Hydrophile-Lipophile Balance Values for O/W Emulsions Stabilized by Nonionic Surfactants. II. "Required Hydrophile-Lipophile Balance Values" of the Oil Mixture

By Noriaki OHBA

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In a preceding paper[1], the HLB values of nonionic surfactants were determined by means of emulsification tests conducted according to the HLB concept presented by Griffin[2]. The HLB values thus obtained were compared with the values calculated from their structural data, and the additivities of these values were discussed in connection with the behaviors of these nonionic surfactants in the systems of O/W emulsions.

In the HLB concept, an algebraic additivity of the HLB values in the mixtures of two or more surfactants is assumed as an important basis, which is expressed as follows[3]:

$$[\mathrm{HLB}]_{\mathrm{m}} = [\mathrm{HLB}]_{\mathrm{a}} x/100 + [\mathrm{HLB}]_{\mathrm{b}}(100-x)/100 \quad (1)$$

Here, $[\mathrm{HLB}]_{\mathrm{m}}$, $[\mathrm{HLB}]_{\mathrm{a}}$ and $[\mathrm{HLB}]_{\mathrm{b}}$ are the HLB values of the mixed emulsifier and of the surfactants "a" and "b" respectively, and x, the percentage content of surfactant "a" in the mixture.

Furthermore, the HLB concept is extended to apply in the case of the oil phase of the emulsion, and the term "required HLB value" is adopted for the given oil in a sense similar to that of the HLB value for the emulsifier. It was shown by Griffin that this required HLB value can be determined by means of emulsification tests, and such values obtained for several oils and waxes were presented by him[3].

In a manner similer to that in the case of the HLB values for emulsifier mixtures, he also assumed that the required HLB value for the oil mixture is obtained as an algebraic additivity from those values for the component oils in the mixture; that is,

$$[\mathrm{HLB}]_{\mathrm{o}} = \sum [\mathrm{HLB}]_i R_i/100 \quad (2)$$

where $[\mathrm{HLB}]_{\mathrm{o}}$ is a required HLB value of the oil mixture, and $[\mathrm{HLB}]_i$ and R_i a required HLB value and the percentage content of the ith component oil in the oil mixture respectively.

In this paper, to study the additivity in the HLB system and the characteristics of oil mixtures, the required HLB values of several oil mixtures were determined by means of emulsification tests[1].

Experimental

Materials. — *Nonionic Surfactants.* — Commercial products of sorbitan monostearate, SMS, and polyoxyethylene sorbitan monostearate, E-SMS-20, which were used in a preceding report[1], were also adopted as the standards for nonionic emulsifiers. The HLB values for these materials are 4.7 for SMS and 14.9 for E-SMS-20. When the required HLB of an oil mixture exceeds 14.9, polyoxyethylene cetyl ether, POEC-20, with the HLB value of 18.4, was adopted instead of E-SMS-20.

Oils and Waxes.—"Carnation White Mineral Oil" produced by the Sonneborn Co. was adopted as the fixed component of the oil mxture to be emulsified, its HLB value being 10.2 and its average viscosity, 70 cp.

Several materials were used as the additive component of the oil mixture; these are listed in Tables II to VI.

These additives, which are usually employed in the emulsion technique, were used without further purification.

TABLE I. REQUIRED HLB VALUES FOR ADDITIVES TO OIL PHASES OF O/W EMULSIONS

Oil phase	Required* HLB value	$[\mathrm{HLB}]_i$**
Acid, stearic	17	33.7∼38.2
Alcohol, cetyl	13	15.7∼16.2
Kerosene	12.5	—
Lanolin, anhydrous	15	10.7∼12.2
Oil		
Mineral, heavy	10.5	—
Mineral, light	10	10.2
Silicone	10.5	—
Petrolatum	10.5	—
Wax		
Beeswax	10∼16	13.9∼16.2
Candelilla	14.5	—
Carnauba	14.5	—
Microcrystalline	9.5	—
Paraffin	9	6.2∼8.9

* Values presented by Griffin
** Apparent values of HLB for additives

1) N. Ohba, This Bulletin., 35, 1016 (1962).
2) W. C. Griffin, *J. Soc. Cosmetic Chemists*, 1, 311 (1949).
3) W. C. Griffin, ibid., 5, 249 (1954).

