Viscosities of O/W Emulsions Stabilized by Nonionic Surfactants. I. Characteristics of Nonionic Surfactants in Emulsion Viscosities

By Noriaki OHBA

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Numerous reports are available on the viscosities of emulsions stabilized by the ionic emulsifiers. Viscosity has been discussed in detail in relation to the several factors affecting viscosity, such as the phase-volume ratio, the particle size distribution, the role of the interfacial films or of the stabilizers, the electroviscous effect, etc.[1]

On the other hand, there are relatively few data on and discussions of the viscosity of emulsions stabilized by the nonionic surfactants. Therefore, we have studied the behavior of nonionic surfactants towards the viscosity of emulsions. We first made the experiments on the emulsifications of mineral oil, using several types of nonionic surfactants; then we measured the viscosities of the emulsions thus obtained with a "MacMichael type" rotating-cup viscometer[2]. From these experiments, we have obtained a conclusion with relation to the HLB concept proposed by Griffin[3] on the nature of nonionic surfactants.

Experimental

Mineral Oil.—"Carnation White Mineral Oil" produced by Sonneborn Co., USA, was used as the oil phase in the emulsification, its average viscosity being 70 cp.

Nonionic Surfactants.—To examine the relative effects of nonionic surfactants on the emulsion viscosity, several samples differing in molecular constitution were selected for use; part of these were the same as those listed in the preceding report[4], and the other samples are listed in Table I.

TABLE I. GLYCERYL MONOSTEARATES

Abbr.	Type[a]	MG, %[b]	
MGS-I	N	45	Free glycerol <10%
MGS-II	N	55	Free glycerol <2%
MGS-III	S	—	MGS-I + K-soap
MGS-IV	S	—	MGS-II + K-soap
MGS-V	S	—	MGS-II + Nonionic surfactant

a : N, Noneself-emulsifying type
S, Self-emulsifying type
b : Monoglyceride content (%) determined with periodate.

Viscosity Measurements.—The viscometer employed in the present experiments was a "MacMichael type" rotating-cup viscometer equipped with a heating device to control the temperature of the emulsions measured. The angular velocity (Ω) of this viscometer can be varied from 25 to 100 r. p. m., and the values of the deflection angle (θ) at 50 r. p. m. were used for comparisons of the relative viscosity.

Results and Discussion

Emulsions of mineral oil were prepared by means of emulsification by inversion[5]. A composition of these emulsions is shown in Table II.

TABLE II. COMPOSITION OF EMULSION

Mineral oil	40.0%
Emulsifier	8.0%
Distilled water	52.0%

The process of emulsification is as follows; Into a mixture of mineral oil and emulsifier, which has been kept at about 90°C, water, which has also been kept at about the same temperature, is gradually added with an adequate stirring. This stirring is continued until the temperature of the emulsion decreases to about 40°C. After the emulsion has been left standing for about 20 hr., the viscosities of these emulsions are measured, at 25°C.

The HLB Method and the Viscosity of the Emulsion.—In the case of emulsifications using nonionic surfactants as stabilizers, there is the well-known HLB method to obtain the most stable emulsion[3]. To study the relations between the stabilities and viscosities of emulsions, sorbitan monostearate (SMS; HLB=4.7) and polyoxyethylene sorbitan monostearate (E-SMS-20; HLB=14.9) were adopted as standards for the emulsifiers[4]. To simplify comparison, one of these two standards was kept as a fixed component in any pair of surfactants in the emulsion studies. In this way, it was possible to study the relative effect of the nonionic surfactant upon the viscosity.

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[1] W. Clayton, "Theory of Emulsions", 4th Ed., The Blakiston Co., Philadelphia (1943); P. Becher, "Emulsions: Theory and Practice", Rheinhold Pub. Corp., New York (1957); etc.

[2] Shimadzu Seisakusho, Kyoto, Japan.

[3] W. C. Griffin, *J. Soc. Cosmetic Chemists*, **1**, 311 (1949).

[4] N. Ohba, This Bulletin, **35**, 1016 (1962).

