{\mathrm{a}}$, and the values calculated by the equations proposed by Griffin, $[\mathrm{HLB}]_{\mathrm{calcd}}$, were compared. The differences between these two values were most remarkable in the case of sorbitan fatty acid esters and became greater at the higher mole numbers of the ethylene oxide in the molecule, excepting polyoxyethylene sorbitan esters and polyethylene glycol stearates.

Some explanations were attempted for such differences and for the deviations from the assumed additive properties of the HLB system, in connection with the role or behavior of nonionic surfactants in emulsification.

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