TABLE II. FATTY ACIDS

Abbr.	Substance	Main component
L-Ac	Lauric	90%
S-Ac	Stearic	80% (20% palmitic)
O-Ac	Oleic	95%

TABLE III. ALCOHOLS

Abbr.	Substance	Main component
L-Alc	Lauryl	85%
C-Alc	Cetyl	80% (20% stearyl)
La-Alc	Lanolin	100% (mixture)

TABLE IV. ESTERS

Abbr.	Substance	Main component
IPM	Isopropyl myristate	97%
BS	Butyl stearate	95%
IPLa	Isopropyl lanolate	100% (mixture)

TABLE V. ACETYLATED ESTERS

Abbr.	Substance	Hydroxyl value
AGMS-I	Acetylated glyceryl monostearate	4
AGMS-II	Acetylated glyceryl monostearate	35
AGMS-III	Acetylated glyceryl monostearate	75
AGMS-IV	Acetylated glyceryl monostearate	155
AGML	Acetylated glyceryl monolaurate	30
AGMO	Acetylated glyceryl monoöleate	4
ALa	Acetylated lanolin	1

TABLE VI. OILS AND WAXES

Abbr.	Substance	Main component
CS-O	Cotton seed oil	Glyceryl trioleate
La	Lanolin	
B-W	Beeswax	
C-W	Ceresin Wax	Paraffin

TABLE VII. COMPOSITION OF O/W EMULSION

Oil mixture	40.0%
Emulsifier	
SMS+E-SMS-20	4.0%
Distilled water	56.0%

Emulsification.—Emulsification was carried out by the phase inversion method reported on in a preceding paper[1]. The composition of the emulsion tested in the present series of experiments is shown in Table VII.

In this table, the oil mixture consists of a mineral oil taken as the fixed component and an additive component, the content of which varies from 0 up to 30% in weight.

The required HLB values of the oil mixtures were determined as the value which was calculated by Eq. 1 for the composition of the mixed emulsifier giving the most stable emulsion in the series of emulsification tests, as described in a preceding paper[1].

Results

In Figs. 1—5, $[\mathrm{HLB}]_o$ vs. R diagrams are shown. In Table VIII, which selects one example from many calculations, the content (R %) of the additive in the oil mixture is listed in the 2nd column, the required HLB value ($[\mathrm{HLB}]_o$) in the 3rd, and the difference ($\varDelta$) between the required HLB value of the oil mixture and the required HLB value of mineral oil ($[\mathrm{HLB}]_m$), in the 4th column. In the last column, the apparent HLB value of the additive,

$$[\mathrm{HLB}]_i = \varDelta(100/R) + [\mathrm{HLB}]_m$$

calculated from $\varDelta$ at each concentration, is shown; $[\mathrm{HLB}]_m = 10.2$ in the present case. If the additivity in Eq. 2 is valid, $[\mathrm{HLB}]_i$ should be constant.

TABLE VIII. REQUIRED HLB VALUES OF MIXTURES OF FATTY ACIDS AND MINERAL OIL

	R, %	$[\mathrm{HLB}]_o$	$\varDelta$	$[\mathrm{HLB}]_i$
L-Ac	0	10.2	—	—
	10	13.4	3.2	42.2
	20	17.2	7.0	45.2
S-Ac	5	11.6	1.4	38.2
	10	12.8	2.6	36.2
	20	14.9	4.7	33.7
O-Ac	5	12.8	2.6	62.2
	7.5	12.8	2.6	44.4
	10	9.8	−0.4	6.2
	20	15.6	5.4	37.2
	30	18.4	8.2	37.5

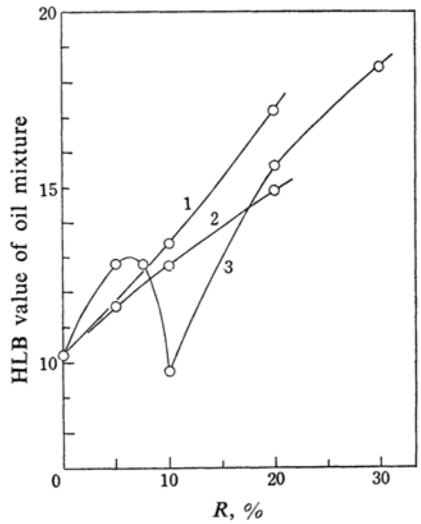

Fig. 1. Required HLB value of oil mixtures, Additives to mineral oil:
1, Lauric acid 2, Stearic acid
3, Oleic acid