[5] N. Ohba, K. Meguro and T. Kondo, Presented at the 12th Symposium of Colloid Chemistry, Hiroshima University, October, 1959.

In Table III, an example of the HLB values for mixtures composed of two emulsifiers, SMS and E-SMS-20, is shown.

To measure the relative viscosity, the resultant angle of deflection (θ) was plotted against the angular velocity (Ω), as is shown in Fig. 1.

TABLE III. HLB VALUES FOR MIXED EMULSIFIERS, θ AT 50 r.p.m., AND STABILITIES OF EMULSIONS

No.	Emulsifier composition (g.)		HLB (Eq.1)	θ at 50 r.p.m.	Stability
	SMS	E-SMS-20			
1	3.4	4.6	10.55	214	+
2	3.5	4.5	10.43	320	++
3	3.6	4.4	10.30	366	+++
4	3.7	4.3	10.18	335	+++
5	3.8	4.2	10.05	445	+++
6	3.9	4.1	9.80	298	++

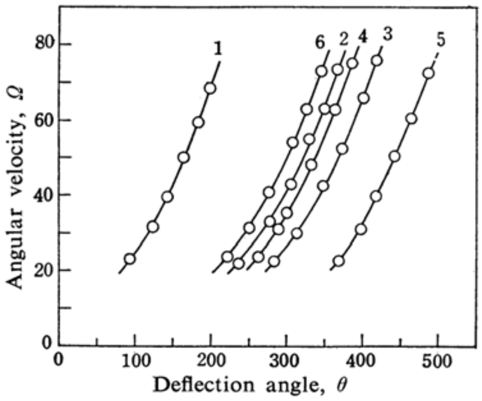

Fig. 1. The relations between deflection angle and angular velocity of viscometer.

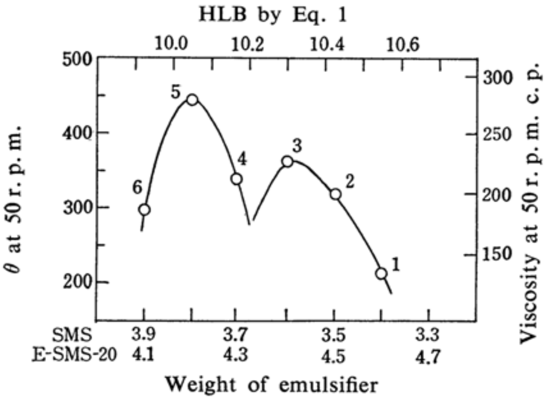

Fig. 2. The relations between the viscosity, the composition of emulsifier, and HLB.

On the basis of this figure, to show the effect of emulsifier composition on the relative viscosities of these emulsions, the values of θ at 50 r.p.m., which is an intermediate value of angular velocity, were listed in the 5th column of Table III and were plotted against the composition of the mxied emulsifiers, as is shown in Fig. 2.

At the top of this figure, a scale of the HLB values for the mixture is shown, calculated from the assumption of the weighed mean of HLB values of their components, using Eq. 1[6].

$$[\mathrm{HLB}] = [\mathrm{HLB}]_a x/100 + [\mathrm{HLB}]_b(100-x)/100 \tag{1}$$

where [HLB], $[\mathrm{HLB}]_a$ and $[\mathrm{HLB}]_b$ are the HLB values of the mixed emulsifier, surfactant "a" and "b" respectively, and x is the percentage content of surfactant "a" in the mixture.

In the case of SMS and E-SMS-20, $[\mathrm{HLB}]_a$ is 4.7, $[\mathrm{HLB}]_b$, 14.9, and

$$x = (\text{weight of SMS}) \times 100/8$$

This scale enables us to follow the $\theta \sim x$ relation with respect to the HLB of the mixed emulsifier.

Following the concept of HLB, it is assumed that the most stable state of emulsions results when the suitable HLB value is attained.

