Viscosities of O/W Emulsions Stabilized by Nonionic Surfactants. II. Effects of Oil Mixtures on the Emulsion Viscosities

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In a preceding paper¹⁾, the effects of nonionic surfactants on the emulsion viscosities were measured, and the relations between the structures of nonionic surfactants and the viscosities of emulsions stabilized by them were studied. In another paper²⁾, the effects of the substances added to the oil on the HLB values of the mixtures thus obtained were determined, according to the concept of HLB suggested by Griffln³⁾, as being equal to the HLB value of that mixed surfactant which gives the most stable emulsion. Thus we studied the relations between the HLB values and the nature of the materials added to the mineral oil.

Several factors which influence the viscosities of the emulsion have been discussed by several workers⁴⁾ in connection with the properties of the oil phase of O/W emulsions. In the practice of emulsion techniques, a certain "thickener" is added to increase the viscosity of a given emulsion. Certain waxes and higher fatty alcohols, such as beeswax, cetyl alcohol and stearyl alcohol, are such examples.

Concerning thses problems, several oil mixtures were selected and were emulsified with nonionic surfactant mixtures of a fixed constituency. The viscosities of the emulsions thus obtained were measured and discussed in relation to the properties of the components of the oil mixture.

Experimental

Nonionic Surfactants.—To make comparison simple, sorbitan monostearate (SMS) and polyoxyethylene sorbitan monostearate (E-SMS-20) were adopted as standards of the nonionic emulsifiers, as has been described in the preceding paper²⁾. The HLB values adopted for these materials are 4.7 for SMS and 14.9 for E-SMS-20. When the required HLB of an oil mixture is over 14.9, polyoxyethylene

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1) N. Ohba, This Bulletin, 35, 1171 (1962).

2) N. Ohba, ibid., 35, 1021 (1962).

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

4) W. Clayton, "Emulsions and their Technical Treatment", 4th Ed., J. and A. Churchill Ltd. (1947); P. Becher, "Emulsions. Theory and Practice", Rheinhold Pub. Corp., New York (1957); etc.

cetyl ether (POEC-20), having the HLB value of 18.4, was adopted in place of E-SMS-20.

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

Several materials were used as the varying component of the oil mixture. They were selected from those described in the foregoing paper[2]; in this paper we distinguish acetylated glyceryl mono-oleate into two, i. e.,

AGMO-I Acetylated mono-oleate (OH. V.=4)
AGMO-II Acetylated mono-oleate and mono-stearate (OH. V.=4).

These materials were used in a varying ratio to the fixed component of mineral oil.

Viscosity Measurements.—The emulsions used in the present experiment were prepared by the same method as has been described in a preceding paper[5], i. e., that method involving phase inversion. The HLB values of these emulsions were also determined by the same method as presented in another paper[2].

TABLE I. COMPOSITION OF O/W EMULSIONS

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

The compositions of these emulsions are shown in Table I. After these emulsions had been left standing for about 20 hr., their viscosities were measured, by a " MacMichael type " rotating-cup viscometer which indicates the values of strain θ as the deflection angle of inner cylinder, for varying angular velocities, Ω, of the cup. For convenience, the values of strain θ at 50 r.p.m. were adopted as the relative viscosities of the emulsions.

Results and Discussion

Viscosity and Composition Diagrams.—The results obtained are illustrated in Figs. 1—4.

In Fig. 1 we can see that the viscosities of S-Ac/mineral oil mixtures increase steeply when the S-Ac content exceeds 10% of the oil mixture. On the other hand, in the case of L-Ac, such an increase was observed in the concentration ranges beyond 15%.

In the case of fatty alcohols, as shown in Fig. 2, the effects of C-Alc were remarkably greater than those of La-Alc and L-Alc. A sudden increase in this viscosity vs. the composition diagram for C-Alc was observed at a 5% content of C-Alc in the oil mixture, while for the cases of the other two alcohols a similar increase was observed at a 20% content.

We can see from these results that, among these fatty acids and alcohols, C-Alc is the most effective additive to the oil phase to increase the emulsion viscosity, both with respect to the amount required and to the degree of viscosity increase. Such an effect of C-Alc can be succcssfully applied in certain fields of emulsion technique.