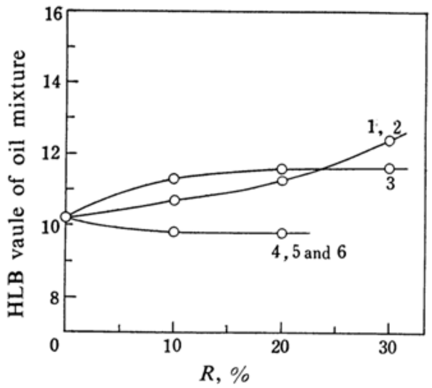

Fig. 2. Required HLB value of oil mixtures. Additives to mineral oil:
1, Lauryl alcohol 2, Cetyl alcohol
3, Lanolin alcohol 4, Isopropyl myristate
5, Butyl stearate 6, Isopropyl lanolate

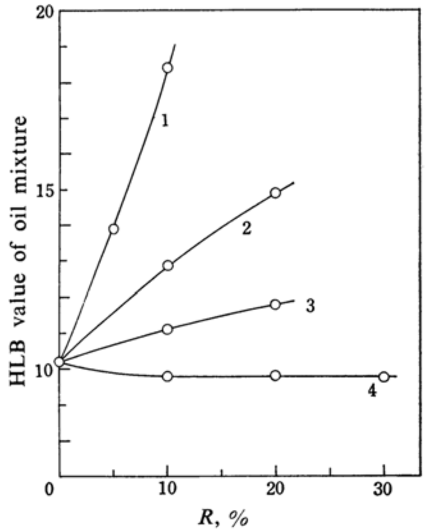

Fig. 3. Required HLB value of oil mixtures. Additives to mineral oil:
1, AGMS-IV 2, AGMS-III 3, AGMS-II
4, AGMS-I

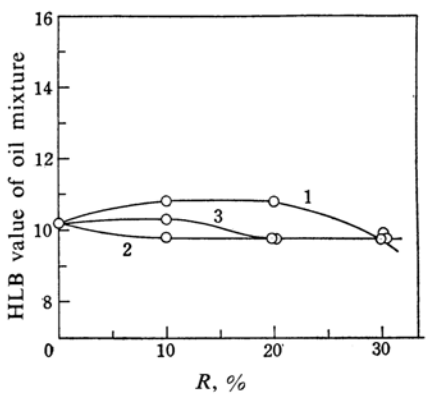

Fig. 4. Required HLB value of oil mixtures. Additives to mineral oil:
1, AGML 2, AGMO 3, ALa

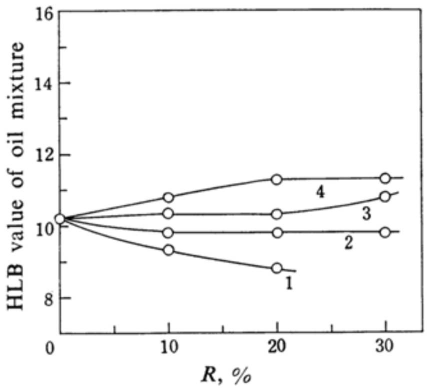

Fig. 5. Required HLB values of oil mixtures. Additives to mineral oil:
1, CS-O 2, C-W 3, La 4, B-W

Discussion

Fatty Acids.—Among the three fatty acids, lauric acid is the nearest of all to the additivity rule expressed by Eq. 2; however, the observed required HLB values, $[HLB]_i$, 42~45, are remarkably large, even considering the required HLB value for stearic acid listed in Table I. We should like to draw attention to the fact that no HLB value exceeding 20 can be evaluated according to the equation presented by Griffin.

Stearic acid also shows a marked deviation from Griffin's value listed in Table I, and the additive property of the HLB value is not distinct.

In the case of oleic acid, the diagram obtained is complicated in the region of R near 10%, where this curve shows a minimum. In the rest of the region studied, the curve runs similar to the other two acids. The value of $[HLB]_i$ for an R larger than 10% is constant and is nearly the same as those for stearic acid.

The elucidation of the anomalous phenomena mentioned above for oleic acid must await further investigation.

Alcohols.—Lauryl alcohol and cetyl alcohol gave coincident results in the region of R examined, and the obtained values of $[HLB]_i$ were 15~17, which are slightly larger than the corresponding values in Table I.

Though the composition and chemical structure of lanolin alcohol is not so simple as those of lauryl alcohol and cetyl alcohol, the curves for these three alcohols run parallel to each other, excepting the curve for lanolin alcohol in the region of R exceeding 10%, where the $[HLB]_o$ is nearly independent of R. Precisely speaking, therefore, the curve for lanolin alcohol is somewhat different from the other two but is, on the other hand, rather similar to that of waxes, as is shown in Fig. 5.