In the case of the series of emulsions shown in Table III, the following relations were found to exist among the HLB values, the particle size by a visual observation, the stability against creaming, and the relative viscosity of these emulsions:

1) The particle size of these emulsions first becomes smaller with the decrease in the HLB value for the emulsions numbered from 1 to 3, and then it becomes larger again with the further decrease in the HLB value for those of 5 and 6:

$$1 > 2 > 3 \geqslant 4 \leqslant 5 < 6$$

2) The stability of these emulsions varied with the decrease in the HLB value as shown in the last column of Table III; that is:

$$1 < 2 < 3 \approx 4 \approx 5 > 6$$

3) The relative viscosity of these emulsions has two maxima with respect to the HLB of the mixed emulsifier, as is shown in Fig. 2. As a whole, the relative viscosity of these emulsions shows two maxima as the HLB decreases with the change in composition of the mixed emulsifiers. Between these two maxima of viscosity, we can observe a deep or flat minima according to the nature of mixed surfactants, as is shown in Fig. 3.

In the case of ionic emulsifiers, it was reported by Richardson[7] that the apparent viscosity of emulsions having the same concen-

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[6] W. C. Griffin, *J. Soc. Cosmetic Chemists*, **5**, 249 (1954).

[7] E. G. Richardson, *J. Colloid Sci.*, **5**, 404 (1950); **8**, 367 (1953).

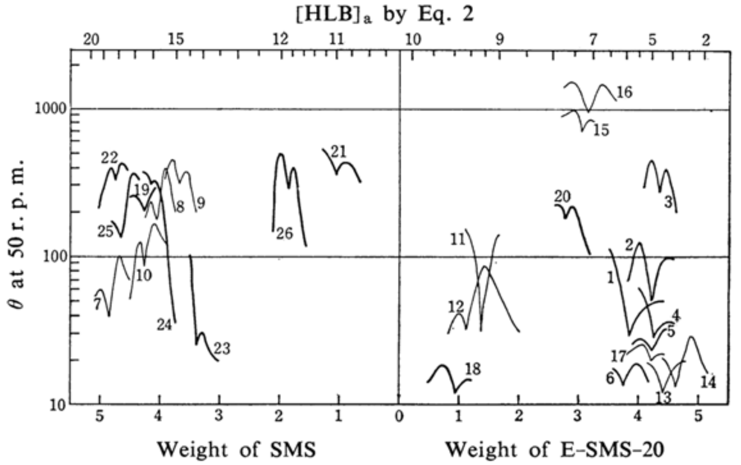

Fig. 3. The relations between the relative viscosity and the composition of mixed emulsifiers.
1, SML 2, SMP 3, SMS 4, SMO 5, SSO
6, STS 7, E-SML-20 8, E-SMP-20 9, E-SMS-20 10, E-SMO-20
11, E-SMS-6 12, E-SMO-6 13, GMS-I 14, GMS-II 15, GMS-III
16, GMS-IV 17, GMS-V 18, POEL-5 19, POEL-10 20, POEC-2
21, POEC-5.5 22, POEC-20 23, POENP-9 24, POENP-10 25, POEOP-10
26, PEGS-10

tration and a similar type of particle size distribution is inversely proportional to their mean grobule diameter. Applying his opinion to our case of the series of emulsions in Table III, the relation between the particle size, the stability and the relative viscosity of these emulsions can reasonably be understood, excepting for the region between the two maxima. To discuss the phenomena occuring in this region, further detailed studies must be made.

Sorbitan Fatty Acid Esters.—In Fig. 3, the cases of sorbitan fatty acid esters, curves 1—6, which were used with E-SMS-20 as the mixed emulsifiers, are shown.

All of the curves have two maxima in relative viscosities, like those shown in Fig. 2. In this figure, the relative viscosities, as a whole, are shown to decrease in the following order:

$$\mathrm{SMS} > \mathrm{SMP} > \mathrm{SML} > \mathrm{SMO} > \mathrm{SSO} > \mathrm{STS}$$

We can see, as a whole, that this order is in agreement with the increasing order of carbon numbers in the fatty acid radicals for saturated fatty acid monoesters and with the melting points of these acids, involving unsaturated acid monoesters. In the case of STS, the emulsions obtained were coarse and gave low relative viscosities.