In Fig. 3, viscosity vs. composition diagrams for acetylated esters are shown. In this figure, it can be seen that AGMS-I, -III and -IV have a greater effect on the viscosities of emulsions than AGMO-I and II. Among these three stearates, AGMS-IV shows a remarkably large effect on the emulsion viscosity, its magnitude being comparable to that of C-Alc. It is also used for the similar purpose of increasing viscosity. AGMS-III and I are effective to the same extent.

The viscosities of emulsions containing AGMO-I and II are considerably different

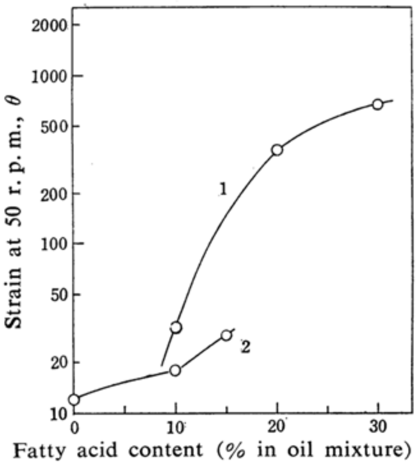

Fig. 1. Viscosity of emulsion.
Oil phase: 1, Mineral oil~stearic acid
2, Mineral oil~lauric acid

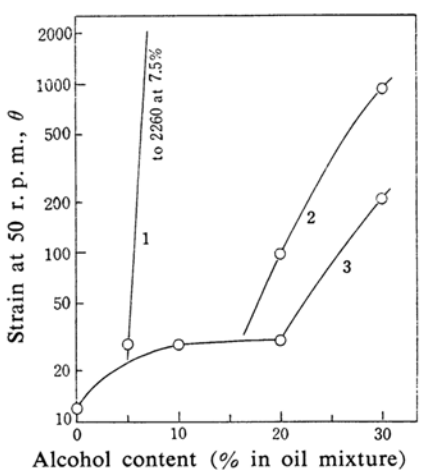

Fig. 2. Viscosity of emulsion.
Oil phase: 1, Mineral oil~cetyl alcohol
2, Mineral oil~lanolin alcohol
3, Mineral oil~lauryl alcohol

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5) N. Ohba, This Bulletin, 35, 1016 (1962).

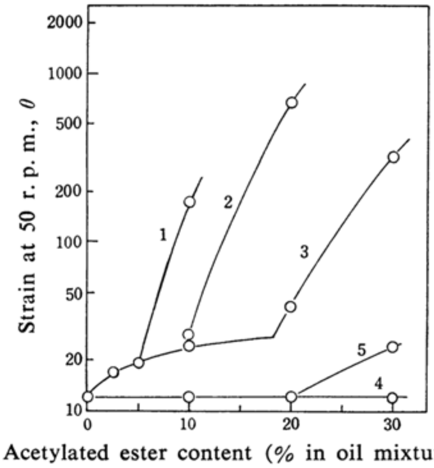

Fig. 3. Viscosity of emulsion.
Oil phase: Mixtures of mineral oil and
1, AGMS-IV 2, AGMS-III 3, AGMS-I
4, AGMO-I 5, AGMO-II

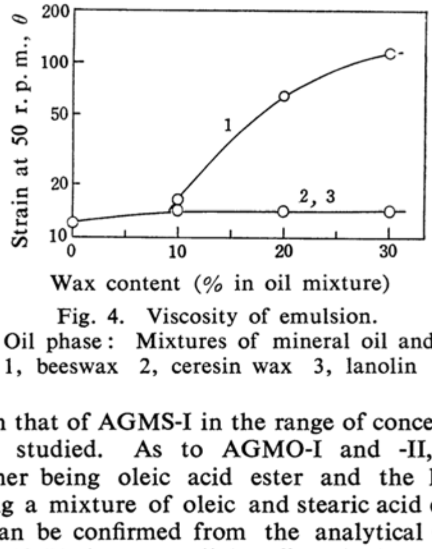

Fig. 4. Viscosity of emulsion.
Oil phase: Mixtures of mineral oil and
1, beeswax 2, ceresin wax 3, lanolin

from that of AGMS-I in the range of concentration studied. As to AGMO-I and -II, the former being oleic acid ester and the latter being a mixture of oleic and stearic acid ester, as can be confirmed from the analytical data, AGMO-II shows a slight effect in increasing the emulsion viscosity, while AGMO-I does not, in the region beyond a 20% content in the oil.