TABLE IX. ANALYTICAL DATA AND THE VALUES of $[HLB]_i$

Additives[1]	$[HLB]_i$	COOH[3]	COOR[3]	OH[3]	C=C
AGMS-IV	82.2	4	210	155	N[2]
O-Ac(7.5%)	44.4	200	N	N	94
L-Ac	42.2	278	N	N	N
O-Ac(20%)	37.2	200	N	N	94
AGMS-III	37.2	3	275	75	N
S-Ac	36.2	202	N	N	N
AGMS-II	20.2	3	315	35	N
La-Alc	21.2	—	40	90	—
L-Alc	16.2	N	N	300	N
C-Alc	16.2	N	N	217	N
AGML	16.2	3	370	30	N
B-W	16.2	18	76	20	9
ALa	11.2	N	120	N	—
La	11.2	5	95	30	22
AGMS-I	6.2	2	330	4	N
AGMO	6.2	2	325	4	80
C-W	6.2	N	N	N	N
O-Ac	6.2	200	N	N	94
IPM	6.2	N	207	N	N
BS	6.2	N	168	N	N
IPLa	6.2	N	—	N	—
CS-O	1.2	N	—	N	90

1) Content of additives is 10% unless otherwise stated.
2) Negligible
3) COOH: acid value, COOR: ester value, OH: hydroxyl value, C=C: iodine value.

Acetylated Esters.—The molecules of this group contain a different number of free hydroxyl radicals, as the result of a varying degree of acetylation. This enables us to study the effects of the increase of the OH-radical on emulsification. Indeed, the results obtained show large differences in $[HLB]_o$ values according to the degree of acetylation, as is shown in Figs. 3 and 4.

The values of the $[HLB]_o$ of acetylated esters increases with the increase in the OH content of the molecules, as indicated in the following series:

AGMS-I < AGMS-II < AGMS-III < AGMS-IV

In the case of AGMS-I, which lacks an OH-radical in the molecule due to the nearly perfect acetylation, the curve is somewhat like that for waxes in Fig. 5. The large difference in the inclinations of curves between these esters and those for alcohols suggests the effect of other factors than the OH content, such as ester linkage and the alkyl chain length of their molecules.

Though the values of $[HLB]_i$ do not fluctuate so much with R, its values are too large in the cases of AGMS-III (33.7～37.2) and AGMS-IV (82.2～84.2).

Oils and Waxes.—Though the natural oils and waxes are of a complicated nature in composition, they behave rather simply, as is shown in Fig. 5. $[HLB]_i$ values are also listed in Table I.

The results obtained for esters are somewhat similar to those for oils and waxes, although their structures are more simple than those for oils and waxes, as is shown in Fig. 2.

Structural Effects.—As far as the present experiments are concerned, the additivity of the required HLB values of the oil mixture from its components, as shown by Eq. 2, if any, is recognized to hold to some extent in the cases of saturated fatty, acids, *n*-fatty alcohols and some acetylated esters.

For the rest of the materials examined, the additivity of the required HLB values is hardly valid. Generally, the required HLB values of oil mixtures varied to some extent with the increase of R up to 10%, and they level off with the further increase of R; in certain cases, as in the AGML in Fig. 4, even an inversion of the sign of Δ from positive to negative is observed with the increase of R.

As for the explanation of these results, it is worth while to list the analytical data of these additives in Table IX. They are arranged in the decreasing order of $[HLB]_i$ at 10% *R*. From this table, it may be concluded as a whole that the intensity of the structural effects on the value of $[HLB]_i$ decreases in the following order:

$$COOH > OH > COOR$$

As seen from this order, the OH-radical by itself does not increase so markedly the values of $[HLB]_i$ as in the case of alcohols, although it increases the value of $[HLB]_i$ when ester-linkage coexists with the OH-radical in a molecule, as seen, for instance, in the case of AGMS-IV.

Summary

To study the additivity of the HLB values of an oil mixture from its component and the characteristics of the oil mixture forming a component of the emulsion, the required HLB values of several oil mixtures were determined by means of the emulsification tests proposed by Griffin.

The oil mixtures examined in this series of experiments consist of two oils, one being a mineral oil of fixed components and the other an oil to be studied as the additive, which is added in varying ratios to the fixed-component mineral oil.

The additivity of the required HLB values in oil mixtures was shown to hold to some extent for the case of saturated fatty acids, *n*-fatty alcohols, and some acetylated esters. For the rest of the additives, the additivity is not valid.

The required HLB values of these additive oils were remarkably large in the case of fatty acids, alcohols and some acetylated esters, excepting the anomalous value for oleic acid.

The structural effects on the increase of required HLB values seem to be in the following order:

$$COOH > OH > COOR$$

Nihon Surfactant Ind. Co.
Itabashi-ku, Tokyo