Polyoxyethylene Sorbitan Fatty Acid Esters.—Derivatives having about 20 and 6 mol. of ethoxy-units in a molecule are used as component emulsifiers, and the results, curves 7—12, are shown in Fig. 3. These curves also gave two maxima, except for the case of E-SMS-6, the magnitude of relative viscosities (and of melting point) being in the following order:

$$\mathrm{E\text{-}SMS\text{-}20} > \mathrm{E\text{-}SMP\text{-}20} > \mathrm{E\text{-}SMO\text{-}20} > \mathrm{E\text{-}SML\text{-}20}$$

We can also see that this order is in agreement with the order of the carbon numbers of the saturated fatty acid esters. Thus we can confirm that the melting points of these varying components run parallel with the above series. However, if we consider the melting point of the fixed emulsifier component, the situation is not so simple. For instance, in the case of mixed emulsifiers consisting of SMS and polyoxyethylene fatty acid esters containing 20 mol. of ethoxy-unit in a molecule, SMS has a higher melting point than the rest of these polyoxyethylene derivatives, while the amounts in the emulsifier mixture required for optimum emulsification increase with the decrease in the relative viscosities. These relations are contrary to what can be expected from simple reasoning based upon the fact that the higher melting component increases the viscosity of the emulsion at its optimum composition.

Glyceryl Monostearates. — In Fig. 3, the results obtained, curves 13—17 are shown; all of these curves show two maxima, like the preceding examples. GMS-I and II gave levels of relative viscosities similar to those of the sorbitan esters. However, in the case of the so-called "self-emulsifying types", GMS-IV and III gave the considerably high levels compared with the rest of the cases examined, although those for GMS-V were in an order of magnitude comparable with that of the other nonionic surfactants.

The relative viscosities of this group decreased

TABLE IV. HLB VALUES BY EMULSIFICATION TEST, (A), VISCOSITY TESTS, (B) AND ASSIGNED, (C)

	(A)	(B)	(C)		(A)	(B)	(C)
SML	5.8	6.0	8.6	E-SML-20	17.3	18.5	16.7
SMP	4.4	5.0	6.7	E-SMP-20	15.6	16.0	15.6
SMS	4.7	4.7	4.7	E-SMS-20	14.9	14.9	14.9
SMO	5.1	5.0	4.3	E-SMO-20	15.0	16.5	15.0
SSO	5.2	5.1	3.7	E-SMS-6	9.4	9.3	9.6
STS	6.5	6.2	2.1	E-SMO-6	9.0	9.5	10.6
POEL-5	9.7	9.6	10.8	MGS-I	4.4	4.5	—
POEL-10	16.4	16.4	14.1	MGS-II	3.7	3.8	—
POEC-2	7.6	7.7	5.1	MGS-III	7.4	7.4	—
POEC-5.5	11.1	11.1	9.8	MGS-IV	7.1	7.2	—
POEC-20	18.4	18.1	15.5	MGS-V	5.5	5.1	—
POENP-9	14.2	14.2	12.9	PEGS-10	11.9	11.9	11.9
POENP-10	15.5	16.1	13.4	POEOP-10	—	17.8	13.6

in the following order:

$$\text{GMS–IV} > \text{GMS–III} \gg \text{GMS–V} > \text{GMS–II} > \text{GMS–I}$$

The anomalous large values of relative viscosity observed for GMS–III and IV are probably due to the presence of K-soap in these self-emulsifying types, that is, to the effects of the ionic surfactants. On the other hand, the relative viscosity observed for GMS–V, which involves nonionic surfactants alone as a component to make the self-emulsifying type, differs from those for those others involving K-soap.

Other Nonionic Surfactants.—For most of this group, two maxima in the curves of relative viscosities were also observed, as is shown in Fig. 3. (curves 18—26). The magnitudes of the relative viscosities did not show a considerable difference or a systematic variation among them, except for the case of POEL–5, which has a lower viscosity level.