Figure 4 shows the results of viscosity measurements for waxes. B-W had a fairly large effect in increasing the emulsion viscosity, while La and C-W showed little influence over the whole range of concentration examined.

The sudden increase in the emulsion viscosity by B-W occurs at a certain content of B-W within the region from 10 to 20% of the oil mixture, as in the case of C-Alc, AGMS-IV, etc., but the increase is smaller for B-W.

As a whole, we can see in Figs. 1—4 that the magnitudes of the effects of these additives on the increasing emulsion viscosity are in the following order, with respect both to the amount required for the sudden increase in viscosity and to the rate of its increase:

C-Alc, AGMS-IV>S-Ac, AGMS-III>La-Alc>
AGMS-I, L-Ac, L-Alc>B-W>AGMO-II,
AGMO-I, C-W, La

Factors Affecting the Emulsion Viscosities.— It was reported in a preceding paper[2] that the effects of additives on the required HLB values of the oil mixtutres vary both with the nature and the amount of the additives in the oil mixture.

Concerning the emulsion viscosities, Toms[6] and Sherman[7] reported that the emulsion viscosity is affected greatly by the chemical nature of the internal phase, while the viscosity of the internal phase is of no consequence.

To make sure of the factors affecting the emulsion viscosities, several data were measured and are listed in Table II; the substances are arranged in the decreasing order of influence on the emulsion viscosities shown above. In this table, the following abbreviations are used:

A: Amount of additive required to increase the emulsion viscosity ten times as much as that of the mineral oil emulsion without any additives; these amounts are determined from the results shown in Figs. 1—4.

Δ: The increase in the required HLB value of the mixture from that of mineral oil[2] at the additive contents corresponding to A.

Figure 5 shows graphically the correlations between "A" and other factors. From these figures we cannot deduce any simple correlation between these factors which may be used to find an effective additive for increasing emulsion viscosity. However, we can safely say that in order to be effective as an additive in increasing emulsion viscosity, a substance's iodine value should be small, while an ineffective additive always shows a low Δ as well as a low hydroxyl value. The melting point of an additive has, on the whole, no correlation with the power of increasing emulsion viscosity. The acid value also shows no correlation with the viscosity of the emulsion formed.

These general tendencies may sometimes become useful guides for the selection of additives to increase emulsion viscosity.

Critical Phenomena. — Throughout all the experiments shown in Figs. 1—4, we can see a fairly distinct critical phenomenon. That is, the viscosities of these O/W emulsions increase steeply beyond a certain critical content of the

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[6] B. A. Toms, *J. Chem. Soc.*, **1941**, 542.
[7] P. Sherman, *Mfg. Chemist*, **26**, 306 (1955); *Kolloid-Z.*, **6**, 141 (1955).

TABLE II. VISCOSITY INCREASE AND CHEMICAL NATURE OF THE ADDITIVES

	A	Δ	COOH*	OH*	C=C*	M. p., °C
C-Alc	5.7	6	N	217	N	50
AGMS-IV	9	74	4	155	N	54
S-Ac	14	28	202	N	N	62
AGMS-III	14	27	3	75	N	39
La-Alc	21	7	N	90	—	—
AGMS-I	25	−2	4	4	N	31
L-Ac	15~25	35	278	N	N	38
L-Alc	27	6	N	300	N	22
B-W	30	4	18	20	9	62
AGMO-II	>30	−1	2	4	40	—
AGMO-I	>30	−1	2	4	80	—
C-W	>30	−1	N	N	N	66
La	>30	2	5	30	22	(30)