HLB and Viscosities of O/W Emulsions.—In Fig. 3, the top scale $[\mathrm{HLB}]_a$ of these figures is of the virtual values of HLB for varying components of the surfactant mixture calculated from the following equations, based upon reasoning similar to that leading to Eq. 1:

$$[\mathrm{HLB}]_a = \{[\mathrm{HLB}]_m - [\mathrm{HLB}]_b x/100\}100/(100-x) \quad (2)$$

where $[\mathrm{HLB}]_m$ indicates the HLB value of standard mineral oil, 10.2[4], $[\mathrm{HLB}]_b$ is the HLB value for the fixed component, 4.7 for SMS and 14.9 for E–SMS–20, and x is the percentage of the fixed component in the emulsifier mixture. Therefore, when SMS is combined with any other surfactants, Eq. 2 becomes

$$[\mathrm{HLB}]_a = (10.2 - 4.7x/100)100/(100-x) \quad (3)$$

while in the case of E–SMS–20, we have

$$[\mathrm{HLB}]_a = (10.2 - 14.9x/100)100/(100-x) \quad (4)$$

Now, from these virtual values of $[\mathrm{HLB}]_a$, we can determine the most probable value of the HLB of the component emulsifier in question from the value of x, which gives the most stable emulsions corresponding to the minima between the two maxima of the $[\mathrm{HLB}]_a$ vs. θ curve. The HLB values thus obtained from the relative viscosities of emulsions can be directly compared with the HLB values of nonionic surfactants determined by emulsification tests by visual observation. In our recent paper[3], the HLB values of several nonionic surfactants by emulsification tests were reported. Although the water-oil-emulsifier ratio in the tests differed from that of the present systems, and this makes comparison somewhat difficult, the HLB values reported and the values corresponding to the viscosity minimum between two maxima as listed in Table IV show a good agreement for all nonionic surfactants. However, these experimental values do not always agree with the values calculated from the structural or analytical data of nonionic surfactants, C in Table IV.

Shapes of the Two Maxima and the Distances between Them.—The shapes of the two maxima and the distance between them may be an important measure to specify the characters of a given nonionic surfactant in emulsifications. Throughout these emulsification tests, it can generally be confirmed that the more distant are the two maxima separated in the viscosity curve, the more insensitive becomes the stability of the emulsion towards its surfactant composition. For this reason, we may introduce the term, "Viscosity Spectra of the Nonionic Surfactant".

Summary

O/W emulsions of mineral oil were prepared, using several types of nonionic surfactants, and their relative viscosities were measured with

a rotating-cup viscometer, together with microscopic and visual observation of the emulsions.

It was found that there are two maxima in the curve of the relative viscosity vs. the ratio of the two surfactants in the mixed emulsifier employed. From these figures, the relative effects of the nonionic surfactants on the emulsion viscosities were discussed.

It was confirmed that the emulsion viscosity at the optimum composition decreases in the following order:
for sorbitan fatty acid esters,

$$SMS > SMP > SML > SMO > SSO > STS$$

for polyoxyethylene sorbitan fatty acid esters,

$$E\text{-}SMS\text{-}20 > E\text{-}SMP\text{-}20 > E\text{-}SMO\text{-}20$$
$$> E\text{-}SML\text{-}20$$

for glyceryl monostearates,

$$GMS\text{-}IV > GMS\text{-}III \gg GMS\text{-}V$$
$$> GMS\text{-}II > GMS\text{-}I$$

For the other types the order of the series was not distinct. In the former two series, the orders of the arrangements are parallel with those of the decreasing carbon atom numbers in the molecule in the case of saturated fatty acid derivatives.

The soap effect is considered to appear in the case of glyceryl monostearates, the so-called self-emulsifying types of the emulsifier.

Using the scale of viscosity vs. virtual HLB value, we can determine by means of emulsification the most probable HLB value of the nonionic surfactants.

Good agreements are seen between the HLB values determined by viscosity minimum and those determined by the emulsification test reported on in the preceding paper.

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Nihon Surfactants Ind. Co.
Itabashi-ku, Tokyo