N: Negligible

* COOH: acid value, OH: hydroxyl value and C=C: iodine value

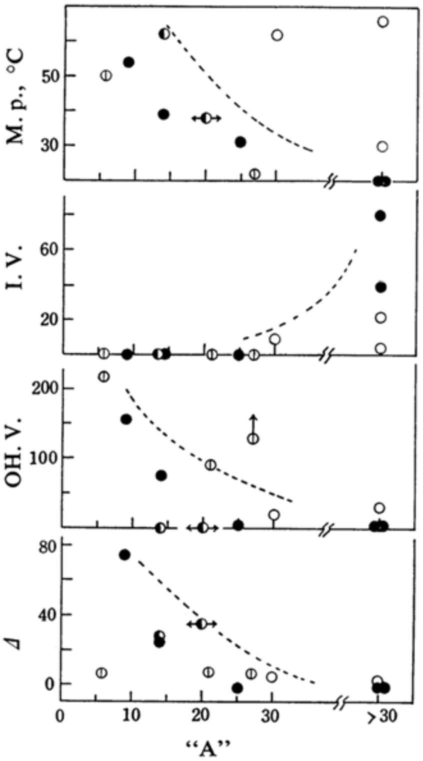

Fig. 5. Correlations between "A" and other factors.

Additives: ◑, Fatty acids; ⦶, Fatty alcohols; ●, Acetylated esters; ○, Waxes

additives, and these critical contents form characteristics of each material. The critical contents determined for the substances are listed, though roughly, in Table III. In this table, the substances are arranged in the decreasing order of their critical contents, which order agrees as a whole with that shown in Table II. That is, a substance having a lower critical content shows a stronger tendency to increase the emulsion viscosity than a substance having a higher critical content.

TABLE III. CRITICAL CONTENTS OF SUBSTANCES

	Critical content, %		Critical content, %
C-Alc	5	L-Ac	10~20
AGMS-IV	5~10	L-Alc	20~30
S-Ac	5~10	AGMO-II	20~30
AGMS-III	10	AGMO-I	>30
B-W	10	C-W	>30
La-Alc	10~20	La	>30
AGMS-I	10~20		

We may also notice that the additive shows no effect in increasing emulsion viscosity when it does not contain any polar group other than ester linkage.

Besides the critical point, the inclination of viscosity vs. additive content diagrams beyond the critical point also offers some measure of the efficiency of additives in increasing emulsion viscosity, with some exceptions, as in the case of B-W, where the small critical content does not always correspond to the steep inclination of the viscosity vs. content diagram beyond the critical point. Precisely speaking, therefore, we should take account of both the critical point and the inclination of the steeper part of the diagram in estimating the efficiency of an additive in increasing emulsion viscosity.

Although many studies on the emulsion viscosities have been carried out by several workers[4,6,7,], none of them is entirely satisfactory in explaining the phenomena. At least, the chemical structure of the additives, and the change in the viscosity of the external phase produced by the solubilization of the oil component into micelles of the emulsifier which is considered to exist in the external phase, are considered to be important in elucidating the phenomena. For the further elucidation of these critical phenomena, however, more details must be studied.

Summary

To study the effects on the viscosities of O/W emulsions of the addition of several materials to the oil phase, oil mixtures were emulsified and the viscosities of the emulsions so obtained were measured with a rotating-cup viscometer,

The effects of these additives in increasing emulsion viscosity are in the following order, with respect both to the amounts required to give a specified increase in viscosity and to the minimum amount required for a sudden increase in viscosity:

C-Alc, AGMS-IV>S-Ac, AGMS-III>La-Alc> AGMS-I, L-Ac, L-Alc>B-W>AGMO-II, AGMO-I, C-W, La

It was confirmed that in order to be effective as an additive in increasing emulsion viscosity, the iodine value should be small, while an ineffective additive always shows a low Δ as well as a low hydroxyl value. The melting point of an additive has, on the whole, no correlation with the power of increasing the emulsion viscosity. The acid value also shows no correlation with the viscosity of the emulsion formed.

A sudden increase in emulsion viscosity was observed beyond a certain amount characteristic of each additive.

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